



**The Numerical Study of Transport and Reaction
Within and Around a Porous Carbonaceous
Particle in a Fluidized Bed**

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ABSTRACT

In response to environmental concerns, a range of advanced coal utilization technologies are currently being developed. As these technologies are primarily based upon various forms of the fluidized bed (FB), much research aimed at improving understanding of coal particle conversion under FB conditions has been undertaken. Taking advantage of recent theoretical advances and modern supercomputer technology, this dissertation presents two advanced modelling studies which address some unresolved FB combustion (FBC) issues.

In the first study, finite element methods were used to solve a transient continuum/percolation model of a single porous char and its surrounding boundary layer so as to generate temperature, O_2 , CO_2 , CO , pressure and porosity distributions for over 100 different FBC conditions. By comparing these results with recent experimental data, the study revealed, amongst other things, that reaction does occur within the boundary layer of a stationary char located within an incipient FB, whilst it is also expected to occur for a stationary char resident within the emulsion phase of a bubbling FB. It was also found that the $CO-O_2$, $C-O_2$ and $C-CO_2$ reactions affect the particle related product ratio, with the influence of each varying with temperature. The $CO-O_2$ and $C-O_2$ reactions are dominant over the intermediate-high and low-intermediate FBC temperature range respectively, whilst the $C-CO_2$ reaction is important at high FBC temperatures for large char particles. These behaviors explain the peculiar product ratio/temperature behavior recently reported by Linjewile and Agarwal (*Fuel*, **74**, 5, 1995).

Continuum models such as that used in the first part of the work presented here require, as input, the effective diffusion coefficients of the fluid-solid system. Using molecular dynamics (MD) and percolation concepts, a new discrete approach for the determination of these coefficients is described and used in the second of the studies reported here. The use of MD not only overcomes many of the problems associated with the more conventional discrete approaches, but also provides an excellent basis for

extending the method to the determination of reaction and other transport parameters. The new method was used to study two gas/porous—graphite systems which may be considered simple prototypes of real gas/char systems. In addition to many other interesting results, this study showed that the tortuosity as normally defined is temperature dependent, and that the diffusivity of a gas within a porous solid varies with temperature in a manner similar to a liquid, not a gas, in the bulk phase.

This work contains no material which has been accepted for the award of any other degree or diploma in any other university or other tertiary institution and, to the best of my knowledge and belief, contains no material previously published or written by another person, except where due reference has been made in the text.

I give consent to this copy of my thesis, when deposited in the University Library, being available for loan and photocopying.

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CHAPTER 1



INTRODUCTION

1.1 BACKGROUND

Of all fossil fuel energy sources, coal is the most abundant. The recent *BP Statistical Review of World Energy* (1994) indicates that at the present rate of production, there is over 230 years of black and brown coal reserves as compared to 43 and 65 for oil and natural gas respectively. This review also indicates that coal reserves are well distributed throughout the world, whilst both oil and gas are concentrated in regions that may be considered politically less stable [approximately 78% of known natural gas and oil reserves are located in the former USSR, Middle East, and Africa]. It is for these reasons that coal is still the world's preferred energy source; almost 40% of the world's electricity is generated by coal-fired power stations [Burnard, 1995]. Despite this fact, coal is being increasingly displaced in the electricity generation industry by natural gas [Patterson, 1993]. This is, of course, due to the world's concern over the impact that coal usage has on both the environment and human health. Of particular concern are:

- **Greenhouse gas emissions.** In relation to fossil fuel utilization, CO₂ is the main offender [Garrett, 1992], with N₂O also being of concern in certain situations [Hayhurst and Lawrence, 1992; Mann et al., 1992; Wojtowicz et al., 1993]. Coal produces approximately double the amount of CO₂ per unit energy output as natural gas [Garrett, 1992].
- **NO_x and SO_x emissions.** These gases are known to affect human health, and are key components for acid rain which is responsible for ecosystem breakdown, and destruction of buildings and monuments [Boardman and Smoot, 1993]. NO_x, when combined with hydrocarbons, is also responsible for ozone and photochemical smog production in the lower atmosphere where it is harmful to humans, flora and crops [Redman, 1989]. For a 600 MW class power plant, natural gas emits no SO_x,

and only half the NO_x of conventional pulverized fuel (PF) combustor based systems per unit energy output [Hassmann, 1993].

- **Carbonaceous emissions.** These include carbon monoxide, and hydrocarbons in both their vapor and condensed (ie: soot) forms. The role of hydrocarbons in the production of photochemical smog has just been outlined, whilst some hydrocarbons have also been identified as cancer-causing [Masclet et al., 1987]. Soot is also responsible for reduced visibility [Boardman and Smoot, 1993].
- **Trace metal emissions.** If temperatures are high enough, naturally occurring trace metals in the coal such as mercury, zinc, cadmium and arsenic may be vaporized and subsequently emitted to the atmosphere with the flue gases [Clarke, 1993] – many are known to be harmful to humans and animals [Querol et al., 1995].
- **Ash disposal.** Some toxic metals are also found in the solid residues [Mojtahedi et al., 1990] – most residues are deposited in precious landfill sites where it may adversely affect the environment in many different ways [Carlson and Adriano, 1993].

In order to compete with natural gas, the coal utilization industry has moved rapidly to address many of these concerns [Patterson, 1993]. For example, NO_x emissions from existing PF combustors have been significantly reduced by retrofitting low NO_x burners, air-staging, reburning, and/or selective catalytic or non-catalytic reduction [Redman, 1989]. Retrofitting has also been used to tackle SO_x [Topper et al., 1994] and particulate emissions [Clarke, 1993]. However, these retrofit strategies are not altogether satisfactory in several respects: (1) they entail increased capital and, sometimes, operating costs [Williams et al., 1994]; (2) some require considerable physical space that may not be readily available [Burnard, 1995]; (3) some can increase other emissions such as toxic hydrocarbons and trace metals [Miller et al., 1994]; (4) some can cause operational problems such as corrosion augmentation [Redman, 1989]; and (5) they can result in lower overall efficiencies and, therefore, higher CO_2 emissions [Summers, 1992]. By applying various NO_x and SO_x reduction strategies to new, more advanced,

PF combustor designs, some of these issues will be addressed [Burnard, 1995]. However, it is expected that coal's future share of the energy market shall be secured by employing advanced coal utilization technologies which use clean burn methods with combined gas/steam cycles [Williams et al., 1994]. These technologies are cleaner, more efficient and, ultimately, cheaper than conventional PF combustion technologies [Summers, 1992; Hassmann, 1993; Topper et al., 1994; Williams et al., 1994].

There are four main types of advanced coal utilization technologies [Topper et al., 1994]: (1) circulating fluidized bed combustion (CFBC); (2) pressurized fluidized bed combustion (PFBC); (3) integrated gasification combined cycle (IGCC) in which either a fixed bed, fluidized bed, or entrained flow gasifier is used; and (4) air blown gasification cycle (ABGC) which uses both pressurized and circulating fluidized bed technology. Clearly, all rely upon the fluidized bed (FB) in one or more of its various forms. The reasons for this are many fold:

- They operate at temperatures significantly lower than those associated with PF combustion – this reduces NO_x and trace metal emissions, and fouling and slagging.
- They are extremely fuel–flexible – this often means significant fuel cost savings as poor quality coals, or even household waste, may be used.
- By using sulphur–sorbent bed materials, SO_x emissions may be largely eliminated without resort to methods such as flue gas desulphurization.

The importance of FB technologies to the future of coal utilization in the power industry has motivated much research into how a burning coal particle behaves within a FB [eg: Prins, 1987; Manzoori, 1990; Chirone et al., 1991; Mann et al., 1992; Linjewile, 1993]. Much of this research is experimental; if models are used, they are invariably simple, and primarily aimed at gaining insights into experimental findings [eg: Stanmore and Jung, 1980], or extrapolating limited experimental data for the purposes of combustor design [eg: Brem and Brouwers, 1990]. The use of simple models is, of course, not perverse on the part of investigators. The complex nature of both coal and the way it responds within

a high temperature environment makes it extremely difficult to model. Lack of readily available computer power has also added to this difficulty. However, as we probe further and further the mysteries of coal combustion in general, and FBC of coal in particular, we are finding simple models more and more inadequate. For example, many of the environmental issues just outlined as well as design and operational considerations require knowledge of burning particle temperatures. These temperatures may in principle be predicted provided we know, amongst other things, the CO/CO₂ product ratio associated with a burning char. This ratio can significantly influence the estimated particle temperature due to the widely different heats-of-reaction associated with the reactions that produce CO and CO₂ [Prins, 1987]. This fact has prompted several recent exhaustive studies that use experiment and simple models and physical arguments to determine how the particle related CO/CO₂ product ratio changes with char particle temperature and size, bed particle size, resident bed phase, and fluidizing conditions [Prins, 1987; Linjewile, 1993]. Despite these efforts, however, none of these relationships have yet to be firmly established, whilst new questions [Linjewile and Agarwal, 1995] have been raised!

This discussion clearly shows that we must bring to bear more advanced modelling techniques. Fortunately, progress has been made in several important respects over the last decade that make this more possible: (1) relatively inexpensive workstations that are as powerful as the supercomputers of the late-1970s are now available [Stadtherr et al., 1993], whilst the most powerful machines of today are over 6000 times faster again [Dongarra et al., 1994]; (2) several new models and theories for describing the *physical* evolution of a char's pore system have been advanced [Sahimi et al., 1990; Bhatia and Gupta, 1992]; and (3) a number of methods and theories for determining and describing effective transport properties of fluids within porous media have either been developed, or have matured [Sahimi et al., 1990]. In this thesis, this recent progress is used as a basis for two advanced modelling studies which relate to porous char particle combustion within FBC environments. As they are largely independent of each other, the studies are

presented in two self-contained chapters. However, where links exist, they are highlighted.

1.2 FIRST STUDY – SINGLE PARTICLE SIMULATION OF CHAR COMBUSTION WITHIN A FLUIDIZED BED

Chapter 2 documents a study in which a newly developed advanced single particle model is used in conjunction with modern supercomputer technology to address the following issues which have been difficult to resolve in the past on the basis of experiment alone, and which could be of significant interest in improving predictive capabilities of mathematical models:

- Does homogeneous reaction occur within the boundary layer of a char resident in the emulsion phase of a fluidized bed ?
- How does the CO/CO₂ product ratio associated with a particle (ie: that which dictates its temperature) vary with char particle temperature and size, bed particle size, and bed hydrodynamics ?
- What is the influence of the normally ignored CO₂ gasification reaction and peripheral disintegration on char conversion as a function of FBC conditions ?

The newly developed model is based upon a continuum formulation for both the porous char and surrounding boundary layer [Jackson, 1977], and percolation concepts [Stauffer and Aharony, 1992] are used to describe the effect that pore evolution has on char effective transport and reaction properties [Sahimi et al., 1990; Sahimi, 1994]. The model is solved using advanced finite element methods and iterative equation solvers that are particularly suited to distributed memory parallel architectures and vector processors used.

1.3 SECOND STUDY – MOLECULAR DYNAMIC SIMULATION OF TRANSPORT AND REACTION WITHIN A POROUS SOLID

Continuum single particle models generally require, as input, the effective transport properties for the fluid/char system – Chapter 3 deals with this aspect of the single particle model problem. Traditionally, three approaches have been used to determine

the transport properties of a fluid–solid system: (1) experiment [eg: Valix et al., 1992]; (2) classical volume averaging techniques in which simple pore system models are used [eg: Sotirchos and Burganos, 1986]; and (3) consistent volume averaging techniques in which the pore system is represented by a discrete network or lattice [eg: Reyes and Jensen, 1986]. The first and second of these have many problems and limitations associated with them. Although the third approach overcomes many of these problems, it is computationally demanding if we wish to treat the pore system in a realistic way (ie: with a general pore model in conjunction with a Monte–Carlo approach rather than, say, a Bethe lattice). An alternative to the conventional approaches is the discrete method [Abbasi et al., 1983; Sahimi, 1990] in which the pore space is modelled using a continuum or discrete percolation system, and the diffusing fluid is represented by discrete elements that execute a random walk through this model pore space, Figure 1.1. Although this approach is also computationally very demanding, its application is much more straightforward compared to the computer based consistent volume averaging techniques, and is both easily vectorized and highly parallel [Sahimi, 1994]. This last makes the discrete approach particularly attractive today, as the latest generation of supercomputers are invariably multiprocessor based, with the individual processors being either vector or highly pipelined scalar units. However, this discrete approach in its present form also suffers from several shortcomings. In Chapter 3, a new discrete approach based upon molecular dynamic [Allen and Tildesley, 1989] and percolation [Stauffer and

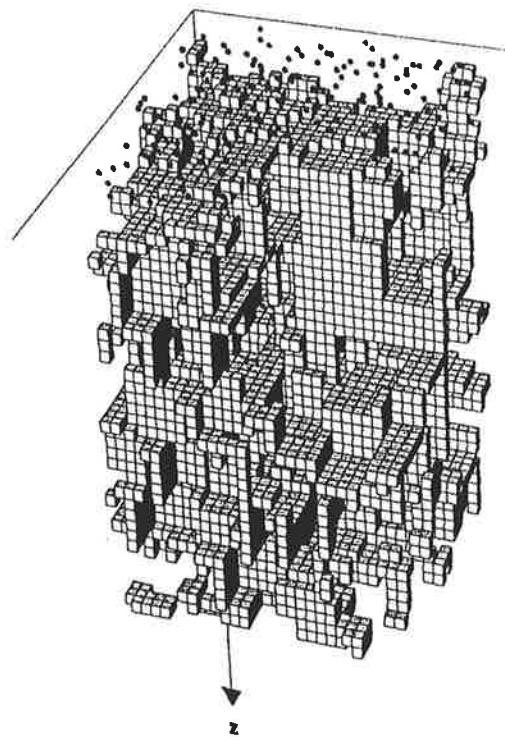


Figure 1.1. Random walkers (black dots) within a continuum percolation model of a porous char [Miccio and Salatino, 1992].

Aharony, 1992; Sahimi, 1994] concepts is described, and subsequently used to study mass diffusion within two non – reactive fluid – solid systems that may be of interest to the coal combustion scientist. This new approach addresses the shortcomings of the more conventional discrete approach, and provides a means by which we may determine all transport coefficients of interest (eg: viscosity, thermal conductivity, Soret and Dufour coefficients), and reaction rate parameters for real solids such as coal and its char.

REFERENCES

1. Abbasi M.H, Evans J.W and Abramson I.S (1983): Diffusion of gases in porous solids: Monte Carlo simulations in the Knudsen and ordinary diffusion regimes, *AIChE Journal*, **29**, 617.
2. Allen M.P and Tildesley D.J (1989): *Computer Simulation of Liquids*, Oxford University Press, Oxford.
3. Bhatia S.K and Gupta J.S (1992): Mathematical modelling of gas–solid reactions: Effect of pore structure, *Rev. Chem. Engng.*, **8**, 178.
4. Burnard G.K (1995): Clean coal technologies: Background and current status, in *Clean Coal Technologies*, Institution on Mechanical Engineers, London.
5. Boardman R.D and Smoot L.D (1993): Pollutant formation and control, in *Fundamentals of Coal Combustion for Clean and Efficient Use*, Smoot L.D (ed.), Elsevier, Amsterdam.
6. Brem G and Brouwers J.J.H (1990): Analytical solutions for non–linear conversion of a porous solid particle in a gas – II. Non–isothermal conversion and numerical verification, *Chem. Engng. Sci.*, **45**, 1915.
7. Carlson C.L and Adriano D.C (1993): Environmental impacts of coal combustion residues, *J. Environ. Quality*, **22**, 227.
8. Chirone R, Massimilla L and Salatino P (1991): Comminution of carbons in fluidized bed combustion, *Prog. Energy Comb. Sci.*, **17**, 297.
9. Clarke L.B (1993): The fate of trace elements during coal combustion and gasification: an overview, *Fuel*, **72**, 731.
10. Dongarra J.J, Meuer H.W and Strohmaier E (1994): *TOP500 Supercomputer Sites*, available by sending “send performance from benchmark” to netlib@ornl.gov.
11. Garrett C.W (1992): On global climate change, carbon dioxide, and fossil fuel combustion, *Prog. Energy Comb. Sci.*, **18**, 369.
12. Hassmann K (1993): Electric power generation, *Proc. IEEE*, **81**, 346.

13. Hayhurst A.N and Lawrence A.D (1992): Emissions of nitrous oxide from combustion sources, *Prog. Energy Comb. Sci.*, **18**, 529.
14. Jackson R (1977): *Transport in Porous Catalysts*, Elsevier, Amsterdam.
15. Linjewile T.M (1993): *Temperature of Burning Carbonaceous Particles in a Fluidized-bed Combustor*, Ph.D Thesis, University of Adelaide.
16. Linjewile T.M and Agarwal P.K (1995): The influence of product CO/CO₂ ratio on the ignition and temperature history of petroleum coke particles in incipiently gas-fluidized beds, *Fuel*, **74**, 13.
17. Mann M.D, Collings M.E and Botros P.E (1992): Nitrous oxide emissions in fluidized-bed combustion: Fundamental chemistry and combustion testing, *Prog. Energy Comb. Sci.*, **18**, 447.
18. Manzoori A.R (1990): *Role of the Inorganic Matter in Agglomeration and Defluidization During the Circulating Fluid Bed Combustion of Low-rank Coals*, Ph.D Thesis, University of Adelaide.
19. Masclet P, Bresson M.A and Mouvier G (1987): Polycyclic aromatic hydrocarbons emitted by power stations, and influence of combustion conditions, *Fuel*, **66**, 556.
20. Miccio F and Salatino P (1992): Monte-Carlo simulation of combustion-induced percolative fragmentation of carbons, *24th Symposium (International) on Combustion*, The Combustion Institute, Pittsburgh, 1145.
21. Miller C.A, Srivastava R.K and Ryan J.V (1994): Emissions of organic hazardous air pollutants from the combustion of pulverized coal in a small-scale combustor, *Environ. Sci. Technol.*, **28**, 1150.
22. Mojtahedi W, Nieminen M, Hulkkonen S and Jahkola A (1990): Partitioning of trace elements in pressurized fluidized-bed combustion, *Fuel Process. Technol.*, **26**, 83.
23. Patterson W.C (1993): *Coal-use Technology. New challenges, new responses*, Financial Times Business Information, London.

24. Prins W (1987): *Fluidized Bed Combustion of a Single Carbon Particle*, Ph.D Thesis, Twente University of Technology, The Netherlands.
25. Querol X, Fernández–Turiel J.L and López–Soler A (1995): Trace elements in coal and their behaviour during combustion in a large power station, *Fuel*, **74**, 331.
26. Redman J (1989): Control of NO_x emission from large combustion plant, *Chem. Eng.*, March, 33.
27. Reyes S and Jensen K.F (1986): Percolation concepts in modelling of gas–solid reactions–II. Application to char gasification in the diffusion regime, *Chem. Engng. Sci.*, **41**, 345.
28. Sahimi M (1990): Diffusion, absorption, and reaction in pillared clays. I. Rod–like molecules in a regular pore space, *J. Chem. Phys.*, **92**, 5107.
29. Sahimi M (1994): *Applications of Percolation Theory*, Taylor and Francis, London.
30. Sahimi M, Gavalas G.R and Tsotsis T.T (1990): Statistical and continuum models of fluid–solid reactions in porous media, *Chem. Engng. Sci.*, **45**, 1443.
31. Sotirchos S.V and Burganos V.N (1986): Intraparticle diffusion and char combustion, *Chem. Engng. Sci.*, **41**, 1599.
32. Stadtherr M.A, Cofer H.N and Camarda K.V (1993): Hardware: Developing the metacomputer, *Chem. Engng. Prog.*, Nov., 27.
33. Stanmore B.R and Jung K (1980): The burnout rates of brown coal char particles in fluidized bed combustors, *Trans. IChemE*, **58**, 66.
34. Stauffer D and Aharony A (1992): *Introduction to Percolation Theory (2nd ed.)*, Taylor & Francis, London.
35. Summers J.S (1992): Reduction of carbon dioxide emissions through efficiency improvements in IGCC electrical power generation, *Energy Convers. Mgmt.*, **33**, 713.

36. Topper J.M, Cross P.J.I and Goldthorpe S.H (1994): Clean coal technology for power and cogeneration, *Fuel*, **73**, 1057.
37. Valix M.G, Trimm D.L, Smith I.M and Harris D.J (1992): Mass transfer effects in coal combustion, *Chem. Engng. Sci.*, **47**, 1607.
38. Williams B.C, McMullan J.T and Campbell P (1994): Clean power generation from coal, *Fuel*, **73**, 1069.
39. Wojtowicz M.A, Pels J.R and Moulijn J.A (1993): Combustion of coal as a source of N₂O emissions, *Fuel Process. Technol.*, **34**, 1.

CHAPTER 2

THE CO/CO₂ PRODUCT RATIO FOR A POROUS CHAR PARTICLE WITHIN AN INCIPIENT FLUIDIZED BED: A NUMERICAL STUDY

2.1 INTRODUCTION

Both particle disintegration [Salatino and Massimilla, 1988; Miccio and Salatino, 1992], and N₂O production [Krammer and Sarofim, 1994], are influenced by the degree of oxygen penetration into a burning char particle. By physically inspecting chars burnt at two different temperatures, Prins (1987) showed that the degree of oxygen penetration is sensitive to particle temperature. As ash viscosity is highly temperature dependent within the fluidized bed combustion (FBC) regime [Raask, 1985], its fate is also dictated by the particle temperature. The importance of these issues from FBC design, operational and environmental perspectives clearly indicates that the temperature of burning particles needs to be modelled with accuracy.

In principle, prediction of char particle temperature requires knowledge of four factors: the relevant heat and mass transfer coefficients, the char combustion kinetics, and the particle related CO/CO₂ product ratio. The last of these has been the subject of two recent experimental and modelling studies [Prins, 1987; Linjewile, 1993]. By measuring flue gas levels of CO and CO₂ and accounting for CO oxidation within the bed and freeboard, Prins (1987) found the particle related CO/CO₂ product ratio varied between 0.17 and 0.5. He was unable, however, to determine any correlation between the ratio and char particle size or temperature, or inert particle size. By developing a novel technique for sampling the gas at or near the surface of a large burning char particle, Linjewile (1993) investigated these issues using 3–11 mm petroleum coke chars within an incipient fluidized bed. Although his product ratios compared well with those of Prins (1987), Linjewile (1993) was unable to establish any correlation between the measured CO/CO₂ product ratio, and either bed or active particle size. He did find, however, a

relationship between the ratio and particle temperature, an example of which is shown in Figure 2.1 – the ratio first increases with temperature to a maximum at $T_a \approx 1000$ K, then decreases until $T_a \approx 1250$ K where, unexpectedly, it starts to increase once again. Using a simplified homogeneous film shrinking core model [Calleja et al., 1981], Linjewile (1993) was able to reproduce the maximum seen in Figure 2.1, but could not obtain the minimum. This lead him to suggest the following hypothesis:

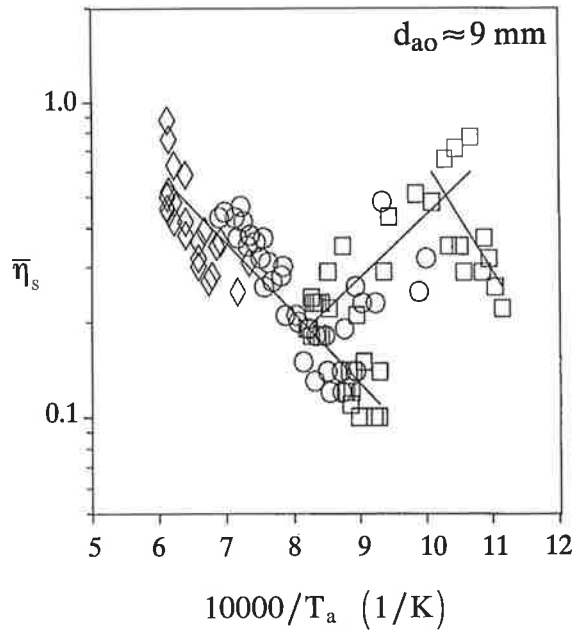


Figure 2.1. Surface CO/CO₂ product ratio vs inverse particle temperature [Linjewile, 1993].

- At low particle temperatures, oxygen penetrates deep into the char so as to react with the solid to form both CO and CO₂ according to the primary CO/CO₂ product ratio. As homogeneous reaction is negligible at these low temperatures, little primary-CO is converted to CO₂ leading to a surface CO/CO₂ product ratio that increases with temperature in accordance with the primary ratio.
- As the particle temperature increases, however, homogeneous conversion of primary-CO to CO₂ *within the pores* becomes increasingly significant, leading to the surface CO/CO₂ product ratio to pass through a local maximum at intermediate FBC temperatures, and then diminish with increasing temperature.
- As particle temperature increases towards the maximum normally encountered under typical FBC conditions, heterogeneous reaction at the particle external surface prevents oxygen penetration into the char. Assuming that the inert particles quench boundary layer reaction [Prins, 1987; Hayhurst, 1991], secondary oxidation of CO no longer occurs leading to the surface CO/CO₂ product ratio to pass through a local minimum, and then increase with particle temperature.

This hypothesis relies upon several assumptions, namely: (1) that both CO and CO₂ are primary products; (2) that homogeneous reaction does not occur within the boundary layer of a particle resident in the emulsion phase; and (3) that significant intraparticle homogeneous reaction does occur.

Although the first assumption has received much attention [Arthur, 1951; Rossberg, 1956; Walker et al., 1959; Phillips et al., 1970; Ayling and Smith, 1972; Basu et al., 1975; Prins, 1987; Tognotti et al., 1990], there is still confusion over whether both CO and CO₂ are primary products at typical FBC temperatures [eg: compare introductions of Tognotti et al. (1990) and Hayhurst (1991)]. Perhaps the most reliable values available to date are those of Tognotti et al. (1990) which are determined by heating single Spherocarb particles within an ambient environment by laser irradiation. By maintaining the surrounding gas at room temperature, this approach elegantly avoids, for a wide range of conditions, one of the main concerns when experimentally determining the primary CO/CO₂ product ratio – secondary oxidation of primary – CO to CO₂ in the particle boundary layer [Tognotti et al., 1990]. Their results strongly suggest that both CO and CO₂ are primary products at typical FBC temperatures.

It is not at all clear if homogeneous oxidation of CO does, or does not, occur within the boundary layer of a particle resident in the emulsion phase. By modelling *steady state* transport and reaction within a *stagnant* boundary layer of an *impervious* char particle, Caram and Amundson (1977) conclude CO oxidation will occur within the boundary layer provided the char diameter is greater than 100 µm. Using a similar but simplified analysis, Ross and Davidson (1982) suggest that the extent of boundary layer reaction tends to increase with particle size, with it being negligible for particles smaller than 500 µm. Normal char particle and bed (inert particles and gas) motion, however, makes extrapolation of these steady state scenarios to FBC conditions uncertain [La Nauze, 1985]. Using experimental observations and physical arguments, Prins (1987) concludes that CO oxidation does not occur within the boundary layer of a char particle resident within the emulsion phase of a bubbling fluidized bed. His adjusted (for reaction in bed

bulk and freeboard) ratio values of 0.17–0.5, however, do not compare well with the primary values of either Arthur (1951) or Tognotti et al. (1990) suggesting that CO conversion to CO₂ must be occurring within the char, the boundary layer, or both. Supporting the conclusions of Prins (1987), Hayhurst (1991) argues, for typical FBC conditions, that promotion of radical recombination by inert particle surfaces inhibits CO oxidation within the boundary layer. On the other hand, both Basu et al. (1975) and Stubington and Chan (1990) show that CO oxidation can occur within the emulsion phase at temperatures typical of FBC.

Even less is known about the occurrence, or not, of intraparticle homogeneous reaction. Some have argued that intraparticle homogeneous CO oxidation will be enhanced by impurities embedded within the pore walls [Blackwood and McGrory, 1958], whilst others have suggested it may in fact be quenched by the pore walls [Hayhurst, 1991].

In view of the many uncertainties associated with the hypothesis of Linjewile (1993) (viz: the three assumptions above), and the fact that he was unable to confirm it using a simplified single particle model, a more sophisticated study was undertaken – this study is described in this chapter. The chapter is set out as follows. In preparation for presentation of the model used here, the following section briefly reviews the various existing single particle FBC models. In Section 2.3, the model used in this work is described, and the results obtained from it are presented and discussed. In particular, by comparing the results obtained here with those of Linjewile (1993), the following questions are considered:

- Does homogeneous reaction occur within the boundary layer of a char resident in the emulsion phase ?
- Does significant intraparticle homogeneous reaction occur ?
- What are the causes of the various phenomena seen in Figure 2.1 ?
- How does the particle related product ratio vary with active particle size ?
- Are the product ratios measured by the Linjewile (1993) approach meaningful ?

The chapter is then concluded with a discussion of possible future work.

2.2 OVERVIEW OF EXISTING SINGLE PARTICLE FBC MODELS

A porous char particle may burn in one of three ways:

- Regime I – kinetic (or reaction) control: the char oxidants fully penetrate throughout the pore structure; the particle size remains constant whilst the density decreases.
- Regime II – pore–diffusion and reaction control (or, simply, diffusion control): the char oxidants partially penetrate the pore structure; both the particle size and density decrease. Oxidant penetration may be significant, partial, or largely restricted to a small zone just under the particle surface.
- Regime III – external mass transfer control: the char oxidants do not penetrate the particle at all due to the slowness of the boundary layer diffusion process relative to reaction; the particle density remains constant whilst its size decreases.

Traditionally [Basu, 1985], single particle FBC models have been based upon the *shrinking core* paradigm in which all heterogeneous combustion is assumed to occur at the external surface of the particle (regime III), or where all intraparticle phenomena are arbitrarily lumped at the external surface [Yagi and Kunii, 1955]. Despite wide usage of the shrinking core model [Basu, 1985], there is extensive experimental evidence indicating that intraparticle combustion does occur under typical FBC conditions [Jung and Stanmore, 1980; Pillai, 1981; Daw and Krishnan, 1982; Jung and La Nauze, 1983; Jung, 1987; Prins, 1987; Vleeskens and Hamburg, 1991; Linjewile 1993; Fuertes et al., 1994], and that the shrinking core model cannot represent many of the phenomena arising from it (eg: non – monotonic variation of char reactivity with conversion). In light of this fact, and given our interest in investigating the various issues raised in the Introduction, the shrinking core model shall receive no further attention here – the reader is referred to the reviews of Basu (1985) and others [Saxena, 1990; Bhatia and Gupta, 1992].

Table 2.1(a). Summary of past single particle FBC models which include intraparticle phenomena [see Table 2.1(b) for key].

Study	A	B	C	D	E	F	G	H
Stanmore and Jung (1980)	a	III(0)	a	I(S)	a	I	a	N
Turnbull et al. (1984)	a	III(1)	b	I(S)	b(S)	I	a	N
Borghi et al. (1985)	b	III(1)	b	I(S)	b(T)	—	b	N
Prins and van Swaaij (1986)	a	II(1)	b	I(S)	b(S)	I	a	N
Brem and Brouwers (1990)	c	I	b	I(S)	c(S)	II	b	Y
Prins (1987) and Prins and van Swaaij (1990)	c	I(1)	b	II(S)	b(S)	II	b	Y
This work [‡]	c	IV(1)	c	II(T)	c(T)	III	c	Y

‡ For comparison purposes.

Although a reasonable number of reported single particle modelling studies consider intraparticle phenomena, the majority are directed towards the study of char combustion in general [review: Sotirchos et al., 1984], the development of new pore evolution models [reviews: Sahimi et al., 1990; Bhatia and Gupta, 1992], or the testing of various intraparticle mass flux models [eg: Sotirchos and Burganos, 1986] – compare Sahimi et al. (1990), Bhatia and Gupta (1992), and Smith et al. (1993) with Basu (1985). The few that specifically address FBC* are summarized in Table 2.1, and are grouped according to their purpose. The first group [Stanmore and Jung, 1980; Turnbull et al., 1984; Borghi et al., 1985; Prins and van Swaaij, 1986] are primarily concerned with the prediction of more general char combustion characteristics such as burnout time, and particle temperature. The study of Brem and Brouwers (1990) is aimed at the development of a model that captures the essential character of the intraparticle combustion process, whilst being simple enough for inclusion within a combustor code [Brem, 1990]. The last

* Studies which consider $923 \leq T_b \leq 1273$ K, $1 \leq d_a \leq 10$ mm, and FB boundary conditions.

Table 2.1(b). Key to Table 2.1(a)

A – Pore system evolution model				
a.	Particle mass conservation (progressive conversion model).			
b.	Single pore model similar to that of Petersen (1957).			
c.	Local mass conservation.			
B – Reactions	I	II	III	IV
$C + O_2 \rightarrow CO_2$	●		●	
$2C + O_2 \rightarrow 2CO$			○	
$C + CO_2 \rightarrow 2CO$				●
$2CO + O_2 \rightarrow 2CO_2$			○	●
Open circle (○) indicates reaction is implicit in overall reaction scheme adopted.				
Shaded ellipse indicates CO and CO ₂ are both primary products of C + O ₂ reaction.				
Open ellipse indicates either CO or CO ₂ are primary products of C + O ₂ reaction, but not both.				
(Number in parenthesis indicates assumed order of C+O ₂ reaction)				
C – Boundary layer treatment				
a.	Negligible boundary layer resistance.			
b.	Implicit inclusion of boundary layer via flux boundary conditions in conjunction with heat and mass transfer coefficients.			
c.	Explicit inclusion of boundary layer.			
D – Mass conservation formulation				
I.	Fick's law.			
II.	Nonisobaric, multicomponent (4 species) Dusty–gas model.			
(S and T in parenthesis indicates either pseudo steady state or transient formulation)				
E – Heat conservation formulation				
a.	Constant temperature particle.			
b.	Isothermal particle.			
c.	Nonisothermal particle.			
(S and T in parenthesis indicates either pseudo steady state or transient formulation)				
F – Dependence of mass transport properties on pore structure and its evolution.				
I.	Conversion independent.			
II.	Empirical correlation [ϕ –dependent only].			
III.	Percolation model as per Mohanty et al. (1982); Shah and Ottino (1987).			
G – Dependence of reactivity parameters on pore structure and its evolution.				
a.	Conversion independent.			
b.	Emperical correlation [ϕ –dependent].			
c.	Percolation model as per Mohanty et al. (1982); Shah and Ottino (1987).			
H – Secondary disintegration [Chirone et al., 1991] included (Y) or not (N).				

[Prins, 1987; Prins and van Swaaij, 1990] is a more fundamental study aimed at investigating how the character of the intraparticle combustion process changes with bed temperature, char particle size and conversion (eg: oxygen penetration depth, particle porosity profiles). The model used in this study is also shown in Table 2.1 for comparison purposes only. In preparation for the development of this model, a detailed review of the earlier models is now undertaken by considering the four physiochemical issues that must be addressed when developing such models: (1) intraparticle mass and energy conservation and transport; (2) the combustion chemistries; (3) the porous char structure and its evolution; and (4) char–FB interaction.

2.2.1 Intraparticle Mass and Energy Conservation and Transport

The standard approach to modelling transport and reaction within a porous solid is to invoke the smooth field approximation (SFA) [Jackson, 1977] in which the fluid/porous solid system is visualized as a continuum over which process parameters vary smoothly in space and time. By applying the SFA to an g –component fluid/porous solid system in which $\mathcal{R}$ reactions are taking place, the conservation of molar concentration for species– i , C_i , may be expressed as

$$\frac{\partial}{\partial t}(\phi_a C_i) + \nabla \cdot \mathbf{N}_i = \sum_{r=1}^{\mathcal{R}} \nu_{ri} \dot{\Omega}_{pr} \quad (2-1)$$

where ν_{ri} and $\dot{\Omega}_{pr}$ are the stoichiometric coefficient of species– i and molar rate–of–reaction per unit porous solid volume for reaction– r respectively, ϕ_a the accessible porosity, and $\mathbf{N}_i$ the molar flux vector of species– i . The conservation equation for total molar concentration, C , is obtained on summing equations (2–1) over the species index

$$\frac{\partial}{\partial t}(\phi_a C) + \nabla \cdot \mathbf{N} = \sum_{i=1}^g \sum_{r=1}^{\mathcal{R}} \nu_{ri} \dot{\Omega}_{pr} \quad (2-2)$$

where we have used the identities

$$\sum_{i=1}^g C_i = C \quad (2-3)$$

and

$$\sum_{i=1}^g \mathbf{N}_i = \mathbf{N} \quad (2-4)$$

and $\mathbf{N}$ is the total molar flux vector. Equations (2-1) and (2-2) form the basis for all of the models of Table 2.1. In every case, spherical symmetry is assumed, whilst most also invoke the pseudosteady state approximation [Froment and Bischoff, 1990].

Constitutive expressions for the fluxes $\mathbf{N}_i$ and $\mathbf{N}$ are also required. Perhaps one of the most advanced, and certainly most popular, flux models, is the Dusty-gas model (DGM), which was developed by Mason and co-workers in the 1960s [Evans et al., 1961, 1962; Mason et al., 1963; Mason and Malinauskas, 1964], and has since been reviewed a number of times [Mason et al., 1967; Jackson, 1977; Mason and Malinauskas, 1983]. In its most general form, the DGM accounts for mass transfer via Knudsen, molecular and surface diffusion, viscous flow, thermal transpiration, and the Soret effect. Ignoring surface and thermal diffusion (Soret effect, thermal transpiration), one possible form of the DGM is [Jackson, 1977]

$$\frac{\mathbf{N}_i}{D_i} + \sum_{j=1}^g \frac{X_j \mathbf{N}_i - X_i \mathbf{N}_j}{D_{ij}} = - \frac{P}{R_u T} \nabla X_i - \frac{X_i}{R_u T} \left(1 + \frac{B_o P}{\mu D_i} \right) \nabla P \quad (2-5)$$

where $X_i = C_i/C$ is the mole fraction of species- i , μ the gas mixture viscosity, P and T the pressure and temperature respectively, and R_u the universal gas constant. The effective transport properties of the fluid/porous solid system are defined by the permeability, B_o , the Knudsen diffusivity

$$D_i = K_o \sqrt{\frac{8 R_u T}{\pi m_i}} \quad (2-6)$$

and, the effective binary diffusivity

$$D_{ij} = K_1 \mathfrak{D}_{ij} \quad (2-7)$$

where m_i is the molecular weight of species- i , and $\mathfrak{D}_{ij}$ the Chapman-Enskog binary diffusion coefficient [Bzowski et al., 1990]. The permeability is a property of the porous solid only, and is defined by the solid's pore structure connectivity, pore size distribution, and porosity. The factor K_o is also exclusively dependent upon these factors, whilst K_1 is determined by the solid's pore structure connectivity and porosity only. The

conceptual model used to derive the DGM, unfortunately, reveals little of how K_o , K_1 and B_o may be related to measurable porous solid structural parameters [Mason et al., 1967]. It is for this reason that Mason et al. (1967) advocate use of transport coefficients determined from diffusion and permeability experiments on the solid in question, rather than those obtained from some simple and unrelated pore system model. This approach is adopted by Prins and co-workers [Prins, 1987; Prins and van Swaaij, 1990] who use the empirical correlations of Blik (1984) to define the local char permeability

$$B_o = 4 \times 10^{-11} \frac{\phi^3}{(1 - \phi)^2} \quad (2-8)$$

and effective binary diffusivity

$$D_{ij} = 0.4\phi^3 D_{ij} \quad (2-9)$$

where ϕ is the the local porosity. They also use the Knudsen diffusivity

$$D_i = \frac{\bar{r}_p}{6} \sqrt{\frac{8R_u T}{\pi m_i}} \quad (2-10)$$

where $\bar{r}_p$ is the mean pore radius. Comparison of these expressions with the definitions set out above clearly indicate their inadequacy – B_o is not (explicitly) dependent upon the pore size distribution, whilst D_i is defined on the basis of an average pore size only, and is therefore limited to unimodal porous solids [Abed and Rinker, 1974]. This highlights the difficulty associated with applying the Mason et al. (1967) philosophy to a burning char where the pore structure is constantly evolving in a non-trivial manner. The network approach of Feng and Stewart (1973) overcomes this problem at the expense of using a well defined pore model. Using the DGM to define fluxes at the pore level where simple and reliable expressions for the transport coefficients exist, Feng and Stewart (1973) determine the macroscopic fluxes by integrating the pore-level flux expressions, N_i^p , over the pore size distribution*

$$N_i = \int_{r_{p,min}}^{r_{p,max}} N_i^p(r_p) \phi(r_p) dr_p \quad (2-11)$$

* It may also be integrated over an orientation distribution if the porous solid is non-isotropic.

where $\phi(r_p)dr_p$ is the pore volume fraction associated with pores whose radii are between r_p and $r_p + dr_p$. By using an appropriate form of the DGM and ignoring both surface and thermal diffusion, equation (2–11) reduces to [Feng and Stewart, 1973; Jackson, 1977]

$$[N_1 \cdots N_g]^T = -\frac{1}{\kappa} \int_{r_{p,\min}}^{r_{p,\max}} \left[[C_1 \cdots C_g]^T \frac{r_p^2}{8\mu} \nabla P + [F(r_p)]^{-1} [\nabla C_1 \cdots \nabla C_g]^T \right] \phi(r_p) dr_p \quad (2-12)$$

where κ is the tortuosity [Epstein, 1989] that accounts for the various non-idealities of the pore system (eg: irregular pore sizes, deadend pores, pore loops), and $F(r_p)$ is an $g \times g$ matrix whose elements are defined by

$$F_{ij} = -\frac{X_i}{\mathcal{D}_{ij}} \text{ for } i \neq j$$

$$F_{ii} = \frac{1}{\mathcal{D}_i} + \sum_{\substack{j=1 \\ j \neq i}}^g \frac{X_j}{\mathcal{D}_{ij}} \quad (2-13)$$

with

$$\mathcal{D}_i = \frac{2r_p}{3} \sqrt{\frac{8R_u T}{\pi m_i}} \quad (2-14)$$

Application of equation (2–12) to the char combustion problem simply requires an initial pore size distribution, a method for integrating this distribution through time, and a tortuosity model. Initial pore size distributions may be determined from experiment [eg: Jung, 1987], whilst there are a variety of pore evolution models, discussion of which is deferred to §2.2.3. The tortuosity may be determined in a number of ways: (1) by fitting the Feng–Stewart flux model to experimental results [eg: Feng et al., 1974]; (2) by using a simple pore model [eg: $\kappa = 3$ for isotropic pore system with no deadend pores; Feng and Stewart, 1973]; (3) indirectly from consistent volume averaging techniques such as EMA and Monte–Carlo (MC) simulations [eg: Kirkpatrick, 1973]; and (4) indirectly from discrete simulations [eg: Abbasi et al., 1983]. Although detailed consideration of these

methods is deferred to the following chapter, it is perhaps pertinent to briefly look at the MC approach of Kirkpatrick (1973), which was used to determine the tortuosity utilized in this work.

In the Kirkpatrick approach, a solid of porosity, ϕ , is represented by a simple three dimensional cubic network in which a random fraction ϕ of the bonds are designated open with an effective diffusivity of one (ie: pores of the same size); the remainder are blocked so as to represent the solid. The effective diffusion coefficient of the “porous solid” is determined by solving the steady state diffusion problem on this network. Using the Kirkpatrick (1973) results, we may define the tortuosity by [Shah and Ottino, 1987]

$$\frac{\phi}{\kappa} = \begin{cases} 0 & \text{for } \phi < 0.32 \\ 1.509(\phi - 0.32)^{1.474} & \text{for } 0.32 < \phi \leq 0.68 \end{cases} \quad (2-15)$$

This function clearly reflects the fact that below $\phi = 0.32$ (the percolation threshold of the pore system), the pore space becomes a series of disconnected pores that do not permit mass transfer on a macroscopic scale. As the tortuosity is defined on the basis of a consistent volume average, the function also captures the effect of pore loops. However, as only the steady state diffusion problem is considered, deadend pores play no role in the simulated diffusion process (they do physically exist within the network), whilst assigning the same diffusivity to each open bond restricts use of equation (2–15) to unimodal porous solids. Although these problems may be addressed [eg: pore sizes may be assigned to the open bonds from an experimentally determined pore size distribution; Sharratt and Mann, 1987], recent studies show that there are more fundamental concerns. For example, use of a regular lattice to determine effective transport properties of a complex irregular pore space is justified on the basis that provided the connectivity of a regular lattice is the same as the average connectivity of an irregular lattice, their percolation properties are the same [Jerauld, 1984a, b]. However, Hollewand and Gladden (1992a, b) have demonstrated that the effective diffusion coefficient of regular and irregular networks having the same average connectivity are not equal for low coordination numbers ($Z \leq 6$), and only show

insignificant differences once $Z \geq 14$. It has also been demonstrated that widely different effective transport properties may be predicted for a system depending upon the network model used [Hollewand and Gladden, 1992a, b]. Finally, effective diffusion coefficients determined under non-reactive conditions may be unsuitable for use with reacting systems [Muthukumar, 1982; Cukier and Freed, 1983; Hollewand and Gladden, 1992a; McGreavy et al., 1992; see, however, Zhang and Seaton, 1994].

Assuming an isotropic unimodal porous solid, the Feng–Stewart model, equation (2–12), reduces to the Dusty–gas model – this permits identification of the DGM parameters K_0 and K_1 , see equations (2–6) and (2–7), with the tortuosity of the Feng–Stewart model

$$K_0 = K_1 = \frac{\phi}{\kappa} \quad (2-16)$$

The relative complexity of the Dusty–gas and network model formulations, means most models of Table 2.1 utilize a Fickian flux expression of the form

$$\mathbf{N}_i = -D_{ie} \nabla C_i \quad (2-17)$$

where D_{ie} is a conversion independent effective diffusion coefficient. This expression is only valid under strict conditions. Some [Stanmore and Jung, 1980; Borghi et al., 1985] set $D_{ie} = D_i$ which may be identified with the small pore limit of the DGM under isothermal–isobaric conditions [Jackson, 1977]. Others [Turnbull et al., 1984; Prins and van Swaaij, 1986; Brem and Brouwers, 1990] assume $D_{ie} = \text{constant}$ which is valid for isothermal–isobaric equimolar counterdiffusion of a binary fluid within a solid whose pores are much larger than the mean free path (large pore limit) [Jackson, 1977]. Whilst some of these assumptions may be appropriate (eg: isothermal), others such as the isobaric condition and equimolar counterdiffusion are known to be generally invalid, and physically inconsistent, under reactive conditions [Jackson, 1977; Hite and Jackson, 1977].

In general, the conservation of energy equation must also be solved in conjunction with the species and total molar concentration equations (2–1) and (2–2). Assuming negligible convective heat transfer, the energy conservation equation becomes

$$C_e \frac{\partial T}{\partial t} - \nabla \cdot (\lambda_e \nabla T) = \sum_{r=1}^{\mathfrak{R}} (-H_r) \dot{\Omega}_{pr} \quad (2-18)$$

where C_e and λ_e are the effective thermal capacitance and conductivity of the fluid/porous solid system respectively, and H_r the enthalpy-of-reaction for reaction- r . The effective thermal capacitance of a char may be defined by

$$C_e = (1 - \phi) \rho_{ct} C_{ct} + \phi \sum_{i=1}^g C_i C_{pi} \quad (2-19)$$

where ρ_{ct} and C_{ct} are the density and specific heat of the char material respectively, and C_{pi} the specific heat at constant pressure of species- i . The recent review of Hanrot et al. (1994) indicates our knowledge of C_{ct} is reasonable. Merrick (1983) proposed a semi-empirical correlation for daf coke based upon Einstein's quantum theory for specific heat of (crystalline) solids

$$C_c = \frac{R_u}{m_c} \left[g\left(\frac{380}{T}\right) + 2g\left(\frac{1800}{T}\right) \right] \quad (2-20)$$

where m_c is the average molecular weight of the char material, 380 K and 1800 K the experimentally determined characteristic Einstein temperatures of the daf char material, and $g(\theta)$ the Einstein specific heat function

$$g(\theta) = \frac{\theta^2 e^\theta}{(e^\theta - 1)^2} \quad (2-21)$$

Although application of Einstein's theory to amorphous solids such as coal char is questionable, equation (2-20) has recently been verified for daf coke [Hanrot et al., 1994]. The effect of ash may be included by a weighted sum [Merrick, 1983; Hanrot et al., 1994]

$$C_{ct} = w_c C_c + w_a C_a \quad (2-22)$$

where C and w are the specific heat and mass fraction of the various char components respectively. Hanrot et al. (1994) summarize existing correlations for C_a . Whilst the weighted average principle is valid for an ideal gas mixture, its applicability for coal chars has only been established recently [Richardson, 1993].

Since the original work of Maxwell (1892), much effort has been directed towards modelling the effective thermal conductivity of porous (composite) solids [reviews:

Winterfeld, 1981; Hahne et al., 1991]. Despite this fact, knowledge of how char effective thermal conductivity varies with conversion is poor [Atkinson and Merrick, 1983; Annamalai and Ryan, 1993]. Sotirchos and Amundson (1984a, b, c, d) suggest

$$\lambda_e = (1 - \phi)^2 \lambda_{ct} + \phi^2 \lambda_g \quad (2-23)$$

where λ_{ct} and λ_g are the thermal conductivities of the char material and interstitial gas mixture respectively. Equation (2-23) is infact a corruption of the Butt (1965) model which is based upon the pore diffusion model of Wakao and Smith (1962) – this explains the presence of the porosity–squared term which has no obvious basis. Despite almost universal usage, the suitability of this equation for describing the effective thermal conductivity of a burning char has not been verified. The only other approach taken in the char combustion literature to calculate λ_e [Shah and Ottino, 1987] is the Effective Medium Approximation [eg: Helte, 1993]; this approach is briefly reviewed in the following chapter.

Knowledge of λ_{ct} is also very poor [Atkinson and Merrick, 1983; van Krevelen, 1993]. Indeed, despite there being a substantial amount of experimental data on the effective thermal conductivity of chars, coals and cokes [see references of: Atkinson and Merrick, 1983; van Krevelen, 1993], no correlation for λ_{ct} is known to this author. Using experimental data of others, Atkinson and Merrick (1983) do propose, however, the following correlation for carbonaceous material

$$\lambda_c = \left(\frac{\rho_c}{4511} \right)^{3.5} T^{0.5} \quad \text{W/mK} \quad (2-24)$$

where ρ_c is the density of carbonaceous material in kg/m^3 , and T the temperature in K.

None of the studies of Table 2.1 use the transient non–isothermal equation (2-18). Brem and Brouwers (1990), however, simulate a non–isothermal particle under steady state conditions

$$\nabla \cdot (\lambda_e \nabla T) + \sum_{r=1}^R (-H_r) \dot{\Omega}_{pr} = 0 \quad (2-25)$$

where the effective thermal conductivity is defined by equation (2-23) in conjunction with unspecified constant values for λ_{ct} and λ_g . Borghi et al. (1985) simulate a transient

isothermal particle

$$C_e \frac{\partial T}{\partial t} = \sum_{r=1}^{\mathfrak{R}} (-H_r) \dot{\Omega}_{pr} - \frac{6h_e}{d_a} (T - T_b) - \frac{6\sigma\epsilon_a}{d_a} (T^4 - T_b^4) \quad (2-26)$$

where d_a is the char particle size, ϵ_a its emissivity, σ the Stefan–Boltzmann constant, and h_e the effective heat transfer coefficient of the char, discussion of which is deferred to a latter section. A constant C_e of unspecified origin is used. Excepting Stanmore and Jung (who assume $T_a = \text{constant}$), the remainder assume a steady state isothermal formulation

$$\sum_{r=1}^{\mathfrak{R}} (-H_r) \dot{\Omega}_{pr} - \frac{6h_e}{d_a} (T - T_b) - \frac{6\sigma\epsilon_a}{d_a} (T^4 - T_b^4) = 0 \quad (2-27)$$

where Prins and co-workers [Prins, 1987; Prins and van Swaaij, 1990] do not include radiation heat transfer (ie: the third term of the left hand side) – radiation has been shown to be an important mode of heat transfer [Sotirchos et al., 1984].

Despite wide adoption of the isothermal assumption, its validity is questionable [Annamalai and Ryan, 1993]. Linjewile et al. (1994) recently found an average 30K temperature difference between the centre and surface of a burning 8mm coke particle in 950K convective flow, with this temperature difference increasing markedly near burnout. Such temperature differences are likely to be exacerbated by conditions which reduce oxygen penetration into the char particle such as high bed temperatures and high reactivity chars. Theoretical calculations [Sotirchos and Amundson, 1984a, b, c, d; Brem and Brouwers, 1990] have demonstrated that inclusion of non–isothermal effects can significantly influence the predicted char particle behaviour.

Without exception, all existing single particle FBC models are based upon a continuum formulation which is arrived at by averaging the non–homogeneous effects of the pore network and solid phase over a volume that is significantly larger than the characteristic dimensions of the char, but small when compared its overall size. If the pore system or solid phase of the char demonstrate some percolation threshold at $\theta = \theta_c$ ($\theta \equiv \phi$ and

$\theta \equiv \bar{\phi}$ for pore system and solid phase respectively)*, then the characteristic dimensions (correlation lengths) of the char scale as [Rammal and Toulouse, 1983]

$$\xi \sim |\theta - \theta_c|^{-\nu} \quad (2-28)$$

where ν is a positive universal scaling exponent. Clearly, as $\theta \rightarrow \theta_c$, $\xi \rightarrow \infty$ (or, more correctly for a char of size $\mathcal{L} \sim V^{1/3}$, $\xi \rightarrow \mathcal{L}$) – this fact cannot be reconciled with the averaging process required for derivation of the continuum equations [Sahimi et al., 1990]. Existing models are also dependent upon the validity of the smooth field approximation which requires:

- the pore structure to be thoroughly cross-linked [Jackson, 1977];
- the pore system to be near-unimodal [Gavalas and Kim, 1981; Burganos and Sotirchos, 1987; Sotirchos and Burganos, 1988; Sotirchos, 1989]; and
- there to be no significant gradients within any pore [Jackson, 1977].

Clearly, both the smooth field and continuum approximations place severe limitations upon any model that adopts them – this issue will receive further airing in relation to future work latter in this chapter.

2.2.2 Combustion Chemistries

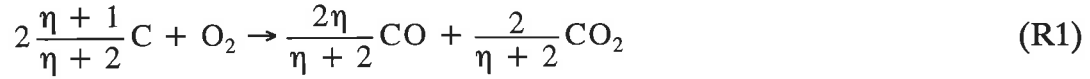
Char consumption within a system containing low levels of moisture primarily proceeds by two gas–solid reactions [Laurendeau, 1978]:

- an exothermic C–O₂ reaction which produces both CO and CO₂; and
- an endothermic C–CO₂ reaction which produces CO.

Although much work has been undertaken [Laurendeau, 1978; Marsh, 1978; Smith, 1982; Smith et al., 1993], kinetic models for these reactions are still poorly developed [Mitchell et al., 1990] – it is either for this reason or the sake of simplicity that all models of Table 2.1 use overall reaction schemes with empirical intrinsic rate expressions. The

* The percolation threshold of the pore system would be that porosity at which the system transitions from a set of isolated pores to one which spans the char, whilst that of the solid phase would be the solid fraction at which it becomes unconsolidated (ie: disintegration onset point).

most general of these schemes is [Sotirchos and Amundson, 1984d]



where η is the primary CO/CO₂ product ratio that may be correlated by the Arrhenius relationship

$$\eta = A e^{-B/T} \quad (2-29)$$

in which A and B are determined from experiment [Arthur, 1951; Tognotti et al., 1990]. The carbon–oxygen reaction scheme, R1, recognizes that both CO and CO₂ may be primary products of this reaction at FBC temperatures. On the basis of early work [eg: Arthur, 1951], however, almost all models of Table 2.1 assume that CO is the sole primary product. Presumably as a result of their own experimental findings (where they argue that the primary CO/CO₂ product ratio is 0.17–0.5), Prins and co-workers [Prins, 1987; Prins and van Swaaij, 1990], assume that CO₂ is the only primary product.

There is considerable uncertainty associated with the intrinsic reaction rate of the carbon–oxygen reaction. For example, after reviewing the available literature, Laurendeau (1978) indicates that the true reaction order, m , will vary according to the following rule-of-thumb: $m \approx 0$ for $T \leq 900$ K, $m \approx 0.5$ for $900 \leq T \leq 1500$ K, and $m \approx 1$ $T \geq 1500$. The review of Smith (1978), however, provides little support for Laurendeau's rough convention – 14 of the 18 *experimental* orders given by Smith do not conform to this hierarchy at all. The review of Suuberg et al. (1988) also suggests that there is no apparent correlation between reaction order and char impurity levels, pretreatment or reaction surface area. There are many reasons proposed for this variability [Laurendeau, 1978; Smith, 1982], but perhaps the most interesting is the recent observation that confidence in the predicted reaction order may be substantially improved by accounting for homogeneous oxidation of CO near and within the particle [Waters et al., 1988]. Uncertainty in the reaction order and the mathematical advantages of using a first order reaction rate, mean most studies of Table 2.1 assume first order dependency on O₂ concentration for the carbon–oxygen reaction

$$\dot{\Omega}_{s1} = k_1 C_{O_2} \quad (2-30)$$

Reported values of the rate constant, k_1 , also show considerable variation. Smith (1978) found, for example, that the intrinsic reactivity of petroleum coke is about four orders of magnitude higher than that of graphon at 775 K. Such large differences may be attributed to varying levels of catalytic and inhibitive activity, and differences in char chemical structure [Smith, 1978, 1982; Garcia and Radovic, 1986; Floess et al., 1988; Ballal et al., 1988; Gopalakrishnan et al., 1994]. Some differences, however, may be ascribed to the range of different models used to determine rate constants, and deficiencies associated with these models. For example, the reaction rate under Regime I of a first order heterogeneous reaction (such as R1 ?) can be expressed as [Laurendeau, 1978]

$$\dot{\Omega}_m(T, X) = k(T) C_s(X) C_g \quad (2-31)$$

where $k(T)$ is the *temperature dependent* rate constant, $C_s(X)$ the *conversion dependent* active site concentration, and C_g the reactant concentration at the gas–solid interfaces. This equation indicates that the rate constant of a char may be determined from experiment by dividing the experimentally measured rate, $\dot{\Omega}_m$, by $C_s C_g$. As direct measurement of C_s and C_g is not possible, a model must be used to determine them on the basis of known quantities such as particle temperature and ambient oxygen concentration. Many models assume $C_s \propto S_t$ where S_t is the *total surface area* (TSA) as measured by either N_2 or CO_2 adsorption [eg: Smith and Tyler, 1972; Hargrave et al., 1986; Valix et al., 1992]. Studies have demonstrated, however, that char consumption is not correlated with TSA in general, and that use of this area to determine rate constants may be much in error [Khan, 1987; Zhu et al., 1989; Lizzio et al., 1990; Radovic et al., 1991]. Other areas of model concern include: (1) intraparticle diffusion coefficients if rates are determined under regime II conditions [Valix et al., 1992]; (2) pore system evolution models [Sandmann and Zygourakis, 1987]; (3) the occurrence or not of homogeneous CO oxidation within the particle and its boundary layer [Waters et al., 1988]; and (4) the primary product ratio [Young and Niksa, 1988]. Rate parameters determined from experiment will depend upon how each of these issues is addressed.

As the intrinsic reaction rate of R2 is *nominally* much less than that of R1 [Laurendeau, 1978], all of the single particle FBC models of Table 2.1 neglect the CO₂ gasification reaction. This assumption, however, may be invalid for those chars which contain significant microporosity [Ballal and Zygourakis, 1987; Sandmann and Zygourakis, 1987] or catalysts that preferentially enhance the reaction [Ballal and Zygourakis, 1986; Ballal et al., 1988], and for those conditions under which oxygen penetration into the particle is slight when compared to that of CO₂ [Smith et al., 1993]. Kinetic studies of the reaction R2 clearly support a first–order dependency on CO₂ concentration for the intrinsic reaction rate at atmospheric pressures [Laurendeau, 1978]

$$\dot{\Omega}_{s2} = k_2 C_{CO_2} \quad (2-32)$$

Once again, rate constants appear to depend upon char type [Dutta et al., 1977], although the degree of variation is less than that associated with the carbon–oxygen reaction [Laurendeau, 1978]. As with reaction R1, this may be attributed to different levels of catalytic activity [Freund, 1986; Furimsky et al., 1988; Floess et al., 1988], and the modeling issues raised previously.

As already indicated in the Introduction, oxidation of CO to CO₂ *may* also occur in the gas phase of the particle and boundary layer provided water is present as a catalyst. On the basis of experiment [Prins, 1987], the workers of Twente University [Prins, 1987; Prins and van Swaaij, 1986, 1990; Brem and Brouwers, 1990] assume no homogeneous reaction occurs within the vicinity of the char. The remainder do admit the occurrence, but only for heat balance purposes by assuming CO is the only primary product of the carbon–oxygen reaction, and that all [Jung and Stanmore, 1980; Borghi et al., 1985] or part [Turnbull et al., 1984] of this is in turn homogeneously converted to CO₂ within the char particle boundary layer. If homogeneous reaction is explicitly included, then the global scheme



is normally used [eg: Sotirchos et al., 1984] in conjunction with the following empirical rate expression of Howard et al. (1973)

$$\dot{\Omega}_{v3} = k_3 C_{CO} \sqrt{C_{O_2} C_{H_2O}} \quad (2-33)$$

Recent studies [Yetter et al., 1986; Wang and Rogg, 1993] have demonstrated, however, that a global reaction mechanism such as this cannot be used to accurately describe carbon monoxide oxidation over the complete range of process parameters. This fact partially accounts for the considerable variation in experimentally determined rate expressions and kinetic parameters [eg: Table I, Yetter et al., 1986; Table II, Howard et al., 1973].

2.2.3 Porous Char Structure and its Evolution

The least complicated of the porous solid models that accounts for intraparticle phenomena is the progressive conversion model. Although this model is used as a basis for several of the single particle FBC models of Table 2.1, its use of average instead of conversion-dependent properties severely limits its value as a char combustion modelling tool. For example, the experimental results of Tomkow et al. (1977) demonstrate that char internal surface area variation with conversion can be considerable and non-monotonic, whilst the correlations (2-8) and (2-9) clearly indicate the sensitivity of the effective transport properties to pore structure change. The model is also limited by the fact that it cannot yield local changes in porosity, only the change in char particle mass. Consequently, determination of burnout time is limited to situations in which the Thiele modulus is large (ie: near Regime III) [eg: Jung and Stanmore, 1980; Turnbull et al., 1984], or small (ie: Regime I). Moreover, as peripheral disintegration is caused by the local solid structure becoming unconsolidated as carbon is consumed, this important process of particle size decrease [Gavalas, 1981] cannot be explicitly included.

The workers of Twente University [Prins, 1987; Prins and van Swaaij, 1990; Brem and Brouwers, 1990] adopt a macroscopic approach in which porosity change throughout the char is determined via local solid mass conservation principles

$$\frac{d\phi(r)}{dt} = - \frac{m_c}{Q_c} \sum_{r=1}^R v_{rc} \dot{\Omega}_{pr}(r) \quad (2-34)$$

Although this approach addresses many of the concerns associated with the progressive conversion model without significantly increasing model complexity, it prevents rigorous* treatment of pore size evolution and its attendant effects (ie: change in effective reactivity and transport properties). Such considerations may be addressed by considering a specific picture of the pore system such as the random pore model [Gavalas, 1980; Bhatia and Perlmutter, 1980, 1981] or pore tree model [Simons, 1983]. By far the most popular is the former, in which the pore system is assumed to be represented by a collection of infinitely long[‡] intersecting cylindrical pores of random orientation. This picture permits derivation of evolution equations for the porosity, total surface area (TSA), and pore size distribution to be solved in parallel with the macroscopic conservation–transport–reaction equations. By assuming infinitely long pores, however, the original random pore model implies that all of the pore space is accessible to the particle surface – this limitation is of major concern as many real chars do contain significant porosity that is initially inaccessible. Delikouras and Perlmutter (1991, 1993) extend the random pore model to consider such porosity. Although in principle this extension is straightforward, closure models are required for the rate at which inaccessible pores are revealed, and the effect this has on the rate of accessible porosity increase. The closure models used by Delikouras and Perlmutter were derived on the basis of simple physical arguments. Whilst adequate, they are not rigorous; Yu and Sotirchos (1987) and Sotirchos and Zarkanitis (1993) use, instead, percolation theory [Stauffer and Aharony, 1992; Sahimi, 1994]. Unlike the random pore and other continuum pore models [Simons, 1983], percolation theory *naturally* accounts for inaccessible porosity and other pore system *connectivity* related issues such as disintegration, and the effect that pore loops and deadends have on the effective transport properties [Sahimi et al., 1990].

Mohanty et al. (1982) were the first to use percolation concepts [Stauffer and Aharony, 1992; Sahimi, 1994] within the continuum framework to naturally describe the influence

* Pore size evolution can be included in an approximate manner using $r_p = 2\phi/S_t$ [Smith, 1982] where S_t is the surface area per unit char particle volume – eg: Reyes and Jensen (1986b).

‡ In comparison to the length scale of interest.

of pore system connectivity on char effective transport and reactivity properties. Although subsequent single particle studies of char combustion and gasification have also used percolation theory within the continuum framework [reviews: Sahimi et al., 1990; Sahimi, 1994], none have been specifically aimed at FBC. Reyes and Jensen (1986a, b) use a Bethe lattice representation of the pore space to study gasification of an isothermal char particle under Regime I and II conditions, whilst Srinivasachar et al. (1988) use a similar approach to study the influence of fragmentation on char combustion. As a discrete network representation of the pore system is adopted, both these studies include pore size evolution and consequent effects. However, the Bethe lattice is an inadequate pore system model in general [Sahimi et al., 1990]. Shah and Ottino (1987) study the effect of peripheral fragmentation on non–isothermal char gasification. By assuming the pore space can be represented by a continuous cubic tessellation in which a random fraction ϕ of the cubic polyhedra are void and the remainder solid, Shah and Ottino (1987) use the results of Mohanty et al. (1982) to estimate the local accessible porosity

$$\phi_a(\phi) = \begin{cases} 0 & 0 \leq \phi \leq 0.32 \\ 0.995(\phi - 0.32)^{0.3938} & 0.32 < \phi \leq 0.5 \\ \phi & 0.5 < \phi \leq 0.68 \end{cases} \quad (2-35)$$

and total surface area

$$\frac{S_t(\phi)}{S_o} = \begin{cases} 0 & 0 \leq \phi \leq 0.32 \\ 34.17(\phi - 0.32) & 0.32 < \phi \leq 0.344 \\ 0.82 + 1.445(\phi - 0.344)^{0.4533} & 0.344 < \phi \leq 0.515 \\ 1.4689 - 3.695(\phi - 0.515)^{1.758} & 0.515 < \phi \leq 0.68 \end{cases} \quad (2-36)$$

from the local porosity, $\phi(r)$. S_o is a reference surface area that is normally determined by fitting the expression (2–36) to surface area data determined from either N_2 or CO_2 adsorption experiments on the char in question. Equation (2–35) clearly demonstrates that the pore system becomes a series of isolated pores at porosities below 0.32, and that all of the inaccessible porosity is exposed for $\phi \geq 0.5$. The non–monotonic surface area expression (2–36) also reflects the interplay between the various *physical* processes that

are *normally* associated with carbon removal during char combustion – pore wall recession and exposure of previously closed porosity on the one hand, and pore coalescence on the other. These equations do not, however, account for other phenomena that may change the porosity and surface area independent of carbon removal such as gasification–induced densification [Hurt et al., 1993]. They are also only strictly valid for a process in which the solid is removed in a completely random fashion [Shah and Ottino, 1987]. This does not, of course, reflect the true reaction process where one would expect solid directly accessible to the particle surface to react preferentially. In other words, the simulated reaction process is random, whereas the real is correlated – it has been demonstrated that random and correlated percolation processes can be significantly different [Stauffer et al., 1982; Sahimi and Tsotsis, 1985; Sahimi, 1985; Shah, 1985; Lane et al., 1986; Shah and Ottino, 1987].

Shah and Ottino (1987) include peripheral disintegration by monitoring the porosity at the particle surface – once this porosity exceeds a critical level, ϕ^* , the local solid matrix is assumed to become unconsolidated with consequent peripheral disintegration. As the particle is assumed pure carbon, the critical porosity is simply

$$\phi^* = 1 - \phi_{pc} \quad (2-37)$$

where ϕ_{pc} is the percolation threshold of the pore system. This critical porosity is unlikely to be valid in general, however, as char makeup (eg: ash content, type of porosity) and external mechanical forces are all known to influence particle disintegration behavior [Hargrave et al., 1986; Kang et al., 1988, 1992; Chirone et al., 1991, 1992].

By way of final note, continuum formulations based upon a microscopic pore structure model[‡] are dependent upon the assumption that the reactive site density is proportional to the TSA (N_2 or CO_2) throughout the conversion process. This assumption is not valid in general [Khan, 1987; Zhu et al., 1989; Lizzio et al., 1990; Radovic et al., 1991], however, as TSA evolution is a physical processes dictated by carbon removal only (ie: pore enlargement and coalescence, exposure of inaccessible porosity), whilst active site density variation with conversion may also be affected by chemical actions such as

[‡] Pore tree model [Simons, 1983], random pore models [Gavalas, 1980; Bhatia and Perlmutter, 1980, 1981], and percolation models [Mohanty et al., 1982].

catalyst deactivation [Cope et al., 1994], and physical processes not directly related to carbon removal such as catalyst particle migration [Gopalakrishnan et al., 1994].

2.2.4 Char–FB Interaction

The standard approach to including heat and mass transfer between a burning char particle and fluidized bed is via flux boundary conditions at the char's external surface, in conjunction with heat and mass transfer coefficients [Basu, 1985]. Until the mid–1980s, these coefficients were completely empirical in nature, and assumed to be either constant [eg: Turnbull et al., 1984], or given by correlations based upon those of Ranz–Marshall [Marshall, 1954] and Frössling [eg: Borghi et al., 1985]. The lack of any sound theoretical basis for these fully–empirical correlations, and their inability to accurately predict heat and mass transfer coefficients over a wide range of FBC parameters, means more soundly based semi–empirical correlations have been developed in recent years [eg: Tamarin, 1982; Prins, 1987; Coelho and Guedes de Carvalho, 1988]. In their most advanced forms, these correlations recognize the effect that bubbles have on heat and mass transfer when the active particle is within the emulsion phase [the so–called “particle convective component”; La Nauze et al., 1984; Xavier and Davidson, 1985; La Nauze and Jung, 1986], and the fact that the active particle moves both between the bubble and emulsion phases, and up and down through the bed [Agarwal et al., 1988; Linjewile and Agarwal, 1990; Agarwal, 1991; Biggs and Agarwal, 1993].

If we are interested in what is going on within the particle *and* the boundary layer, then we must, of course, model both. Whilst we should solve the full multidimensional boundary layer flow, heat transfer and combustion problem in addition to that associated with the burning porous char particle, computational limitations mean this approach is not presently possible. An alternative, whilst only approximate, is to solve the spherically symmetric mass and heat transfer equations on a boundary layer whose thickness is defined to give the desired mass and heat transfer properties. Amundson and co–workers [Srinivas and Amundson, 1981; Sotirchos and Amundson, 1984a, b, c, d;

Morell et al., 1990] define their thermal and concentration boundary layer sizes via

$$\text{Nu and Sh} = \frac{2}{1 - a/b} \quad (2-38)$$

which is valid for mass and heat transfer through a stagnant boundary layer of thickness, $b - a$, surrounding a sphere of radius, a . Unfortunately, this equation is unlikely to be of much use when considering FBC problems. However, as no other mechanism exists whereby boundary layer sizes may be defined a priori, it must do. Our inability to model the actual problem rigorously, and the limitations associated with the alternative, means our ability to undertake a systematic quantitative study of the effect of bed parameters on char combustion behavior is limited. However, Mon and Amundson (1978) did find that the boundary layer thickness does not significantly affect the qualitative nature of the solution.

In general, mass fluxes within the boundary layer would be defined by the large pore limit of the DGM [Jackson, 1977]. This requires knowledge of the effective binary diffusion coefficients within, and the permeability of, the boundary layer. A number of different effective diffusivities have been used [eg: Avedesian and Davidson, 1973; Agarwal and O'Neill, 1988], whilst the permeability is traditionally defined by the Carman–Kozeny equation

$$B_o = \frac{d_b^2 \phi_b^3}{36k(1 - \phi_b)^2} \quad (2-39)$$

where d_b and ϕ_b are the bed particle diameter and porosity respectively, and k a constant of $O(5)$ [Carman, 1956]. Although more accurate and rigorous expressions are available [review: Sahimi, 1994], equation (2–39) yields similar values to these expressions for $\phi \lesssim 0.5$ (ie: porosities typical of the bulk phase of a fluidized bed) [Sahimi, 1994]. As reaction induced pressure differences are unlikely to be large within the boundary layer, an alternative to the DGM is a Fickian model in which the diffusivities are replaced by dispersion coefficients that account for both molecular diffusion and bulk fluid flow [eg: Linjewile et al., 1995]. In the case of the energy equation, the Fourier flux expression is normally used in conjunction with one of a number of well tested models for the

effective thermal conductivity [eg: Argo and Smith, 1953; Yagi and Kunii, 1957; Kunii and Smith, 1961; Duncan et al., 1989; review: Hahne et al., 1991]; these models in general include radiation and convective effects arising from interstitial fluid flow.

2.3 SIMULATION OF A BURNING POROUS CHAR PARTICLE WITHIN AN INCIPIENT FLUIDIZED BED: THE CO/CO₂ PRODUCT RATIO

2.3.1 Model Details

Assuming: (1) spherical symmetry; (2) a highly crosslinked pore structure; (3) the continuum limit; (4) an interstitial gas mixture of O₂, CO₂, CO, and N₂ only ($i = 1, 2, 3$ & 4); and (5) the global reaction schemes R1, R2, and R3 ($r = 1, 2$ & 3), mass conservation within the porous char particle and its surrounding boundary layer was described by

$$\frac{\partial}{\partial t}(\phi_a C_i) + \frac{1}{r^2} \frac{\partial}{\partial r}(J_i + X_i N) = \sum_{r=1}^4 v_{ri} \dot{\Omega}_{pr} = \dot{\Omega}_i \quad \text{for } i = 1, \dots, 4 \quad \begin{matrix} (2-40a) \\ \text{to} \\ 2-40d) \end{matrix}$$

and

$$\frac{\partial}{\partial t}(\phi_a C) + \frac{1}{r^2} \frac{\partial N}{\partial r} = \sum_{r=1}^3 \sum_{i=1}^4 v_{ri} \dot{\Omega}_{pr} = \dot{\Omega} \quad (2-41)$$

Ignoring thermal and surface diffusion, the species molar diffusion fluxes, J_i , and total molar flux, N , were defined by the DGM expressions

$$\sum_{j=1}^4 \frac{X_j J_i - X_i J_j}{\Delta_{ij}} = -r^2 \frac{\partial C_i}{\partial r} - A_{im} r^2 \frac{\partial C}{\partial r} - A_{iT} r^2 \frac{\partial T}{\partial r} \quad \begin{matrix} (2-42a) \\ \text{for } i = 1, \dots, 4 \\ \text{to} \\ 2-42b) \end{matrix}$$

and

$$N + \sum_{j=1}^4 \frac{J_j}{\Delta_j} = -A_{mm} r^2 \frac{\partial C}{\partial r} - A_{mT} r^2 \frac{\partial T}{\partial r} \quad (2-43)$$

where the parameters Δ_{ij} , Δ_i , A_{im} , A_{iT} , A_{mm} , and A_{mT} are defined in Table 2.2. These expressions were derived on the following basis: (1) within the char, it was assumed that heterogeneous reaction was restricted to the smaller pores, whilst the macropores acted as the main gas carriers [Morell et al., 1990] – this permitted d_p to be identified with a single unchanging average macropore diameter, and use of the tortuosity function

Table 2.2. Parameters for DGM equations (2–42) and (2–43).

Parameter	$\frac{1}{\Delta_{ij}}$	A_{im}	A_{iT}	A_{mm}
Particle	$\frac{1}{D_{ij}} + \frac{1}{D_j \Delta_i}$	$-\frac{X_i}{\Delta_i}$	$\frac{C_i}{T} \left(1 - \frac{1}{\Delta_i}\right)$	$\frac{1}{\Delta} + \frac{B_o P}{\mu}$
Boundary Layer	$\frac{1}{D_{ij}}$	$-\frac{X_i}{\Delta_i}$	$\frac{C_i}{T} \left(1 - \frac{1}{\Delta_i}\right)$	$\frac{B_o P}{\mu}$
Parameter	A_{mT}	Δ_i	Δ	D_{ij}
Particle	$\frac{C}{T} \left(\frac{1}{\Delta} + \frac{B_o P}{\mu}\right)$	$D_i \Delta$	$\sum_{j=1}^4 \frac{X_j}{D_j}$	$\mathfrak{D}_{ij} \frac{\phi}{\varkappa}$
Boundary Layer	$\frac{C B_o P}{T \mu}$	$\frac{\Delta}{\sqrt{m_i}}$	$\sum_{j=1}^4 X_j \sqrt{m_j}$	$\mathfrak{D}_{ij} \frac{\phi}{\varkappa}$
Parameter	D_i	B_o	$\mathfrak{B}_o$	$\frac{\phi}{\varkappa}$
Particle	$\mathfrak{D}_i \frac{\phi}{\varkappa}$	$\mathfrak{B}_o \frac{\phi}{\varkappa}$	$\frac{d_p^2}{32}$	Eq. (2–15)
Boundary Layer	—	$\mathfrak{B}_o$	Eq. (2–39)	ϕ_b^2
Parameter	$\mathfrak{D}_{ij}$	$\mathfrak{D}_i$	μ_i	
Interstitial Gas	$\frac{3}{8} \left(\frac{m_i + m_j}{2\pi m_i m_j}\right)^{1/2} \frac{(k_b T)^{3/2}}{P \sigma_{ij}^2 \Omega_{ij}^{11}}$	$\frac{d_p}{3} \left(\frac{8 R_u T}{\pi m_i}\right)^{1/2}$	$\frac{5}{16} \left(\frac{m_i k_b T}{\pi}\right)^{1/2} \frac{1}{\sigma_i^2 \Omega_i^{22}}$	
Parameter	μ	Φ_{ij}		
Interstitial Gas	$\sum_{i=1}^4 \left[X_i \mu_i / \sum_{j=1}^4 X_j \Phi_{ij} \right]$	$\frac{\left[1 + (\mu_i / \mu_j)^{1/2} (m_j / m_i)^{1/4} \right]^2}{\left[8 + 8 m_i / m_j \right]^{1/2}}$		

$\mathfrak{D}_{ij}$ and μ_i follow Bzowski et al. (1990); $\mathfrak{D}_i$ and $\mathfrak{B}_o$ for char based on circular pore cross section; tortuosity follows Shah and Ottino (1987) [Kirkpatrick, 1973; Mohanty et al., 1982], and the large pore limit of Wakao and Smith (1962) for char and boundary layer respectively; μ follows Wilke (1950).

(2–15); (2) the large pore limit of the DGM was assumed to apply within the boundary layer; (3) the bed permeability was defined by the Kozeny–Carman correlation, equation (2–39) [Carman, 1956]; and (4) the bed tortuosity was defined by the large pore limit of the Wakao and Smith (1962) pore model.

Assuming solid reaction within the smaller pores may be described by a random removal of polyhedra from a cubic tessellation of space, the rates-of-reaction per unit char-volume for the heterogeneous reactions R1 and R2 ($r = 1 \text{ \& } 2$) were determined from the intrinsic rates via

$$\dot{\Omega}_{pr} = S_t \dot{\Omega}_{sr} \quad (2-44)$$

where S_t is the accessible TSA as defined by equation (2–36) [Mohanty et al., 1982; Shah and Ottino, 1987]. The intrinsic rate expressions (2–30) and (2–32) were used in conjunction with the rate constants of Table 2.3 [Smith, 1978; Dutta et al., 1977]. Assuming an ash free char, the primary CO/CO₂ product ratio, η , was defined by the correlation of Tognotti et al. (1990), equation (2–29) with $A = 70$ and $B = 3070 \text{ K}$.

Small traces of water (3.5%) were also assumed to be present, but only as a catalyst to the homogeneous reaction R3 (ie: concentration assumed uniform and constant). The rate-of-reaction per unit char volume for the homogeneous reaction was determined from the volumetric rate using

$$\dot{\Omega}_{p3} = \phi_a \dot{\Omega}_{v3} \quad (2-45)$$

where ϕ_a is the accessible porosity as defined by equation (2–35). The volumetric rate was defined by equation (2–33) in conjunction with the rate constant of Table 2.3 [Howard et al., 1973].

Table 2.3. Rate constants.

r	1	2	3
E_r	179400	248120	125600
A_r	$1.2708 \times 10^5 \frac{R_u}{P_o}$	$5.3010 \times 10^7 \frac{R_u}{P_o}$	$9.6670 \times 10^{15} \frac{R_u^2}{P_o^2}$
n_r	1	0	0

$k_r = A_r T^{n_r} \exp(-E_r/R_u T)$; k_1 and k_2 in m/s, k_3 in m³/mol s, and E_r in J/mol.

Assuming negligible convection, heat transfer within the particle and its surrounding boundary layer was described by the conservation equation

$$C_e \frac{\partial T}{\partial t} + \frac{1}{r^2} \frac{\partial J_T}{\partial r} = \sum_{r=1}^3 (-H_r) \dot{\Omega}_r = \dot{Q} \quad (2-46)$$

and Fourier flux model

$$J_T = -\lambda_e r^2 \frac{\partial T}{\partial r} \quad (2-47)$$

where λ_e is the effective thermal conductivity as defined in Table 2.4, H_r the enthalpies-of-reaction of Table 2.5, and C_e the effective thermal capacitance. Assuming an ash free char, the thermal conductivity of the char material, λ_{ct} , was defined by the model of Atkinson and Merrick (1983), equation (2-24). The effective thermal capacitance of both the char and boundary layer were defined by equation (2-19) with the specific heat model of Merrick (1983), equation (2-20), being used within the char; a constant specific heat was assumed for the bed material (see Table 2.9).

Table 2.4. Effective thermal conductivity formula.

Char particle

$$\lambda_e = \lambda_g \phi_e + \lambda_{ct} \bar{\phi}_e \quad \phi_e = 1.509(\phi - 0.32)^{1.474} \quad \bar{\phi}_e = 1.509(0.68 - \phi)^{1.474}$$

Boundary layer [Yagi and Kunii, 1957]

$$\lambda_e = \phi_b d_b h_{rv} + \frac{1 - \phi_b}{\frac{1}{\lambda_b} + \frac{1}{\lambda_g \chi}} \quad h_{rs} = \frac{4\sigma\epsilon T^3}{2 - \epsilon} \quad h_{rv} = \frac{8\sigma\epsilon(1 - \phi_b)T^3}{2\epsilon(1 - \phi_b) + \phi_b(1 - \epsilon)}$$

$$\chi = \frac{1}{\psi} + \frac{d_b h_{rs}}{\lambda_g} \quad \psi = \psi_a \left(\frac{\lambda_g}{\lambda_a} \right)^{0.36} \quad \psi_a = \exp(1.81 \ln \phi_b - 1.714)$$

Interstitial fluid [Mason & Saxena, 1958; White, 1974]

$$\lambda_g \approx \sum_{i=1}^4 \left[X_i \lambda_i / \sum_{j=1}^4 X_j \phi_{ij} \right] \quad \phi_{ij} = \frac{\left[1 + (\lambda_i / \lambda_j)^{1/2} (m_i / m_j)^{1/4} \right]^2}{\left[8 + 8m_i / m_j \right]^{1/2}}$$

$$\lambda_i \approx \lambda_{oi} \left(\frac{T}{T_o} \right)^{3/2} \frac{T_o + S_i}{T + S_i}$$

Table 2.5. Heats of Reaction.

r	1	2	3
$\mathcal{H}_1$	$-\frac{230542\eta + 783290}{\eta + 2}$	161988	-577905
$\mathcal{H}_2$	$\frac{151.032\eta - 293.703}{\eta + 2}$	174.856	-198.680
$\mathcal{H}_3$	$\frac{0.00144\eta - 0.00775}{\eta + 2}$	0.00531	-0.00919
$\mathcal{H}_4$	$-\frac{21.072\eta - 49.540}{\eta + 2}$	-24.77	28.47

$H_r = \mathcal{H}_1 + \mathcal{H}_2 T + \mathcal{H}_3 T^2 + \mathcal{H}_4 T \ln T$; J/mol – O₂ for reaction R1, J/mol – CO₂ for reaction R2, J/mol – O₂ for reaction R3.

Assuming that the char contains no ash, the porosity throughout the char was determined via local mass balance considerations

$$\frac{d\phi(r)}{dt} = -\frac{m_c}{Q_c} \sum_{r=1}^2 v_{rc} \dot{\Omega}_{pr}(r) = -\frac{m_c}{Q_c} \dot{\Omega}_c(r) \quad (2-48)$$

where v_{rc} is the stoichiometric coefficient for carbon in reaction-r. Finally, disintegration was assumed to occur if the local porosity exceeded the value [cf: equation (2-37)]

$$\phi^* = 1 - 0.32 = 0.68 \quad (2-49)$$

where $\phi_{pc} = 0.32$ is an approximate value for the percolation threshold of a random cubic tessellation of space.

2.3.2 Model Solution

As equations (2-42) are not independent, the constraint

$$\sum_{i=1}^4 J_i = 0 \quad (2-50)$$

was used to replace all occurrences of the flux J_4 in equations (2-42a) to (2-42c) and (2-43), to yield, when combined with the heat flux equation (2-47), an implicit

expression for the fluxes $\mathbf{n} = [J_1 \ J_2 \ J_3 \ N \ J_T]^T$

$$\mathbf{B}\mathbf{n} = -\mathbf{A}r^2 \frac{\partial \mathbf{x}}{\partial r} \quad (2-51)$$

where the matrices $\mathbf{A}$ and $\mathbf{B}$ are defined in Table 2.6, and $\mathbf{x} = [C_1 \ C_2 \ C_3 \ C \ T]^T$ is the state-variable vector.

Using the dimensionless groups of Table 2.7, this equation was combined with the coupled conservation equations, (2-40a) to (2-40c), (2-41) and (2-46), to yield the system of nonlinear partial differential equations (PDEs)

$$\mathbf{C} \frac{\partial \bar{\mathbf{x}}}{\partial \tau} + \mathbf{D}\bar{\mathbf{x}} + \frac{1}{\zeta^2} \frac{\partial}{\partial \zeta} \left(\mathbf{X}\mathbf{B}^{-1}\mathbf{A} \zeta^2 \frac{\partial \bar{\mathbf{x}}}{\partial \zeta} \right) = \bar{\mathbf{s}} \quad (2-52)$$

where $\bar{\mathbf{x}} = [\bar{C}_1 \ \bar{C}_2 \ \bar{C}_3 \ \bar{C} \ \bar{T}]^T$ is the dimensionless state-variable vector, and $\mathbf{C}, \mathbf{D}, \mathbf{X}$ and $\bar{\mathbf{s}}$ are defined in Table 2.8.

This system of PDEs was discretized on the char/boundary layer domain using the Galerkin finite element method [Zienkiewicz and Taylor, 1989] to yield the system of ordinary differential equations (ODEs)

$$\mathbf{M}_f \frac{d\hat{\mathbf{x}}}{d\tau} + \mathbf{K}_f \hat{\mathbf{x}} = \mathbf{f}_f \quad (2-53)$$

where $\hat{\mathbf{x}}, \mathbf{f}_f, \mathbf{M}_f$ and $\mathbf{K}_f$ are the nodal state variable vector, force vector, mass matrix and stiffness matrix respectively. Gaussian quadrature was used to evaluate $\mathbf{f}_f, \mathbf{M}_f$ and $\mathbf{K}_f$.

As this system of ODEs is highly nonlinear and extremely stiff, the backward-Euler variant ($\alpha=1$) of the Winget and Hughes (1985) Newton-Raphson (NR) predictor-corrector algorithm was used to

Table 2.7. Dimensionless parameters.

$\tau = \frac{D_o t}{r_o^2}$	$\zeta = \frac{r}{r_o}$	$C_o = \frac{P_b}{R_u T_b}$
$\bar{C} = \frac{C}{C_o}$	$\bar{C}_i = \frac{C_i}{C_o}$	$\bar{T} = \frac{T - T_b}{T_b - T_o}$

integrate it through time. The primary computer requirement of this technique is the need, for each NR iteration, to calculate and form a global matrix, $\mathbf{M}^*$, and subsequently solve the global non-symmetric linear system

$$\mathbf{M}^* \Delta \mathbf{v} = \Delta \mathbf{f} \quad (2-54)$$

This is especially the case for distributed memory computers such as the Thinking Machines CM-5 where interprocessor communications must be kept to a minimum (assembly and solution of this global system would require significant interprocessor communications), and for vector architectures such as the Fujitsu VP2200 where solution procedures of such systems are not easily vectorized (eg: the vectorized linear equation solver supplied with the VP2200 places very strict conditions on the nature of M^* ; they were not satisfied in this case). As such machines were used for this work, the nonsymmetric Cholesky element-by-element preconditioned generalized minimum residual (NC-EBE-PC-GMRES) algorithm of Shakib et al. (1989) was used to solve the system (2-54). Use of this iterative method means: (1) assembly of the global M^* matrix is never undertaken; (2) all computationally intensive tasks are done on an element-by-element basis; and (3) the equation (2-54) need only be solved to an accuracy commensurate with maintenance of NR iteration convergence – this is fundamentally more efficient than a direct

Table 2.6. Definition of matrices of equations (2-51).

$$A = \begin{bmatrix} 1 & 0 & 0 & A_{1m} & A_{1T} \\ 0 & 1 & 0 & A_{2m} & A_{2T} \\ 0 & 0 & 1 & A_{3m} & A_{3T} \\ 0 & 0 & 0 & A_{mm} & A_{mT} \\ 0 & 0 & 0 & 0 & \lambda_e \end{bmatrix}$$

$$B = \begin{bmatrix} B_{11} & B_{12} & B_{13} & 0 & 0 \\ B_{21} & B_{22} & B_{23} & 0 & 0 \\ B_{31} & B_{32} & B_{33} & 0 & 0 \\ B_{m1} & B_{m2} & B_{m3} & 1 & 0 \\ 0 & 0 & 0 & 0 & 1 \end{bmatrix}$$

Elements of matrix B.

$$B_{11} = \frac{X_1}{\Delta_{14}} + \frac{X_2}{\Delta_{12}} + \frac{X_3}{\Delta_{13}} + \frac{X_4}{\Delta_{14}}$$

$$B_{22} = \frac{X_1}{\Delta_{12}} + \frac{X_2}{\Delta_{24}} + \frac{X_3}{\Delta_{23}} + \frac{X_4}{\Delta_{24}}$$

$$B_{33} = \frac{X_1}{\Delta_{13}} + \frac{X_2}{\Delta_{23}} + \frac{X_3}{\Delta_{34}} + \frac{X_4}{\Delta_{34}}$$

$$B_{21} = \frac{X_2}{\Delta_{24}} - \frac{X_2}{\Delta_{12}}$$

$$B_{31} = \frac{X_3}{\Delta_{34}} - \frac{X_3}{\Delta_{13}}$$

$$B_{12} = \frac{X_1}{\Delta_{14}} - \frac{X_1}{\Delta_{12}}$$

$$B_{32} = \frac{X_3}{\Delta_{34}} - \frac{X_3}{\Delta_{23}}$$

$$B_{13} = \frac{X_1}{\Delta_{14}} - \frac{X_1}{\Delta_{13}}$$

$$B_{23} = \frac{X_2}{\Delta_{24}} - \frac{X_2}{\Delta_{23}}$$

$$B_{m1} = \frac{1}{\Delta_1} - \frac{1}{\Delta_4}$$

$$B_{m2} = \frac{1}{\Delta_2} - \frac{1}{\Delta_4}$$

$$B_{m3} = \frac{1}{\Delta_3} - \frac{1}{\Delta_4}$$

solution technique where the accuracy of the solution is equal to that of the machine used; this degree of accuracy is, of course, totally unnecessary as most of it is lost in the limited accuracy of the NR iteration.

Using the dimensionless groups of Table 2.7 once again, the non-dimensional form of the porosity evolution equation (2-48) was also discretized using the Galerkin finite element method to yield the system of ODEs

$$\mathbf{M}_s \frac{d\hat{\phi}}{d\tau} = \mathbf{f}_s \quad (2-55)$$

where $\hat{\phi}$, $\mathbf{f}_s$ and $\mathbf{M}_s$ are the nodal porosity vector, force vector and mass matrix respectively. Gaussian quadrature was used to evaluate the force vector. The particle porosity distribution at the new time step was determined by simply diagonalizing the mass matrix, $\mathbf{M}_s$, and using a forward Euler time integrator.

Reaction at the particle external surface and peripheral disintegration meant the particle external surface moved with time. Rather than using a transformation to immobilize the particle surface [Gavalas, 1981; Crank, 1984; Sotirchos and Amundson, 1984b; Reyes and Jensen, 1986b], the node located at the particle surface was explicitly moved using a procedure similar to that described by Shah and Ottino (1987) – interpolation was made on a finite element basis.

Table 2.8. Definition of matrices and vectors of equation (2-52).

$$\mathbf{C} = \begin{bmatrix} \phi_a & 0 & 0 & 0 & 0 \\ 0 & \phi_a & 0 & 0 & 0 \\ 0 & 0 & \phi_a & 0 & 0 \\ 0 & 0 & 0 & \phi_a & 0 \\ 0 & 0 & 0 & 0 & C_c \end{bmatrix} \quad \mathbf{X} = \frac{1}{D_0} \begin{bmatrix} 1 & 0 & 0 & X_1 & 0 \\ 0 & 1 & 0 & X_2 & 0 \\ 0 & 0 & 1 & X_3 & 0 \\ 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 1 \end{bmatrix}$$

$$\mathbf{D} = \frac{\partial \phi_a}{\partial \tau} \begin{bmatrix} 1 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 \end{bmatrix} \quad \bar{\mathbf{s}} = \frac{r_o^2}{D_0} \left[\frac{\dot{\Omega}_1}{C_o} \quad \frac{\dot{\Omega}_2}{C_o} \quad \frac{\dot{\Omega}_3}{C_o} \quad \frac{\dot{\Omega}}{C_o} \quad \frac{\dot{Q}}{\Delta T} \right]^T$$

2.3.3 Model Code and its Validation

The solution algorithm described in the previous section was implemented on a 32 node/128 vector processor Thinking Machines CM-5. The code was run on the CM-5 in one of two modes: as a single simulation utilizing all 32 nodes (SIMD); or as 32 separate simulations, each utilizing one node (SPMD). The former is suitable for very large problems, whilst the latter is good for smaller models. The code was primarily written in CM FORTRAN, a parallel FORTRAN90 language, with some CMMD code also included (CMMD is a library of message-passing routines). A FORTRAN77 version was also written for execution on a Fujitsu VP2200 vector supercomputer, although this code was not used for production purposes.

The code was validated in a number of ways:

- Each component of the code (eg: routine used to calculate enthalpies-of-reaction, NC-EBE-PC-GMRES routine) was thoroughly tested. In the case of the various solvers, these were tested on small problems with known answers.
- By making judicious modifications to the code, the problem solved was reduced to transient heat conduction within a sphere; the results produced were compared with published data (Heisler chart).
- The code was checked to ensure no mass or heat fluxes were generated under no-reaction/no-gradient conditions.
- The results obtained were inspected thoroughly for any major inconsistencies – as will become obvious from discussion in the following section, the results were consistent and showed many trends seen in previous experimental and modelling studies.

2.3.4 Simulation Details

Results were generated for over 100 different combinations of bed temperature and oxygen concentration, inert particle size, and active particle size (Table 2.9).

So as to investigate the various issues raised in the Introduction, dual simulations were conducted for many of the combinations. In the

Table 2.9. Simulation conditions.

$T_b = 973, 1073, 1173, 1273 \text{ K}$ $X_{1b} = 0.07, 0.14, 0.21 (P_b = 1 \text{ atm})$ $d_{ao} = 1, 5 \text{ mm}$ $d_b = 200, 600, 1100 \text{ }\mu\text{m}$		$\left. \vphantom{\begin{matrix} T_b \\ X_{1b} \\ d_{ao} \\ d_b \end{matrix}} \right\} \text{BLRS} \\ 1 \text{ \& } 2$
$S_o = 3.2 \times 10^7 \text{ m}^2/\text{m}^3$	$\rho_b = 1500 \text{ kg}/\text{m}^3$	
$\rho_c = 2000 \text{ kg}/\text{m}^3$	$\lambda_b = 0.33 \text{ W}/\text{mK}$	
$m_c = 0.013 \text{ kg}/\text{mol}$	$C_b = 800 \text{ J}/\text{kgK}$	
$d_p = 1 \text{ }\mu\text{m}$	$\varepsilon = 0.8$	

first, reaction R3 occurs in both the particle and boundary layer (boundary layer reaction scenario 1; BLRS = 1), whilst in the second, its occurrence within the boundary layer is assumed to be inhibited by the bed particles (BLRS = 2).

Although the concentration and thermal boundary layers are likely to be of different size and dependent upon the bed hydrodynamics, both were assumed to extend over the region $r_a(t) < r \leq 2r_{ao}$ in all simulations. Whilst recognizing the limitations associated with this assumption (see §2.4), numerical studies have demonstrated that the assumed boundary layer thickness does not affect the qualitative nature of the results [Mon and Amundson, 1978; Sotirchos et al., 1984]. Assuming carbon oxide bed concentrations are small relative to those of oxygen and nitrogen, the boundary conditions used in all simulations were

$$r = 0 : \frac{\partial C_i}{\partial r} = \frac{\partial C}{\partial r} = \frac{\partial T}{\partial r} = 0$$

$$r = 2r_{ao} : C_1 = C_b X_{1b}, C_2 = C_3 = 0, C = C_b = \frac{P_b}{R_u T_b}, T = T_b$$

whilst reaction at the external surface of the char particle was included within the finite element formulation via source terms. The char and boundary layer initial conditions were set equal to those of the bed (ie: a soaked particle). Finally, the char was assumed

to have an initial uniform porosity of 0.4 ($\phi_a \approx 0.368$), whilst the boundary layer porosity was assumed uniform and constant at $\phi_b = 0.42$.

As the GMRES iterative linear equation solver is embedded within a non-linear solution procedure, the GMRES solution accuracy need not be that great [Winget and Hughes, 1985]. It was found, in this study, that a GMRES solution accuracy of 50% in combination with a NR accuracy, ϵ_{NR} , of 1–4% yielded accurate results in a reasonable time. Accuracy of this convergence criterion combination was assessed by comparing results obtained under this combination with those generated using stricter convergence requirements (ie: down to $\epsilon_{NR} = 0.1\%$).

Depending upon the time rate-of-change of the concentrations and temperature, and the convergence behavior of the NR and GMRES iterative procedures, the timestep size was allowed to vary up to a maximum of 0.1 ms. Although at lower bed temperatures it was found that significantly greater timestep sizes could be accommodated on this basis, the simple time integration procedure used to solve equation (2–55) often meant predicted porosity distribution accuracy was significantly degraded. As this limited the extent to which large particle burnout could be followed, future implementations of this model shall adopt a more sophisticated time integration procedure for the solid evolution equation.

Using relative errors calculated in the L_2 -norm from recovered element concentration and temperature gradients, the adaptive mesh refinement strategy of Zienkiewicz and Zhu (1987) was implemented on the basis of an $O(h)$ assumed error rate-of-convergence. The element concentration and temperature gradients were recovered via the Zienkiewicz and Zhu (1992) technique – this is a particularly efficient technique for vector and distributed memory machines, as it is done on an element-by-element basis. In all simulations, the relative errors were not allowed to exceed 4% for any element, and only element subdivision was permitted (ie: element recombination was not implemented).

2.3.5 Results and Discussion

The equation systems (2–53) and (2–55) were solved through time so as to yield the particle porosity distribution, and the temperature and species concentrations throughout the particle/boundary layer system. These results are detailed and discussed in the following sections. Results are presented in terms of the particle conversion

$$X = \frac{m_a - m_{a0}}{m_{a0}} = 1 - \frac{3}{1 - \phi_o} \int_0^{\zeta_a} (1 - \phi) \zeta^2 d\zeta \quad (2-56)$$

where m_{a0} and m_a are the initial and instantaneous char particle masses respectively, and ζ_a the dimensionless char particle radius (see Table 2.7).

As Table 2.9 indicates, simulations were performed for three different inert particle sizes. Unfortunately, it was realized well into the results production programme that the inert particle size did not significantly influence the mass transfer characteristics of the boundary layer, whilst it did affect the boundary layer thermal conductivity in a linear manner. Consequently, changing the inert particle size resulted in trends that were contrary to experimental observations. For example, Figure 2.6 shows that the particle over-temperature diminishes as the inert particle size increases – this is inconsistent with experimental observations [La Nauze and Jung, 1983; Linjewile, 1993] where the particle over-temperature increases with inert particle size due to a diminishing Nu/Sh ratio [Linjewile, 1993]. As the effect of inert particle size does not follow that obtained experimentally, comparison on an inert particle size basis has been de-emphasized except where we wish to highlight the effect of particle-bed heat transfer properties on the character of the burning char particle behavior. In any case, it was found that for the model used here, the inert particle size had little qualitative influence (about the only exception was the maximum temperature difference across the char – see Figure 2.12). Given this, and the fact that the most complete set of results obtained for the 1 mm and 5 mm chars were for $d_b = 200 \mu\text{m}$ and $d_b = 1100 \mu\text{m}$ respectively, these have been used. Comparison of results obtained for the different sized chars is only made on a qualitative basis except for the average surface CO/CO₂ product ratio where it was found that inert

particle size had neither a qualitative or quantitative effect (see, for example, Figure 2.15).

As both particle temperature and depth of oxygen penetration affect the CO/CO₂ product ratio, these issues are discussed prior to a detailed consideration of the ratio. These discussions are then followed by an analysis of how disintegration influences char conversion behavior.

2.3.5.1 Intraparticle Oxygen Distribution

Figure 2.2 illustrates the intraparticle oxygen distribution for the 1 mm and 5 mm chars at various conditions and particle conversion levels. This figure indicates that, qualitatively, the intraparticle oxygen distribution changes little with boundary layer reaction scenario, whilst it is influenced considerably by bed temperature and active particle size and, to varying degrees, by bed oxygen concentration and particle conversion. Insight into these trends may be obtained by considering Figures 2.3 and 2.4 in conjunction with Figure 2.2. Figure 2.3 shows, for the same conditions as Figure 2.2, the rate of the heterogeneous reaction R₁, and homogeneous reaction R₃ at $X \approx 0.2$ (these are the reactions responsible for oxygen consumption), whilst Figure 2.4 illustrates the char particle porosity distribution for the same conditions and conversion levels as Figure 2.2.

For $T_b = 973$ K, the small intraparticle oxygen concentration gradients indicate the 1 mm char combustion process at this temperature is controlled by both diffusion and reaction, with the latter being the most important. Figure 2.3 shows that the homogeneous reaction rate is maximum at the particle center for all bed oxygen concentrations, and that the rates of the two reactions increase substantially with X_{1b} . The latter is reflected in the decreasing and increasing intraparticle oxygen concentrations and gradients respectively. The slowness of the boundary layer reaction relative to those within the particle means there is no perceptible difference between the two BLRS oxygen distributions (less than 1% difference in surface oxygen concentrations). Finally, as the char pore structure evolves with conversion (see Figure 2.4), resistance to intraparticle

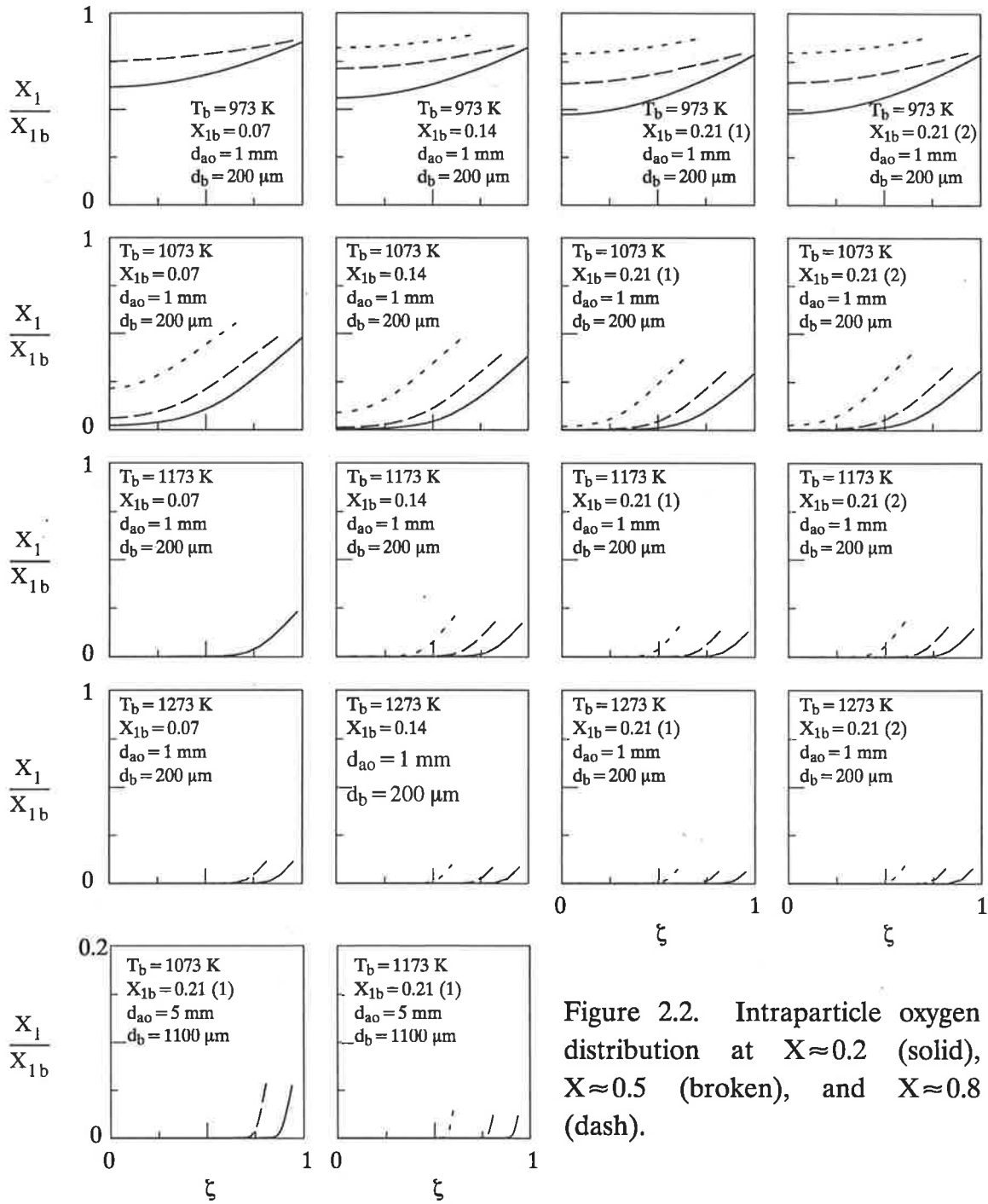


Figure 2.2. Intraparticle oxygen distribution at $X \approx 0.2$ (solid), $X \approx 0.5$ (broken), and $X \approx 0.8$ (dash).

mass transport diminishes (cf: Table 2.2) leading to a greater and more uniform distribution of oxygen within the char at higher conversion levels.

This effect is even more obvious for the 1 mm char at $T_b = 1073$ K, where higher rates of oxygen consumption mean intraparticle transport exerts greater control. At $X_{1b} = 0.07$, for example, the particle center oxygen concentration increases from almost zero at $X \approx 0.2$, to 25% of the bed level at $X \approx 0.8$. Once again, Figure 2.3 shows that as

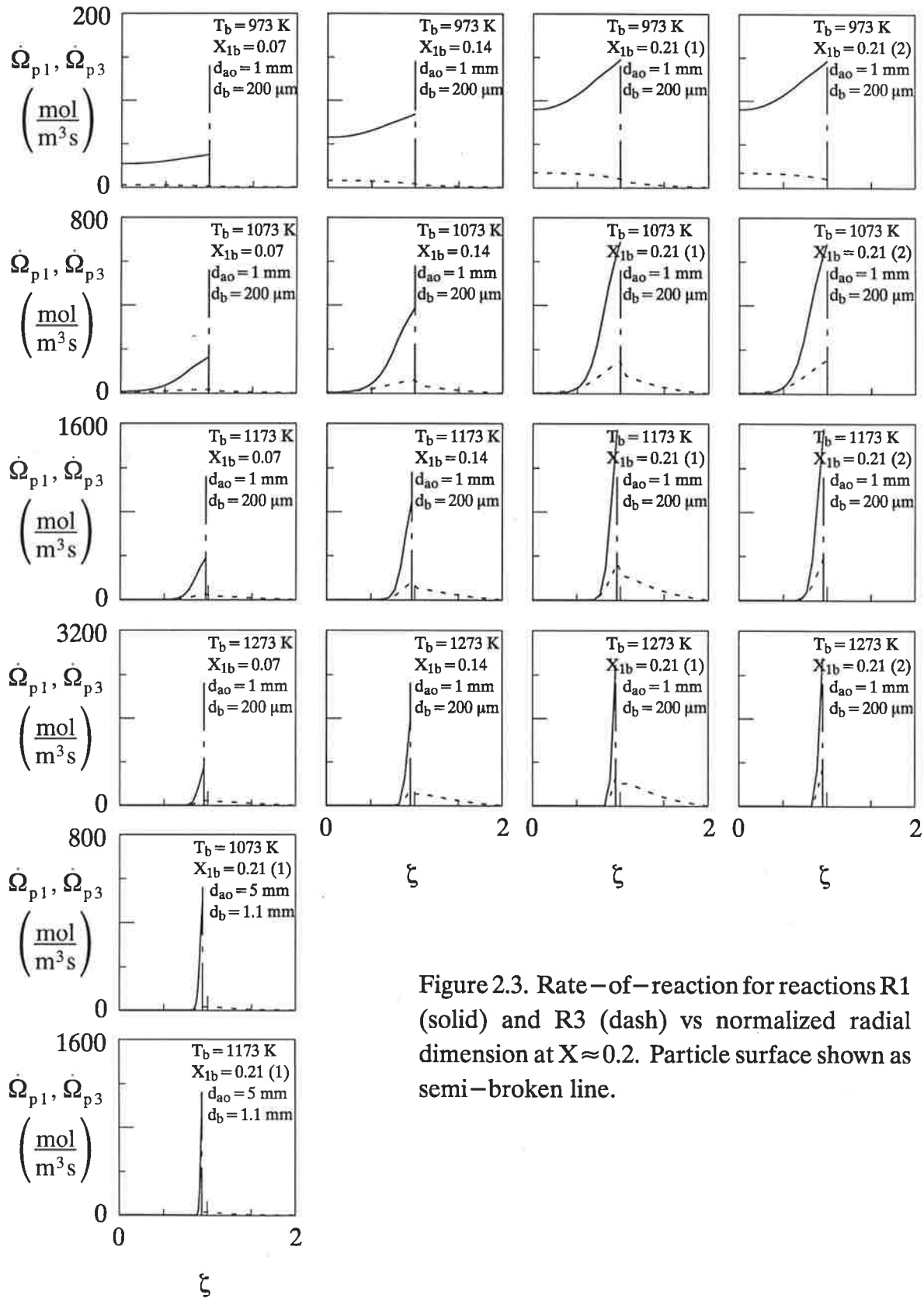


Figure 2.3. Rate-of-reaction for reactions R1 (solid) and R3 (dash) vs normalized radial dimension at $X \approx 0.2$. Particle surface shown as semi-broken line.

X_{1b} increases, the rate of intraparticle reaction also substantially increases leading to a decrease in oxygen concentration and penetration depth. The figure also shows that the

maximum rate of homogeneous reaction has now moved towards the periphery of the char particle. The rate of homogeneous reaction within the boundary layer is still only a fraction of the intraparticle rate of oxygen consumption ($\sim 6\%$ difference between the two BLRS surface oxygen concentrations).

For the 1 mm char at the higher bed temperatures of 1173 K and 1273 K, high rates of reaction mean the char combustion process is primarily controlled by boundary layer transport – oxygen penetration into the particle is only slight (outer 30% of particle at $T_b = 1173$ K and $X_{1b} = 0.07$; outer 10% at $T_b = 1273$ K and $X_{1b} = 0.21$), whilst particle surface oxygen concentration varies from 20% of the bed level at $T_b = 1173$ K and $X_{1b} = 0.07$, to 7% at $T_b = 1273$ K and $X_{1b} = 0.21$. Although intraparticle rates of oxygen consumption are still considerable in comparison to those of the boundary layer, the fact that intraparticle reaction is largely restricted to the particle periphery means boundary layer reaction is much more significant than at lower bed temperatures – the surface oxygen concentration at $X_{1b} = 0.21(2)$ is approximately 15 and 30 percent greater than that at $X_{1b} = 0.21(1)$ for $T_b = 1173$ K and $T_b = 1273$ K respectively. As also noted by Prins (1987), restriction of reaction to the particle periphery also means the intraparticle oxygen concentration distribution remains largely unaffected by the char conversion process.

For a given bed temperature, comparison of the $d_{a0} = 1$ mm and $d_{a0} = 5$ mm results of Figure 2.2 show that the oxygen surface concentration and depth of penetration of the smaller char are significantly greater than those of the larger*. This is reflected in Figure 2.3 where reaction rates associated with the 5 mm char are considerably smaller than those of the 1 mm char despite similar or larger particle over – temperatures (see Figure 2.6). As equation (2–38) indicates that $Sh(5\text{mm char}) \approx Sh(1\text{mm char})$, these behaviors arise from the fact that the effective mass transfer coefficient of the larger char is only approximately 20% of the smaller.

* Note: As: (1) the 5 mm char combustion process was largely controlled by boundary layer processes, and (2) the inert particle size only affects boundary layer thermal conductivity, it was found that inert particle size had little effect on the intraparticle oxygen distribution obtained for this char. Consequently, comparison of 1 mm/200 μm and 5 mm/1100 μm results is adequate.

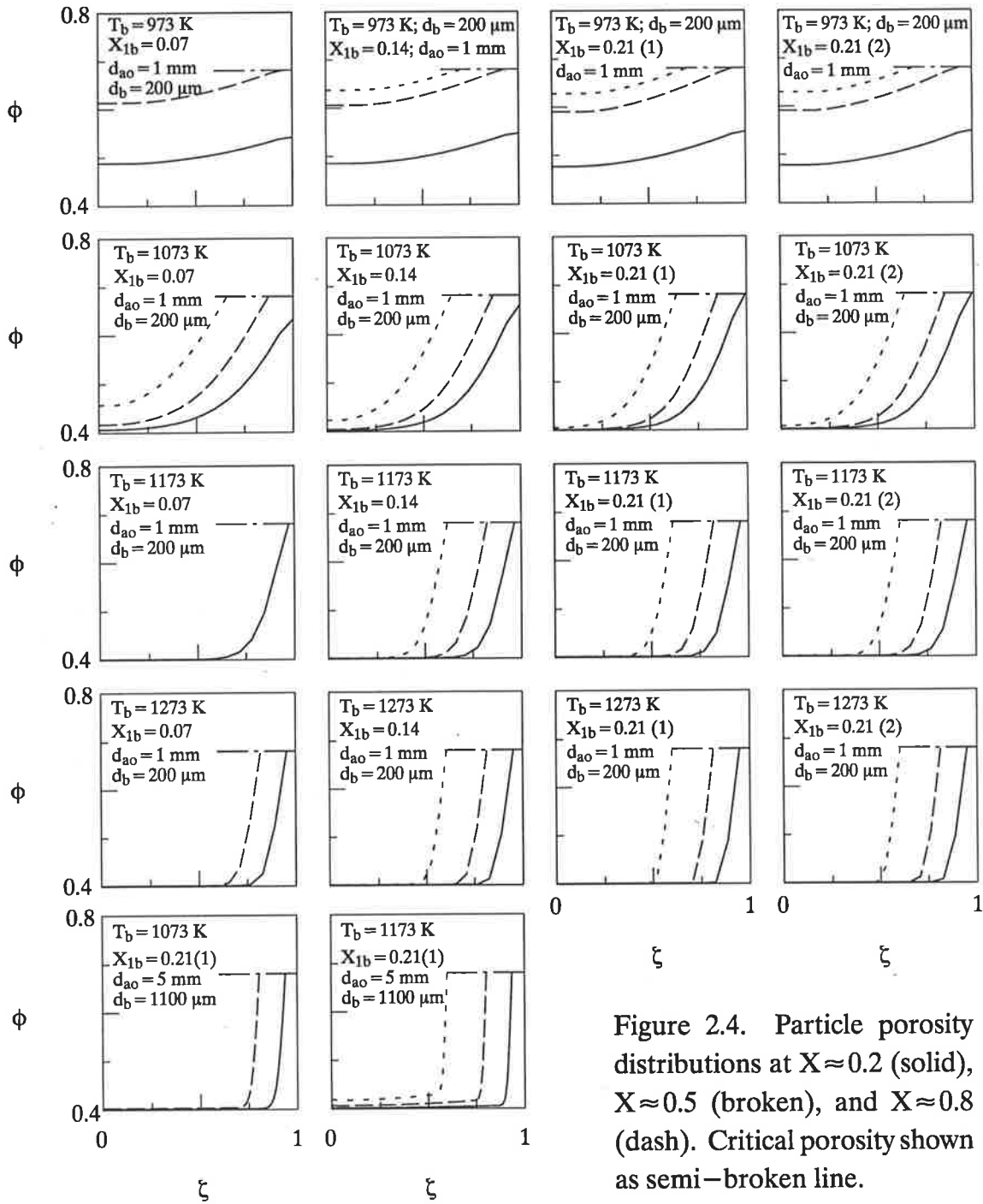


Figure 2.4. Particle porosity distributions at $X \approx 0.2$ (solid), $X \approx 0.5$ (broken), and $X \approx 0.8$ (dash). Critical porosity shown as semi-broken line.

In spite of the small oxygen penetration depth, the $d_{ao} = 5$ mm results of Figure 2.4 show that significant porosity development occurs throughout this char at $T_b = 1173$ K. The reason for this may be seen by considering Figure 2.5 which shows how the ratio of overall carbon consumption rates of the two heterogeneous reactions

$$\frac{\dot{\Omega}_{t1c}}{\dot{\Omega}_{t2c}} = \frac{\int_{r_{1p}}^{r_a} \dot{\Omega}_{p1c} r^2 dr}{\int_{r_{2p}}^{r_a} \dot{\Omega}_{p2c} r^2 dr} \quad (2-57)$$

varies with bed temperature for both the 1mm and 5mm chars; r_{ip} is the penetration radius of species- i . This figure shows that the CO_2 gasification reaction for the 5 mm char accounts for approximately 10% of the total conversion at $T_b = 1173$ K, and more than 25% at $T_b = 1273$ K. This clearly indicates the importance of including the CO_2 gasification reaction within single particle FBC models. This figure also suggests that reaction R2 increases in importance with active particle size, whilst it also shows bed oxygen concentration has little effect, at least for smaller chars.

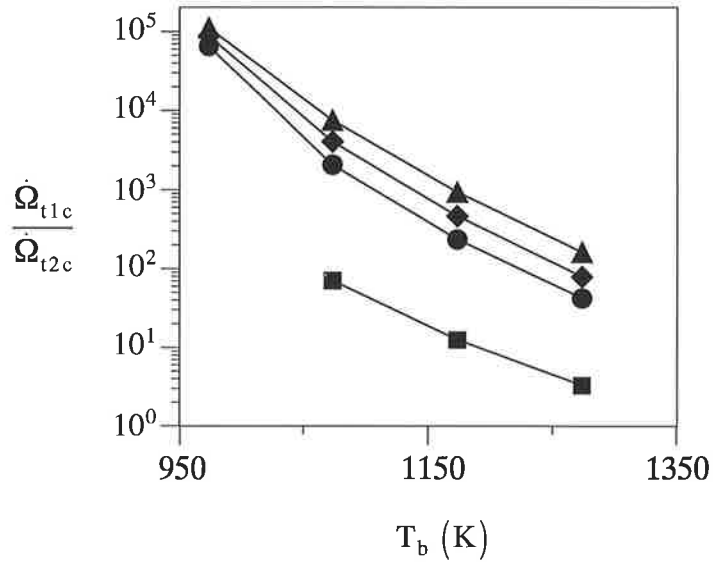


Figure 2.5. Ratio of total heterogeneous reaction rates vs bed temperature for $d_{a0} = 1$ mm, $d_b = 200$ μm , $X \approx 0.2$: $X_{1b} = 0.07$ $\blacktriangle$; $X_{1b} = 0.14$ $\blacklozenge$; $X_{1b} = 0.21$ (1) $\bullet$; and $d_{a0} = 5$ mm, $d_b = 1100$ μm , $X \approx 0.03$: $X_{1b} = 0.21$ (1) $\blacksquare$.

2.3.5.2 Char Particle Temperature

For 1 mm and 5 mm chars, Figure 2.6 shows how particle over-temperature changes with conversion for various bed temperatures, bed oxygen concentrations, inert particle sizes, and BLRS. Ignition occurs in every case with a consequent rapid rise in char particle temperature. At the lower bed temperatures of 973 K and 1073 K, the initial rapid rate associated with 1mm char ignition decays but remains positive until ΔT_{ab} reaches a maximum at $X \approx 0.3$. The over-temperature then slowly decreases until

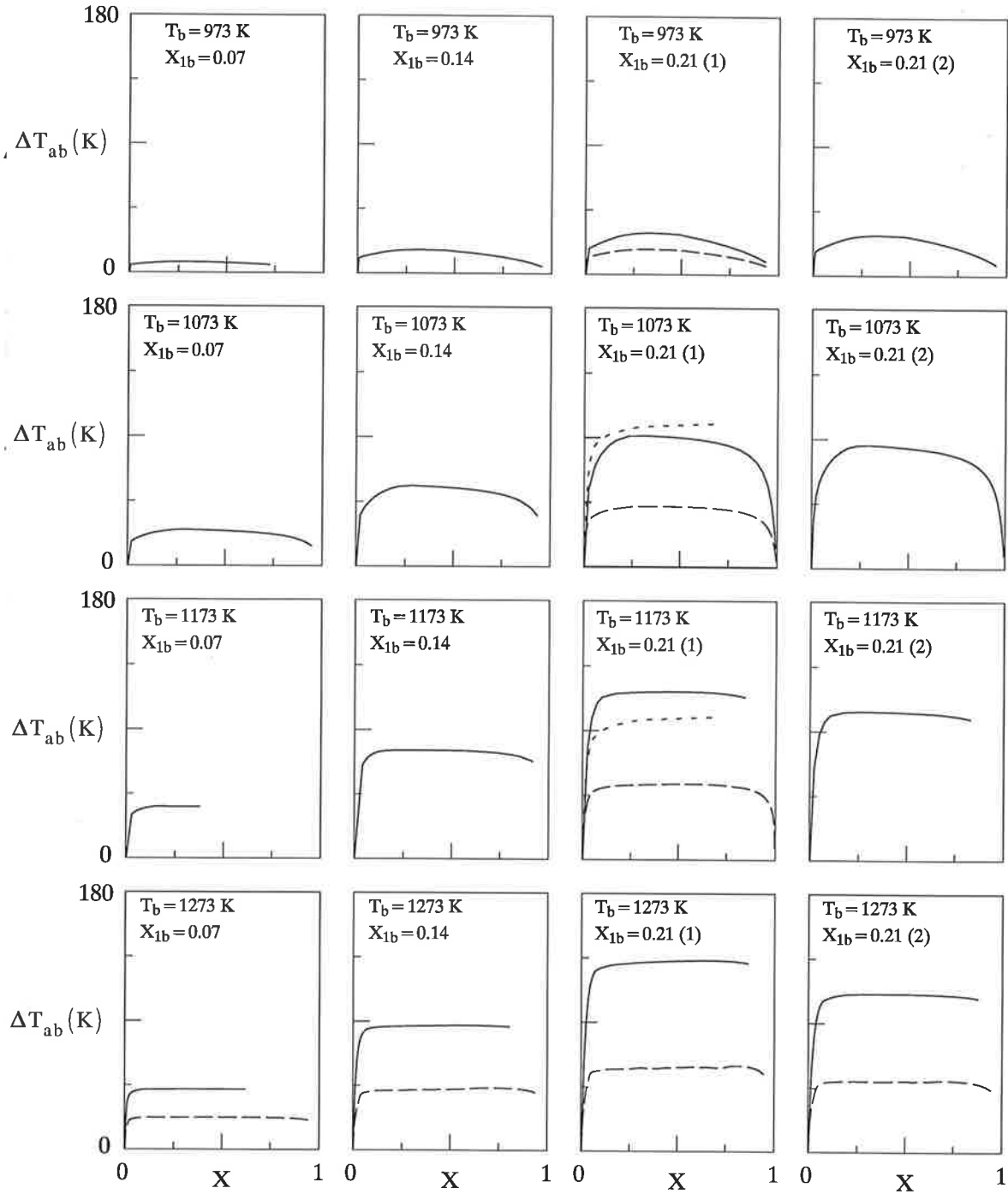


Figure 2.6. Average char particle over-temperature vs conversion for $d_p = 1 \mu\text{m}$: $d_{ao} = 1 \text{ mm}$ and $d_b = 200 \mu\text{m}$ (solid); $d_{ao} = 1 \text{ mm}$ and $d_b = 1100 \mu\text{m}$ (broken); $d_{ao} = 5 \text{ mm}$ and $d_b = 1100 \mu\text{m}$ (dash).

extinction. At the higher bed temperatures, ΔT_{ab} for the 1 mm char quickly reaches a maximum and remains there for the majority of the conversion process. For the 5mm char, the initial high rate associated with ignition also decays rapidly. Unlike the smaller char, however, it appears as if ΔT_{ab} continues to rise over the complete conversion

process for both of the bed temperatures shown – similar behavior has been seen experimentally [Linjewile, 1993]. Bed oxygen concentration and BLRS appear to have little effect on the way ΔT_{ab} varies with conversion (eg: the conversion at which $\Delta T_{ab}^{\max}$ occurs for the lower bed temperatures appears to be independent of X_{1b} , d_b and BLRS).

Some understanding of these trends may be gained by considering the heat balance associated with a burning char particle. Realizing that the char is near–isothermal (see below), the rate of heat accumulation within the char must equal the difference between that produced due to reaction and that removed via heat transfer to the bed

$$\frac{4\pi}{3} r_a^3 \rho_c C_c \frac{dT_a}{dt} = 4\pi \int_0^{r_a} \dot{Q} r^2 dr - 4\pi r_a^2 h_e \Delta T_{ab} \quad (2-58)$$

where $\dot{Q}$ is the rate of heat production per unit char–volume, and h_e the heat transfer coefficient embodying both convection and radiation

$$h_e = h + \sigma \epsilon_a (T_a + T_b) (T_a^2 + T_b^2) \quad (2-59)$$

Rearranging equation (2–58), realizing that reactions R2 and R3 do not greatly influence the particle heat balance, and using the $\dot{Q}$ definition of equation (2–46) with the char–volume reaction rate (2–44) gives

$$\frac{d\Delta T_{ab}}{dt} \approx \frac{3}{r_a^3 \rho_c C_c} \int_{r_{1p}}^{r_a} S_t H_1 k_1 C_1 r^2 dr - \frac{3h_e}{r_a \rho_c C_c} \Delta T_{ab} \quad (2-60)$$

where r_{1p} is the oxygen penetration radius. The complex combination of conversion dependent parameters (ie: r_a , r_{1p} , S_t , h_e and C_1) in this equation means it is difficult to isolate to what extent each influence ΔT_{ab} . Comparison of Figure 2.22 with Figure 2.6 indicates that particle over–temperature for the 1 mm char at $T_b = 973$ K and 1073 K may be linked to the rate of char combustion (ie: the first term on the RHS). No correlation appears to exist, however, between combustion rate and particle over–temperature for the 1mm char at the higher bed temperatures, and for the larger char at both temperatures shown. As char particle size decrease is substantial and begins early in the conversion process (see Figure 2.20 for 1 mm char whilst $X_d \leq 0.05$ for the

5 mm char), it is likely that the change in particle over-temperature under these conditions is driven by an interplay between the decreasing surface area available for heat loss, the increasing heat transfer coefficient, and the decreasing intraparticle reaction volume.

Homogeneous reaction within the particle boundary layer will affect particle over-temperature via two competing mechanisms. As already discussed, O_2 consumption within the boundary layer reduces the amount of oxygen available for reaction with the char – this will tend to reduce the char reaction rate, and with it, particle over-temperature.

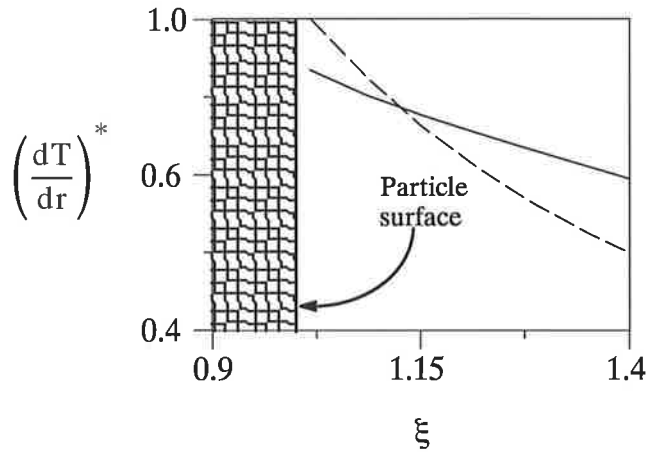


Figure 2.7. Normalized temperature gradient within boundary layer under $BLRS = 1$ (solid) and $BLRS = 2$ (broken), for $d_{ao} = 1$ mm, $T_b = 1273$ K, $X_{1b} = 0.21$, $d_b = 200$ μ m.

Figure 2.7 demonstrates,

however, that heat production in the boundary layer induces a reduced temperature gradient *near* the particle surface – this will reduce the rate of particle heat loss leading to a tendency for particle temperature increase. As Figure 2.6 clearly illustrates, the second of these mechanisms is more dominant – for a given bed temperature, homogeneous reaction within the boundary layer [$X_{1b} = 0.21(1)$] brings about a higher particle temperature relative to that obtained when no CO oxidation occurs within the boundary layer [$X_{1b} = 0.21(2)$]. However, the influence of boundary layer reaction on particle over-temperature appears to diminish as inert particle size increases, or as bed temperature decreases. The latter trend is due to the decreasing rate of the homogeneous reaction (ignition temperature ~ 923 K), whilst the former arises from the increased capacity of the boundary layer to conduct away heat produced within it (ie: $h_e \propto d_b$).

The previous discussion highlights the importance of knowing whether or not reaction occurs within the boundary layer. By definition, the char–bed heat transfer coefficient is defined by

$$h_e = \frac{J_{Ts}}{\Delta T_{ab}} \quad (2-61)$$

where J_{Ts} is the heat flux at the external surface of the char particle. As boundary layer reaction reduces the heat flux at the particle surface so as to raise the particle over–temperature, equation (2–61) clearly shows boundary layer reaction serves to reduce the char–bed heat transfer coefficient. However, not only does the occurrence of boundary layer reaction modify the char–bed heat transfer coefficient, but, as the rate varies substantially over the range of FBC temperatures, so to does its effect on this transport property. Consequently, *if* reaction does occur within the boundary layer, several key points must be considered when seeking to determine the particle–bed heat transfer coefficient from experiment, and when using these coefficients in models:

- In addition to h_e 's dependence on active particle size and its motion, properties of the fluidizing gas and bed materials, and the bed hydrodynamics, explicit consideration of boundary layer reaction will also be required, presumably via a Damköhler Number of the form $Da = \dot{Q}R^2/\lambda\Delta T$.
- Correlations determined for h_e under non–reactive conditions [eg: Pal'chenok and Tamarin, 1983; Prins, 1987; Linjewile, 1993] will not be valid for char combustion applications.
- Correlations determined for h_e under reactive conditions [eg: Ross and Davidson, 1982; La Nauze and Jung, 1983; Baskakov et al., 1987] will implicitly include the effect of boundary layer reaction (eg: via a modification of the powers of Pr and Re). However, as the rate of boundary layer reaction is determined by, amongst other things, the moisture content and the CO concentration, these correlations shall not in general be valid for conditions and chars other than those used in determining the correlation.

Figure 2.6 indicates that the average particle over-temperature of the 1mm char increases with both bed temperature and oxygen concentration. Once again, these trends may be understood by considering the heat balance associated with the char particle. By taking the steady-state limit of the heat balance, equation (2-60) becomes

$$\Delta T_{ab} \approx \frac{1}{r_a^2 h_c} \int_{r_{1p}}^{r_a} S_t H_1 k_1 C_1 r^2 dr \quad (2-62)$$

This equation clearly illustrates that system temperature will primarily affect particle over-temperature via two mechanisms. The Arrhenius form of k_1 means particle over-temperature will tend to increase with system temperature. As Figure 2.2 indicates, however, this effect is increasingly offset by the decreasing depth of oxygen penetration (ie: r_{1p} approaches r_a). These two competing mechanisms are reflected in

Figure 2.8 which shows, for all X_{1b} and both BLRS, that the (maximum) particle over-temperature for the 1 mm char increases at a diminishing rate with bed temperature. At a high enough bed temperature, oxygen penetration shall be negligible, and the combustion process largely controlled by the rate of mass transfer through the boundary layer. In this situation, any further increase in bed temperature will not affect particle temperature (as the rate remains unaffected), but will only

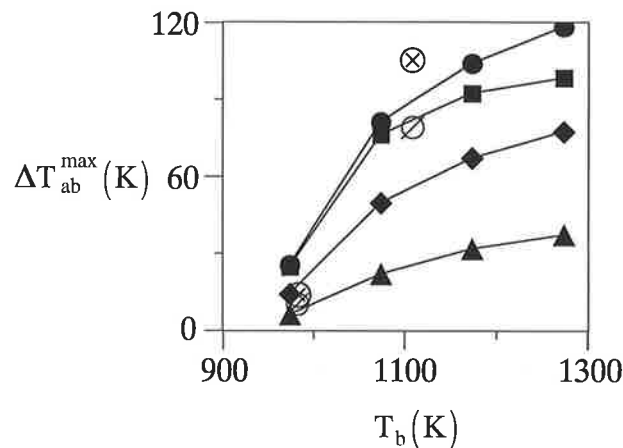


Figure 2.8. Maximum particle over-temperature vs bed temperature for $d_{ao} = 1$ mm, $d_b = 200$ μ m: $X_{1b} = 0.07$ ▲; $X_{1b} = 0.14$ ◆; $X_{1b} = 0.21$ (1) ●; $X_{1b} = 0.21$ (2) ■. ASPC results of Prins (1987) for $d_{ao} = 0.8$ mm, ∅; and $d_{ao} = 1$ mm ⊗.

serve to decrease the temperature difference between the bed and particle. This behavior is clearly illustrated in Figure 2.9 which shows, for the 5 mm char, ΔT_{ab} at two different bed temperatures for the first 40% of the conversion process (they cross over soon after this point). This trend has also been observed in recent experiments [Linjewile

et al., 1994]. The temperature dependent enthalpy–of–reaction and boundary layer heat transfer coefficient will also affect the way ΔT_{ab} changes with bed temperature. The relative temperature– insensitivity of H_1 (see Table 2.5) and h_e suggest, however, that these are likely to be of secondary importance relative to the former mechanisms.

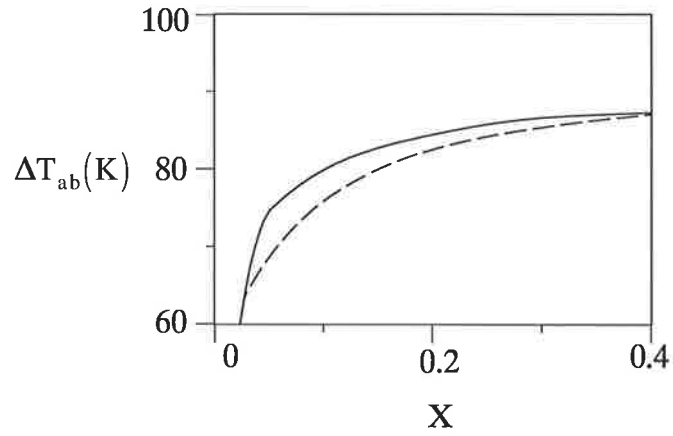


Figure 2.9. Particle over–temperature vs bed temperature for $d_{ao}=5$ mm, $d_b=1100$ μ m, BLRS=1: $T_b=1073$ K (solid); $T_b=1173$ K (broken).

For comparison, the maximum particle over–temperatures obtained by Prins (1987) from his ASPC model at $T_b=985$ K and 1110 K are also shown in Figure 2.8. Two sets of values have been plotted: (1) that set obtained by Prins for $d_{ao}=0.8$ mm; and (2) a set for $d_{ao}=1$ mm derived from the first set using the scaling relationship: $\Delta T_{ab} \sim d_a^{1.3}$ [Prins, 1987]. Differences between the models, char properties and simulation conditions makes comparison difficult. However, by comparing effective heat transfer coefficients, char combustion rates, and enthalpies–of–reaction [cf: equation (2–62)], we should be able to reconcile any differences between the values of Prins and those predicted in this study. Table 2.10 shows rough estimates for these parameters – these

Table 2.10. Values used to compare maximum over–temperatures of Prins (1987) with those determined in this study for a 1mm char.

Parameter	Prins (985K)	This work (973K)	Prins (1110K)	This work (1073K)
$R_{max}(10^{-9} \text{ kg/s})^{\ddagger}$	~ 0.8	~ 3.8	~ 6.1	~ 13.7
$t_{90}(\text{s})$	~ 1212	~ 96	~ 140	~ 30
$h_e(\text{W/m}^2\text{K})^{\dagger}$	~ 800	~ 710	~ 860	~ 750
$H_r(\text{MJ/kg of C})$	~ 33	~ 35	~ 33	~ 35

$\dagger$ Prins values are for a 1 mm char obtained from 0.8 mm char via $h \sim d_a^{-0.26}$

$\ddagger$ Prins values are for a 1 mm char obtained from 0.8 mm char via $R \sim d_a^{1.5}$

figures indicate that Prins' over-temperatures should be smaller than those predicted in this study. As Figure 2.8 shows, this is true at the lower bed temperature, but not at the higher. This discrepancy may be due to our use of the scaling relationship $\Delta T_{ab} \sim d_a^{1.3}$ which is infact only valid for Regime I burning [Prins, 1987]. At the higher bed temperature, Prins found that the 0.8 mm char burnt in a Regime II manner. His scaling for Regime III burning – $\Delta T_{ab} \sim d_a^{-0.2}$ – suggests, therefore, that the adjusted value shown in Figure 2.8 for $T_b = 1110$ K may be an over-estimate; the true value will most likely lie somewhere in between the calculated value for the 0.8 mm char, and the estimated value for the 1mm char.

Figure 2.10 shows how the maximum particle over-temperature for the 1 mm char varies with bed oxygen concentration – this points to an increasing linear relationship between these two parameters for all bed temperatures. The particle heat balance, equation (2-62), shows that particle over-temperature is roughly proportional to the oxygen concentration within the particle (remember that intraparticle homogeneous reaction has been

neglected in this simple explanation since it was found that it accounted for only a small proportion of the intraparticle heat generated – its rate is proportional to $\sqrt{C_1}$, and hence it may become more dominant at small oxygen concentration levels). For $\Delta T_{ab} \sim C_{1b}$, therefore, the intraparticle oxygen distribution must also be proportional to the bed oxygen concentration – this dependence does indeed hold, at least approximately, as shown in Figure 2.11 where, for different bed temperatures, C_1 at

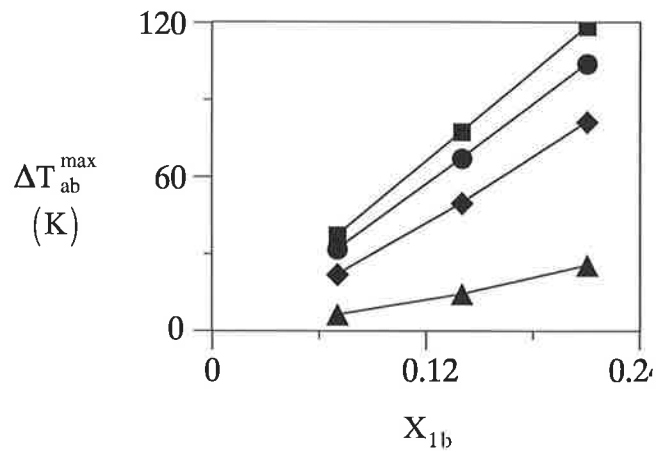


Figure 2.10. Maximum particle over-temperature vs bed oxygen concentration for $d_{ao} = 1$ mm, $d_b = 200$ μ m: $T_b = 973$ K ▲; $T_b = 1073$ K ◆; $T_b = 1173$ K ●; $T_b = 1273$ K (1) ■.

several points within the 1 mm char have been plotted against bed oxygen concentration at $X \approx 0.2$.

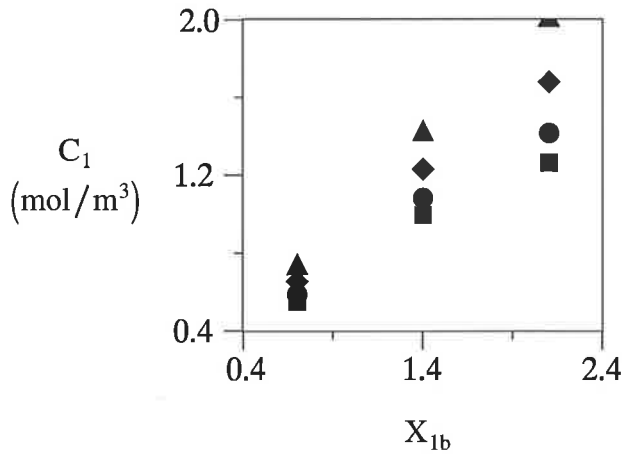


Figure 2.11(a). Oxygen Concentration vs Bed Oxygen Concentration at different positions within the char at $X \approx 0.2$ for $d_{ao} = 1$ mm, $T_b = 973$ K, $d_b = 200$ μm : $\zeta \approx 1.0$ $\blacktriangle$; $\zeta \approx 0.73$ $\blacklozenge$; $\zeta \approx 0.47$ $\bullet$; $\zeta \approx 0.20$ $\blacksquare$.

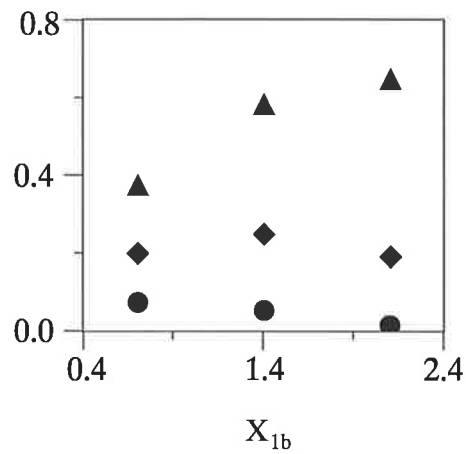


Figure 2.11(b). Oxygen Concentration vs Bed Oxygen Concentration at different positions within the char at $X \approx 0.2$ for $d_{ao} = 1$ mm, $T_b = 1073$ K, $d_b = 200$ μm : $\zeta \approx 1.0$ $\blacktriangle$; $\zeta \approx 0.73$ $\blacklozenge$; $\zeta \approx 0.47$ $\bullet$.

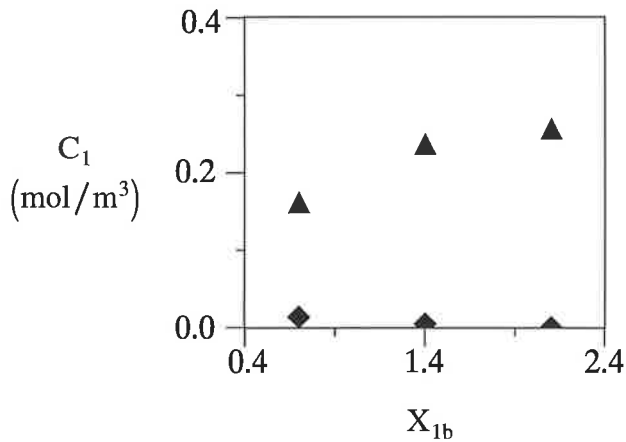


Figure 2.11(c). Oxygen Concentration vs Bed Oxygen Concentration at different positions within the char at $X \approx 0.2$ for $d_{ao} = 1$ mm, $T_b = 973$ K, $d_b = 200$ μm : $\zeta \approx 0.97$ $\blacktriangle$; $\zeta \approx 0.71$ $\blacklozenge$.

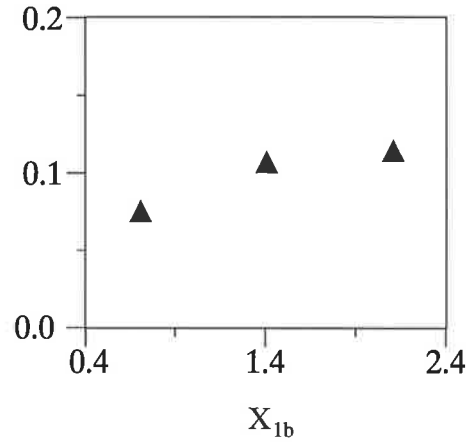


Figure 2.11(d). Oxygen Concentration vs Bed Oxygen Concentration at different positions within the char at $X \approx 0.2$ for $d_{ao} = 1$ mm, $T_b = 1073$ K, $d_b = 200$ μm : $\zeta \approx 0.95$ $\blacktriangle$.

Comparing gradients, Figure 2.10 also shows that bed temperature affects ΔT_{ab} 's sensitivity to bed oxygen concentration. This is due to the shift in char combustion behavior with system temperature. At the lowest bed temperature, char combustion is primarily controlled by reaction leading to a relative insensitivity to bed oxygen concentration. At the higher bed temperatures, however, particle over-temperature becomes increasingly sensitive to bed oxygen concentration as the char combustion process becomes more and more controlled by boundary layer and intraparticle mass transport.

For the same conditions and char as Figure 2.6, Figure 2.12 shows how the maximum temperature difference across the char, ΔT_a , varies with conversion. To reveal behavior near ignition, ΔT_a has been plotted against log-conversion. Although this figure shows that near-isothermal behavior prevailed for all of the conditions simulated here (largest sustained ΔT_a of ~ 3 K occurred at $T_b = 1073$, $X_{1b} = 0.21$), trends still permit identification of situations in which more non-isothermal behavior may occur. For the 1 mm char at the lower bed temperatures of 973 K and 1073 K, the ΔT_a increase with conversion is a result of intraparticle solid consumption (see Figure 2.4) causing the effective thermal conductivity of the porous solid to decrease towards that of the interstitial gas mixture. The increase of ΔT_a with bed oxygen concentration at these bed temperatures indicates the degree of non-isothermality is determined by, amongst other things, the rate of heat production (ie: the reaction rates). Thus, ΔT_a should increase with bed temperature. At the higher bed temperatures, however, small oxygen penetration depths (see Figure 2.2) mean there is no opportunity for significant internal carbon consumption. An opportunity for greater non-isothermality would exist, though, if the char was initially highly porous. An estimate of ΔT_a for such chars at high bed temperatures may be obtained from the results given here. Figure 2.3 indicates that as bed temperature increases from 973 K to 1273 K, the rate of reaction internal to the char increases by over an order of magnitude, and becomes increasingly restricted to the periphery of the char. If the char was initially highly porous, then this increase should

result in a similar change in ΔT_a (ie: an order of magnitude increase on that predicted for the lower bed temperatures at high conversions; ~ 30 K at $X_{1b} = 0.21$).

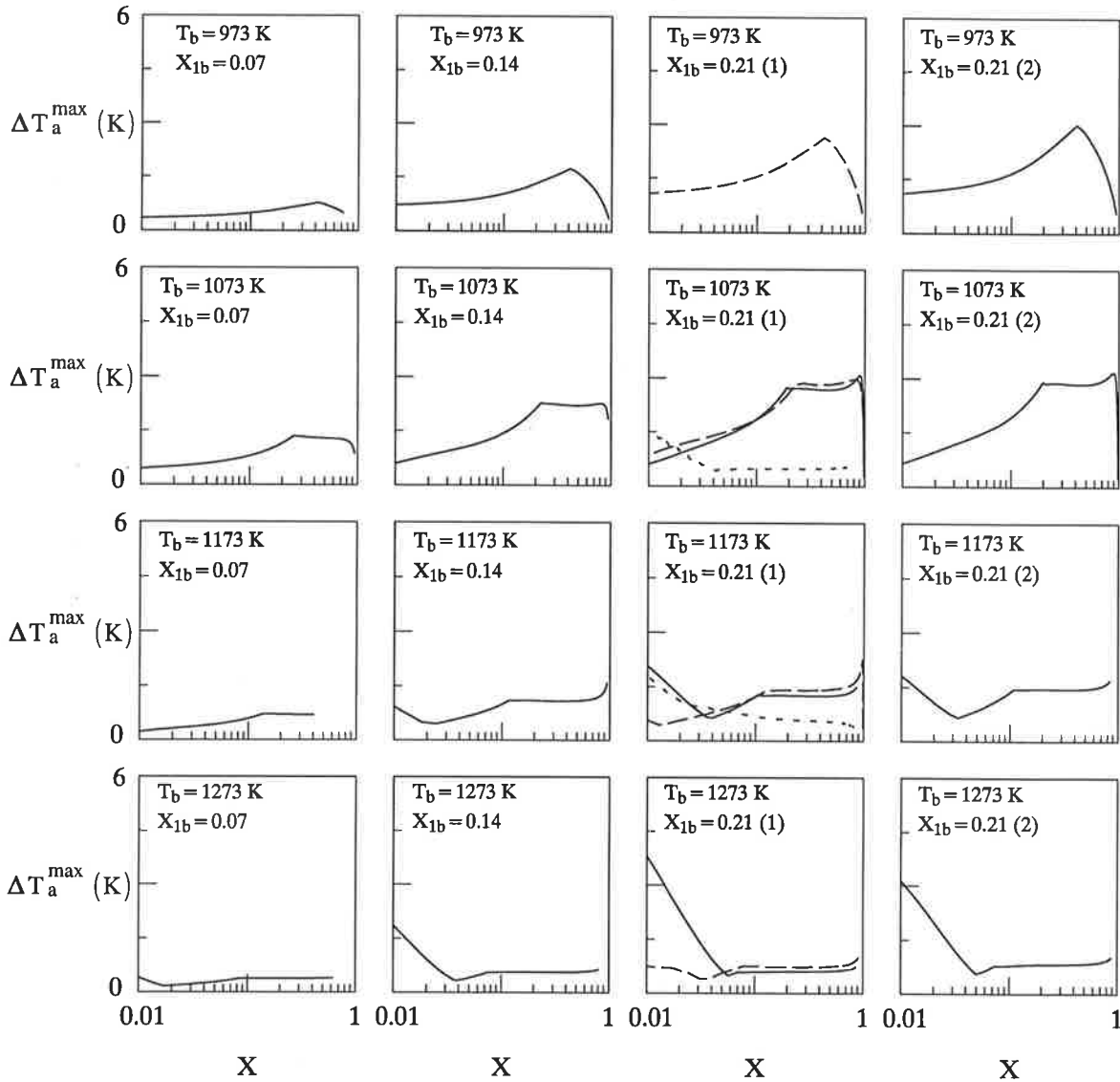


Figure 2.12, Maximum temperature difference across char particle vs log-conversion: $d_{ao} = 1$ mm and $d_b = 200$ μm (solid); $d_{ao} = 1$ mm and $d_b = 1100$ μm (broken); $d_{ao} = 5$ mm and $d_b = 1100$ μm (dash).

Figure 2.12 also shows that as bed temperature increases for $d_b = 200$ μm , ΔT_a increases to a maximum at ignition, and then rapidly decays as a pseudo-steady state is approached. Comparing the behavior of the 5mm char with that of the 1mm char at $T_b = 1073$ K also indicates that the bed temperature necessary for this behavior decreases with increasing active particle size. Although the degree of non-isothermality is not great here [largest ΔT_a of ~ 4 K occurred for $d_{ao} = 1$ mm at

$T_b = 1273$, $X_{1b} = 0.21$], it does suggest that significant non-isothermal behavior may occur when the following three conditions hold: (1) reaction is largely restricted to the char particle periphery; (2) heat transfer from the char is poor; and (3) the char combustion process is highly transient. This scenario is likely to arise for mobile char particles within a bubbling FB. Experimental observations [Nienow et al., 1978; Agarwal, 1987] indicate that when large char particles are present in low concentrations within a bubbling FB, a circulation pattern is set up due to the slow sinking of the particles in the dense phase, and a jerky upwards movement provided by short rides in the bubble phase. Recent simulation results [Biggs and Agarwal, 1993] indicate that such mobile char particles may experience rapid and substantial changes in temperature as they move between the emulsion phase (where mass transfer is poor and heat transfer good) and the bubble phase (where mass and heat transfer are good and poor respectively). Future work will seek confirmation of this hypothesis.

2.3.5.3 Surface CO/CO₂ Product Ratio

Figure 2.13 shows, for both the 1 mm and 5 mm chars, the average surface CO/CO₂ product ratio as a function of inverse particle temperature for the second boundary layer reaction scenario. This figure indicates that if boundary layer reaction does not occur, the surface CO/CO₂ product ratio simply increases with particle temperature for both the small and large active particles. The same plot for the 1 mm char under both boundary layer reaction scenarios is illustrated in Figure 2.14 – this figure shows that if boundary layer reaction does occur, a maximum is seen at intermediate FBC temperatures. Comparing these results with those of Linjewile (1993), Figure 2.1, clearly indicates that homogeneous reaction does occur within the boundary layer of a *stationary char particle resident within an incipient fluidized bed*.

Two phase theory of fluidization [Davidson and Harrison, 1963] tells us that gas flow through the emulsion phase of a bubbling fluidized bed is the same as that passing through an incipient fluidized bed, any excess gas simply passes through the bed as bubbles. We therefore appear to have a sound basis for extending the above conclusion

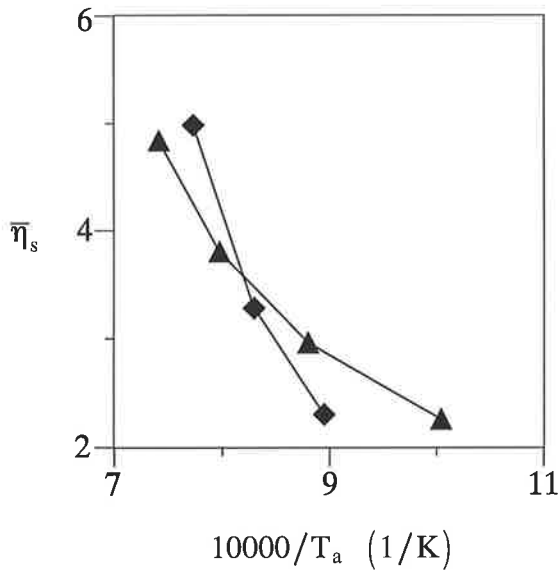


Figure 2.13. Average CO/CO₂ product ratio vs inverse particle temperature for $d_{ao}=1$ mm/ $d_b=200$ μ m ($\blacktriangle$) and $d_{ao}=5$ mm/ $d_b=1100$ μ m ($\blacklozenge$) chars when no boundary layer reaction occurs ($X_{1b}=0.21$).

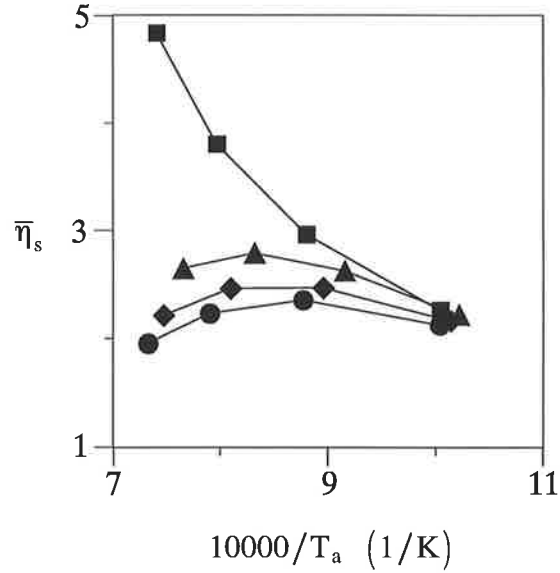


Figure 2.14. Average CO/CO₂ product ratio vs inverse particle temperature for $d_{ao}=1$ mm, $d_b=200$ μ m: $X_{1b}=0.07$ ($\blacktriangle$); $X_{1b}=0.14$ ($\blacklozenge$); $X_{1b}=0.21$ (1) ($\bullet$); $X_{1b}=0.21$ (2) ($\blacksquare$).

to stationary chars resident within the emulsion phase of a bubbling fluidized bed. However, this ignores bed particle convection induced by the bubbles passing through the bed [La Nauze et al., 1984; Xavier and Davidson, 1985]. By enhancing mass and heat transfer between the char and the bed, bed particle convection leads to a reduction of the boundary layer temperature, and of the time spent by CO within the boundary layer – both serve to reduce the extent of boundary layer reaction. This is infact the basis of Prins' argument for why significant homogeneous reaction will not occur within the boundary layer of a char resident within the emulsion phase of a bubbling fluidized bed [Prins, 1987]. As the effective mass transfer coefficient associated with the 5 mm char is significantly less than that of the 1 mm char, we may indirectly assess the validity of Prins' argument by comparing the surface CO/CO₂ product ratios of these chars. Figure 2.15 shows the surface CO/CO₂ product ratio for the 1 mm and 5 mm chars at $T_b = 1073$ K – the trends seen in this figure infact hold for all bed temperatures, $T_b = 1073$ K was selected because the char over-temperatures are similar (see Figure 2.6). This figure

shows that the surface product ratio of the larger char is significantly less than that of the smaller (for both $d_b = 1100 \mu\text{m}$ and $200 \mu\text{m}$) clearly supporting the notion that the extent of boundary layer reaction for a stationary char resident within the emulsion phase of a bubbling fluidized bed will be less than that for a char within an incipient fluidized bed. As the boundary layer thickness used here cannot easily be related to real bed conditions, it is unfortunately not possible to make a systematic quantitative assessment of how the extent of boundary layer reaction changes with superficial gas velocity.

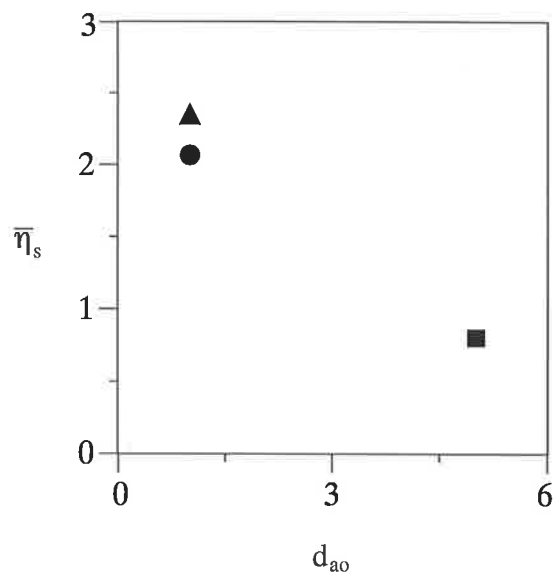


Figure 2.15. Average surface CO/CO₂ product ratio vs initial char particle size for $T_b = 1073 \text{ K}$ and $X_{1b} = 0.21$ (1): $d_{ao} = 1 \text{ mm}$ and $d_b = 200 \mu\text{m}$ ▲; $d_{ao} = 1 \text{ mm}$ and $d_b = 1100 \mu\text{m}$ ●; $d_{ao} = 5 \text{ mm}$ and $d_b = 1100 \mu\text{m}$ ■.

In the approach of Linjewile (1993), the char is fixed to the end of a gas sampling probe – this means we cannot make any definitive statement with regards CO oxidation within the boundary layer of a mobile char. However, the rapid and often sudden movements seen for large chars within a bubbling fluidized bed [Nienow et al., 1978; Agarwal, 1987] do suggest the extent of boundary layer reaction will be less for a mobile char within such beds [La Nauze, 1985].

The above discussions are clearly at odds with the findings of Hayhurst (1991) who argues that promotion of radical recombination by inert particle surfaces [Dennis et al., 1982] inhibits reaction within the boundary layer of a char resident within the emulsion phase for typical FBC temperatures. His argument, however, is based upon the assumption that the porosity within the boundary layer is equal to that of the bulk bed. Review of

the literature [Basu, 1985] infact shows that, when compared to the gas interstices of the bulk bed, significant inert – free void zones may occur within the boundary layer of larger char particles – following the analysis of Hayhurst (1991), this would act to reduce the temperature required for ignition of the boundary layer CO–O₂ gas mixture.

Figures 2.13 and 2.14 also show that intraparticle homogeneous reaction in its own right is unlikely to be sufficient to generate a maximum in the η_s vs $1/T$ curve, boundary layer reaction is also required. This is clearly supported by the discussion of Section 2.3.5.1 where we saw that despite a substantial increase in the maximum intraparticle rate (ie: peak values of Figure 2.3), significantly reduced oxygen penetration depths (ie: reaction volumes) mean the overall rate of intraparticle homogeneous reaction does not change substantially with temperature.

Figure 2.16 shows, for the 5 mm char, the average surface CO/CO₂ product ratio as a function of inverse particle temperature when boundary layer reaction does occur – unlike the 1 mm char, a minimum is obtained at higher particle temperatures in addition to the maximum at intermediate temperatures. The reason why a minimum is obtained becomes obvious when we plot the carbon oxide and CO/CO₂ product ratio distributions within the 5 mm char, Figure 2.17. At

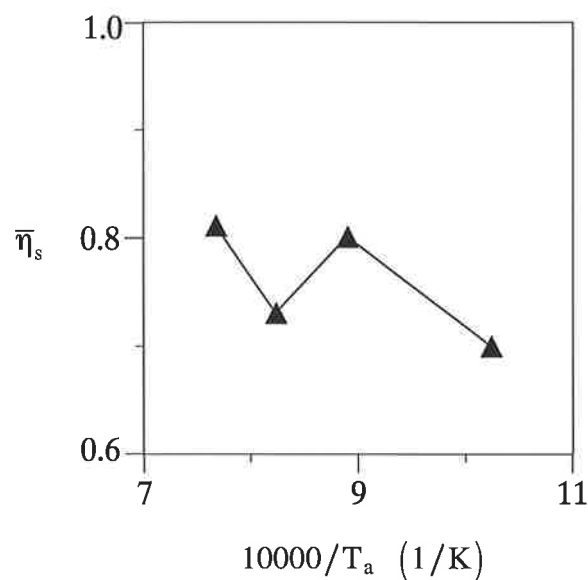


Figure 2.16. Average surface CO/CO₂ product ratio vs inverse particle temperature for $d_{a0}=5$ mm, $d_b=1100$ μ m; $X_{1b}=0.21$ (1).

the lower bed temperatures, the intraparticle CO/CO₂ product ratio is the order of 1–5. At $T_b=1273$ K, however, this increases to the order of 1–70 due to a massive loss of CO₂ in favour of CO. This is, of course, due to the increased importance of the heterogeneous reaction



relative to the C–O₂ reaction as already discussed in §2.3.5.1, and shown in Figure 2.5. The fact that the surface CO/CO₂ product ratio at $T_b = 1273$ K for the second boundary layer reaction scenario is much greater than that of the first, compare Figures 2.13 and 2.16, indicates the surface ratio value for the first scenario is defined by the combined action of the CO₂ gasification and boundary layer reactions which act to decrease and increase the carbon dioxide concentration respectively.

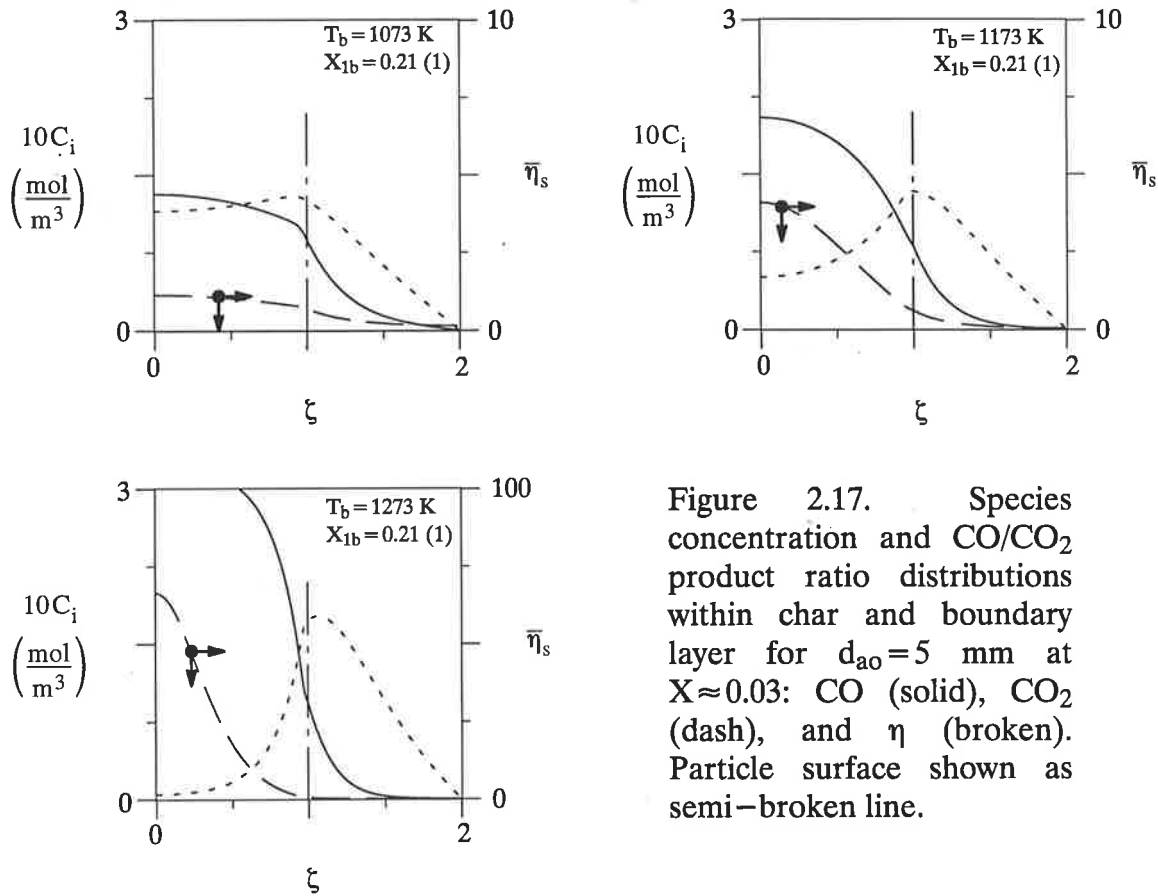


Figure 2.17. Species concentration and CO/CO₂ product ratio distributions within char and boundary layer for $d_{a0} = 5$ mm at $X \approx 0.03$: CO (solid), CO₂ (dash), and η (broken). Particle surface shown as semi-broken line.

Figure 2.5 has been replotted in Figure 2.18 along with the overall rate ratio used by Linjewile (1993) in his simple, homogeneous film, shrinking core model. Extrapolation of the 1 mm char curves to the level of the 5 mm char at $T_b = 1273$ K (dash lines), indicates that the particle temperature required before a minimum is seen in the η_s vs $1/T$ curve increases as active particle size diminishes, and is the order of 1400–1500 K for the 1 mm char simulated here. As smaller chars burn at lower temperatures for a given set of conditions, it is unlikely that a minimum would be obtained for such chars under typical

FBC conditions. This figure also shows that Linjewile (1993) could not predict the high temperature minimum because the overall reaction rate used for the CO₂ gasification reaction was too small relative to that of the C–O₂ reaction.

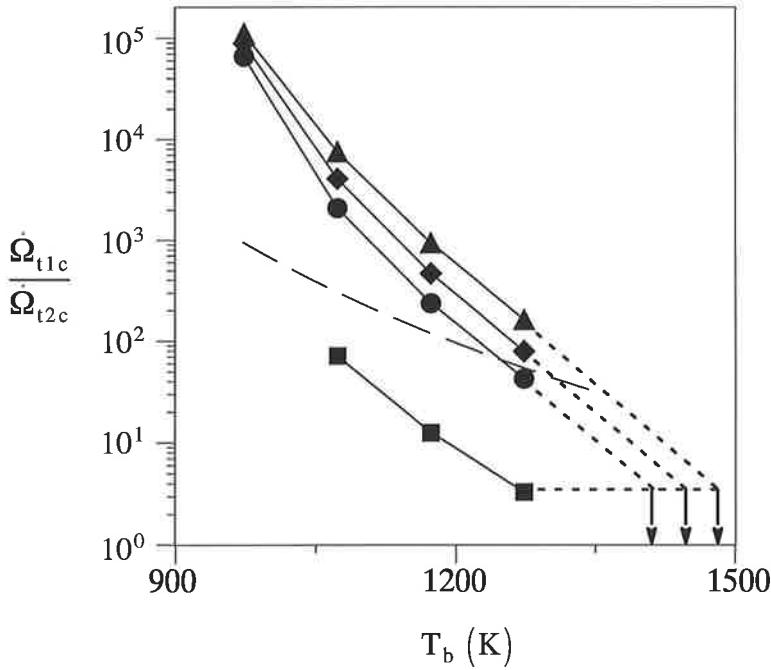


Figure 2.18. Ratio of total heterogeneous reaction rates vs bed temperature for $d_{ao}=1$ mm, $d_b=200$ μ m, $X \approx 0.2$: $X_{1b}=0.07$ $\blacktriangle$; $X_{1b}=0.14$ $\blacklozenge$; $X_{1b}=0.21$ (1) $\bullet$; and $d_{ao}=5$ mm, $d_b=1100$ μ m, $X \approx 0.03$: $X_{1b}=0.21$ (1) $\blacksquare$. Ratio of Linjewile et al. (1995) is shown as a broken line.

As the CO/CO₂ product ratio measured by the technique of Linjewile (1993) at high bed temperatures represents something other than the net effect of the two reactions R1 and R3, the ratio cannot be used to accurately estimate the enthalpy–of–reaction from the often used expression [eg: Field et al., 1967; La Nauze and Jung, 1983; Prins, 1987; Linjewile and Agarwal, 1995]

$$H_r^t = 33054 \left(\frac{2}{\Delta_m} - 1 \right) + 9791 \left(2 - \frac{2}{\Delta_m} \right) \quad \text{kJ per kg of carbon} \quad (2-63)$$

where Δ_m is the mechanism factor that smoothly varies between 2, indicating the product of the net reaction R1 + R3 is CO only, to 1 where CO₂ is the sole product. However, as the CO₂ gasification reaction is moderately endothermic (~ 12 MJ per kg of C), use of the Linjewile (1993) ratio in equation (2–63) does yield the correct trend between temperature and enthalpy–of–reaction.

2.3.5.4 Char Particle Conversion Behaviour

Figure 2.19 shows the char particle density and size variation with conversion for the 1 mm and 5 mm chars at various conditions – these variations are qualitatively similar to those obtained by others [eg: Gavalas, 1981; Sotirchos and Amundson, 1984d; Reyes and Jensen, 1986b; Prins, 1987; Srinivasachar et al., 1988]. This figure clearly indicates that for all cases, particle density initially decreases in a linear manner due to internal

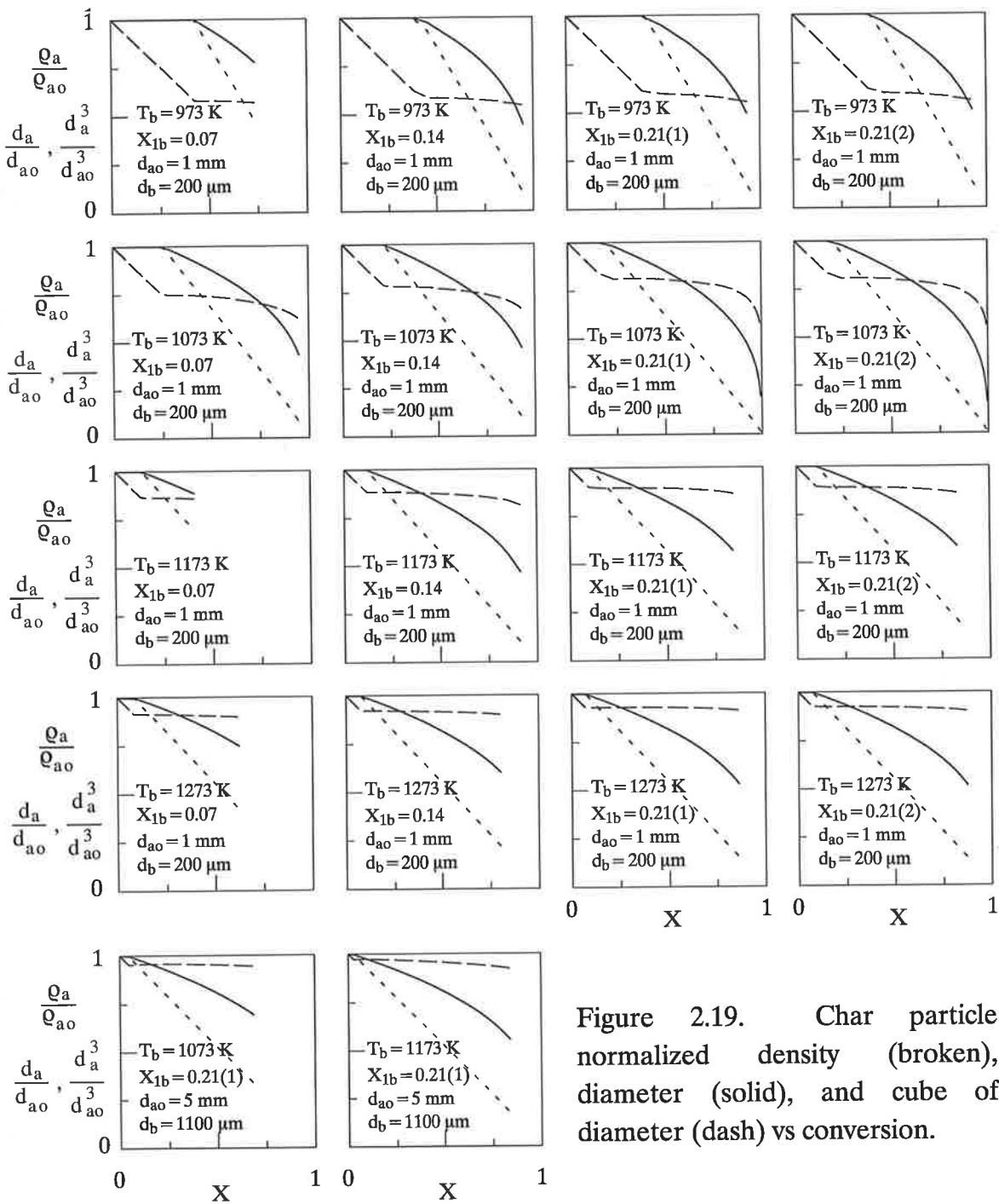


Figure 2.19. Char particle normalized density (broken), diameter (solid), and cube of diameter (dash) vs conversion.

combustion, whilst reaction at the external surface causes virtually no change in particle size. Once the porosity at the particle surface reaches the critical value, however, density change almost ceases, and the particle size starts to decrease. This behavior persists until high conversion levels ($X \geq 0.85$) where the rate of particle density decrease once again picks up as the combustion process passes into the kinetic regime.

As char particle size does not change prior to the onset of disintegration, the change in normalized particle density up to this point is infact equal to X_d , the conversion at which disintegration starts. Figure 2.20 shows how X_d varies with bed temperature and active particle size. This figure clearly illustrates that X_d decreases at a diminishing rate with increasing char particle size and bed temperature, whilst it remains largely unaffected by bed oxygen concentration and BLRS. This behavior is dictated by the mode of char combustion, and the way it changes with these parameters. For a combustion process primarily controlled by reaction, a high degree of oxygen penetration means considerable pore development occurs throughout the char prior to the surface porosity reaching the critical value. When combustion is largely controlled by the rate of mass transport, however, negligible oxygen penetration means pore evolution is isolated to the particle periphery where it directly contributes to the initiation of peripheral

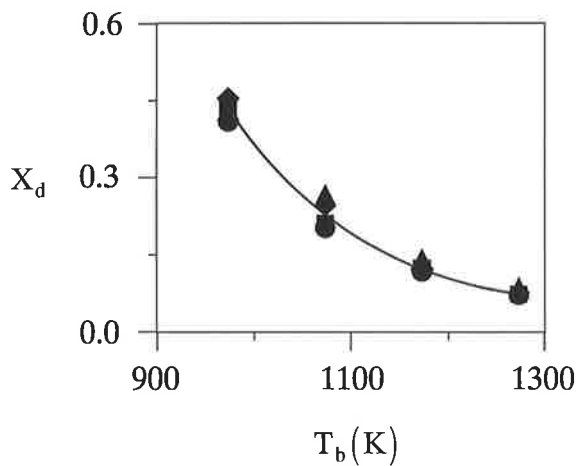


Figure 2.20(a). Conversion at onset of disintegration vs bed temperature for $d_{ao} = 1$ mm, $d_b = 200$ μ m: $X_{1b} = 0.07$ $\blacktriangle$; $X_{1b} = 0.14$ $\blacklozenge$; $X_{1b} = 0.21$ (1) $\bullet$; $X_{1b} = 0.21$ (2) $\blacksquare$.

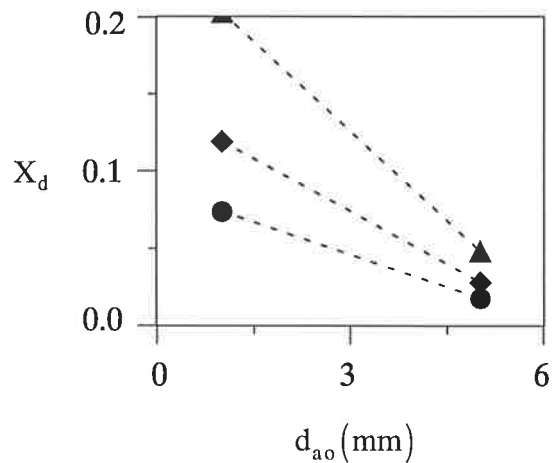


Figure 2.20(b). Conversion at onset of disintegration vs active particle size for $X_{1b} = 0.21$ (1): $T_b = 1073$ K $\blacktriangle$; $T_b = 1173$ K $\blacklozenge$; $T_b = 1273$ K $\bullet$.

disintegration. As discussed in a previous section, transition between these regimes is chiefly dictated by bed temperature and active particle size (with their influence decreasing at higher values of these parameters as char combustion becomes more and more controlled by mass transfer), whilst bed oxygen concentration has a lesser effect*, and BLRS no effect. The degree of particle density change for $X > X_d$ is also determined by the combustion regime. For example, at high bed temperatures or for large char particles, the particle density change for $X_d < X \leq 0.85$ is almost zero due to reaction being primarily restricted to the particle periphery.

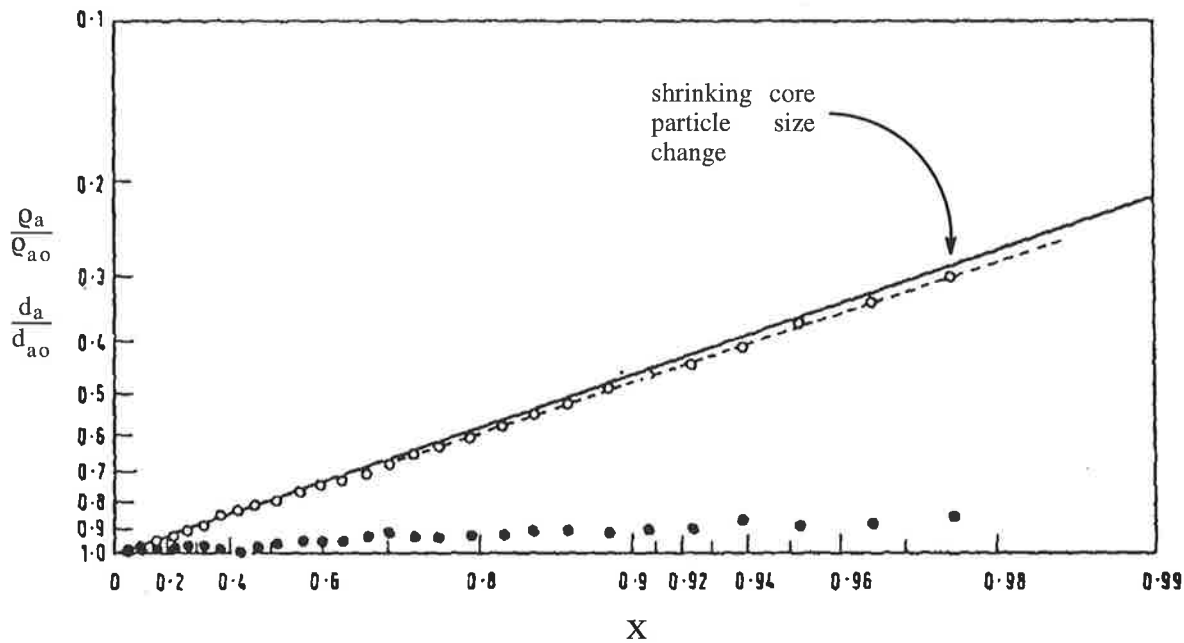


Figure 2.21. Experimentally determined char particle normalized density (●) and diameter (○) vs conversion for $d_{ao} = 11.8$ mm and $T_b = 1173$ K [La Nauze and Jung, 1983].

Figure 2.21 shows an experimentally determined particle density and size variation with conversion for an 11.8 mm char at $T_b = 1173$ K [La Nauze and Jung, 1983]. Based upon these results, La Nauze and Jung (1983) suggest that chars down to 3 mm in size will burn in a shrinking core manner with some internal combustion that may become significant for smaller sized char particles (ie: < 3 mm). This last comment was motivated by the deviations seen in Figure 2.21 from that expected of a shrinking core (ie: particle radius

* The effect X_{1b} has on the O_2 distribution is most marked at $T_b = 1073$ K which is the bed temperature where we see the greatest difference in X_d as shown in Figure 2.20(a).

follows solid line and density remains unchanged from its initial value). The results obtained here suggest, however, that even for large char particles, internal combustion causing peripheral disintegration may infact be the major cause of particle size decrease, not combustion at the external surface. However, as X_d for large chars is quite small [see Figure 2.20(b)], arriving at this conclusion on the basis of experimental observations such as Figure 2.21 would be extremely difficult.

The contribution of disintegration to the char conversion process is also clearly illustrated in Figure 2.22 which shows, for a range of conditions and char sizes, the variation with conversion of the char combustion rate, $\dot{m}_{ar}$, and the total rate of char mass loss $\dot{m}_{at} = \dot{m}_{ar} + \dot{m}_{ad}$ where $\dot{m}_{ad}$ is the rate of mass loss via disintegration. The total rate (solid line) initially follows the combustion rate curve (broken line) until onset of disintegration where it discontinuously jumps to a maximum, and then decreases with conversion in a monotonic fashion (this is because incremental mass loss diminishes with particle size). The ratio of these two rates, shown in Figure 2.22 as a dashed line, indicates that once it commences, disintegration is the major source of particle mass loss for all conditions – for the 1 mm char at $T_b = 973$ K, mass loss due to reaction only accounts for approximately 10% of the total rate, with this increasing to 30–40% for both sized chars at the higher bed temperatures. Clearly, disintegration should be included in any model used to predict char particle burnout time.

Comparison of burnout times (time at $X = 0.9$) predicated here with those of Prins (1987), Table 2.10, also clearly indicates the significance of disintegration when attempting to estimate burnout time. At the lower bed temperature, Prins' burnout time is over 12 times larger than that predicted in this work, despite his maximum combustion rate* being about 1/5th of ours. This large difference is caused by Prins' char ($\phi_o = 0.2$, $\phi^* = 0.95$, $\rho_c = 2250$ kg/m³) not exhibiting peripheral disintegration at any stage during the conversion process, whereas the char simulated in this study ($\phi_o = 0.4$, $\phi^* = 0.65$, $\rho_c = 2000$ kg/m³) started to disintegrate at $X \approx 0.38$. Although the predicted burnout

* This is being used as a measure of the rate of char consumption due to reaction.

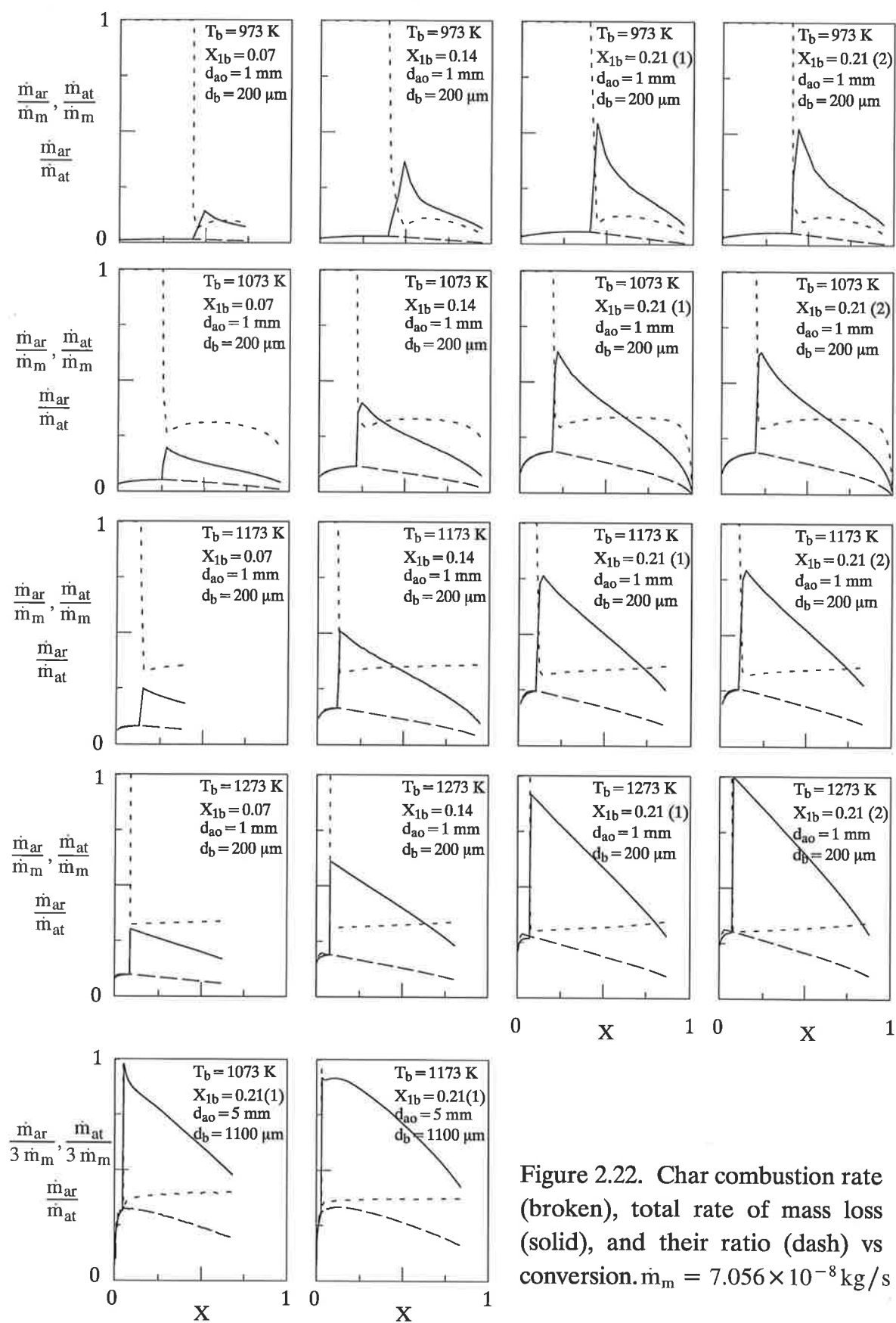


Figure 2.22. Char combustion rate (broken), total rate of mass loss (solid), and their ratio (dash) vs conversion. $\dot{m}_m = 7.056 \times 10^{-8} \text{ kg/s}$

times compare more favorably at the higher bed temperature (that of Prins is 5 times larger), this is because Prins' maximum rate has increased to about half that determined here. In this case, Prins' char does exhibit disintegration, but it does not start until $X \approx 0.55^*$ as compared to $X \approx 0.18$ for our char.

2.3.6 Summary of Results

By comparing results generated here with the experimental results of Linjewile (1993), we were able to conclude that homogeneous reaction does occur within the boundary layer of a stationary char particle resident within an incipient fluidized bed. Reaction is also expected to occur within the boundary layer of a stationary char particle resident within the emulsion phase of a bubbling fluidized bed, with the extent of reaction diminishing as superficial gas velocity increases. However, it is still unclear what effect active particle motion has on the the extent of boundary layer reaction, and whether or not intraparticle homogeneous reaction does occur.

As a result of this work, we can propose a modified form of the Linjewile (1993) hypothesis to explain the behavior seen in Figure 2.1:

- At low particle temperatures, oxygen penetrates deep into the char so as to react with the solid to form both CO and CO₂ according to the primary CO/CO₂ product ratio. As homogeneous reaction is negligible at these low temperatures, little primary-CO is converted to CO₂ leading to a surface CO/CO₂ product ratio that increases with temperature in accordance with the primary ratio.
- As the particle temperature increases, however, homogeneous conversion of primary-CO to CO₂ in the boundary layer and, possibly, the pores becomes increasingly significant, leading to the surface CO/CO₂ product ratio to pass through a local maximum at intermediate FBC temperatures, and then diminish with increasing temperature.

* This is equal to over 60% of the conversion process on the basis of 90% conversion being equal to burnout.

- As particle temperature increases towards the maximum normally encountered under typical FBC conditions, heterogeneous reaction at the particle external surface and homogeneous reaction within the boundary layer prevents substantial oxygen penetration into the char. The considerably lower intrinsic reactivity of the CO_2 gasification reaction on the other hand means it still occurs throughout the char volume to produce CO at the expense of CO_2 . Provided the particle volume (CO_2 reactive surface area really) is sufficiently high, the overall rate of the gasification reaction becomes comparable to that of the $\text{C}-\text{O}_2$ reaction leading to a minimum at a temperature dependent upon the char particle size and char type [ie: pore structure and catalytic impurities; Ballal and Zygourakis, 1986, 1987; Sandmann and Zygourakis, 1987; Ballal et al., 1988; Smith et al., 1993].

The results generated in this study indicate that the simplified, homogeneous film, shrinking core model used by Linjewile (1993) could not predict the high temperature minimum of Figure 2.1 because the overall reaction rate used by him for the CO_2 gasification reaction was too small relative to that of the $\text{C}-\text{O}_2$ reaction – this issue will be explored further in future work.

Since the CO_2 gasification reaction makes a significant contribution to the CO/CO_2 product ratio for larger active particles at higher FBC temperatures, the surface CO/CO_2 product ratio determined under such conditions by the method of Linjewile (1993) cannot be used to accurately predict enthalpies-of-reaction when used with the standard expression (2–63). It also means that experimentally measured CO/CO_2 product ratios will vary with active particle size. On the basis of work presented both here and in the literature, it is hypothesized that the particle related CO/CO_2 product ratio can in fact increase or decrease with active particle size depending upon the temperature/combustion regime:

- At low FBC temperatures typical of the kinetic regime for the $\text{C}-\text{O}_2$ reaction (ie: $\sim 900\text{--}1000\text{ K}$), both the homogeneous and CO_2 gasification reactions are unimportant (cf: §2.3.5.1), and active particles of all sizes are near-isothermal

[this is reasonable in light of the analysis in §2.3.5.2 where it was shown that non-isothermal effects are only likely to be of importance if reaction is largely restricted to the particle periphery and: (1) the char is initially highly porous; and/or (2) the char-bed heat transfer is poor and the combustion process highly transient] – in this case the product ratio will be equal to the primary value, and independent of active particle size.

- At intermediate temperatures typical of reaction and intraparticle diffusion control for the C–O₂ reaction (ie: ~1000–1100 K), boundary layer reaction starts to become important (cf: §2.3.5.1), with the degree of importance increasing with active particle size [La Nauze, 1985] – in this case the product ratio will tend to decrease as active particle size increases.
- At high temperatures typical of low oxygen penetration and considerable boundary layer transport control (ie: ~1100–1300 K), the importance of the CO₂ gasification reaction increases with active particle size relative to the C–O₂ reaction (cf: §§2.3.5.1 and 2.3.5.3) – in this case the product ratio will tend to increase with active particle size.

The above hypothesis is very tentative, especially in the intermediate temperature regime where intraparticle homogeneous reaction for smaller chars, if it occurs, is likely to be more significant than that associated with larger chars. The fact that the variation of product ratio with active particle size is determined by an interplay between the various reactions, means it is subject to all the factors that influence the behaviors of these reactions (eg: bed hydrodynamics and char properties) – it is perhaps no small wonder that a relationship between the particle related product ratio and active particle size has eluded experimental determination.

Interplay between the various reactions also affects the particle over-temperature. Particle over-temperature first increases with bed temperature to a maximum, where it then starts to diminish with any further increase in bed temperature due to the C–O₂ reaction becoming boundary layer transport controlled, and the endothermic C–CO₂

reaction more significant. The rate of particle over-temperature decrease at high bed temperatures will be moderated, however, by boundary layer reaction which acts to reduce the char-bed heat transfer coefficient. As boundary layer reaction affects the char-bed heat transfer coefficient:

- this should be explicitly accounted for in any correlation for this transport coefficient via a Damköhler Number of the form $Da = \dot{Q}R^2/\lambda\Delta T$;
- bed-char heat transfer correlations determined under non-reactive conditions will not be valid in char combustion applications; and
- bed-char heat transfer correlations determined under reactive conditions but which do not explicitly consider boundary layer reaction (via a Damköhler Number) will implicitly include its effect, but will not in general be valid for conditions and chars other than those used in determining them.

Finally, it was found that the CO_2 gasification reaction can be responsible for significant solid consumption within larger char particles at high FBC temperatures, and that peripheral disintegration is the major source of char particle mass loss if it occurs, with its contribution being greatest under near-Regime I (for $\text{C}-\text{O}_2$ reaction) conditions.

2.4 CONCLUDING REMARKS AND FUTURE WORK

In this chapter, an advanced single particle FBC model has been developed and subsequently used to study the behavior of burning porous char particles within an incipient fluidized bed for over 100 different combinations of bed temperature and oxygen concentration, inert particle size, and active particle size. The model is based upon a spherically symmetric, transient, continuum multicomponent mass and heat conservation formulation for both the porous char and surrounding boundary layer. Mass fluxes are defined via the Dusty-gas model, and percolation concepts are used to describe the effect that pore evolution has on available reactive surface area, accessible porosity, and intraparticle mass transport coefficients. Both homogeneous ($\text{CO}-\text{O}_2$) and heterogeneous ($\text{C}-\text{O}_2$ and $\text{C}-\text{CO}_2$) reactions are modelled, with the primary

CO/CO₂ product ratio of the carbon–oxygen reaction being defined by an Arrhenius type expression. This model represents an improvement upon that of Prins [Prins, 1987; Prins and van Swaaij, 1990] which the review of §2.2 shows to be the most advanced of existing single particle FBC models.

By comparing results obtained from this model with the experimental results of Linjewile (1993), we successfully addressed many of the issues raised in the Introduction to this chapter. For example, we were able to show that homogeneous reaction does occur within the boundary layer of a char resident within an incipient fluidized bed, and that for higher bed temperatures and larger char particles, the normally neglected C–CO₂ reaction is significant, and responsible for considerable production of CO at the expense of CO₂. Both these issues are critical for explanation of the high temperature maximum and low temperature minimum seen in Figure 2.1. It was also found that the simplified, homogeneous film, shrinking core model used by Linjewile (1993) could not predict the high temperature minimum, because the overall reaction rate used by him for the CO₂ gasification reaction was too small relative to that of the C–O₂ reaction – this issue will be explored further in the near future. A more comprehensive summary of the results may be found in §2.3.6.

Despite the success of this study and the advanced nature of the model, the brief literature review of §2.2 indicated the following precluded a full quantitative study: (1) use of the continuum and smooth field approximations; (2) inadequate modelling of char morphological and transport properties; (3) our inability to solve the full boundary layer problem in conjunction with that of the burning char; and (4) poor kinetic models for both the heterogeneous and homogeneous reaction processes. Issues associated with addressing the first three are briefly discussed below, whilst consideration of the last is deferred to the end of the following chapter.

2.4.1 The Breakdown of the Continuum Approximation, Fractals, and Non-classical Transport Equations

If the continuum approximation breaks down [cf: equation (2–28) and associated text], then the medium in question may be considered fractal [Sahimi et al., 1990]. Although use of a macroscopic theory based upon differential equations to describe transport and/or reaction on such a medium is strictly invalid [Sahimi et al., 1990], anything else is generally unattractive from an engineering perspective – it is for this reason that much effort has been devoted to the development of such theories in recent years. The first was that of O’Shaughnessy and Procaccia (1985a, b) who proposed a modified form of Fick’s second law for a spherically symmetric fractal body (OSP equation)

$$\frac{\partial C}{\partial t} = \frac{K_f}{r^{d_f-1}} \frac{\partial}{\partial r} \left(r^{d_f-1-\theta} \frac{\partial C}{\partial r} \right) \quad (2-64)$$

where d_f and $d_w = \theta + 2$ are the fractal and random walk fractal dimensions respectively, and K_f the pre-factor of the length-dependent “diffusion coefficient” scaling relationship [Gefen et al., 1983]

$$D = K_f r^{-\theta} \quad (2-65)$$

The OSP equation has since been used in the study of diffusion and reaction on fractal structures [Clément et al., 1989; 1990], and spherical porous catalyst particles [Giona, 1991, 1992]. Various fundamental criticisms of the OSP equation have motivated the development of several new, more sound, theories [Giona and Roman, 1992a, b, c; Roman and Giona, 1992; Muralidhar and Ramkrishna, 1993; Barta, 1994; Metzler et al., 1994]. Perhaps the most promising of these new theories is that of Cushman (1991) where the flux is governed by an integro-differential equation in which the diffusion coefficient is both position and time dependent

$$\frac{\partial C(\mathbf{r}, t)}{\partial t} = \nabla \cdot \int_0^t \int_{\mathbf{r}} D(\mathbf{r}', t') \nabla C(\mathbf{r} - \mathbf{r}', t - t') d\mathbf{r}' dt' \quad (2-66)$$

Unlike the previous theories, this equation can be applied to any body of interest, and permits us to define the length scale over which the body may be considered fractal (eg: average pore length). It also naturally reduces to Fick’s law if the diffusion process is assumed local in both time and space. Despite all this activity, there is still a long way

to go. In particular, we must resolve issues relating to: (1) application and solution of these non–classical equations for real problems (eg: those problems that include reaction, multicomponent fluids, and coupled processes); (2) how to determine the relevant transport coefficients [eg: $D(r, t)$ of equation (2–66)] and their variation with various morphological parameters (eg: porosity); and (3) how to include non–linear effects [eg: effect of temperature on $D(r, t)$]. The last two of these issues may be tackled using the equilibrium molecular dynamic approach of the next chapter [Biggs and Agarwal, 1992, 1994], and its nonequilibrium variant [Evans and Morriss, 1984, 1990] – this work will be undertaken in the near future by this author.

2.4.2 The Discrete Approach and Lattice Gas Automata – The Way Forward

Despite the fact that the non–classical equations of the previous section describe transport on a fractal, they are still reliant upon the smooth field approximation. Indeed, O’Shaughnessy and Procaccia (1985a, b) make very clear that their equation does not describe the real, highly discontinuous, behavior, but, rather, a function that “envelopes” it. The only way to avoid both the smooth field and continuum approximations is to explicitly model the porous solid of interest either via continuum tessellation/ random inclusion models such as are illustrated in Figure 2.23, or a discrete network, examples of which are shown in Figure 2.24. The latter are computationally less demanding, but are restricted to systems where: (1) transport within the pore bodies is much more significant compared to their necks [Sahimi, 1994]; (2) where significant pore development* does not occur; and (3) where transport within the complementary phase is not of interest. Clearly, the discrete lattice is inadequate when we wish to model the full char combustion process where the last two are extremely important, and the first a consideration that can not be ruled out.

* Significant pore development is where adjacent pores begin to overlap, and original pore shape is lost.

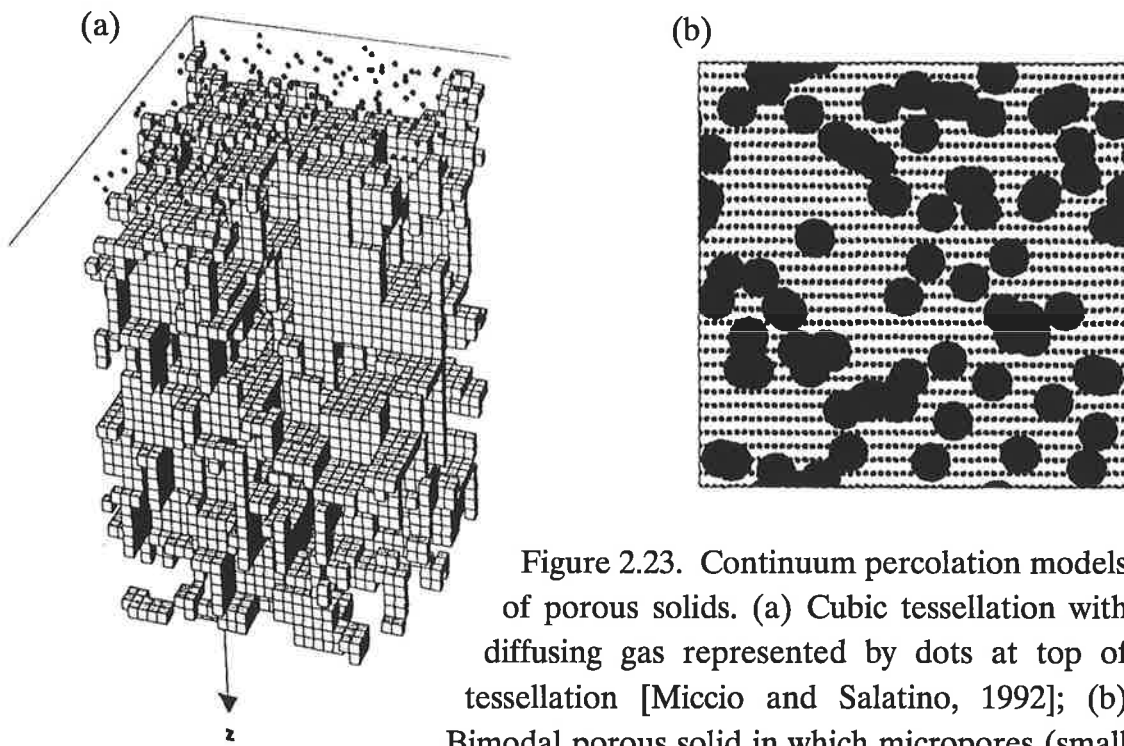


Figure 2.23. Continuum percolation models of porous solids. (a) Cubic tessellation with diffusing gas represented by dots at top of tessellation [Miccio and Salatino, 1992]; (b) Bimodal porous solid in which micropores (small black circles) are ordered, and the macropores randomly distributed (interpenetrated black circles) [Zygourakis and Sandmann, 1988].

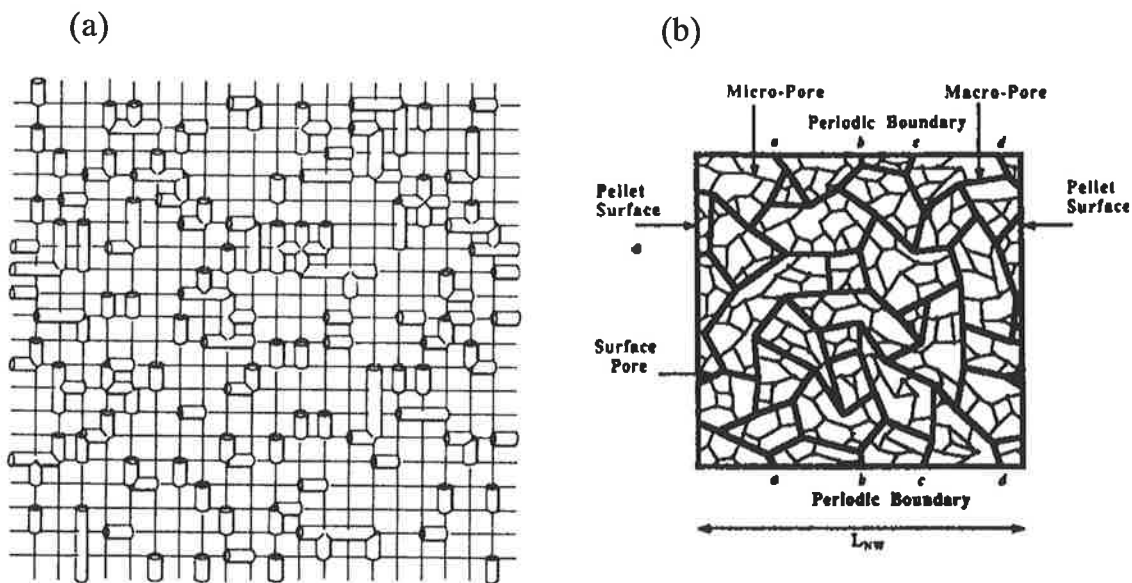


Figure 2.24. Discrete percolation models of porous solids. (a) Regular network representing a bimodal porous solid in which the thin lines are micropores, and tubes macropores [Sharratt and Mann, 1987]; (b) Random network representing a bimodal porous solid in which the thin lines are micropores, and bold lines macropores [Hollewand and Gladden, 1992b].

Continuum percolation models such as those illustrated in Figure 2.23 also offer an opportunity to improve upon our treatment of the effective transport and reactivity properties of the char:

- Morphological elements (eg: elements derived from the different macerals, and inerts) of different reactivity may be explicitly included – this will permit more realistic simulation of burnout and disintegration phenomena [Hargrave et al., 1986; Kang et al., 1988, 1992; Chirone et al., 1991, 1992].
- The transport properties of the char/fluid system may be treated more effectively. For example, the brief literature review of §2.2 indicates that little is known about how char thermal conductivity varies with char type, or conversion. If our discrete model distinguishes between those morphological elements that derive themselves from the different macerals of the parent coal, then we need only determine the thermal conductivity of these elements^{*}, and then let the model automatically take care of the effect of char particle composition, and conversion.

Although explicit solution of the reaction–transport differential equations for char combustion on continuum tessellations is possible [eg: via finite element methods; Winterfeld, 1981], the need to solve huge linear equation systems, and numerical considerations such as stability and timestep size, mean it is unlikely to be ever a feasible option. An alternative is to represent the interstitial fluid with discrete elements (molecules) that execute a random walk (RW) through the model pore space [Sahimi and Tsotsis, 1987; Sahimi, 1991]. If a molecule collides with an element of the solid phase (ie: tessellation cell, lattice bond or site), then reaction occurs with a probability proportional to the intrinsic reactivity [Sahimi, 1994]. If reaction does occur, the colliding fluid molecule and impinged solid element are removed (infact, as the solid element invariably represents a large number of solid atoms, it is only removed once it has reacted with a number of impinging molecules). As this approach does not require

* The effective thermal conductivity of these elements may be determined by first separating the individual macerals from their parent coal [Crelling, 1989], charring them under the same conditions they are likely to experience in the combustor of interest [Jones et al., 1985], and then using the technique of Weiss et al. (1994).

numerical solution of any differential equations and can be both parallelized and vectorized easily, it is particularly attractive when simulating real porous solids. Similar, but different, discrete approaches were also independently developed by Kerstein and Edwards (1987), and Zygourakis and Sandmann (1988). Instead of explicitly including the interstitial fluid, both these approaches simulate diffusion controlled reaction by assigning different burn times to the elements of the solid phase depending upon their position within the model char. Whilst the methods of Kerstein and Edwards (1987), and Zygourakis and Sandmann (1988) are computationally less demanding than that of Sahimi and Tsotsis (1987), they are also less general. Since this initial work, all three approaches have been widely used to investigate coal combustion related issues such as secondary fragmentation [eg: Miccio and Salatino, 1992], ash fate [eg: Kang et al., 1988], and char burnout behavior [Sandmann and Zygourakis, 1987].

If we are interested in including bulk fluid flow in addition to diffusion (eg: situations involving non–equimolar reaction schemes, or flow in the boundary layer of a char), homogeneous reaction, and realistic fluid densities, then an alternative to the standard RW method must be sought. An extremely promising approach is lattice gas automata (LGA) in which the fluid is represented by mesoscopic (ie: super–atomic but sub–hydrodynamic) discrete particles that move on a regular lattice and interact at its sites according to a set of relatively simple rules [good basic description given in d’Humières and Lallemand, 1987]. It turns out that this very simple, and perhaps crude, representation of the fluid yields a macroscopic behavior that is close to that described by the continuum differential equations we normally use to model fluid flow [Frisch et al., 1987], heat and mass transfer, and reaction [Chen et al., 1995]. Whilst details are unimportant here [reviews: Doolen et al., 1990; Boon, 1992; Verheggen, 1992; Ershov, 1994; Chen et al., 1995], it is perhaps worthwhile mentioning the features of the method that recommend it to this author for future solution of the char combustion/boundary layer flow problem:

- Codes are extremely simple when compared to those based upon the more traditional approaches.
- As all particle interactions are local (ie: collision outcomes at a lattice site are defined by the site's state only), the method is easily vectorized, and highly parallel. This is particularly good in light of the latest generation of distributed memory machines such as the Thinking Machines CM-5 and Fujitsu VP500 which combine both vector and parallel technologies. It is also good for machines like the CRAY T3D as the DEC Alpha processors used in this machine are highly pipelined and therefore benefit from vector coding.
- The bit-basis of standard (ie: Boolean) LGA methods mean an extremely large number of sites may be simulated on modern parallel machines*. This fact combined with the mesoscopic nature of the fluid particles, and the relatively simple particle interaction rules, gives us the ability to consider a range of length scales far greater than would be possible with either continuum methods such as finite elements, or more conventional particle methods such as molecular dynamics.
- The bit representation of the fluid also means that mass, momentum and energy are exactly conserved at the lattice site level, and that round-off errors are zero – this makes the method unconditionally stable irrespective of the nature of the problem.
- The mesoscopic level of the LGA method also means we can capture the many phenomena that are lost when using the continuum approximation [eg: the possibility of non-classical reaction phenomena; Chopard et al., 1994].

* For example, according to Shimomura et al. (1990), 5000 million sites with an update rate of 300–500 million sites per second could be simulated on a CRAY X-MP/416 (512×64 Mbits of memory) – in light of computer technology advances since this time [Dongarra et al., 1994; this article includes a list of the 500 fastest computers in the world as of late 1994; no CRAY X-MP machines are mentioned and the oldest machine on the list (CRAY Y-MP/432) is c1990], this figure should be many orders of magnitude higher today [eg: Chen et al. (1995) mention that 100000 million site updates per second are now possible for simple LGA simulations on a 4224 vector processor CM-5 (number of processors actually used is unspecified, but it is unlikely that all would have been used)].

- Complex, irregular, geometries and associated boundary conditions may be easily modelled making it a straightforward exercise to simulate processes within porous solids represented by continuum percolation constructs such as those illustrated in Figure 2.23 [eg: Sahimi, 1993].

The method is, of course, not without its problems. These include non-Galilean invariance, velocity dependent equation-of-state, limitations to slow flow (flows in which the speeds are much less than the speed of sound) [Frisch et al., 1987], and noisy simulation results [Verheggen et al., 1992]. The first two problems may be dealt with in a relatively straightforward manner provided the flows are slow [Frisch et al., 1987], whilst the third issue is unlikely to be of concern for our problem of interest [Ershov, 1994]. Noisy results, on the other hand, are of particular concern as it means the raw simulation results must be averaged over a finite number of lattice sites so as to yield smooth data suitable for subsequent analysis – this means much finer lattices must be used to obtain the same resolution as the more conventional techniques [Verheggen et al., 1992]. An alternative solution to this problem is to use more particles than the minimum per site [ie: remove the exclusion principle; Chopard et al., 1994]. Although this increases computational requirements, it ends up that for reaction problems such as those we're interested in, more than the minimum number of particles have to be used anyway [Chopard et al., 1994]. Another alternative is to use the lattice Boltzmann variant of the method [McNamara and Zanetti, 1988; Chen et al., 1991, 1992; Qian et al., 1992] in which the state of a particle is now represented by a floating point number (between 0 and 1) rather than a single bit. Although this also naturally overcomes the problems of non-Galilean invariance and the velocity dependent equation-of-state, its use of floating point numbers instead of bits means it is much more demanding both in terms of CPU and memory requirements, and is only a conditionally stable method equivalent to an explicit finite difference scheme [Chen et al., 1995]; it does, of course, retain the highly parallel nature and mesoscopic character of the Boolean LGA approach.

Since its initial development in the mid–1980s [Frisch et al., 1986], LGA has been applied to a wide range of problems [see Doolen et al., 1990; Boon, 1992; Verheggen, 1992; Sahimi, 1993; Ershov, 1994; Chen et al., 1995 and references therein for a wide cross section of applications]. In recent years, the method has been used to study reactive systems including those involving both homogeneous and heterogeneous reaction within porous media [reviews: Ershov, 1994; Chen et al., 1995; see also Chopard et al., 1994]. Not surprisingly, algorithms for reactive systems are markedly more complex compared to their non–reactive counterparts [Chen et al., 1995], and for this reason they are less advanced [Chopard et al., 1994]. Despite this fact, the LGA method has already been used to study problems that include transport and reaction with pore enlargement [Wells et al., 1991] – this bodes well for the solution of the char combustion/boundary layer problem via this method.

Despite its obvious rigor, LGA simulation of transport and reaction on a discrete model of a porous solid is extremely demanding from a computational resource perspective. The question then arises: over what range of length scales may we reasonably simulate when considering the char combustion/boundary layer problem? An answer to this question may be obtained by considering the resources required relative to those available today. For Boolean LGA, the number of sites needed to simulate a region of volume, V , in $d = 2$ or 3 dimensional space is given by

$$N_s = \left(\frac{10L}{l} \right)^d \quad (2-67)$$

where $L = V^{1/d}$ is the extent of the region, and l the smallest feature of interest (eg: pore size). The factor of 10 in this equation accounts for the Rothman (1988) requirement; ie: the lattice spacing must be approximately one tenth of the smallest feature of interest [Sahimi, 1993]. On the basis of 8 bits per byte, and using an average of N_b bits (ie: particles) per site (ie: we are not imposing the exclusion principle), the total amount of memory required is

$$N_m = \frac{N_b}{8} \left(\frac{10L}{l} \right)^d \quad (2-68)$$

This equation is plotted in Figure 2.25 over several decades of the length ratio for two different N_b values per dimension. The lowest values of N_b shown for 2D and 3D (ie: 6 and 24 respectively) are for the standard lattices normally used with the exclusion principle in force [Frisch et al., 1987]. The higher values of N_b in both dimensions (ie: 40 and 160) are average values for when the exclusion principle is not imposed – these values were estimated on the basis of the work of Chopard et al. (1994). Also shown for comparison purposes are the memory capacities of two different modern distributed memory parallel computers: a 128 vector processor (VP) CM–5 [this machine is identical to that used for the work reported in this chapter, and is listed as the 288th fastest in the world; Dongarra et al., 1994], and a 4224 VP version of the same machine [this is equivalent to the Sandia National Laboratory machine which is listed as second fastest in the world; Dongarra et al., 1994]. This figure shows that existing supercomputers of

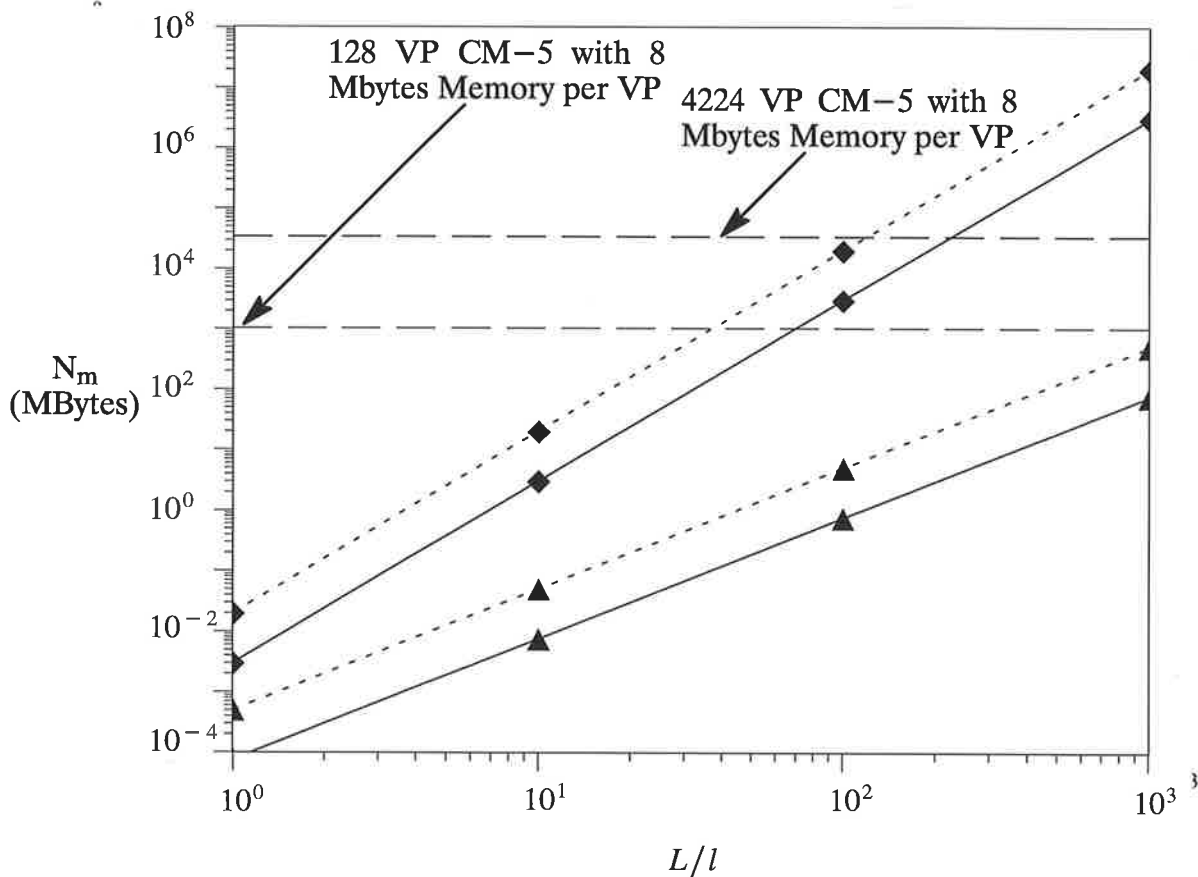


Figure 2.25. Memory requirements versus length scale ratio. 2D $\triangle$: 6 particles per site (solid); 40 particles per site (dash). 3D $\diamond$: 24 particles per site (solid); 160 particles per site (dash). Memory capacity of two different CM–5 machines shown as broken lines.

modest capabilities (the 128 VP CM-5) should be able to accommodate 2D char combustion/boundary layer problems in which the length scales vary from the μm level to the mm level. The 3D situation is not as rosy, however, as even the large CM-5 can only cover two decades of the length ratio.

The memory requirements are, of course, only part of the equation; we must also be concerned with the rate at which the lattice sites are updated. Using the site update rate data of Chopard et al. (1994) for 40+ bits per site, and scaling it from a CM-200/8k to a 128 VP CM-5*, gives an update rate of approximately 1.7 MUPS (millions of site updates per second). Whilst this rate is extremely poor compared to simulations in which the exclusion principle is enforced (these are normally 200 times faster), it must be remembered that the greater number of particles per site means the results are more smooth, therefore reducing the number of realizations required to obtain accurate results. For a length ratio of 10^3 , equation (2-67) yields a site number of $N_s = 100$ million in 2D. Comparing the expected update rate of 1.7 MUPS with this number of sites indicates each time step would require about 60 seconds of CPU time. This figure would improve to approximately 1-2 seconds per timestep if the 4224 VP CM-5 were to be used (the vector lengths will still be substantial as each VP would operate on approximately 25000 sites). These times clearly indicate that CPU speed is the main constraint on the LGA simulation of the char combustion/boundary layer problem.

The fact that we are limited to within the μm to mm range means we must invoke the smooth field approximation for those regions that contain the smaller macropores, mesopores, and micropores. Although this clearly runs counter to the whole philosophy of discrete simulation, our ability to explicitly consider smaller scale features will improve as computer technology further matures. For example, past trends indicate that the performance of the individual supercomputer improves at a rate of 10^2 MFLOPS per decade [Stadtherr et al., 1993], whilst the practice of coupling geographically dispersed

* The scaling was done using data taken from the article of Dongarra et al. (1994). The R_{max} value of a CM-200/8k machine (no CM-2a was given in the list) was compared with the R_{peak} value of a 128 VP CM-5. R_{max} , which is smaller than R_{peak} , was used for the CM-2 because interprocessor communications for this machine would be far greater than for the CM-5.

supercomputers via highspeed network links means this rate can be improved upon considerably provided the problem is highly parallel. As this is the case for LGA, we should be in a position to explicitly consider scales of the $O(100)$ nm in 2D by early next decade [we need a 10^d MFLOPS increase to see a factor of 10 drop in length scale for a d -dimensional system; refer equation (2-67)].

2.4.3 Generating Discrete Porous Solid Models

Most discrete models to date simply assume that the pore space may be represented by an uncorrelated percolation system. Studies [Lane et al., 1986; Sandmann and Zygourakis, 1987; Hollewand and Gladden, 1992a, b] in recent years have shown, however, that such models are generally inadequate. For example, using the same experimentally determined pore size distribution (PSD) for a bimodal porous catalyst, Hollewand and Gladden (1992b) generated two different models of the catalyst, and determined the tortuosity of each. In the first, all pores of a random network were assigned a size from the PSD in an uncorrelated manner – an example of this type of system is shown on a regular lattice in Figure 2.24(a). The second structure, which is illustrated in Figure 2.24(b), was generated by overlaying two monodisperse random networks and then connecting them at their points of intersection. They found that the predicted tortuosity of the first could be greater than that of the second by over an order of magnitude, and that the difference between the predicted values varied with both network connectivity and porosity. This clearly demonstrates that “classical” parameters such as porosity and PSD are generally insufficient in their own right for generating a representative model, and that it is extremely important to be able to produce accurate and realistic models of the solid to be simulated.

A complete but compact description of a complex porous solid is possible using statistical mechanics of space filling tessellations [Joshi, 1974; Quiblier, 1984; Adler et al., 1990; Adler, 1992; Thovert et al., 1993]. In this approach, an experimentally derived digitized image of the solid is described by a distribution (phase) function

$$Z(\mathbf{r}) = \begin{cases} 1 & \text{if } \mathbf{r} \text{ belongs to the pore space} \\ 0 & \text{otherwise} \end{cases} \quad (2-69)$$

where $\mathbf{r}$ is the position vector of any point on the image. A compact description of the solid is then arrived at by calculating various moments of this distribution function. The most commonly used moments are the zeroth and first, the former being equal to the porosity, although higher order moments may also be used if desired [Adler, 1992]. These experimentally determined moments are then manipulated into a form that can be utilized at any time to “reconstruct” the solid on a tessellation of space. This reconstructed solid is not, of course, an exact replica of the original digitized image, but, rather, a statistically equivalent likeness. Whilst this approach has been widely used to study sandstone related phenomena [Adler et al., 1990; 1992], it has not been applied to more complex solids such as coal or char. It is this author’s opinion that this approach could be an excellent tool for the study of coal and char down to the μm level provided it can be generalized to include a multicomponent solid phase (ie: to allow us to consider the coal macerals or their derived features in the char, and mineral inclusions). Although other approaches have appeared in recent years, they are either subsumed by the method just described [Sevick et al., 1989], or centered around surface descriptions [Mann and Wasilewski, 1990] which are not of use when we wish to construct models that contain both the the pore space and complementary phase.

Digitized images with a resolution down to the μm level may be obtained for use with the above approach via modern quantitative microscopy methods [Zygourakis and Glass, 1988; Lymberopoulos and Payatakes, 1992; David and Fermont, 1993; Lester et al., 1994; McEnaney and Mays, 1994; Cloke et al., 1995]. Techniques such as NMR [Hollewand and Gladden, 1992c; Gladden 1993; Hou et al., 1994] and Synchrotron [Spanne et al., 1994] tomography may also be of use in the future if their resolution can be made comparable to that of quantitative microscopy. Quantitative microscopy should allow us to model the larger macropores, mineral inclusions, and those morphological regions that derive themselves from the original coal maceral groups (ie: vitrinite, liptinite and inertinite) [Jones et al., 1985]. Provided we can establish a relationship between the

individual macerals within the parent coal (eg: Sporinite, etc.) with their descendants in the char, the resolution of quantitative microscopy should also permit us to include these.

As indicated at the end of the previous section, we should be in a position to explicitly consider features as small as $O(100)$ nm by early next decade. Unfortunately, quantitative microscopy techniques are unlikely to be of use at these length scales, and we therefore have to look for an alternative way of generating a “digitized image” of the pore space suitable for use with the reconstruction approach of Adler and others [Joshi, 1974; Quiblier, 1984; Adler et al., 1990; Adler, 1992; Thovert et al., 1993]. Provided we can buildup a molecular picture of the char at this level* (this is likely to be the structure of the individual maceral derived morphological elements), we can perform an energy calculation so as to define the “pore space” (ie: those regions of low potential energy) for each gas of interest [eg: Gusev et al., 1993]. Overlaying this energy map with a tessellation will then permit the synthesis of a digitized image by differentiating between those cells that lie in the high and low energy regions (ie: color those in the high and low energy regions black and white respectively). We could also identifying the likely reactivities of the various parts of this digitized image (ie: in the same way as we would at the maceral level), by performing equilibrium molecular dynamic simulations on the molecular models. The reader is referred to the following chapter for a more fuller discussion of this issue.

By way of final note, despite our ability to study and accurately describe real porous solids down to the μm level, we are faced with one major problem when studying coal char – the morphology of a coal char particle is governed by both the morphology of the parent coal particle, and the heating process the coal particle undergoes to become a char. This, of course, means that we are faced with the task of either: (1) considering all the permutations of the coals and heating processes of interest; or (2) of developing a model that quantitatively describes the coal-to-char conversion process. The massive changes that occur during coal pyrolysis makes the last an extremely difficult proposition

* Refer to next chapter for a discussion of this issue.

at this stage. We, therefore, must resort to the first of these approaches until such a model is developed [eg: Ballal and Zygourakis, 1986; Sandmann and Zygourakis, 1987; Ballal et al., 1988].

NOMENCLATURE

Latin

a	radial position of active (char) particle external surface
A	pre-exponential factor for primary CO/CO ₂ product ratio correlation
$\mathbf{A}$	matrix as defined in Table 2.6
A_{im}	element of the matrix $\mathbf{A}$ as defined in Table 2.2
A_{iT}	element of the matrix $\mathbf{A}$ as defined in Table 2.2
A_{mm}	element of the matrix $\mathbf{A}$ as defined in Table 2.2
A_{mT}	element of the matrix $\mathbf{A}$ as defined in Table 2.2
A_r	collision frequency constant for reaction $-r$
b	radial position of boundary layer edge
B	exponential factor for primary CO/CO ₂ product ratio correlation
$\mathbf{B}$	matrix as defined in Table 2.6
B_{ij}	elements of matrix $\mathbf{B}$ as defined in Table 2.6
B_{mj}	elements of matrix $\mathbf{B}$ as defined in Table 2.6
B_o	effective permeability of porous solid
$\mathfrak{B}_o$	permeability of pore
C	total molar concentration
$\mathbf{C}$	matrix as defined in Table 2.8
$\overline{C}$	dimensionless total molar concentration
C_a	specific heat of ash
C_b	specific heat of bed material
C_c	specific heat of carbonaceous material
C_{CO_2}	molar concentration of carbon dioxide

C_{CO}	molar concentration of carbon monoxide
C_{ct}	specific heat of char material (ie: carbonaceous material and ash)
C_e	effective thermal capacitance of fluid/porous solid system
C_g	molar concentration of oxidant
C_{H_2O}	molar concentration of water
C_i	molar concentration of species—i
$\bar{C}_i$	dimensionless molar concentration of species—i
C_o	reference molar concentration
C_{O_2}	molar concentration of molecular oxygen
C_{pi}	specific heat at constant pressure of species—i
$C_s(X)$	conversion dependent concentration of reactive sites
d	Euclidean dimension
D	length—dependent “diffusion coefficient” of Gefen et al. (1983)
$\mathbf{D}$	matrix as defined in Table 2.8
d_a	active (char) particle diameter
Da	Damköhler number
d_{a0}	initial active (char) particle diameter
d_b	bed particle size
D_i	effective Knudsen diffusion coefficient of species—i
$\mathcal{D}_i$	Knudsen diffusion coefficient of species—i within a pore
D_{ie}	effective diffusion coefficient of species—i in a mixture
D_{ij}	effective binary diffusion coefficient of species pair i—j
$\mathcal{D}_{ij}$	Chapman—Enskog binary diffusion coefficient of species pair i—j

d_f	fractal dimension
D_o	reference diffusion coefficient
d_p	pore diameter
d_w	random walk fractal dimension
E_r	activation energy for reaction—r
$\mathbf{F}$	diffusion coefficient matrix of Feng—Stewart mass flux model
$\mathbf{f}_f$	force vector associated with FE formulation of conservation equations
F_{ij}	elements of matrix $\mathbf{F}$
$\mathbf{f}_s$	force vector associated with FE formulation of mass conservation equation
$g(\theta)$	Einstein specific heat function for solids
h	FE length parameter
h_e	effective heat transfer coefficient of char particle
$\mathcal{H}_i$	coefficients for H_r function
H_r	enthalpy—of—reaction for reaction—r
h_{rs}	heat transfer coefficient for bed solid surface to bed solid surface radiative heat transfer
H_r^t	total enthalpy—of—reaction
h_{rv}	heat transfer coefficient for bed void to bed void radiative heat transfer
g	total number of diffusing species
$\mathbf{J}_i$	molar diffusion flux vector of species—i
$\mathbf{J}_T$	heat flux vector
J_{Ts}	heat flux at active (char) particle surface
k	Kozeny constant
K_o	Knudsen diffusivity DGM parameter

K_1	binary diffusivity DGM parameter
$k(T)$	temperature dependent rate constant
k_b	Boltzmann constant
K_f	pre-factor of the length-dependent “diffusion coefficient” of Gefen et al. (1983)
$\mathbf{K}_f$	stiffness matrix associated with FE formulation of conservation equations
k_r	rate constant for reaction—r
l	size of smallest feature to be explicitly simulated
L	extent of simulation region
$\mathcal{L}$	size of porous solid
m	true reaction order
$\mathbf{M}^*$	effective mass matrix
m_a	mass of active (char) particle
$\dot{m}_{ad}$	rate of active (char) particle mass loss due to disintegration only
m_{ao}	initial mass of active (char) particle
$\dot{m}_{ar}$	rate of active (char) particle mass loss due to reaction only
$\dot{m}_{at}$	total rate of active (char) particle mass
m_c	average molecular weight of char material
$\mathbf{M}_f$	mass matrix associated with FE formulation of conservation equations
m_i	molecular weight of species—i
$\dot{m}_m$	maximum of $\dot{m}_{at}$ over all conditions simulated for particular active (char) size
$\mathbf{M}_s$	mass matrix associated with FE formulation of mass conservation equation
$\mathbf{n}$	flux vector
$\mathbf{N}$	total molar flux vector

N_b	number of bits
N_i	molar flux vector of species $-i$
N_i^p	molar flux vector of species $-i$ at the pore level
N_m	amount of memory
n_r	collision frequency temperature $-$ exponent for reaction $-r$
N_s	number of sites
Nu	Nusselt number
P	pressure
P_b	bed pressure
$\dot{Q}$	rate of heat production per unit char volume
r	radius
r'	dummy length variable
R	characteristic radius
$\mathcal{R}$	total number of reactions
r_{1p}	radial position at which molecular oxygen within active (char) particle falls to zero (ie: $r_a - r_{1p}$ is the penetration depth of molecular oxygen)
r_a	active (char) particle radius
r_{ao}	initial active (char) particle radius
R_{max}	maximum overall char reaction rate
R_{max}	actual peak speed achieved in LINPACK benchmark
r_p	pore radius
$\bar{r}_p$	mean pore radius
$r_{p,max}$	maximum pore radius
$r_{p,min}$	minimum pore radius

R_{peak}	theoretical peak speed of supercomputer
R_u	Universal Gas Constant
$\bar{s}$	vector as defined in Table 2.8
Sh	Sherwood number
S_i	temperature parameter for Sutherland formula for thermal conductivity
S_o	reference value of S_t
S_t	total surface area per unit char volume
t	time
t'	dummy time variable
T	temperature
$\bar{T}$	dimensionless temperature
t_{90}	time at 90% conversion
T_a	active (char) particle temperature
T_b	bed temperature
T_o	reference temperature for Sutherland formula for thermal conductivity; or reference temperature for dimensionless temperature
V	volume
w_a	weight fraction of ash in char particle
w_c	weight fraction of carbonaceous material in char particle
$\mathbf{x}$	state variable vector
X	conversion
$\mathbf{X}$	matrix as defined in Table 2.8
$\bar{\mathbf{x}}$	dimensionless state variable vector

$\hat{\mathbf{x}}$	nodal state variable vector associated with FE formulation of conservation equations
X_{1b}	bed mole fraction of molecular oxygen
X_d	conversion at onset of disintegration
X_i	mole fraction of species—i
Z	connectivity
$Z(\mathbf{r})$	phase function

Greek

α	time integrator parameter ($0 \leq \alpha \leq 1$)
Δ	parameters as defined in Table 2.2
$\Delta \mathbf{f}$	out—of—balance force vector
Δ_i	parameters as defined in Table 2.2
Δ_{ij}	parameters as defined in Table 2.2
Δ_m	mechanism factor
ΔT	characteristic temperature difference
ΔT_a	maximum temperature difference across active (char) particle
$\Delta T_a^{\max}$	conversion—maximum maximum active (char) particle over—temperature
ΔT_{ab}	active (char) particle over—temperature
$\Delta T_{ab}^{\max}$	conversion—maximum active (char) particle over—temperature
$\Delta \mathbf{v}$	velocity error vector
ϵ	emissivity
ϵ_a	emissivity of active (char) particle
ϵ_{NR}	NR accuracy
η	primary CO/CO ₂ product ratio

η_s	primary CO/CO ₂ product ratio at active (char) particle surface
$\bar{\eta}_s$	average primary CO/CO ₂ product ratio at active (char) particle surface
κ	tortuosity
λ	thermal conductivity
λ_a	thermal conductivity of air
λ_b	thermal conductivity of bed material
λ_c	thermal conductivity of carbonaceous material
λ_{ct}	thermal conductivity of char material
λ_e	effective thermal conductivity of fluid/porous solid system
λ_g	thermal conductivity of interstitial gas mixture
λ_i	thermal conductivity of species—i
λ_{oi}	thermal conductivity of species—i at temperature T _o
μ	viscosity
μ_i	viscosity of species—i
ν	correlation length universal scaling exponent
ν_{ri}	stoichiometric coefficient of species—i in reaction—r
ν_{rc}	stoichiometric coefficient of carbonaceous material in reaction—r
ϕ	porosity
ϕ_a	accessible porosity
ϕ^*	critical porosity at which solid matrix becomes unconsolidated
$\bar{\phi}$	complement of the porosity
$\hat{\phi}$	nodal state variable vector associated with FE formulation of mass conservation equation
ϕ_b	bed porosity

ϕ_{ij}	Wilke [Wilke, 1950; Mason and Saxena, 1958; White, 1974] parameter for mixture viscosity and thermal conductivity
ϕ_o	initial active (char) particle porosity
ϕ_{pc}	percolation threshold associated with pore system
ϕ_{sc}	percolation threshold associated with solid phase
ρ_a	density of active (char) particle
ρ_{ao}	initial density of active (char) particle
ρ_b	density of bed material
ρ_c	density of carbonaceous material
ρ_{ct}	density of char material
σ	Stefan–Boltzmann constant
σ_i	Lennard–Jones potential interaction length parameter of species–i
σ_{ij}	Lennard–Jones potential interaction length parameter of species pair i–j
τ	dimensionless time
ψ	ratio of film thickness of fluid between adjacent bed particles and their size
ψ_a	ψ for motionless air in a bed of porosity ϕ
χ	parameter of Yagi and Kunii (1957) model
ζ	dimensionless radius
ζ_a	dimensionless active (char) particle radius
ξ	correlation length
$\dot{\Omega}_c$	molar rate–of–production of carbonaceous material per unit porous solid volume
Ω_{ij}^{11}	collision integral of Chapman–Enskog theory

Ω_i^{22}	collision integral of Chapman–Enskog theory
$\dot{\Omega}_m$	experimentally measured rate–of–reaction
$\dot{\Omega}_{pr}$	molar rate–of–reaction per unit porous solid volume for reaction–r
$\dot{\Omega}_{sr}$	molar rate–of–reaction per unit surface area for reaction–r = 1, 2
$\dot{\Omega}_{trc}$	total molar rate–of–consumption of carbonaceous material for reaction–r
$\dot{\Omega}_{v3}$	molar rate–of–reaction per unit volume for homogeneous reaction

Acronyms

BLRS	boundary layer reaction scenario
CM–2	Thinking Machines CM–2 massively parallel supercomputer (model preceding CM–5)
CM–5	Thinking Machines CM–5 massively parallel/vector supercomputer
CMMD	message passing library for Thinking Machines CM–5
CPU	central processing unit
DGM	Dusty–gas model
EBE	element–by–element
EMA	effective–medium approximation
FBC	fluidized bed combustion
GMRES	generalized minimum residual
LGA	lattice gas automata
Mbits	millions of bits
Mbytes	millions of bytes
MC	Monte–Carlo
MFLOPS	millions of floating point operations per second

MUPS	millions of (site) updates per second
NC	non-symmetric Cholesky
NMR	nuclear magnetic resonance
NR	Newton-Raphson
ODE	ordinary differential equation
OSP	O'Shaughnessy and Procaccia (equation)
PC	pre-conditioned
PDE	partial differential equation
PSD	pore size distribution
R1	carbon/oxygen reaction
R2	carbon/carbon dioxide reaction
R3	carbon monoxide/oxygen reaction
RW	random walk
SFA	smooth field approximation
SIMD	single instruction, multiple data
SPMD	single program, multiple data
TSA	total surface area
VP	vector processor
VP500	Fujitsu VP500 massively parallel/vector supercomputer
VP2200	Fujitsu VP2200 vector supercomputer

REFERENCES

1. Abbasi M.H, Evans J.W and Abramson I.S (1983): Diffusion of gases in porous solids: Monte Carlo simulations in the Knudsen and ordinary diffusion regimes, *AIChE Journal*, **29**, 617.
2. Abed R and Rinker R.G (1974): Isobaric diffusion, permeability, and simultaneous flow and diffusion in commercial catalysts, *J. Catalysis*, **34**, 246.
3. Adler P.M (1992): *Porous Media: Geometry and Transports*, Butterworth–Heinemann, Boston.
4. Adler P.M, Jacquin C.G and Quiblier J.A (1990): Flow in simulated porous media, *Int. J. Multiphase Flow*, **16**, 691.
5. Adler P.M, Jacquin C.G and Thovert J.F (1992): The formation factor of reconstructed porous media, *Water Resour. Res.*, **28**, 1571.
6. Agarwal P.K (1987): The residence phase of active particles in fluidized beds of smaller inert particles, *Chem. Engng. Sci.*, **42**, 2481.
7. Agarwal P.K (1991): Transport phenomena in multi–particle systems – IV. Heat transfer to a large freely moving particle in gas fluidized bed of smaller particles, *Chem. Engng. Sci.*, **46**, 1115.
8. Agarwal P.K, Mitchell W.J and La Nauze R.D (1988): Transport phenomena in multi–particle systems – III. Active particle mass transfer in fluidized beds of inert particles, *Chem. Engng. Sci.*, **43**, 2511.
9. Agarwal P.K and O'Neill B.K (1988): Transport phenomena in multi–particle systems – I. Pressure drop and friction factors: Unifying the hydraulic–radius and submerged–object approaches, *Chem. Engng. Sci.*, **43**, 2487.
10. Annamalai K and Ryan W (1993): Interactive processes in gasification and combustion – II. Isolated carbon, coal and porous char particles, *Prog. Energy Comb. Sci.*, **19**, 383.

11. Argo W.B and Smith J.M (1953): Heat transfer in packed beds, *Chem. Engng. Prog.*, **49**, 443.
12. Arthur J.R (1951): Reactions between carbon and oxygen, *Trans. Faraday Soc.*, **47**, 164.
13. Atkinson B and Merrick D (1983): Mathematical models of the thermal decomposition of coal. 4. Heat transfer and temperature profiles in a coke—oven charge, *Fuel*, **62**, 553.
14. Avedesian M.M and Davidson J.F (1973): Combustion of carbon particles in a fluidized bed, *Trans. Inst. Chem. Eng.*, **51**, 121.
15. Ayling A.B and Smith I.W (1972): Measured temperatures of burning pulverized fuel particles and the nature of the primary reaction product, *Comb. Flame*, **18**, 173.
16. Ballal G and Zygourakis K (1986): Gasification of coal chars with carbon dioxide and oxygen, *Chem. Eng. Comm.*, **49**, 181.
17. Ballal G and Zygourakis K (1987): Evolution of pore surface area during noncatalytic gas—solid reactions. 2. Experimental results and model validation, *Ind. Eng. Chem. Res.*, **26**, 1787.
18. Ballal G, Amundson N.R and Zygourakis K (1988): Pore structural effects in catalytic gasification of coal chars, *AIChE Journal*, **34**, 426.
19. Barta S (1994): Anomalous diffusion on percolating clusters, *Physica A*, **203**, 163.
20. Baskakov A.P, Filippovskii N.F, Munts V.A and Ashikhmin A.A (1987): Temperature of particles heated in a fluidized bed of inert material, *J. Engng. Phys.*, **52**, 574.
21. Basu P (1985): A review of combustion of single coal particles in fluidized beds, *Trans. CSME*, **9**, 142.
22. Basu P, Broughton J and Elliott D.E (1975): Combustion of single coal particles in fluidized beds, in *Fluidized Combustion*, The Institute of Fuel, London.

23. Bhatia S.K and Perlmutter D.D (1980): A random pore model for fluid–solid reactions: I. Isothermal, kinetic control, *AIChE Journal*, **26**, 379.
24. Bhatia S.K and Perlmutter D.D (1981): A random pore model for fluid–solid reactions: II. Diffusion and transport effects, *AIChE Journal*, **27**, 247.
25. Bhatia S.K and Gupta J.S (1992): Mathematical modelling of gas–solid reactions: Effect of pore structure, *Rev. Chem. Engng.*, **8**, 178.
26. Biggs M.J and Agarwal P.K (1992): Mass diffusion of atomic fluids in random micropore spaces using equilibrium molecular dynamics, *Phys. Rev. A*, **46**, 3312.
27. Biggs M.J and Agarwal P.K (1993): Mathematical modelling of oscillations in the temperature of freely moving burning carbonaceous particles in bubbling fluidized beds, *Fuel*, **72**, 805.
28. Biggs M.J and Agarwal P.K (1994): Mass diffusion of diatomic fluids in random micropore spaces using equilibrium molecular dynamics, *Phys. Rev. E*, **49**, 531.
29. Blackwood J.D and McGrory F (1958): The carbon–steam reaction at high pressure, *Aust. J. Chem.*, **11**, 16.
30. Blik A (1984): *Mathematical Modelling of a Cocurrent Fixed Bed Gasifier*, Ph.D Thesis, Twente University of Technology, The Netherlands.
31. Boon J.P, Ed. (1992): *Proceedings of Advanced Research Workshop on Lattice Gas Automata Theory, Implementation, and Simulation*, in *J. Stat. Phys.*, **68**(3/4).
32. Borghi G, Sarofim A.F and Beer J.M (1985): A model of coal devolatilization and combustion in fluidized beds, *Comb. Flame*, **61**, 1.
33. Brem G (1990): *Mathematical Modelling of Coal Conversion Processes*, Ph.D Thesis, Twente University of Technology, The Netherlands.
34. Brem G and Brouwers J.J.H (1990): Analytical solutions for non–linear conversion of a porous solid particle in a gas – II. Non–isothermal conversion and numerical verification, *Chem. Engng. Sci.*, **45**, 1915.

35. Burganos V.N and Sotirchos S.V (1987): Diffusion in pore networks: Effective medium theory and smooth field approximation, *Chem. Engng. Sci.*, **33**, 1678.
36. Butt J.B (1965): Thermal conductivity of porous catalysts, *AIChE Journal*, **11**, 106.
37. Bzowski J, Kestin J, Mason E.A and Uribe F.J (1990): Equilibrium and transport properties of gas mixtures at low density: Eleven polyatomic gases and five noble gases, *J. Phys. Chem. Ref. Data*, **19**, 1179.
38. Calleja G, Sarofim A.F and Georgakis C (1981): Effect of gasification order on the bounding solutions for char combustion, *Chem. Engng. Sci.*, **36**, 919.
39. Caram H.S and Amundson N.R (1977): Diffusion and reaction in a stagnant boundary layer about a carbon particle, *Ind. Eng. Chem. Fundam.*, **16**, 171.
40. Carman P.C (1956): *Flow of Gases Through Porous Media*, Butterworths, London.
41. Chen S, Chen H, Martinez D and Matthaeus W.H (1991): Lattice Boltzmann model for simulation of magnetohydrodynamics, *Phys. Rev. Lett.*, **67**, 3776.
42. Chen S, Chen H and Matthaeus W.H (1992): Recovery of the Navier–Stokes equations using a lattice gas Boltzmann method, *Phys. Rev. A*, **45**, 5339.
43. Chen S, Dawson S.P, Doolen G.D, Janecky D.R and Lawniczak A (1995): Lattice methods and their applications to reacting systems, *Comp. Chem. Engng.*, **19**, 617.
44. Chirone R, Massimilla L and Salatino P (1991): Comminution of carbons in fluidized bed combustion, *Prog. Energy Comb. Sci.*, **17**, 297.
45. Chirone R, Masi S, Salatino P and D’Amore M (1992): The influence of coal macerals on carbon attrition during the fluidized bed combustion of coal char, *Comb. Sci. Tech.*, **83**, 135.
46. Chopard B, Frachebourg L and Droz M (1994): Multiparticle lattice gas automata for reaction diffusion systems, *Intnl. J. Mod. Phys. C*, **5**, 47.

47. Clément E, Sander L.M and Kopelman R (1989): Steady-state diffusion-controlled $A + A \rightarrow 0$ reaction in Euclidean and fractal dimensions: Rate laws and particle self-ordering, *Phys. Rev. A*, **39**, 6472.
48. Clément E, Kopelman R and Sander L.M (1990): Bimolecular reaction $A + B \rightarrow 0$ at steady state on fractals: anomalous rate law and reactant self-organization, *Chem. Phys.*, **146**, 343.
49. Cloke M, Lester E, Allen M and Miles N.J (1995): Automated maceral analysis using fluorescence microscopy and image analysis, *Fuel*, **74**, 659.
50. Coelho M.A.N and Guedes de Carvalho J.R.F.G (1988): Transverse dispersion in granular beds Part II – Mass transfer from large spheres immersed in fixed or fluidized beds of small inert particles, *Chem. Eng. Res. Des.*, **66**, 178.
51. Cope R.F, Arrington C.B and Hecker W.C (1994): Effect of CaO surface area on intrinsic char oxidation rates for Beulah Zap chars, *Energy Fuels*, **8**, 1095.
52. Crank J (1984): *Free and Moving Boundary Problems*, Oxford University Press, Oxford.
53. Crelling J.C (1989): Separation and characterization of coal macerals: Accomplishments and future possibilities, *Am. Chem. Soc. Div. Fuel Chem. Preprints*, **34**, 249.
54. Cukier R.I and Freed K.F (1983): Diffusion controlled processes among stationary reactive sinks: Effective medium approach, *J. Chem. Phys.*, **78**, 2573.
55. Cushman J.H (1991): On diffusion in fractal porous media, *Water Resour. Res.*, **27**, 643.
56. David P and Fermont W.J.J (1993): Application of color image analysis in coal petrology, *Org. Geochem.*, **20**, 747.
57. Davidson J.F and Harrison D (1963): *Fluidized Particles*, Cambridge University Press, Cambridge.

- 
58. Daw C.S and Krishnan R.P (1982): Direct combustion of solid carbonaceous fuels: The diffusionally controlled regime, *Engineering Foundation Conference on Combustion of Tomorrow's Fuels*, Santa Barbara, 39.
 59. Delikouras E.A and Perlmutter D.D (1991): Inaccessible porosity in gasification reactions under kinetic control, *AIChE Journal*, **37**, 1607.
 60. Delikouras E.A and Perlmutter D.D (1993): Combined effects of mass transfer and inaccessible porosity in gasification reactions, *AIChE Journal*, **39**, 829.
 61. Dennis J.S, Hayhurst A.N and Mackley I.G (1982): The ignition and combustion of propane/air mixtures in a fluidized bed, *19th Symposium (International) on Combustion*, The Combustion Institute, Pittsburgh, 1205.
 62. d'Humières D and Lallemand P (1987): Numerical simulations of hydrodynamics with lattice gas automata in two dimensions, *Complex Systems*, **1**, 599.
 63. Dongarra J.J, Meuer H.W and Strohmaier E (1994): *TOP500 Supercomputer Sites*, available by sending "send performance from benchmark" to netlib@ornl.gov.
 64. Doolen G.D, Frisch U, Hasslacher B, Orszag S and Wolfram S, Eds. (1990): *Lattice Gas Methods for Partial Differential Equations*, Addison – Wesley, New York.
 65. Duncan A.B, Peterson G.P and Fletcher L.S (1989): Effective thermal conductivity within packed beds of spherical particles, *ASME J. Heat Trans.*, **111**, 830.
 66. Dutta S, Wen C.Y and Belt R.J (1977): Reactivity of coal and char. 1. In carbon dioxide atmosphere, *Ind. Eng. Chem., Process Des. Dev.*, **16**, 20.
 67. Epstein N (1989): On tortuosity and tortuosity factor in flow and diffusion through porous media, *Chem. Engng. Sci.*, **44**, 777.
 68. Ershov A.P (1994): Gas dynamics of cellular automata (Review), *Comb. Exp. and Shock Waves*, **30**, 107.
 69. Evans D.J and Morriss G.P (1984): Non–Newtonian molecular dynamics, *Comput. Phys. Rep.*, **1**, 297.

70. Evans D.J and Morriss G.P (1990): *Statistical Mechanics of Nonequilibrium Liquids*, Academic Press, London.
71. Evans R.B, Watson G.M and Mason E.A (1961): Gaseous diffusion in porous media at uniform pressure, *J. Chem. Phys.*, **35**, 2076.
72. Evans R.B, Watson G.M and Mason E.A (1962): Gaseous diffusion in porous media. II. Effect of pressure gradients, *J. Chem. Phys.*, **36**, 1894.
73. Feng C.F and Stewart W.E (1973): Practical models for isothermal diffusion and flow of gases in porous solids, *Ind. Eng. Chem. Fundam.*, **12**, 143.
74. Feng C.F, Kostrov V.V and Stewart W.E (1974): Multicomponent diffusion of gases in porous media. Models and experiments, *Ind. Eng. Chem. Fundam.*, **13**, 5.
75. Field M.A, Gill D.W, Morgan B.B and Hawksley P.G.W (1967): *Combustion of Pulverized Coal*, BCURA, Leatherhead.
76. Floess J.K, Longwell J.P and Sarofim A.F (1988): Intrinsic reaction kinetics of microporous carbons. 2. Catalyzed chars, *Energy Fuels*, **2**, 756.
77. Freund H (1986): Gasification of carbon by CO₂: a transient kinetics experiment, *Fuel*, **65**, 63.
78. Frisch U, d'Humières D, Hasslacher B, Lallemand P, Pomeau Y and Rivet J–P (1987): Lattice gas hydrodynamics in two and three dimensions, *Complex Systems*, **1**, 649.
79. Frisch U, Hasslacher B and Pomeau Y (1986): Lattice–gas automata for the Navier–Stokes Equation, *Phys. Rev. Lett.*, **56**, 1505.
80. Froment G.F and Bischoff K.B (1990): *Chemical Reactor Analysis and Design (2nd ed.)*, John Wiley & Sons, NY.
81. Fuertes A.B, Marban G and Pis J.J (1994): Combustion kinetics of coke particles in a fluidized bed reactor, *Fuel Process. Technol.*, **38**, 193.

82. Furimsky E, Sears P and Suzuki T (1988): Iron–catalyzed gasification of char in CO₂, *Energy Fuels*, **2**, 634.
83. Garcia X and Radovic (1986): Gasification reactivity of Chilean coals, *Fuel*, **65**, 292.
84. Gavalas G.R (1980): A random capillary model with application to char gasification at chemically controlled rates, *AIChE Journal*, **26**, 577.
85. Gavalas G.R (1981): Analysis of char combustion including the effect of pore enlargement, *Comb. Sci. Tech.*, **24**, 1981.
86. Gavalas G.R and Kim S (1981): Periodic capillary models of diffusion in porous solids, *Chem. Engng. Sci.*, **36**, 1111.
87. Gefen Y, Aharony A and Alexander S (1983): Anomalous diffusion on percolating clusters, *Phys. Rev. Lett.*, **50**, 77.
88. Giona M (1991): Statistical analysis of anomalous transport phenomena in complex media, *AIChE Journal*, **37**, 1249.
89. Giona M (1992): First–order reaction–diffusion kinetics in complex fractal media, *Chem. Engng. Sci.*, **47**, 1503.
90. Giona M and Roman H.E (1992a): A theory of transport phenomena in disordered systems, *Chem. Engng. Journal*, **49**, 1.
91. Giona M and Roman H.E (1992b): Fractional diffusion equation for transport phenomena in random media, *Physica A*, **185**, 87.
92. Giona M and Roman H.E (1992c): Fractional diffusion equation on fractals: one–dimensional case and asymptotic behaviour, *J. Phys. A*, **25**, 2093.
93. Gladden L.F (1993): Nuclear magnetic resonance studies of porous media, *Trans. IChemE*, **71**, 657.

94. Gopalakrishnan R, Fullwood M.J and Bartholomew C.H (1994): Catalysis of char oxidation by calcium minerals: Effects of calcium compound chemistry on intrinsic reactivity of doped Spherocharb and Zap chars, *Energy Fuels*, **8**, 984.
95. Gusev A.A, Arizzi S and Suter U.W (1993): Dynamics of light gases in rigid matrices of dense polymers, *J. Chem. Phys.*, **99**, 2221.
96. Hahne E, Song Y.W and Gross U (1991): Measurements of thermal conductivity in porous media, *Convective Heat and Mass Transfer in Porous Media*, Kluwer Academic, Boston, 849.
97. Hanrot F, Ablitzer D, Houzelot J.L and Dirand M (1994): Experimental measurement of the true specific heat capacity of coal and semicoke during carbonization, *Fuel*, **73**, 305.
98. Hargrave G, Pourkashanian M, Williams A (1986): The combustion and gasification of coke and coal chars, *21st Symposium (International) on Combustion*, The Combustion Institute, Pittsburgh, 221.
99. Hayhurst A.N (1991): Does carbon monoxide burn inside a fluidized bed? A new model for the combustion of coal char particles in fluidized beds, *Comb. Flame*, **85**, 155.
100. Helte A (1993): Radiative and conductive heat transfer in porous media: Estimation of the effective thermal conductivity, *J. Appl. Phys.*, **73**, 7167.
101. Hite R.H and Jackson R (1977): Pressure gradients in porous catalyst pellets in the intermediate diffusion regime, *Chem. Engng. Sci.*, **32**, 703.
102. Hollewand M.P and Gladden L.F (1992a): Representation of porous catalysts using random pore networks, *Chem. Engng. Sci.*, **47**, 2757.
103. Hollewand M.P and Gladden L.F (1992b): Modelling of diffusion and reaction in porous catalysts using a random three – dimensional network model, *Chem. Engng. Sci.*, **47**, 1761.

104. Hollewand M.P and Gladden L.F (1992c): Visualization of phases in catalyst pellets and pellet mass transfer processes using magnetic resonance imaging, *Trans. IChemE*, **70**, 183.
105. Hou L, Cody G.D, Hatcher P.G, Gravina S and Mattingly M.A (1994): Imaging the microstructure of low rank coals. A study combining nuclear magnetic resonance, scanning electron and optical microscopic imaging, *Fuel*, **73**, 199.
106. Howard J.B, Williams G.C and Fine D.H (1973): Kinetics of carbon monoxide oxidation in postflame gases, *14th Symposium (International) on Combustion*, The Combustion Institute, Pittsburgh, 975.
107. Jackson R (1977): *Transport in Porous Catalysts*, Elsevier, Amsterdam.
108. Jerauld G.R, Hatfield J.C, Scriven L.E and Davis H.T (1984a): Percolation and conduction on Voronoi and triangular networks: a case study in topological disorder, *J. Phys. C*, **17**, 1519.
109. Jerauld G.R, Scriven L.E and Davis H.T (1984b): Percolation and conduction on the 3D Voronoi and regular networks: a second case study in topological disorder, *J. Phys. C*, **17**, 3429.
110. Jones R.B, McCourt C.B, Morley C and King K (1985): Maceral and rank influences on the morphology of coal char, *Fuel*, **64**, 1460.
111. Joshi M.Y (1974): *A Class of Stochastic Models for Porous Media*, Ph.D Thesis, University of Kansas, Lawrence, Kansas.
112. Jung K (1987): Internal burning of petroleum coke particles in a fluidized bed, *Fuel*, **66**, 774.
113. Jung K and Stanmore B.R (1980): Fluidized bed combustion of wet brown coal, *Fuel*, **59**, 74.
114. Jung K and La Nauze R.D (1983): Particle size and density changes during fluidized-bed combustion, *Can. J. Chem. Engng.*, **61**, 262.

115. Kang S–G, Helble J.J, Sarofim A.F and Beer J.M (1988): Time–resolved evolution of fly ash during pulverised coal combustion, *22nd Symposium (International) on Combustion*, The Combustion Institute, Pittsburgh, 231.
116. Kang S–G, Sarofim A.F and Beer J.M (1992): Effect of char structure on residual ash formation during pulverised coal combustion, *24th Symposium (International) on Combustion*, The Combustion Institute, Pittsburgh, 1153.
117. Kerstein A.R and Edwards (1987): Percolation model for simulation of char oxidation and fragmentation time–histories, *Chem. Engng. Sci.*, **42**, 1629.
118. Khan M.R (1987): Significance of char active surface area for appraising the reactivity of low– and high– temperature chars, *Fuel*, **66**, 1626.
119. Kirkpatrick S (1973): Percolation and conduction, *Rev. Mod. Phys.*, **45**, 574.
120. Krammer G.F and Sarofim A.F (1994): Reaction of char nitrogen during fluidized bed coal combustion – Influence of nitric oxide and oxygen on nitrous oxide, *Comb. Flame*, **97**, 118.
121. Kunii D and Smith J.M (1961): Heat transfer characteristics of porous rocks: II. Thermal conductivities of unconsolidated particles with flowing fluids, *AIChE Journal*, **7**, 29.
122. La Nauze R.D (1985): Fundamentals of coal combustion in fluidized beds, *Chem. Eng. Res. Des.*, **63**, 3.
123. La Nauze R.D and Jung K (1983): Combustion kinetics in fluidized beds, *Proceedings of the 7th International Conference on Fluidized Bed Combustion*, **2**, 1040.
124. La Nauze R.D and Jung K (1986): Mass transfer relationships in fluidized bed combustors, *Chem. Engng. Sci.*, **43**, 275.
125. La Nauze R.D, Jung K and Kastl J (1984): Mass transfer to large particles in fluidized beds of smaller particles, *Chem. Engng. Sci.*, **39**, 1623.

126. Lane A, Shah N and Curtis–Conner Wm (1986): Measurement of the morphology of high–surface–area solids: Porosimetry as a percolation process, *J. Colloid Int. Sci.*, **109**, 235.
127. Laurendeau N.M (1978): Heterogeneous Kinetics of Coal Char Gasification and Combustion, *Prog. Energy Comb. Sci.*, **4**, 221.
128. Lester E, Allen M, Cloke M and Miles N.J (1994): An automated image analysis system for major maceral group analysis in coals, *Fuel*, **73**, 1729.
129. Linjewile T.M (1993): *Temperature of Burning Carbonaceous Particles in a Fluidized–bed Combustor*, Ph.D Thesis, University of Adelaide.
130. Linjewile T.M and Agarwal P.K (1990): Heat transfer behavior and temperature of freely moving burning carbonaceous particles in fluidized beds, *23rd Symposium (International) on Combustion*, The Combustion Institute, Pittsburgh, 917.
131. Linjewile T.M and Agarwal P.K (1995): The influence of product CO/CO₂ ratio on the ignition and temperature history of petroleum coke particles in incipiently gas–fluidized beds, *Fuel*, **74**, 13.
132. Linjewile T.M, Hull A.S and Agarwal P.K (1994): Optical probe measurements of the temperature of burning particles in fluidized beds, *Fuel*, **73**, 1880.
133. Linjewile T.M, Gururajan V.S and Agarwal P.K (1995): The CO/CO₂ product ratio from the combustion of single petroleum coke spheres in an incipiently fluidized bed, accepted for publication, *Chem. Engng. Sci.*
134. Lizzio A.A, Jiang H, and Radovic L.R (1990): On the kinetics of carbon (char) gasification: Reconciling models with experiment, *Carbon*, **28**, 7.
135. Lymberopoulos D.P and Payatakes A.C (1992): Derivation of topological, geometrical, and correlational properties of porous media from pore–chart analysis of serial section data, *J. Coll. Inter. Sci.*, **150**, 61.
136. McEnaney B and Mays T.J (1994): Characterization of macropores using quantitative microscopy, in *Characterization of Porous Solids III*, Elsevier.

137. McGreavy C, Andrade J.S and Rajagopal K (1992): Consistent evaluation of effective diffusion and reaction in pore networks, *Chem. Engng. Sci.*, **47**, 2751.
138. McNamara G.G and Zanetti G (1988): Use of the Boltzmann equation to simulate lattice–gas automata, *Phys. Rev. Lett.*, **61**, 2332.
139. Mann R and Wasilewski M.C (1990): Towards a fractal computer graphic basis for characterization of catalyst pore structure by image reconstruction, *Trans. IChemE*, **68**, 177.
140. Marsh H (1978): How oxygen molecules gasify carbons, *Chem. Soc. London Spec. Pub.*, **32**, 133.
141. Marshall W.R (1954): Atomization and spray drying, *Chem. Engng. Prog.*, **50**, 82.
142. Mason E.A, Evans R.B and Watson G.M (1963): Gaseous diffusion in porous media. III. Thermal transpiration, *J. Chem. Phys.*, **38**, 1808.
143. Mason E.A and Malinauskas A.P (1964): Gaseous diffusion in porous media. IV. Thermal diffusion, *J. Chem. Phys.*, **41**, 3815.
144. Mason E.A, Malinauskas A.P and Evans R.B (1967): Flow and diffusion of gases in porous media, *J. Chem. Phys.*, **46**, 3199.
145. Mason E.A and Malinauskas A.P (1983): *Gas Transport in Porous Media: The Dusty–gas Model*, Elsevier, Amsterdam.
146. Mason E.A and Saxena S.C (1958): Approximate formula for the thermal conductivity of gas mixtures, *Phys. Fluids*, **1**, 361.
147. Maxwell J.C (1892): *A Treatise on Electricity and Magnetism*, Oxford University Press, London.
148. Merrick D (1983): Mathematical models of the thermal decomposition of coal. 2. Specific heats and heats of reaction, *Fuel*, **62**, 540.
149. Metzler R, Glöckle W.G and Nonnenmacher T.F (1994): Fractional model equation for anomalous diffusion, *Physica A*, **211**, 13.

150. Miccio F and Salatino P (1992): Monte–Carlo simulation of combustion–induced percolative fragmentation of carbons, *24th Symposium (International) on Combustion*, The Combustion Institute, Pittsburgh, 1145.
151. Mitchell R.E, Kee R.J, Glarborg P, and Coltrin M.E (1990): The effect of CO conversion in the boundary layers surrounding pulverised–coal char particles, *23rd Symposium (International) on Combustion*, The Combustion Institute, Pittsburgh, 1169.
152. Mohanty K.K, Ottino J.M and Davis H.T (1982): Reaction and transport in disordered media: Introduction of percolation concepts, *Chem. Engng. Sci.*, **37**, 905.
153. Mon and Amundson (1978): Diffusion and reaction in a stagnant boundary layer about a carbon particle. 2. An extension, *Ind. Eng. Chem. Fundam.*, **17**, 313.
154. Morell J.I, Amundson N.R and Park S–K (1990): Dynamics of a single particle during char gasification, *Chem. Engng. Sci.*, **45**, 387.
155. Muralidhar R and Ramkrishna D (1993): Diffusion in pore fractals: A review of linear response models, *Transport in Porous Media*, **13**, 79.
156. Muthukumar M (1982): Concentration dependence of diffusion controlled processes among static traps, *J. Phys. Chem.*, **76**, 2667.
157. Nienow A.W, Rowe P.N and Chiba T (1978): Mixing and segregation of a small proportion of large particles in gas fluidized beds of considerably smaller ones, *AIChE Symp. Series*, **74**(176), 45.
158. O'Shaughnessy B and Procaccia I (1985a): Analytical solutions for diffusion on fractal objects, *Phys. Rev. Lett.*, **54**, 455.
159. O'Shaughnessy B and Procaccia I (1985b): Diffusion on fractals, *Phys. Rev. A*, **32**, 3073.
160. Pal'chenok G.I and Tamarin A.I (1983): Study of heat exchange between a model particle and fluidized bed, *J. Engng. Phys.*, **45**, 427.

161. Petersen E.E: Reaction of porous solids, *AIChE Journal*, **3**, 443 (1957).
162. Phillips R, Vastola F.J and Walker P.L Jr. (1970): Factors affecting the product ratio of the carbon–oxygen reaction–II. Reaction temperature, *Carbon*, **8**, 205.
163. Pillai K.K (1981): Burning rates of coal in fluidized–coal combustion, *Fuel*, **60**, 163.
164. Prins W (1987): *Fluidized Bed Combustion of a Single Carbon Particle*, Ph.D Thesis, Twente University of Technology, The Netherlands.
165. Prins W and van Swaaij W.P.M (1986): Fluidized bed combustion of a single carbon particle, in *Fluidized Bed Combustion*, Radovanovic M (ed.), Springer–Verlag, Berlin.
166. Prins W and van Swaaij W.P.M (1990): The influence of transport phenomena on the fluidized bed combustion of a single carbon particle, *Fuel Process. Technol.*, **24**, 355.
167. Qian Y.H, d’Humières D and Lallemand P (1992): Lattice BGK models for Navier–Stokes equation, *Europhys. Lett.*, **17**, 479.
168. Quiblier J.A (1984): A new three–dimensional modeling technique for studying porous media, *J. Coll. Inter. Sci.*, **98**, 84.
169. Radovic L.R, Jiang H and Lizzio A.A (1991): A transient kinetics study of char gasification in carbon dioxide and oxygen, *Energy Fuels*, **5**, 68.
170. Raask E (1985) Mineral impurities in coal combustion, Springer–Verlag, Berlin.
171. Rammal R and Toulouse G (1983): Random walk on fractal structures and percolation clusters, *J. Physique Lett.*, **44**, 13.
172. Reyes S and Jensen K.F (1986a): Percolation concepts in modelling of gas–solid reactions. I. Application to char gasification in the kinetic regime, *Chem. Engng. Sci.*, **41**, 333.

173. Reyes S and Jensen K.F (1986b): Percolation concepts in modelling of gas–solid reactions. II. Application to char gasification in the diffusion regime, *Chem. Engng. Sci.*, **41**, 345.
174. Richardson M.J (1993): The specific heats of coals, cokes and their ashes, *Fuel*, **72**, 1047.
175. Roman H.E and Giona M (1992): Fractional diffusion equation on fractals: three–dimensional case and scattering function, *J. Phys. A*, **25**, 2017.
176. Ross I.B and Davidson J.F (1982): The combustion of carbon particles in a fluidized bed, *Trans. IChemE*, **60**, 108.
177. Rossberg M (1956): Experimentelle ergebnisse über die primärreaktionen bei der kohlenstoffverbrennung, *Z Electrochem*, **60**, 952.
178. Rothman D.H (1988): Cellular automaton fluids: A model for flow in porous media, *Geophysics*, **53**, 509.
179. Sahimi M (1985): Fractal dimension in a percolation model of fluid displacement, *Phys. Rev. Lett.*, **55**, 1698.
180. Sahimi M (1991): Transport, reaction, and fragmentation in evolving porous media, *Phys. Rev. A*, **43**, 5367.
181. Sahimi M (1993): Flow phenomena in rocks: from continuum models to fractals, percolation, cellular automata, and simulated annealing, *Rev. Mod. Phys.*, **65**, 1393.
182. Sahimi M (1994): *Applications of Percolation Theory*, Taylor and Francis, London.
183. Sahimi M and Tsotsis T.T (1985): A percolation model of catalyst deactivation by site coverage and pore blockage, *J. Catalysis*, **96**, 552.
184. Sahimi M and Tsotsis T.T (1987): Dynamic scaling for the fragmentation of reactive porous media, *Phys. Rev. Lett.*, **59**, 888.
185. Sahimi M, Gavalas G.R and Tsotsis T.T (1990): Statistical and continuum models of fluid–solid reactions in porous media, *Chem. Engng. Sci.*, **45**, 1443.

186. Salatino P and Massimilla L (1988): The role of peripheral percolation in detachment of fines from burning carbon particles, *22nd Symposium (International) on Combustion*, The Combustion Institute, Pittsburgh, 29.
187. Sandmann C.W and Zygourakis K (1987): Pore structure evolution during non-catalytic gas-solid reactions: IV. Studies with demineralized chars, *Chem. Eng. Comm.*, **58**, 139.
188. Saxena S.C (1990): Devolatilization and combustion Characteristics of Coal Particles, *Prog. Energy Comb. Sci.*, **16**, 55.
189. Sevick E.M, Monson P.A and Ottino J.M (1989): Morphology and transport using the Ising lattice as a morphology description, *Chem. Engng. Sci.*, **44**, 21.
190. Shah N (1985): *Development and Application of Models for Transport and Reaction in Composite Media*, PhD Thesis, University of Massachusetts.
191. Shah N and Ottino J.M (1987): Transport and reaction in evolving, disordered composites – I. Gasification of porous solids, *Chem. Engng. Sci.*, **42**, 63.
192. Shakib F, Hughes T.J.R and Johan Z (1989): A multi-element group preconditioned GMRES algorithm for nonsymmetric systems arising in finite element analysis, *Comp. Meth. App. Mech. Engng.*, **75**, 1989.
193. Sharratt P.N and Mann R (1987): Some observations on the variation of tortuosity with Thiele Modulus and pore size distribution, *Chem. Engng. Sci.*, **42**, 1565.
194. Shimomura T, Doolen G.D, Hasslacher B and Fu C (1990): Calculations using lattice gas techniques, in *Lattice Gas Methods for Partial Differential Equations*, Addison-Wesley, New York, 3.
195. Simons G.A (1983): The role of pore structure in coal pyrolysis and gasification, *Prog. Energy Comb. Sci.*, **9**, 269.
196. Smith I.W (1978): The intrinsic reactivity of carbons to oxygen, *Fuel*, **57**, 409.
197. Smith I.W and Tyler R.J (1972): Internal burning of pulverized semi-anthracite: the relationship between particle structure and reactivity, *Fuel*, 313.

198. Smith I.W (1982): The combustion rates of coal chars: A review, *19th Symposium (International) on Combustion*, The Combustion Institute, Pittsburgh, 1045.
199. Smith K.L, Smoot L.D and Fletcher T.H (1993): Coal characteristics, structure, and reaction rates, in *Fundamentals of Coal Combustion for Clean and Efficient Use*, Smoot L.D (ed.), Elsevier, Amsterdam.
200. Sotirchos S.V (1989): Multicomponent diffusion and convection in capillary structures, *AIChE Journal*, **35**, 1953.
201. Sotirchos S.V and Amundson N.R (1984a): Dynamic behaviour of a porous char particle burning in an oxygen-containing environment, *AIChE Journal*, **30**, 537.
202. Sotirchos S.V and Amundson N.R (1984b): Dynamic behaviour of a porous char particle burning in an oxygen-containing environment. Part II: Transient analysis of a shrinking particle, *AIChE Journal*, **30**, 549.
203. Sotirchos S.V and Amundson N.R (1984c): Diffusion and reaction in a char particle and in the surrounding gas phase. Two limiting models, *Ind. Eng. Chem. Fundam.*, **23**, 180.
204. Sotirchos S.V and Amundson N.R (1984d): Diffusion and reaction in a char particle and in the surrounding gas phase. A continuous model, *Ind. Eng. Chem. Fundam.*, **23**, 191.
205. Sotirchos S.V, Srinivas B and Amundson N.R (1984): Modelling of the combustion of single char particles, *Rev. Chem. Engng.*, **2**, 175.
206. Sotirchos S.V and Burganos V.N (1986): Intraparticle diffusion and char combustion, *Chem. Engng. Sci.*, **41**, 1599.
207. Sotirchos S.V and Burganos V.N (1988): Analysis of multicomponent diffusion in pore networks, *AIChE Journal*, **34**, 1106.
208. Sotirchos S.V and Zarkanitis S (1993): A distributed pore size and length model for porous media reacting with diminishing porosity, *Chem. Engng. Sci.*, **48**, 1487.

209. Spanne P, Thovert J.F, Jacquin C.J, Lindquist W.B, Jones K.W and Adler P.M (1994): Synchrotron computed microtomography of porous media: Topology and transports, *Phys. Rev. Lett.*, **73**, 2001.
210. Srinivas B and Amundson N.R (1981): Intraparticle effects in char combustion. II. Steady state analysis, *Can. J. Chem. Engng*, **59**, 60.
211. Srinivasachar S, Toqan M.A, Beér J.M and Ettouney H.M (1988): Percolation model for coal char particle combustion and fragmentation, *Comb. Sci. Tech.*, **57**, 55.
212. Stadtherr M.A, Cofer H.N and Camarda K.V (1993): Hardware: Developing the metacomputer, *Chem. Engng. Prog.*, Nov., 27.
213. Stanmore B.R and Jung K (1980): The burnout rates of brown coal char particles in fluidized bed combustors, *Trans. IChemE*, **58**, 66.
214. Stauffer D, Coniglio A and Adam M (1982): Gelation and critical phenomena, *Adv. Polymer Sci.*, **44**, 103.
215. Stauffer D and Aharony A (1992): *Introduction to Percolation Theory (2nd ed.)*, Taylor & Francis, London.
216. Stubington J.F and Chan S.W (1990): On the phase location and rate of volatiles combustion in bubbling fluidized bed combustors, *Trans. IChemE*, **68**, 195.
217. Suuberg E.M, Wojtowicz M and Calo J.M (1988): Reaction order for low temperature oxidation of carbons, *22nd Symposium (International) on Combustion*, The Combustion Institute, Pittsburgh, 79.
218. Tamarin A.I (1982): Mass transfer between the gas and solid particles in a fluidized bed, *J Engng. Phys.*, **41**, 1346.
219. Thovert J.F, Salles J and Adler P.M (1993): Computerized characterization of the geometry of real porous media: Their discretization, analysis and interpretation, *J. Microscopy*, **170**, 65.

220. Tognotti L, Longwell J.P and Sarofim A.F (1990): The products of the high temperature oxidation of a single char particle in an electrodynamic balance, *23rd Symposium (International) on Combustion*, The Combustion Institute, Pittsburgh, 1207.
221. Tomków K, Jankowska A, Czechowski F and Siemieniowska T (1977): Activation of brown-coal chars with oxygen, *Fuel*, **56**, 101.
222. Turnbull E, Kossakowski E.R, Davidson J.F, Hopes R.B, Blackshaw H.W and Goodyer P.T.Y (1984): Effect of pressure on combustion of char in fluidized beds, *Chem. Eng. Res. Des.*, **62**, 223.
223. Valix M.G, Trimm D.L, Smith I.W and Harris D.J (1992): Mass transfer effects in coal combustion, *Chem. Engng. Sci.*, **47**, 1607.
224. van Krevelen D.W (1993): *Coal: Topology-Physics-Chemistry-Constitution*, Elsevier, Amsterdam.
225. Verheggen T.M.M, Ed. (1992): *Introduction to Numerical Methods for the Simulation of Multi-phase and Complex Flow*, Springer-Verlag, Berlin.
226. Verheggen T.M.M, Rem P and Somers J (1992): Introduction, in *Introduction to Numerical Methods for the Simulation of Multi-phase and Complex Flow*, Springer-Verlag, Berlin.
227. Vleeskens J.M and Hamburg G (1991): Depth of combustion inside char from evidence of oxidized pyrite, *Fuel*, **70**, 1377.
228. Wakao N and Smith J.M (1962): Diffusion in catalyst pellets, *Chem. Engng. Sci.*, **17**, 825.
229. Walker P.L Jr., Rusinko F Jr. and Austin L.G (1959): Gas reactions of carbon, *Advances in Catalysis*, **11**, 133.
230. Wang W and Rogg B (1993): Reduced kinetic mechanisms and their numerical treatment I: Wet CO flames, *Comb. Flame*, **94**, 271.

231. Waters B.J, Squires R.G, Laurendeau N.M and Mitchell R.E (1988): Evidence for formation of CO₂ in the vicinity of burning pulverized carbon particles, *Comb. Flame*, **74**, 91.
232. Weiss Y, Benari Y, Kantorovich I.I, Bar–Ziv E, Krammer G, Modestion A and Sarofim A.F (1994): Evolution of porosity and thermal conductivity during char oxidation, *25th Symposium (International) on Combustion*, The Combustion Institute, Pittsburgh, 519.
233. Wells J.T, Janecky D.R and Travis B.J (1991): A lattice gas automata model for heterogeneous chemical reactions at mineral surfaces and in pore networks, *Physica D*, **47**, 115.
234. White F.M (1974): *Fluid Mechanics*, John Wiley, New York.
235. Wilke C.R (1950): A viscosity equation for gas mixtures, *J. Chem. Phys.*, **18**, 517.
236. Winget J.M and Hughes T.J.R (1985): Solution algorithms for non–linear transient heat conduction analysis employing element–by–element iterative strategies, *Comp. Meth. App. Mech. Engng.*, **52**, 711.
237. Winterfeld P.H (1981): *Percolation and Conduction Phenomena in Disordered Composite Media*, PhD Thesis, University of Minnesota.
238. Xavier A.M and Davidson J.F (1985): Heat transfer in fluidized beds: Convective heat transfer in fluidized beds, *Fluidization (2nd ed.)*, Academic Press, London, 437.
239. Yagi S and Kunii D (1955): Studies on combustion of carbon particles in flames and fluidized beds, *5th Symposium (International) on Combustion*, Reinbold Publishing Corp., New York, 231.
240. Yagi S and Kunii D (1957): Studies on effective thermal conductivities in packed beds, *AIChE Journal*, **3**, 373.
241. Yetter R.A, Dryer F.L and Rabitz H (1986): Complications of one–step kinetics for moist CO oxidation, *21st Symposium (International) on Combustion*, The Combustion Institute, Pittsburgh, 749.

242. Young B.C and Niksa S (1988): Combustion rates for selected low-rank coal chars, *Fuels*, **67**, 155.
243. Yu H-C and Sotirchos S.V (1987): A generalized pore model for gas-solid reactions exhibiting pore closure, *AIChE Journal*, **33**, 382.
244. Zhang L and Seaton N.A (1994): The application of continuum equations to diffusion and reaction in pore networks, *Chem. Engng. Sci.*, **49**, 41.
245. Zhu Z-B, Furusawa T, Adschiri T and Nozaki T (1989): Characterization of coal char reactivity by the number of active sites during CO₂ gasification, *Am. Chem. Soc. Div. Fuel Chem. Preprints*, **34**(1), 87.
246. Zienkiewicz O.C and Taylor R.L (1989): *The Finite Element Method (4th ed.)*, McGraw-Hill, London.
247. Zienkiewicz O.C and Zhu J.Z (1987): A simple error estimator and adaptive procedure for practical engineering analysis, *Int. J. Num. Meth. Engng.*, **24**, 337.
248. Zienkiewicz O.C and Zhu J.Z (1992): The superconvergent patch recovery and a posteriori error estimates. Part I. The recovery technique, *Int. J. Num. Meth. Engng.*, **33**, 1331.
249. Zygorakis K and Glass M.W (1988): Macropore size analysis using digital image processing and a stereological model, *Chem. Engng. Comm.*, **70**, 39.
250. Zygorakis K and Sandmann C.W (1988): Discrete structural models and their application to gas-solid reacting systems, *AIChE Journal*, **34**, 2030.

CHAPTER 3

DETERMINATION OF EFFECTIVE TRANSPORT PROPERTIES OF FLUIDS IN POROUS SOLIDS

3.1 INTRODUCTION

In order to model reaction within a porous solid, we generally require effective transport properties for the fluid–solid system in question. Knowledge of how the effective transport properties vary with pore system evolution is also critical if reaction causes considerable change in the pore structure. Consequently, much attention has been given to the development of techniques for determining effective transport properties of fluids within porous solids, and how these effective properties change with pore system geometry and morphology [Sahimi et al., 1990]. Traditionally, three approaches have been used: (1) experiment; (2) classical volume averaging techniques in which simple pore system models are used; and (3) consistent volume averaging techniques in which the pore system is represented by a lattice. Each is briefly reviewed in Section 3.2 with particular emphasis placed on their shortcomings. Review articles are referred to for details. The many problems and limitations associated with these more conventional techniques have motivated the development of approaches in which the pore system and fluid are represented by discrete entities – discussion of these discrete approaches shall also be undertaken in Section 3.2. In Section 3.3, a new discrete approach based upon molecular dynamic [Allen and Tildesley, 1989] and percolation [Stauffer and Aharony, 1992; Sahimi, 1994] concepts is described, and subsequently used to study mass diffusion within two non–reactive fluid–solid systems that may be of interest to the coal combustion scientist. This is followed by a discussion on the application of this new approach to more realistic systems, and its extension to the determination of other transport coefficients, and reaction rate parameters.

3.2 OVERVIEW OF TECHNIQUES FOR STUDY OF DIFFUSION OF FLUIDS WITHIN POROUS MEDIA

3.2.1 Experimental Techniques

Experimental techniques for the determination of effective diffusion coefficients may be broken up into three broad groupings: (1) steady state; (2) unsteady state; and (3) nuclear magnetic resonance (NMR). A review of (1) and (2) may be found in Haynes (1988), whilst application of NMR to the study of fluids within porous solids is reviewed by Gladden (1993). Each of these methods require interpretation of data by some assumed model – this may limit subsequent usage of the derived data, and can lead to significant errors if important phenomena are not included. Haynes (1988), for example, highlights the potential for error if heat or non-linear isotherm effects are neglected when interpreting sorption rate experiments, whilst the nature of the pore structure must be carefully considered so as to avoid misinterpretation of NMR data [Gladden, 1993].

Most experimental approaches are limited to relatively low temperatures where reaction does not occur, whilst extrapolation to higher temperatures typical of combustion may be much in error [Valix et al., 1992]. This last has been confirmed by a number of recent simulation studies which demonstrate that the occurrence of reaction can significantly influence the effective transport properties [Muthukumar, 1982; Cukier and Freed, 1983; Hollewand and Gladden, 1992a; McGreavy et al., 1992; see, however, Zhang and Seaton, 1994]. Reaction also leads to a change in pore system morphology – the ability to determine tortuosity variation with conversion via experiment is limited.

Individual techniques have various shortcomings that must also be considered when determining effective diffusion coefficients. For example: (1) static experiments cannot account for deadend pores; (2) axial dispersion in chromatography experiments restrict the range of applicability [Sarmah and Haynes, 1989]; (3) instrument response restricts sorption rate methods to slow diffusion processes [Haynes, 1988]; and (4) NMR techniques are limited to the study of fast diffusion of fluids with high concentrations of unpaired nuclear spins [Ruthven, 1984].

3.2.2 Classical Volume Averaging Techniques

Classical volume averaging techniques first determine an averaged diffusion coefficient by using an average pore size [Satterfield, 1970], or by averaging the pore level behavior over pore size and orientation distributions [Johnson and Stewart, 1965; Feng and Stewart, 1973; Wang and Smith, 1983]. A tortuosity factor, κ [Epstein, 1989], is then introduced to account for the various non-idealities of the pore structure such as irregular pore shape, deadend pores, and loops. The tortuosity factor, and its variation with porosity, is usually determined by assuming some simple pore system model amenable to straightforward mathematical analysis. Well known results include that of Wakao and Smith (1962) who found $\kappa=1/\phi$ in the large pore limit, and Johnson and Stewart (1965) who derived $\kappa=3$ for a non-interconnected isotropic random pore system. A review of the various averaging processes and tortuosity factors may be found in Cunningham and Williams (1980).

Except in the simplest cases, the classical volume averaging approach is inconsistent. As mass conservation is violated at intersections of different sized pores [Gavalas and Kim, 1981; Burganos and Sotirchos, 1987], significant errors are introduced for non-unimodal pore systems [Burganos and Sotirchos, 1987; Sotirchos and Burganos, 1988; Sotirchos, 1989]. Moreover, as the averaging process does not account for mass transfer contributions at pore junctions, it is invalid for systems in which pore overlap is significant, and where pore dimensions (radius and length) are comparable [Sotirchos and Burganos, 1988].

The use of simple pore system models to calculate tortuosity factors and their variation with conversion may also be much in error. They are, for example, incapable of rigorously accounting for pore system topology and connectivity. This is often reflected in the large discrepancies seen between estimated and experimental tortuosities [Satterfield and Cadle, 1968]. Moreover, it has been demonstrated that the tortuosity is not only a property of the solid, but may also depend upon temperature, mixture composition and pressure [Bhatia, 1986].

3.2.3 Consistent Volume Averaging Techniques

The many problems and limitations associated with experimental and classical volume averaging techniques have motivated the development of averaging methods in which the pore system is represented by a discrete lattice. The most commonly used techniques include: the effective medium approximation (EMA) [Kirkpatrick, 1973]; the position–space renormalization group (PSRG) methods [Shah and Ottino, 1986 and references therein]; and Monte–Carlo (MC) simulations [Winterfeld, 1981]. Brief reviews of these and other less common methods such as the renormalized EMA [Sahimi et al., 1983; Sahimi, 1988], and critical path method [Katz and Thompson, 1987] may be found in Sahimi (1988, 1993, 1994) and Sahimi et al. (1990).

These approaches do not require use of the smooth field approximation, and average, in a consistent manner, the pore level behavior over the pore system volume. As the averaging process naturally accounts for both pore system geometry and topology, a tortuosity factor is not required, and percolation behavior is revealed when appropriate (alternatively, we may back–out a tortuosity that naturally incorporates both pore system geometry and topology). Despite this, recent work has demonstrated these techniques are not without problems. It is normally assumed a complex pore system may be represented by a regular network. This is supported by the work of Jerauld and others [Jerauld et al., 1984a, b; Winterfeld, 1981], who demonstrated that percolation properties of regular and irregular (synonymous with real pore spaces) lattices are the same provided their average connectivities are equal. However, Hollewand and Gladden (1992a, b) have recently shown effective diffusion coefficients of regular and irregular networks with the same average connectivity are not equal for low coordination numbers ($Z \leq 6$), and only show insignificant differences once $Z \geq 14$. It has also been illustrated that widely different effective transport properties may be predicted for a given system depending upon the network representation used [Hollewand and Gladden, 1992a, b].

Individual techniques also have faults that restrict their application. For example, the

EMA incorrectly predicts the percolation threshold in three dimensions, and the functional behavior of the effective diffusion coefficient near the percolation threshold in two dimensions. The PSRG methods, whilst more accurate than the EMA, perform poorly in three dimensions due to computational limitations. Finally, use of a discrete lattice is not justified when the effect of pore bodies and pore intersections are comparable [Sahimi, 1994; Burganos and Sotirchos, 1989]. In this case, continuum percolation models must be used in conjunction with MC simulations. As this requires numerical solution of a multidimensional PDE or system of PDEs, computational resource limitations are often a consideration.

3.2.4 Discrete Methods

By assuming a continuum description of the pore level transport/reaction behavior, consistent volume averaging techniques do not permit study of transport and reaction within porous media from a fundamental perspective. This and other issues raised in the previous section may be dealt with by retaining the percolation representation of the pore space, and replacing the continuum fluid by discrete fluid elements, the most basic being the molecule. Fluid flow is then simulated via the discrete fluid elements executing a random walk (RW) throughout the pore space. By representing the fluid as discrete elements, this approach is much more efficient than MC simulations when large continuum percolation systems are of interest, especially when modern vector and parallel computer architectures are to be used [Sahimi, 1994]. To date, two variants of the RW approach have been used to estimate effective diffusion coefficients of model porous solids: the transmission probability method, and the mean square displacement method.

The former involves the injection of a large number of particles at one end of the model porous solid and then counting the fraction of particles that successfully walk through to an opposing plane a distance $\mathcal{L}$ away. The effective diffusivity is then determined at large $\mathcal{L}$ from the slope of the P_t vs $1/\mathcal{L}$ curve, where P_t is the fraction of particles transmitted through a distance $\mathcal{L}$. This approach has been used by Evans and co-workers [Evans

et al., 1980; Nakano and Evans, 1983; Abbasi et al., 1983] to determine, as a function of porosity and mean pore size, tortuosity factors for ordinary and Knudsen diffusion within pore spaces defined by regular non-overlapping, and random overlapping assemblages of spheres. Burganos and Sotirchos (1988) have also used this approach to study Knudsen diffusion through a system of unimodal or bimodal randomly overlapping parallel cylindrical capillaries.

The mean square displacement (MSD) method relies upon the accumulation of the MSD, $R^2(t)$, of many particles executing a random walk throughout the model porous solid. The effective diffusion coefficient for a d -dimensional porous solid is then determined using the Einstein relationship

$$D_e = \frac{R^2}{2dt} \quad (3-1)$$

in the long time limit. Burganos and Sotirchos (1989) compared these two methods and found that whilst they gave similar results, the MSD approach may be computationally more efficient if high accuracy results are required. Sahimi (1990) studied diffusion of flexible chains through pillared clays with absorption, whilst Tomadakis and Sotirchos (1991a, b, 1993a, b) studied mass transport within unimodal and bimodal systems of overlapping cylindrical fibres. Melkote and Jensen (1989) undertook similar [Tomadakis and Sotirchos, 1993a] studies using the transmission probability method.

Much attention has also been given to the use of the discrete approach for theoretical study of diffusion within disordered media. This work has been reviewed a number of times in recent years [Havlin and Ben-Avraham, 1987; Havlin and Bunde, 1991]. Perhaps one of the most important conclusions to come from these theoretical studies is the fact that diffusion within a percolating porous medium may be fundamentally different to that described by Fick's law. Such diffusion processes are termed anomalous [Alexander and Orbach, 1982], sub-diffusive, or non-Fickian. The fundamental basis for anomalous diffusion may be perceived if we consider the correlation length of the pore system. Amongst other things, this is the distance a particle must travel within the pore structure before it forgets its initial state. The correlation length of a percolation

system near the percolation threshold, ϕ_c , scales as [Rammal and Toulouse, 1983]

$$\xi \sim |\phi - \phi_c|^{-\nu} \quad (3-2)$$

where ϕ is the porosity and ν a positive universal critical scaling exponent. Clearly, the correlation length, and therefore memory, increases to infinity as the percolation threshold is approached (or, for a finite sized body of size $\mathcal{L}$, $\xi \rightarrow \mathcal{L}$). If the Fickian formulation is used, we are assuming the diffusion process is memoryless. Equation (3-2) indicates this assumption is invalid near the percolation threshold. Infact, a diffusion process is anomalous for times less than the correlation time of the system, τ_c , where τ_c is directly related to the correlation length of the system and the speed of the diffusing particles. Anomalous diffusion manifests itself in a number of ways:

- The particle distribution of a memoryless diffusion process is Gaussian [Kubo et al., 1985]. It has been demonstrated that this distribution for an anomalous diffusion process is non-Gaussian [O'Shaughnessy and Procaccia, 1985; Guyer, 1985; Havlin and Ben-Avraham, 1987; Sahimi, 1987; Roman et al., 1989; Giona and Roman, 1992].
- The long time limit of the mean square displacement for a Gaussian diffusion process scales as $R^2 \sim t$ [Kubo et al., 1985]. This differs from that of anomalous diffusion where $R^2 \sim t^\alpha$ for $\alpha < 1$ [Gefen et al., 1983]. It may be easily shown that the diffusion coefficient defined by the Einstein relation (3-1) does not exist for an anomalous diffusion process; indeed, this relationship is only true for a Gaussian process.
- The velocity autocorrelation function may contain oscillatory components and will possess a long negative time-tail [Bruin, 1972, 1974; James and Evans, 1987; Muralidhar et al., 1990; Biggs and Agarwal, 1992, 1994].

Random walk techniques are powerful tools that permit study of mass diffusion within porous media at a fundamental level, and provide a means of determining effective diffusion coefficients without the many problems attendant upon the more traditional approaches. However, there are still problems:

- Although the nature of the various interactions are known to be critical [Sahimi, 1990], the fluid–substrate and fluid–fluid interactions are usually assumed “hard”, and inclusion of multiple species in a realistic manner (ie: not only by size variation but also potential, shape, and mass distribution) is difficult.
- Absorption, reaction and surface diffusion are also known to be important [Muthukumar, 1982; Cukier and Freed, 1983; Sahimi, 1990] – inclusion of such considerations is not straightforward, and is usually done in an ad–hoc manner or as a model parameter.
- The tortuosity factor is known to be temperature dependent [Bhatia, 1986] – the lack of any clear connection between the RW time steps and real time means temperature effects may not be directly investigated.

3.3 MOLECULAR DYNAMIC SIMULATION OF TRANSPORT AND REACTION WITHIN POROUS MEDIA

Many of the shortcomings associated with the present discrete approaches may be effectively and easily dealt with using molecular dynamics [Sahimi, 1990]. In molecular dynamics (MD), the fluid is represented as discrete particles (atoms or molecules) whose positions and velocities are integrated through time using classical particle dynamic techniques [Allen and Tildesley, 1989]. The technique provides a microscopic picture of a system which may reveal fundamental behaviors, and yields macroscopic quantities of interest via statistical mechanics [McQuarrie, 1976].

The versatility and power of MD is witnessed by the wide range of problems that it has been applied to. For example, it has been used to study solids [Yip, 1986], atomic fluids [Pas and Zwolinski, 1991], and molecular fluids such as hydrocarbons [Edberg et al., 1986], proteins [Berendsen, 1986], and molten salts [Tissen and Janssen, 1990]. It has also been used to study multicomponent liquids [Heyes, 1992], phase transitions [Nicholson and Parsonage, 1982], reaction [Brown, 1991], gas–in–metal systems [Gillan, 1986], fluids within single pores [Murad et al., 1993], and diffusion within zeolite cages [El Amrani and Kolb, 1993]. The method may be used to determine, as a function

of temperature, pressure and density, equilibrium parameters such as the specific heats, and non – equilibrium quantities like the self and binary diffusion coefficients, shear and bulk viscosities, thermal conductivity, and the thermotransport coefficients.

I report here an approach based upon MD and percolation [Stauffer and Aharony, 1992; Sahimi, 1994] concepts which may be used to study diffusion (and reaction) within porous media. The method of porous solid generation, which utilizes percolation concepts, is first described. This is followed by a description of the MD algorithms used to study diffusion, without reaction, of atomic and molecular monocomponent fluids within the porous solid. Finally, application of this technique to the study of two model systems is detailed.

3.3.1 Porous Solid Generation

The porous solid is generated in two consecutive stages: (1) creation of a two phase solid/void skeleton on a regular space filling tessellation; and (2) insertion of substrate atoms into the solid phase. Each stage is described below, whilst a brief description may also be found in Biggs and Agarwal (1992).

The skeleton of a simple uncorrelated porous solid of porosity ϕ may be generated on an $L \times L \times L$ regular space filling tessellation using the algorithm

```

do 10 i = 1, L
  do 10 j = 1, L
    do 10 k = 1, L
      cell(i, j, k) = VOID
      r = RAN
      if (r <  $\phi$ ) cell(i, j, k) = SOLID
    10 continue
  10 continue
10 continue

```

(A1)

where SOLID and VOID indicate solid or fluid occupancy of the cell respectively, and RAN is a [0:1] uniform random number. The skeleton generated using this algorithm includes accessible and inaccessible pore volume. As the inaccessible pore space does not contribute to the mass transfer process, a modified version of the Hoshen and Kopelman (1976) algorithm is used to remove any isolated pores under periodic

boundary conditions. An alternative to this method of skeleton generation is that of Alexandrowicz (1980) which generates only the sample spanning pore. It should be noted, however, that removing or ignoring isolated pores may be inappropriate if cell sizes are smaller than the potential cutoff distance, or if reaction is included (see §3.4.2) where isolated pores will be eventually exposed.

Having generated the porous solid skeleton, the substrate atoms must be positioned within the solid phase. The positions of the substrate atoms within a solid cell are defined by the desired microscopic details of the substrate structure, and the status (solid or void) of the adjacent unit cells. This last consideration is important so as to prevent the occurrence of coincident substrate atoms. The substrate structure may be as simple or complex as we like. For example, a coke-like structure (graphite without order between the planes) with organically bound inorganics may be modelled with ease. Not surprisingly, storage of the substrate atom positions requires significant memory. If this is a problem, the algorithm described in Biggs and Agarwal (1992) may be used. The method significantly reduces storage overhead in exchange for a small increase in CPU cost (although code complexity is significantly increased).

The above process of pore system generation is attractive for several reasons: (1) the algorithms for generating percolation systems on regular tessellations are relatively simple; (2) the properties of percolation systems built on regular space filling tessellations are well understood; (3) the atomic nature of the substrate may be generated with relative ease; and (4) the cell structure of the solid permits efficient force calculation during the MD simulation. However, this process produces a solid in which the *substrate structure is defined by the pore system configuration*. This is clearly an approximation for real microporous solids where the *pore system is defined by the solid's molecular structure*. On the other hand, the mesoporous/macroporous structure of a real porous solid is generally not defined by the solid molecular structure, but rather in spite of it. These issues must be considered when generating computer models of real porous solids for use with the MD approach (see §3.4.1).

3.3.2 Molecular Dynamic Algorithms

3.3.2.1 Preliminaries

The standard MD simulation of a fluid at equilibrium (this sort of simulation is known as equilibrium molecular dynamics or EMD) involves tracking through time the trajectories of a finite number of particles (atoms or molecules) under periodic boundary conditions. Periodic boundary conditions reduce finite size effects [Allen and Tildesley, 1989]. For an N particle simulation, we integrate, through time, Newton's equations of motion for each particle $i = 1, 2, \dots, N$

$$\frac{d\mathbf{v}_i}{dt} = \frac{\mathbf{f}_i}{m_i} \quad \frac{d\mathbf{r}_i}{dt} = \mathbf{v}_i \quad (3-3)$$

where $\mathbf{v}$ and $\mathbf{r}$ are the particle velocity and position vectors respectively, m the particle mass, and $\mathbf{f}$ the force acting on the particle. The total force acting on a particle may include forces induced by an external field, and the potential interactions between the particle and other surrounding (fluid and solid) particles. The total potential induced by these interactions may be expressed as [Allen and Tildesley, 1989]

$$u_i = u_f + u_2 + u_3 + \dots \quad (3-4)$$

where u_f is the external field potential, and u_n , $n = 2, 3, \dots, \infty$, the sum of the n -body potential interactions. Computational limitations mean that even today, most simulations neglect all but the external field and two-body interactions. Using this assumption, the force acting on the i^{th} atom due to the surrounding fluid and solid, under no external fields, is

$$\mathbf{f}_i = - \sum_{\substack{j=1 \\ j \neq i}}^N \nabla_{\mathbf{r}_{ij}} u_{ij} \quad (3-5)$$

where u_{ij} is the pair potential between atom pair $i-j$ a distance r_{ij} apart. The Laplacian operator in Cartesian space is defined as

$$\nabla_{\mathbf{r}_{ij}} = \frac{d}{dr_{ij}} \hat{\mathbf{r}}_{ijx} + \frac{d}{dr_{ij}} \hat{\mathbf{r}}_{ijy} + \frac{d}{dr_{ij}} \hat{\mathbf{r}}_{ijz} \quad (3-6)$$

where $\hat{\mathbf{r}}_{ij} = (\hat{\mathbf{r}}_{ijx}, \hat{\mathbf{r}}_{ijy}, \hat{\mathbf{r}}_{ijz})$ is the unit vector defining the position of atom i with respect to atom j . As most of the simulation time is spent calculating the force term (3-5), a truncated force potential is often used if long range forces are negligible [Allen and

Tildesley, 1989]

$$\bar{u}_{ij} = \begin{cases} u_{ij} - \left| \frac{du_{ij}}{dr_{ij}} \right|_{r_{ij}=r_c} (r_{ij} - r_c) - |u_{ij}|_{r_{ij}=r_c} & \text{for } r_{ij} < r_c \\ 0 & \text{for } r_{ij} \geq r_c \end{cases} \quad (3-7)$$

where the cutoff radius, r_c , is selected such that the summation of equation (3-5) is now over $N_b \ll N$ atoms

$$\mathbf{f}_i = - \sum_{j=1}^{N_b} \nabla_{r_{ij}} \bar{u}_{ij} \quad (3-8)$$

If long range forces are important (eg: charge–charge interactions of ion systems, and dipole–dipole interactions of some molecular fluids such as carbon dioxide), several techniques are available to efficiently calculate them [Allen and Tildesley, 1989; Hansen, 1986].

The form of the potential may be as simple or as complex as one likes. The main limitations on the potential selected are the available potential models for the system under investigation, and computational resources. A well known and used potential is the simple, but realistic, Lennard–Jones (LJ) interaction

$$u_{ij} = 4\epsilon \left[\left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^6 \right] \quad (3-9)$$

where ϵ and σ are the pair potential energy and length parameters respectively. As these parameters are determined from experiment, the potential, whilst lacking rigorous theoretical basis, provides a good approximation for determining macroscopic properties. Moreover, as the potential includes both long range attractive and short range repulsive components, it is also suitable for qualitative study of the system's microscopic behavior.

Simulations using equations (3-3) ensure conservation of energy, mass and volume – this corresponds to the microcanonical ensemble (constant NVE). As we are often interested in how properties vary with temperature and pressure, results generated in

this ensemble are of limited practical use (although, of course, the microscopic behavior is still of great interest). Simulations in the canonical (constant NVT), isothermal–isobaric (constant NPT), and other (constant μ VT) ensembles are possible using the constraint techniques developed by Hoover et al. (1982) and Evans (1983). As we are interested in the behavior of the system at a given temperature, MD simulation of atomic and molecular fluids in the canonical ensemble is now described.

3.3.2.2 Atomic Fluids in the Canonical Ensemble

Simulations in the canonical ensemble may be simply performed by integrating equations (3–3) through time with occasional rescaling of the atom velocity's so as to maintain an average kinetic energy (and hence temperature) [Woodcock, 1971]. Alternatively, we may solve the classical trajectory equations modified by Gauss's Principle of Least Constraints [Bradbury, 1968; Hoover et al., 1982; Evans, 1983]

$$\frac{d\mathbf{v}_i}{dt} = \frac{\mathbf{f}_i}{m_i} - \zeta \mathbf{v}_i \qquad \frac{d\mathbf{r}_i}{dt} = \mathbf{v}_i \qquad (3-10)$$

where ζ is the Lagrangian multiplier

$$\zeta = \frac{\sum_{i=1}^N \mathbf{v}_i \cdot \mathbf{f}_i}{\sum_{i=1}^N m_i \mathbf{v}_i \cdot \mathbf{v}_i} \qquad (3-11)$$

which enforces the desired temperature. Unlike the velocity rescaling process, this technique has a sound theoretical basis. The temperature is enforced in such a way as to minimize the difference between the constrained and Newtonian trajectories. Studies have found that equilibrium and non–equilibrium properties determined using this constraint technique do not differ, within statistical error, to those produced from Newtonian simulations [Brown and Clarke, 1984]. Although other techniques have also been reported, they are cumbersome and, if not carefully used, yield incorrect results [Allen and Tildesley, 1989].

There are a variety of techniques for integrating equations (3–10) to (3–11) through time: Gear predictor–corrector schemes [Gear, 1971]; Runge–Kutta methods; and

Verlet integrators [Verlet, 1967]. These methods have been reviewed by Berendsen and van Gunsteren (1986), and Allen and Tildesley (1989). As Runge–Kutta methods require at least two force evaluations every time step, they are rarely used. The predictor–corrector schemes are more accurate for systems in which there are no constraints or random forces, whilst the Verlet leapfrog method [Hockney, 1970] is most suited to systems containing constraints and random forces. The Verlet leapfrog method is also simple, requires little memory, is more stable at larger timestep sizes, is self–starting, and time reversible [Allen and Tildesley, 1989]. The random nature of the potential field induced by the porous medium, and the use of constraints to simulate atomic fluids (and rigid/semi–rigid molecular fluids) in the canonical ensemble, means the Verlet technique is most suited to the work reported here. Consequently, the damped force technique of Brown and Clarke (1984) was used. This method is particularly attractive as the constraint (3–11) is not explicitly enforced at each time step, but manifests itself as a scaling of the old velocity, $\mathbf{v}_i(t - \Delta t/2)$, and new force, $\mathbf{f}_i(t)$, when calculating the new (constrained) velocity $\mathbf{v}_i(t + \Delta t/2)$.

3.3.2.3 Molecular Fluids in the Canonical Ensemble

The motion of any atom within a molecule is made up of four modes: translation, rotation, torsion and vibration. The last two are typically much higher in frequency and smaller in amplitude when compared with the first two modes. If these higher frequency modes are included, much smaller simulation timestep sizes are required. Moreover, the modelling of vibrational motion using classical dynamics is questionable. These facts have motivated the development of MD techniques in which various modes are frozen. A review of these techniques may be found in Allen and Tildesley (1989). If a molecule is assumed completely rigid, its motion may be modelled using Euler angles [Goldstein, 1981]. However, Euler angle formulations exhibit computational singularities that require time consuming and complex work–arounds [Barojas et al., 1973]. To overcome these problems, Evans and co–workers [Evans, 1977; Evans and Murad, 1977] proposed a formulation based upon quaternions [Goldstein, 1981]. However, it has been demonstrated [Allen and Tildesley, 1989] that whilst freezing vibrational modes is

reasonable, intramolecular rotation (molecule bending) and torsion (molecule twisting) may be important. Both the Euler and quaternion approaches are unable to cope with partially rigid molecules. Using Gauss's Principle of Least Constraints [Bradbury, 1968], several groups have developed techniques which allow simulation of partially rigid molecules [Ryckaert et al., 1977; Memon et al., 1981; Ciccotti et al., 1982; Andersen, 1983; Edberg et al., 1986; Baranyai and Evans, 1990]. Although the study here has been restricted to diatomic fluids, it may be extended to molecules of any complexity including hydrocarbons [Edberg et al., 1986], and proteins [Berendsen, 1986].

An EMD simulation in the canonical ensemble (constant NVT) of a rigid heteronuclear diatomic fluid involves the solution for both atoms (1 and 2) of each molecule ($p = 1, \dots, P$) the equations

$$\begin{aligned} \frac{d\mathbf{v}_{1,p}}{dt} &= \frac{\mathbf{f}_{1,p}}{m_1} + \mathbf{n}_{1,p} + \mathbf{b}_p & \frac{d\mathbf{r}_{1,p}}{dt} &= \mathbf{v}_{1,p} \\ \frac{d\mathbf{v}_{2,p}}{dt} &= \frac{\mathbf{f}_{2,p}}{m_2} + \mathbf{n}_{2,p} - \mathbf{b}_p & \frac{d\mathbf{r}_{2,p}}{dt} &= \mathbf{v}_{2,p} \end{aligned} \quad (3-12)$$

where $\mathbf{n}$ and $\mathbf{b}$ are the Nosé–Hoover (NH) thermostat and bond constraint vectors respectively.

The NH thermostat vector for each of the atoms ($i = 1, 2$) of a diatomic molecule are given by [Nosé, 1984; Hoover, 1985; Evans and Holian, 1985]

$$\mathbf{n}_{i,p} = -\zeta \mathbf{v}_{i,p} \quad (3-13)$$

and

$$\dot{\zeta} = \frac{1}{\tau^2} \left(\frac{2K_e}{M_d k_b T} - 1 \right) \quad (3-14)$$

where ζ is the NH Lagrangian multiplier, K_e the total kinetic energy of the system, $M_d = 5P - 4$ the total number of degrees-of-freedom in the system, k_b the Boltzmann constant, T the desired temperature, and τ the thermostat characteristic time which controls its efficiency [Evans and Holian, 1985]. The total kinetic energy may be estimated from the individual atom velocities by

$$K_e = \frac{1}{2} \sum_{i=1}^N m_i v_i^2 \quad (3-15)$$

where $N=2P$ is the total number of fluid atoms. The bond constraint vector for a molecule is given by

$$\mathbf{b}_p = \lambda_p \mathbf{r}_{12,p} \quad (3-16)$$

where λ is the bond constraint Lagrangian multiplier, and $\mathbf{r}_{12}$ the bond length vector

$$\mathbf{r}_{12,p} = \mathbf{r}_{2,p} - \mathbf{r}_{1,p} \quad (3-17)$$

The bond constraint Lagrangian multiplier is selected for each molecule such that the bond length constraint

$$r_{12,p}^2 - d_{12}^2 = 0 \quad (3-18)$$

and the orthogonality condition

$$\dot{\mathbf{r}}_{12,p} \cdot \mathbf{r}_{12,p} = 0 \quad (3-19)$$

are satisfied.

The force summations of (3-5) and (3-8) are obvious for atomic fluids. However, their implementation for molecular fluids with bond and angle constraints requires a little explanation. If two atoms within a molecule are constrained with respect to each other, no explicit potential is considered to act between them – the constraint effectively represents a high strength potential. Thus, if no external field exists, the force acting on an atom within a molecule is the sum of all intermolecular forces, and those intramolecular forces between it and the other atoms with which it has no mutual constraint. If we consider a water molecule, for example, in which the O–H bond lengths have been constrained but not the H–O–H angle, then the hydrogen atoms would be subject to forces from all other surrounding atoms, and that induced by the opposing hydrogen atom of the molecule.

As already stated, the Verlet time integrator is perhaps the most appropriate for systems involving constraints and random forces. Consequently, the Pierleoni and Ryckaert (1992) implementation of the RATTLE algorithm [Andersen, 1983] was used to integrate equations (3-12).

3.3.3 Study of Two Model Systems

3.3.3.1 Preliminaries

The new discrete technique was used to study two model systems that may be considered prototypical of real systems: atomic argon within a completely random microporous graphite [Biggs and Agarwal, 1992], and a CO-like molecular fluid within a similar structure [Biggs and Agarwal, 1994]. For both studies, the solid skeleton of the microporous graphite was generated on a regular tessellation of unit cells, each cell measuring $1.2762 \times 0.9839 \times 1.3436 \text{ nm}^3$. The graphite was of hexagonal form with a stacking spacing of 0.3354 nm [Grayson and Eckroth, 1985]. All simulations were performed at a nominal pressure of 1 atmosphere where nominal pressure in this context is the pressure exerted by the molecules if assumed part of a perfect gas in the bulk phase. The simulations were performed in reduced units [Allen and Tildesley, 1989] based upon the arithmetic average of the fluid atom parameters. Examples of reduced quantities include temperature $T^* = Tk_b/\epsilon$, time $t^* = t\sigma(m/\epsilon)^{0.5}$, and distance $r^* = r/\sigma$.

In the first of these studies [Biggs and Agarwal, 1992], four realizations were undertaken for each of the porosities 0.312, 0.4, 0.6 and 0.8 at the single temperature of 140 K. The interaction potential parameters* of Maitland et al. (1981) and Crowell and Steele (1961) were used with a cutoff radius of 2.5σ . Each realization was conducted on a pore space generated using a unique seed, and porosities were achieved to at least $\pm 0.1\%$ of the desired value. The atoms were randomly distributed throughout the accessible pore space, each being placed at the center of the assigned unit cell so as to avoid initial large forces which can cause problems with time integration. Each fluid atom was assigned a velocity with a completely random direction, and magnitude uniformly distributed about the value which would give an ensemble temperature equal to the desired temperature (140 K in the atomic simulation). To ensure system equilibration, the particle trajectories were first advanced 20000 timesteps using a timestep size of 0.01 ps. Production runs were then carried out over a further 180000 timesteps using the same

* Ar–Ar parameters: $\sigma=0.341 \text{ nm}$, $\epsilon/k_b=119.8 \text{ K}$, $m=6.6357 \times 10^{-26} \text{ kg}$. Ar–C parameters: $\sigma=0.384 \text{ nm}$, $\epsilon/k_b=58.3 \text{ K}$.

timestep size.

The molecular study was far more extensive – the same porosities of the argon study were investigated for a range of temperatures between 100 K and 1500 K. The potential interaction parameters[‡] of a CO–like molecule and graphite–like substrate were used with a cutoff radius of 2.5 in reduced units. Interaction parameters between unlike atoms were determined using the Lorentz–Berthelot rules [Allen and Tildesley, 1989] for $i \neq j = 1, 2$, and s

$$\sigma_{ij} = \frac{1}{2}(\sigma_i + \sigma_j) \quad (3-20a)$$

$$\epsilon_{ij} = (\epsilon_i \epsilon_j)^{1/2} \quad (3-20b)$$

The larger scope of the molecular study meant only two realizations per system configuration could be undertaken. The technical details are similar to that of the atomic study (see previous paragraph) except: (1) the geometric center of each molecule was placed at the centre of the allocated cell; (2) the atom velocities for each molecule were also influenced by the need to satisfy constraint equation (3-19); and (3) 30000 and 370000 timesteps of 0.005 ps were used for equilibration and production respectively.

The results of these two studies are presented and discussed in the following. Of primary interest are the mean square displacement (MSD)

$$R^2(t) = \left\langle [\mathbf{r}(t_0 + \tau_A) - \mathbf{r}(t_0)]^2 \right\rangle \quad (3-21)$$

and velocity autocorrelation function (VACF)

$$\psi_v(t) = \langle \mathbf{v}(t_0 + \tau_B) \cdot \mathbf{v}(t_0) \rangle \quad (3-22)$$

which can reveal much about the fluid behaviour, and be used to generate the effective diffusion coefficient via the Einstein relationship (3-1), or the Green–Kubo integral [McQuarrie, 1976]

$$D_e = \frac{1}{3} \int_0^\infty \psi_v(t) dt \quad (3-23)$$

[‡] Parameters: $\sigma_1 = 0.335$ nm, $\epsilon_1/k_b = 51.2$ K, $m_1 = 1.99265 \times 10^{-26}$ kg; $\sigma_2 = 0.295$ nm, $\epsilon_2/k_b = 61.6$ K, $m_2 = 2.65686 \times 10^{-26}$ kg; $d_{12} = 0.1128$ nm; $\sigma_s = 0.384$ nm, $\epsilon_s/k_b = 58.3$ K where atoms 1, 2 and s are C(gas), O(gas) and C(solid) respectively.

The MSD and VACF were generated using the equilibrium time averages

$$\left\langle \left[\mathbf{r}(t_o + \tau_A) - \mathbf{r}(t_o) \right]^2 \right\rangle = \frac{1}{MN} \sum_{j=1}^M \sum_{i=1}^N \left[\mathbf{r}_i(t_{oj} + \tau_A) - \mathbf{r}_i(t_{oj}) \right]^2 \quad (3-24)$$

$$\left\langle \mathbf{v}(t_o + \tau_B) \cdot \mathbf{v}(t_o) \right\rangle = \frac{1}{MN} \sum_{j=1}^M \sum_{i=1}^N \mathbf{v}_i(t_{oj} + \tau_B) \cdot \mathbf{v}_i(t_{oj}) \quad (3-25)$$

where N is the number of particles, $M \approx 20000$ the number of time origins over which the average is taken, and $\tau_A = 100\Delta t$ and $\tau_B = 10\Delta t$ the times between successive quantities used in the calculation of the MSD and VACF respectively. Also of interest is the memory kernel, $K(t)$, associated with the VACF which may be generated by inverting the Volterra equation

$$\frac{d\psi_v(t)}{dt} = - \int_0^t K(t') \psi_v(t - t') dt' \quad (3-26)$$

using the technique of Berne and Harp (1970).

3.3.3.2 Mean Square Displacement

Irrespective of the mass transport process, the MSD scales with time as

$$R^2 \sim t^\alpha \quad (3-27)$$

where α is an exponent that reflects the nature of the particle transport process [Muralidhar et al., 1990]. For example, it may be shown that for a fluid in the bulk state

$$\alpha = 2 \quad \text{as} \quad t \rightarrow 0 \quad (3-28)$$

and

$$\alpha = 1 \quad \text{as} \quad t \rightarrow \infty \quad (3-29)$$

For a percolation system [Gefen et al., 1983]

$$\alpha < 1 \quad (3-30)$$

for all time provided $\phi \leq \phi_c$, and for times less than the correlation time of the system, τ_c , when $\phi > \phi_c$ – this corresponds to anomalous diffusion (see §3.2.4). For $t \gg \tau_c$, the percolating cluster appears homogeneous, and equality (3-29) holds. Despite extensive use of the MSD for the study of fluids within porous media, little is known on how its behavior changes with temperature or porosity – this is investigated in the following.

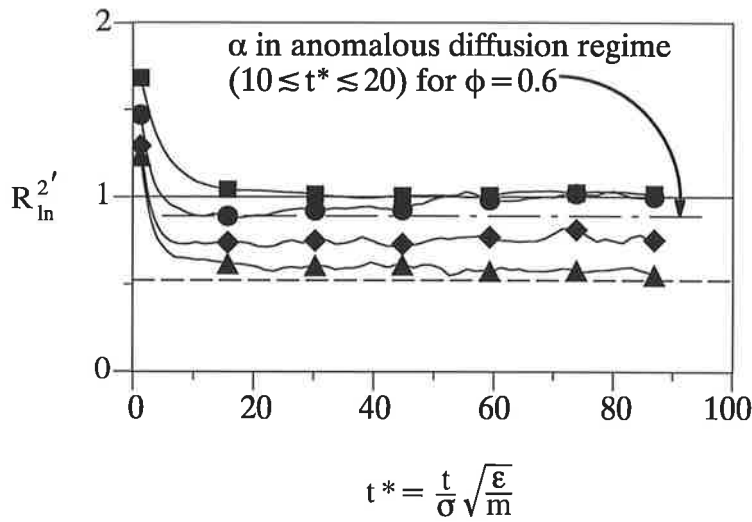


Figure 3.1. Derivative of log-MSD w.r.t log-time vs time for molecular fluid at $T = 500\text{K}$ showing MSD transition behavior: $\phi = 0.312$ ▲; $\phi = 0.4$ ◆; $\phi = 0.6$ ●; $\phi = 0.8$ ■.

The transition from short to long time behavior of the molecular system for different porosities at $T = 500\text{ K}$ is shown in Figures 3.1 and 3.2. When equation (3-27) is valid,

Figure 3.1 will display a horizontal straight line equal to α . Both figures clearly show the exponent for $\phi = 0.6$ at $T = 500\text{ K}$ transitions from $\alpha > 1$ at short times, to $\alpha < 1$ (anomalous diffusion) in the range $10 \leq t^* \leq 20$, and finally to $\alpha = 1$ (normal diffusion) for $t^* \geq 50$. This behavior is similar to that reported by Gusev and coworkers [Figure 4, Gusev et al., 1993; Figures 6 and 7, Gusev and Suter, 1993] who study, using transition-state theory, the motion of small gas

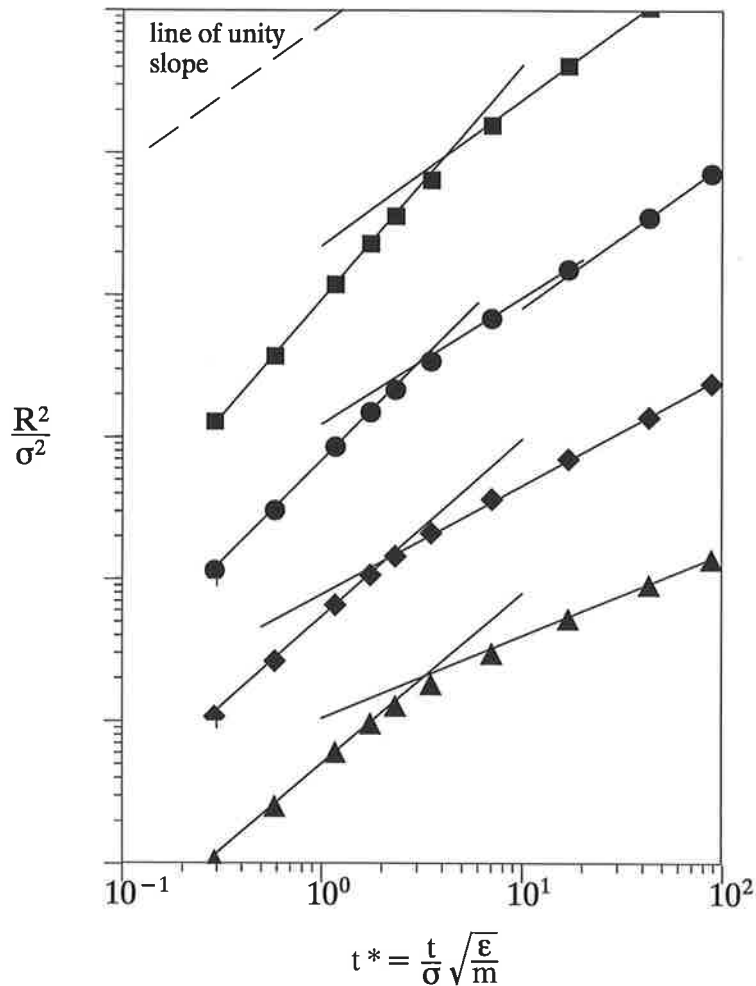


Figure 3.2. Log-log plot of MSDs for molecular fluid at $T = 500\text{K}$ showing lines of best fit for various regimes: $\phi = 0.312$ ▲; $\phi = 0.4$ ◆; $\phi = 0.6$ ●; $\phi = 0.8$ ■.

molecules within dense polymer matrices. The short to intermediate time behavior for the porosities 0.312 and 0.4, are similar to that of $\phi = 0.6$. However, although expected at some point, there is no transition to normal diffusion within the time span shown here. The process for $\phi = 0.8$ is very different to that of the other porosities where it moves from $\alpha > 1$ at short times to $\alpha = 1$ at longer times without passing through an anomalous diffusion regime. Figures 3.1 and 3.2 clearly indicate memory (ie: the time taken to transition to the normal diffusion regime) increases as the percolation threshold is approached, and that this rate of increase is highly nonlinear. This last agrees with the nature of the correlation length near ϕ_c [cf: equation (3-2)], and with the observations of Lowe and Masters (1993) who find the onset of asymptotic behavior shifts rapidly to longer times as the percolation threshold is approached.

Figure 3.1 demonstrates an unexpected behavior – α in the anomalous diffusion regime appears to be porosity dependent. The exponent in the anomalous diffusion regime is defined by

$$\alpha = \frac{2}{d_w} \quad (3-31)$$

where d_w is the fractal dimension of a random walk on the percolating cluster at $\phi = \phi_c$. This is defined by [Gefen et al., 1983]

$$d_w = 2 + \frac{\mu - \beta_p}{\nu} \quad (3-32)$$

where μ , ν and β_p are universal scaling exponents dependent upon system dimensionality only. As these exponents are universal, α must also be universal, and therefore independent of porosity. There are several possible explanations for the apparent porosity dependence:

- One of the key concerns associated with any MD (MC or RW) simulation is the effect of system size. Although use of periodic boundary conditions should ensure finite size effects are rendered insignificant, pathological cases have been recorded [Allen and Tildesley, 1989]. As Figure 3.1 is based upon simulations involving approximately 32 molecules, finite size effects may be important, especially near the percolation threshold. The effect of system size was investigated for the

configuration $\phi = 0.4$ and $T = 500$ K for system sizes $P = 64, 100$, and 150 molecules. The corresponding anomalous exponents determined from a straight line fit of the log–log plot of the MSD in the region $10 \leq t^* \leq 20$ are shown in Table 3.1 – these suggest there is no system size dependence. Despite this, our inability to undertake a more comprehensive study due to lack of resources, means we cannot be certain system size plays no part in the porosity dependence of the exponents.

Table 3.1. α for various sized systems at $\phi = 0.4$ and $T = 500$ K.

P	α
32	0.77
64	0.75
100	0.75
150	0.78
ave.	0.77

- A second concern is the number of realizations used for any given system configuration. Ideally, a large number should be used, especially near the percolation threshold. However, lack of computational resources restricted the number of realizations for any configuration to two. Consequently, much uncertainty is associated with the values of the exponent, and this uncertainty cannot be determined. The only exception is the configuration $\phi = 0.4$ and $T = 500$ K, where a total of five realizations were undertaken to assess system size effects. The exponent values for each of the realizations shown in Table 3.1, indicate that whilst there is some variation, it is not large. However, once again, lack of resources prevents a definitive statement being made.

Using the critical exponent values of Sahimi (1993) for random percolation in three dimensions yields

$$\alpha \approx \frac{2}{2 + \frac{2 - 0.41}{0.88}} \approx 0.52 \quad (3-33)$$

which is shown as a dashed line in Figure 3.2. The obvious difference between this value and those predicted by our simulations may also be related to the above concerns.

Figure 3.3 demonstrates the change in MSD transition behavior with temperature. As the variations with temperature for the other porosities remain essentially unchanged from those of Figure 3.2, they are not shown. Comparison of the $T = 300$ K, 500 K and

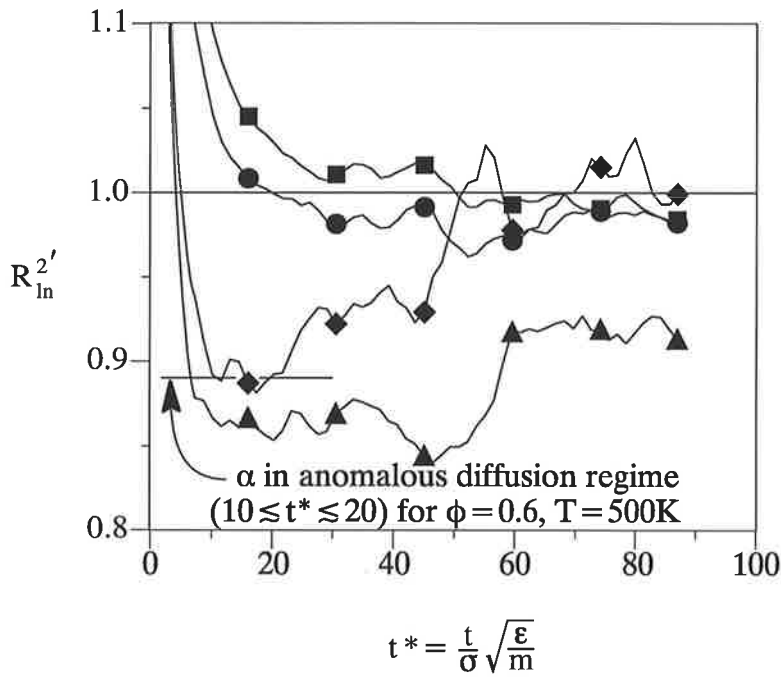


Figure 3.3. Derivative of log-MSD with respect to log-time vs time for molecular fluid showing MSD transition behavior:
 $T=300$ K, $\phi=0.6$ ▲;
 $T=500$ K, $\phi=0.6$ ◆;
 $T=700$ K, $\phi=0.6$ ●;
 $T=700$ K, $\phi=0.8$ ■.

700 K curves for $\phi=0.6$ strongly suggests that the time taken to transition from anomalous to normal diffusion decreases with increasing temperature. The similarity between $\phi=0.6$ and $\phi=0.8$ curves at $T=700$ K also suggests that at high enough temperatures, anomalous diffusion may not occur at all.

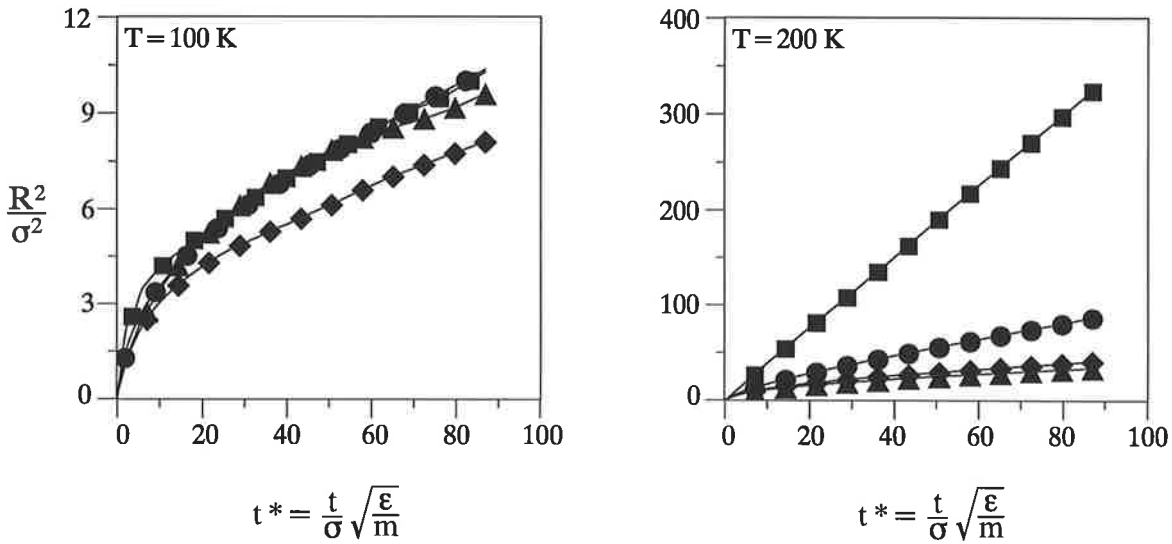


Figure 3.4. MSD for molecular fluid: $\phi=0.312$ ▲; $\phi=0.4$ ◆; $\phi=0.6$ ●; $\phi=0.8$ ■.

Comparing the MSDs shown in Figure 3.4 clearly shows that the particle motion is highly restricted at $T=100$ K. This reflects the ease with which a low kinetic energy particle typical of this temperature may become trapped within the nooks, crannies, and cages

of the pore structure.

3.3.3.3 Velocity Autocorrelation Function

The VACFs for the molecular fluid at the temperatures of 100 K and 200 K are shown in Figures 3.5 and 3.6 respectively. Similar oscillatory behavior has been seen in MD studies of the Lorentz gas [Bruin, 1972, 1974; James and Evans, 1987; Alder, 1986], and in random walk simulations on percolation clusters [Jacobs and Nakanishi, 1990; Muralidhar et al., 1990]. These oscillations reflect changes in the direction and magnitude of the particle velocities as they interact with the substrate potential field, and

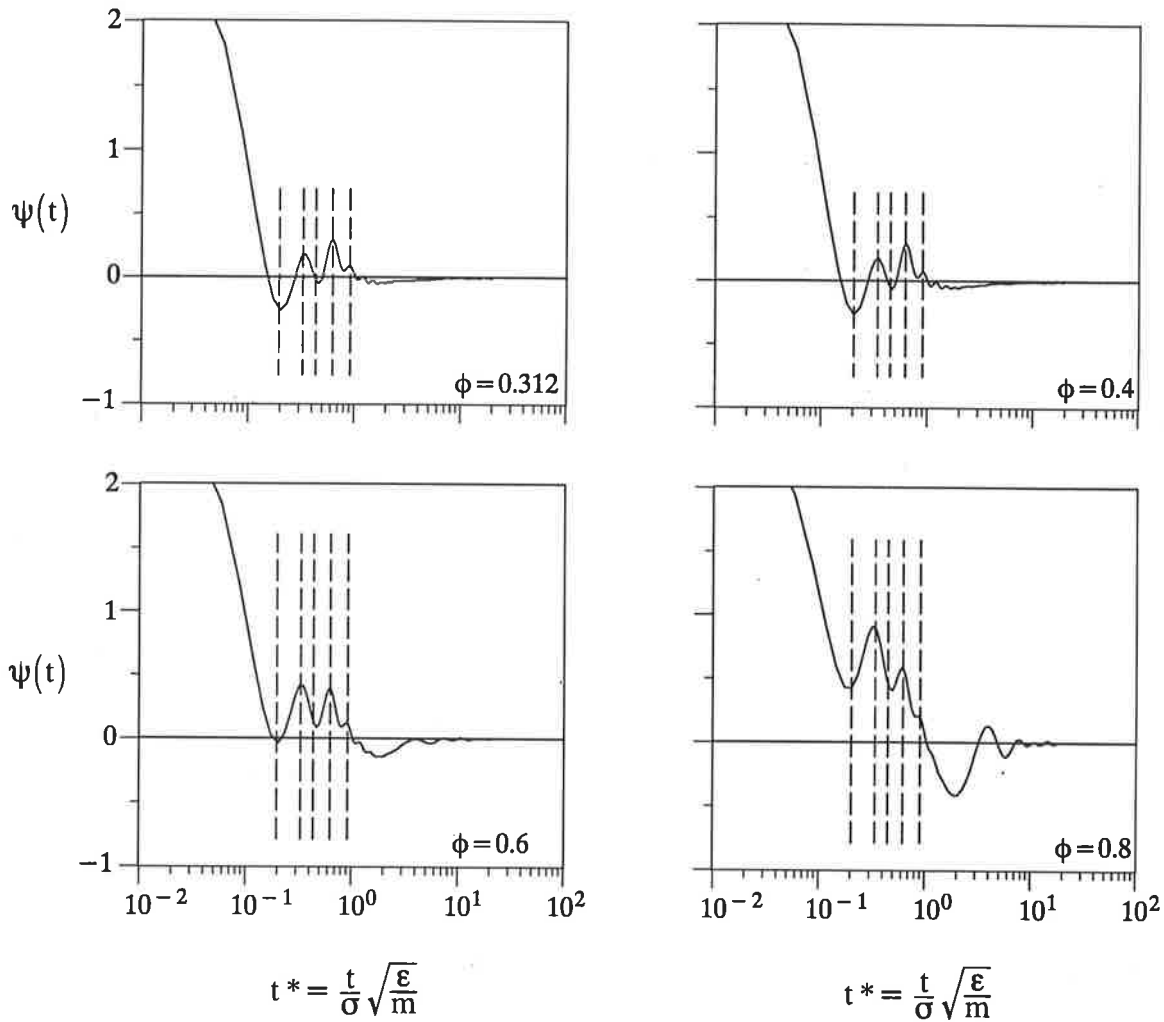


Figure 3.5. VACFs for molecular fluid at $T = 100\text{K}$.

the pore structure as a whole. The negative troughs for $\phi = 0.312$ and $\phi = 0.4$ at $T = 100$ K indicate frequent particle trajectory reversal [Toukubo et al., 1977]. This reflects the fact that at low porosities, forces from a large number of competing directions restrict

particles to definite paths, with little freedom to avoid potential barriers and pore turns. The positive oscillations at the higher porosities for both temperatures indicate a diminishing likelihood of frequent particle reversal in favour of substantial particle trajectory deviation – as the particles encounter forces from only a few directions, they have greater freedom to avoid the much fewer potential barriers and pore turns. It is interesting to note that despite the random nature of the pore structure, the positions of the maxima and minima at small times appear to be porosity invariant (see dashed lines on Figures 3.5 and 3.6). As the only “uniform” characteristic of the pore structure is the

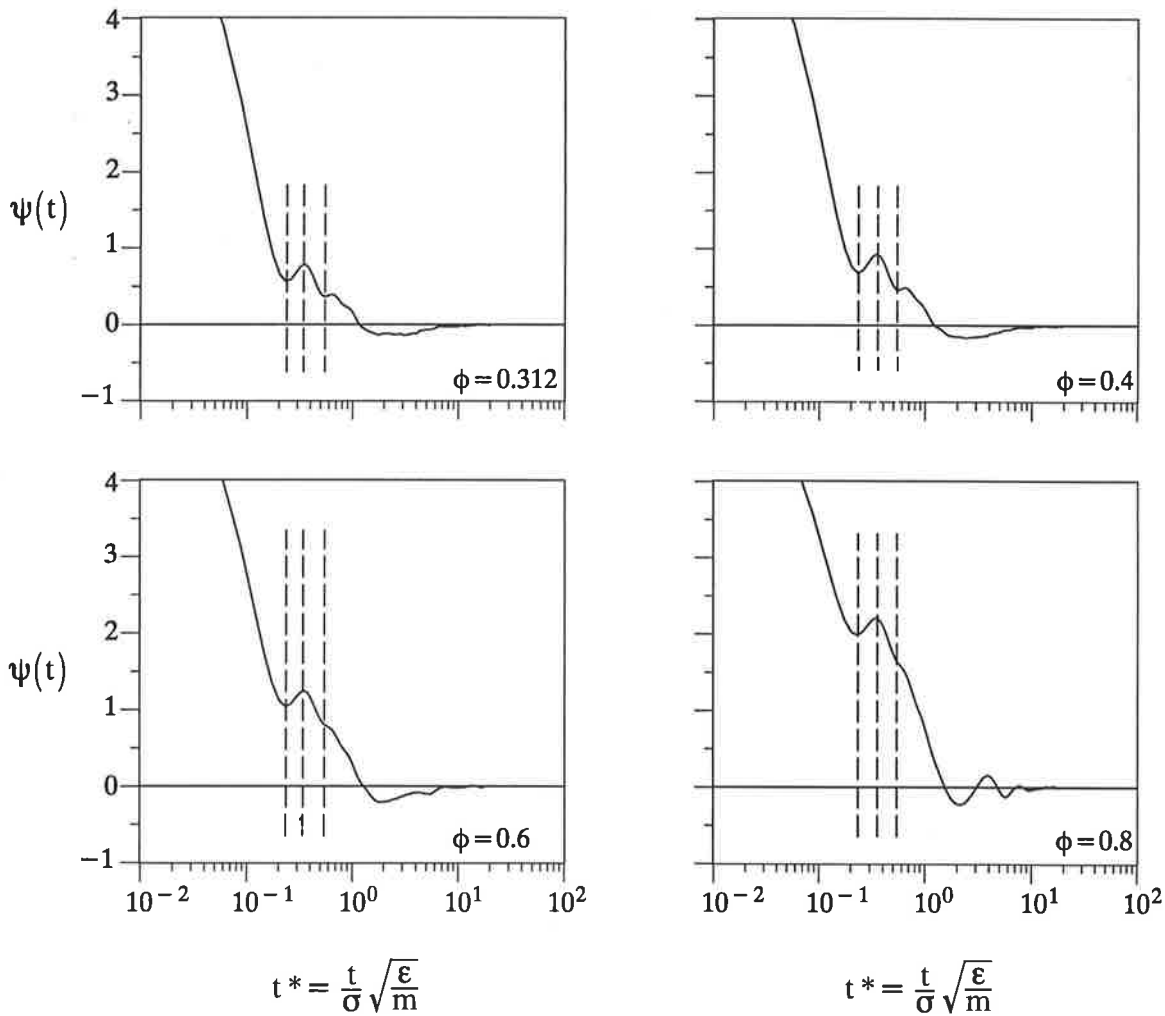


Figure 3.6. VACFs for molecular fluid at $T = 200\text{K}$.

substrate over a unit cell length, these extrema, which are related to the moment at which particle accelerations change sign, may be related to the substrate structure over small length scales.

Particles possessing high kinetic energy will be less affected by the force field of the surrounding solid as they would tend to punch through most energy barriers with little deviation. This explains the significant reduction in oscillatory behavior as temperature increases – compare the VACFs for $T=100$ K and 200 K with those of the higher temperatures 300 K and 900 K shown in Figure 3.7 and Figure 3.8 respectively. This effect has important consequences for the apparent tortuosity of the solid. A particle with a kinetic energy significantly greater than the majority of the potential energy barriers of the solid will see a less tortuous path than a particle whose energy is comparable to, or less than, these barriers. Thus, tortuosity is not only a property of the solid, but also of temperature.

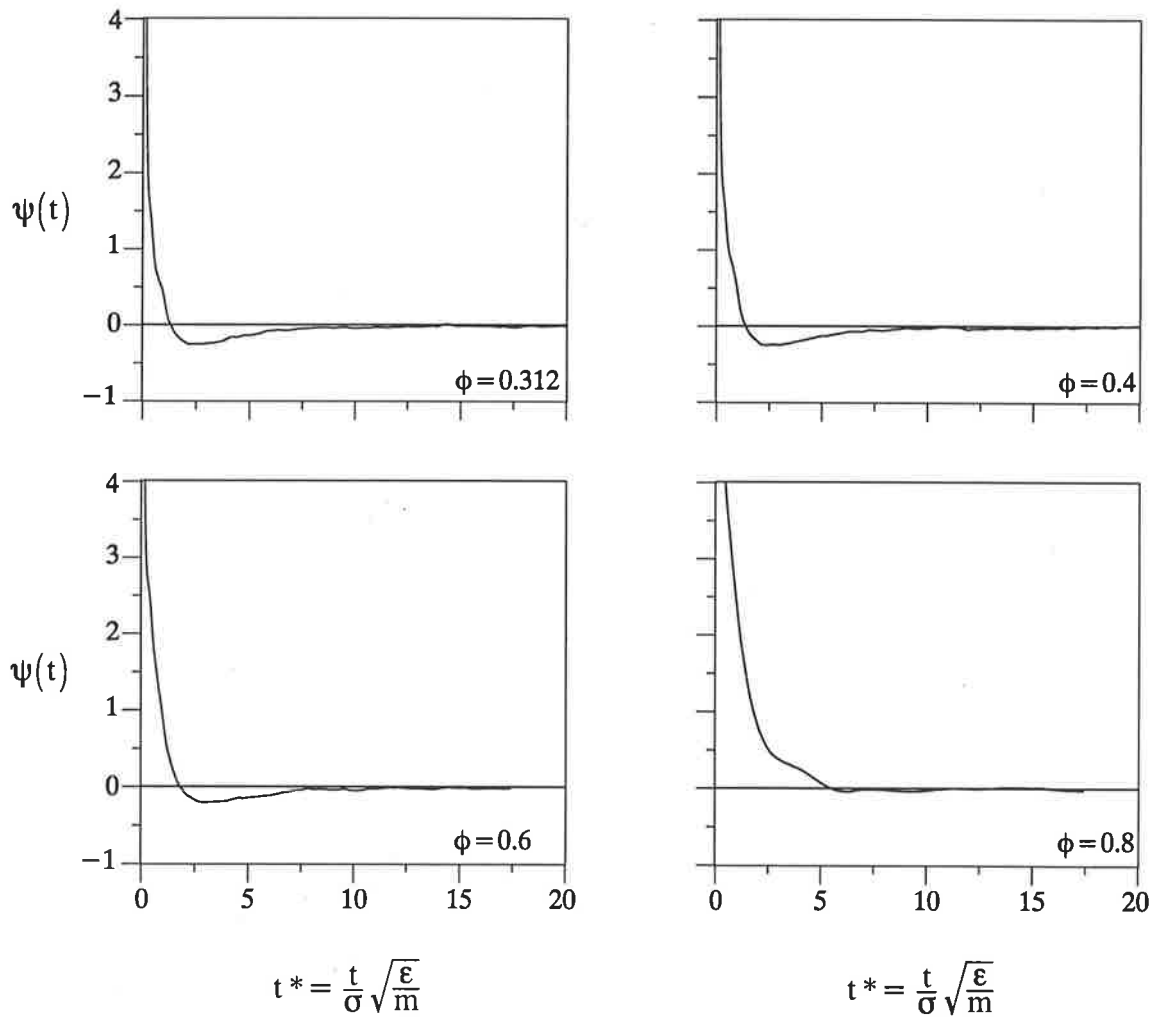


Figure 3.7. VACFs for molecular fluid at $T = 300$ K.

As decay of the VACF is a direct result of collision events, it is expected that the rate of VACF decay shall be greater at lower porosities where such events are more likely. The variation in VACF behavior with porosity shown in Figure 3.8 clearly supports this.

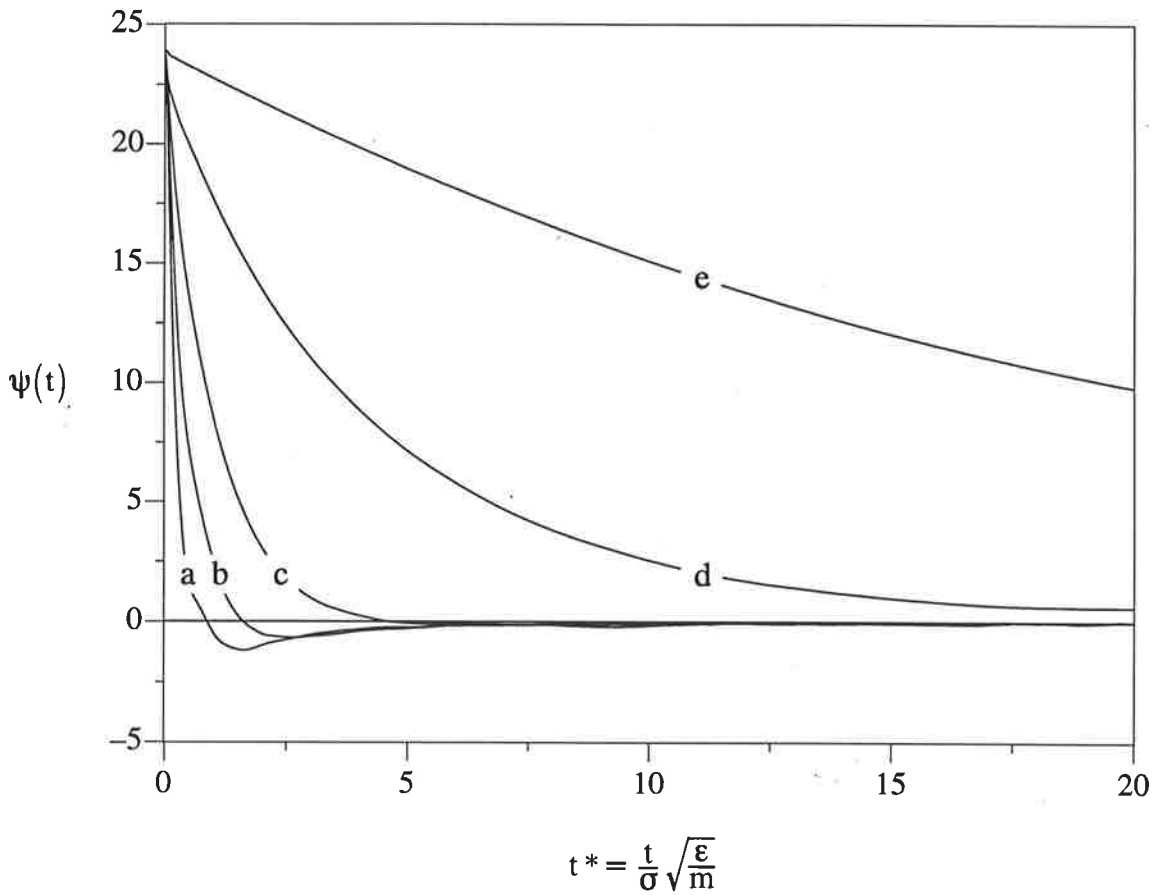


Figure 3.8. VACFs for molecular fluid at $T = 900\text{K}$: (a) $\phi = 0.312$; (b) $\phi = 0.6$; (c) $\phi = 0.8$; (d) $\phi = 0.95$; (e) $\phi = 0.99$.

Figure 3.8 also indicates the change in VACF tail character with porosity typical of all temperatures. The VACFs for the porosities 0.312, 0.4 and 0.6 demonstrate long negative time-tails, the behavior at $\phi = 0.8$ is similar to that of a liquid away from its critical point [Boon and Yip, 1980], whilst the VACFs at $\phi = 0.95$ and $\phi = 0.99$ are more like those of a low density gas. A long negative time-tail indicates a particle will eventually move in the opposite direction to its initial travels [Alder and Wainwright, 1970; Alder and Alley, 1978; Alley and Alder, 1979]. The greater number of deadend pores at the lower porosities mean these events are more likely – this accounts for the persistence of the negative time-tail at the lower porosities.

3.3.3.4 Memory Kernel

The memory kernel (MK) associated with the VACF, $K(t)$, for the atomic fluid at each of the simulated porosities are shown in Figure 3.9. None of the MKs for the porosities $\phi \leq 0.8$ decay to zero for the accumulation time span used. The decay for $\phi = 1.0$ is rapid, and similar to other reported results [Boon and Yip, 1980]. As for the VACFs, shown here in Figure 3.10, oscillations occur which diminish in size with time, and whose position in time appear porosity invariant. The only significant difference between MKs for the different porosities is the initial negative trough, the depth of which increases with porosity.

The normalized total force autocorrelation function (TFACF) for each of the porosities are also shown in Figure 3.9. The total force may be written as [Kubo et al., 1985]

$$f_t(t) = f_s(t) + f_r(t) \quad (3-34)$$

where f_r is the random force, and f_s the systematic force

$$f_s(t) = - \int_{t_0}^t mK(t-s)v(s)ds \quad (3-35)$$

It may be proven that [Kubo, 1966]

$$\frac{1}{\gamma_r} = \frac{1}{\gamma_t} - \frac{1}{i\omega} \quad (3-36)$$

where i is the imaginary identity,

$$\gamma_r(\omega) = \frac{1}{\langle v(t_0) \cdot v(t_0) \rangle} \int_0^\infty \langle f_r(t_0 + \tau_B) \cdot f_r(t_0) \rangle e^{-i\omega t} dt \quad (3-37a)$$

the spectra (Fourier–Laplace transforms) of the RFACF, and

$$\gamma_t(\omega) = \frac{1}{\langle v(t_0) \cdot v(t_0) \rangle} \int_0^\infty \langle f_t(t_0 + \tau_B) \cdot f_t(t_0) \rangle e^{-i\omega t} dt \quad (3-37b)$$

the spectra of the TFACF. Simplification of equation (3–36) to

$$\frac{1}{\gamma_r} \approx \frac{1}{\gamma_t} \quad (3-38)$$

may be made under certain conditions [Kubo, 1966] and hence the TFACF and the RFACF are approximately equal for these conditions. The second

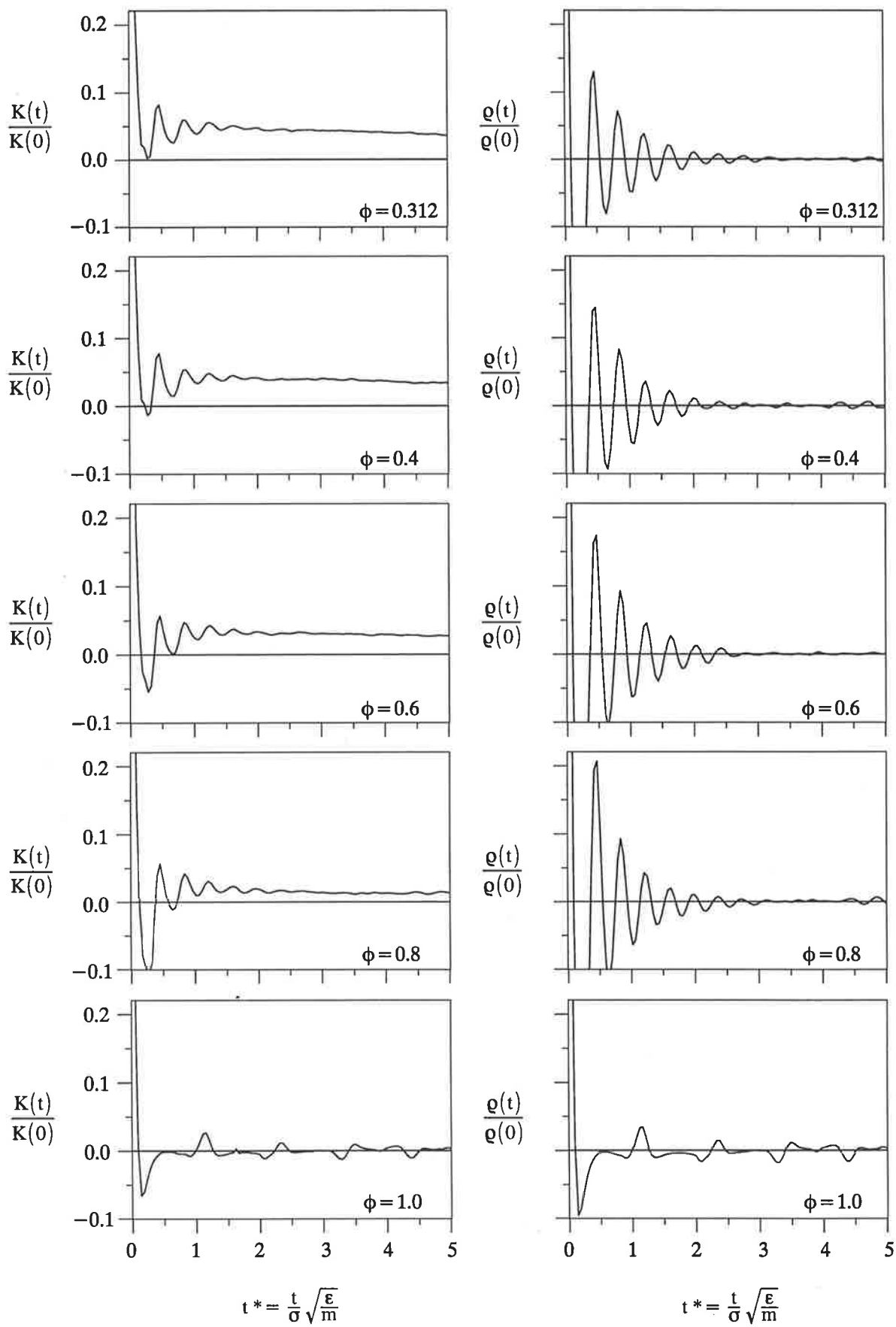


Figure 3.9. MK and TFACF vs time for atomic fluid.

fluctuation–dissipation theorem states [Kubo, 1966]

$$m^2 \langle \mathbf{v}(t_0) \cdot \mathbf{v}(t_0) \rangle K(t) = \langle \mathbf{f}_r(t_0 + \tau_B) \cdot \mathbf{f}_r(t_0) \rangle \quad (3-39)$$

indicating that the MK shall also approximately equal the TFACF when equation (3–38) is valid. As the normalized memory kernel and the TFACF for $\phi = 1.0$ are identical in shape, approximation (3–38) holds for a dilute gas in the bulk phase. There is, however, no such correspondence for $\phi < 1.0$ indicating that approximation (3–38) is invalid for fluids within porous media.

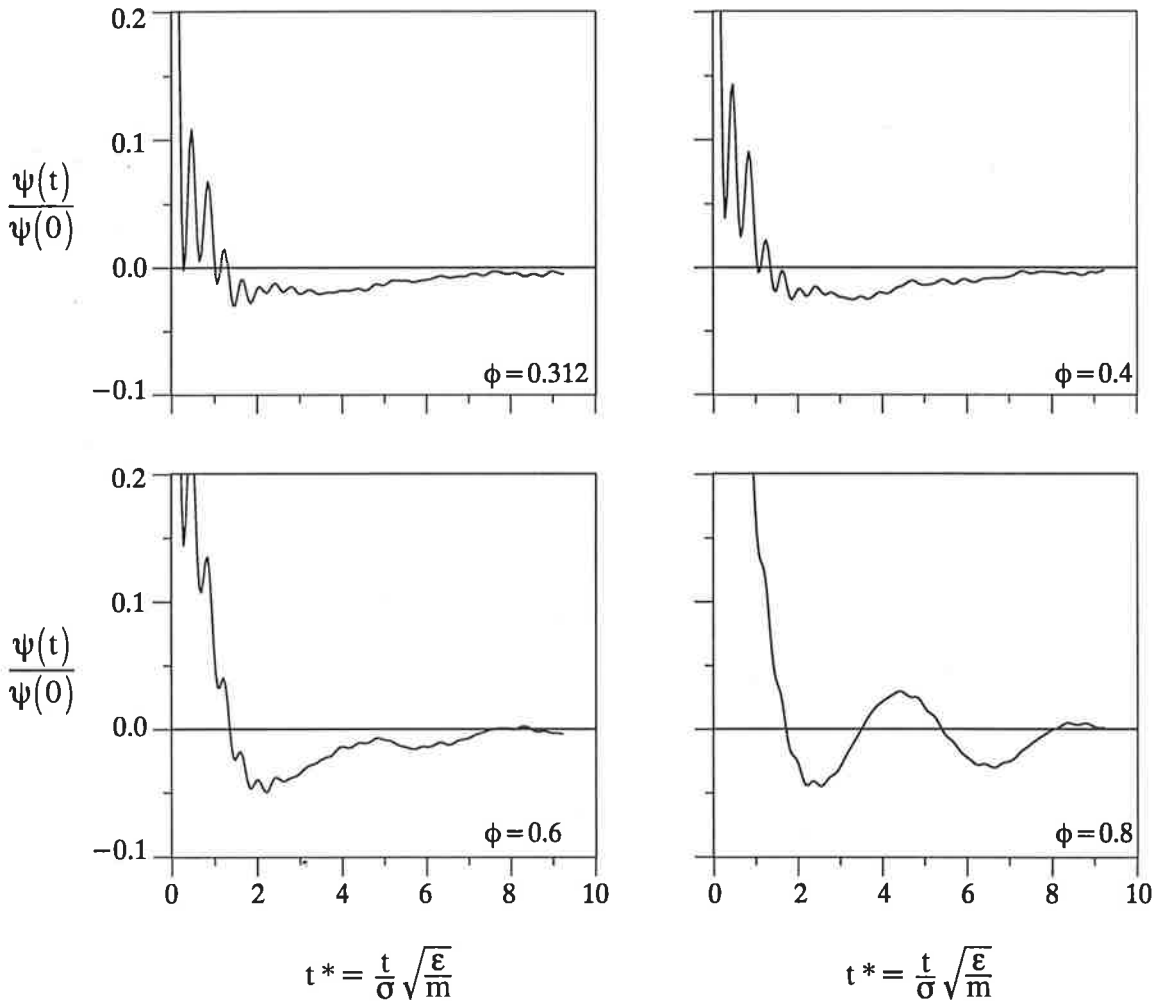


Figure 3.10. VACFs for atomic fluid at $T = 300\text{K}$.

3.3.3.5 Effective Diffusion Coefficients

From a practical perspective, one of the primary questions we are faced with is how the effective diffusion coefficient varies with porosity and temperature. The reduced effective diffusion coefficient of the molecular fluid, as a function of porosity for selected

temperatures, is plotted in Figure 3.11. It should be noted that use of the Green–Kubo integral (3–23) will result in overestimated diffusion coefficients for those systems which have not yet made the transition to the normal diffusion regime in the VACF accumulation time span (mainly for $\phi = 0.312$ and 0.4). Shah and Ottino (1987) express the effective diffusivity of a fluid within a cubic tessellation of space as (they set $\phi_c \approx 0.32$)

$$D_e \sim (\phi - 0.32)^{1.474} \quad 0.32 < \phi \leq 0.7 \quad (3-40)$$

whilst percolation theory predicts

$$D_e \sim (\phi - \phi_c)^{\mu - \beta_p} \quad \phi \rightarrow \phi_c^+ \quad (3-41)$$

where $\mu - \beta_p$ is a critical exponent. The nonlinear profiles of Figure 3.12 clearly demonstrate equation (3–40) does not describe the results generated here. The lack of detailed information in the vicinity of ϕ_c precludes any definitive statement being made on the suitability of equation (3–41) to describe our data. However, the critical

exponent, $\mu - \beta_p$, what ever its value, is known to be dependent upon the dimension of the system only – it should be temperature independent. The insert of Figure 3.12 indicates that this condition is approximately satisfied by our data where the gradients for each of the selected temperatures between $\phi = 0.312$ and $\phi = 0.4$ are within 15% of their mean value.

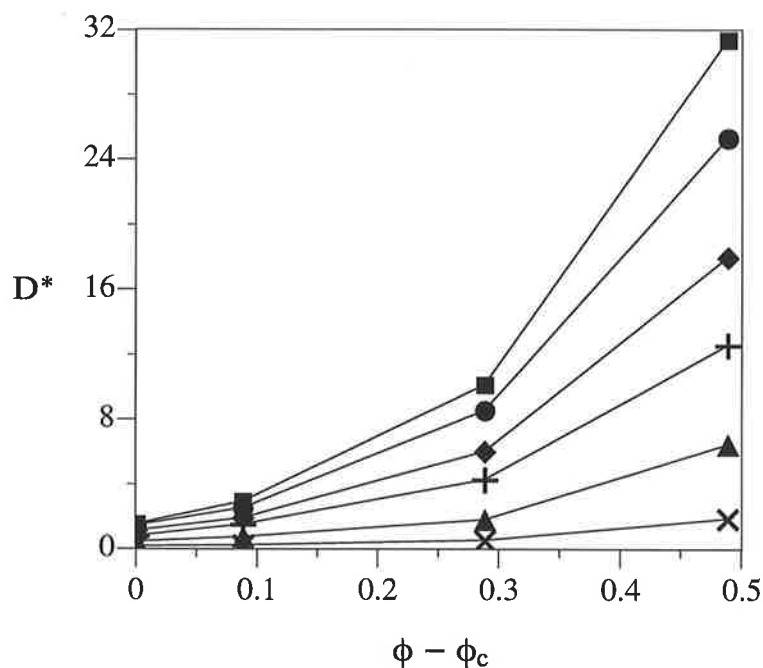


Figure 3.11. Effective diffusion coefficient of molecular fluid vs porosity above percolation threshold: $T = 200 \text{ K}$ ×; $T = 300 \text{ K}$ ▲; $T = 500 \text{ K}$ +; $T = 700 \text{ K}$ ◆; $T = 1100 \text{ K}$ ●; $T = 1500 \text{ K}$ ■.

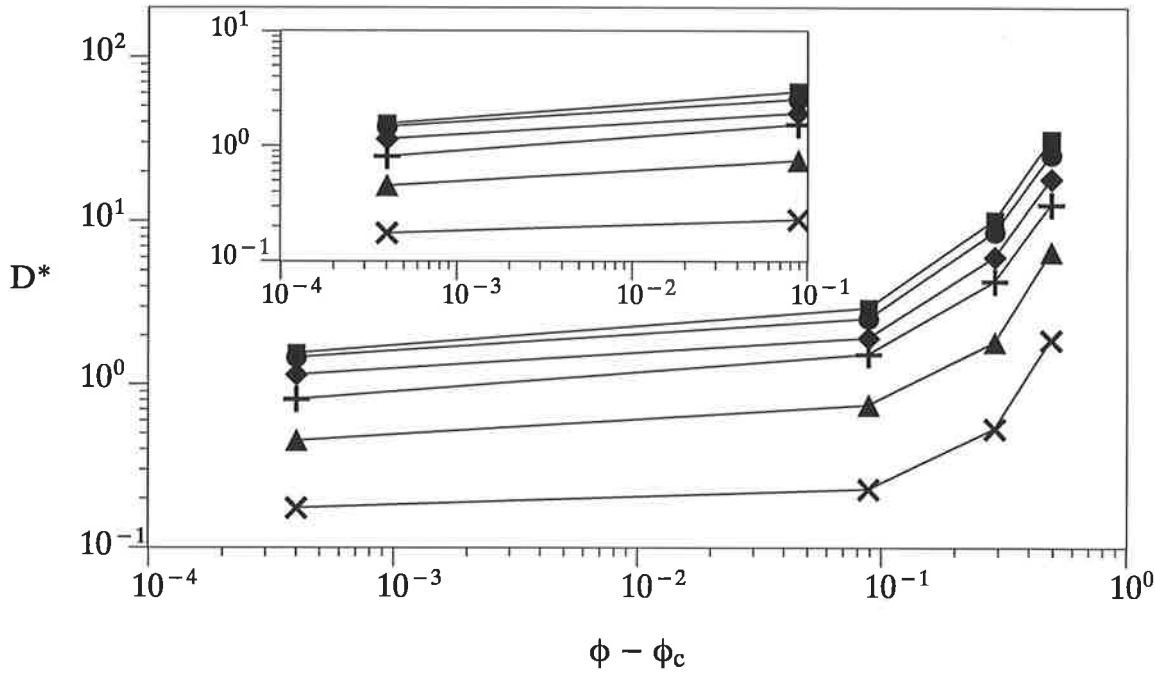


Figure 3.12. Log-log plot of effective diffusion coefficient for molecular fluid vs porosity above percolation threshold: $T = 200 \text{ K}$ $\times$; $T = 300 \text{ K}$ $\blacktriangle$; $T = 500 \text{ K}$ $+$; $T = 700 \text{ K}$ $\blacklozenge$; $T = 1100 \text{ K}$ $\blacksquare$.

Figure 3.13(a) suggests the effective diffusion coefficient away from the percolation threshold may be modelled by

$$D_e = k_1 e^{\beta \phi} \quad (3-42)$$

where the variation of β and k_1 with temperature is shown in Figures 3.13(b) and 3.13(c) respectively. The pre-exponential factor appears to be a weak function of temperature whilst it is unclear if β varies with temperature at all due to the large error bands.

The differences between equations (3-40) and (3-42) deserve some discussion. Equation (3-40) represents the effective diffusivity of a system at steady state. In such a system, only the backbone of the pore space actively transports fluid – the accessible deadend fraction of the pore system is unused. The MD technique allows the fluid particles to pass into and travel down the deadend pores. The utilization of the deadend pore space significantly influences the calculated effective diffusion coefficient. We may understand why by looking at the VACF. The diffusion coefficient is given by the integral of this function over time; equation (3-23). The negative time-tail acts to reduce the

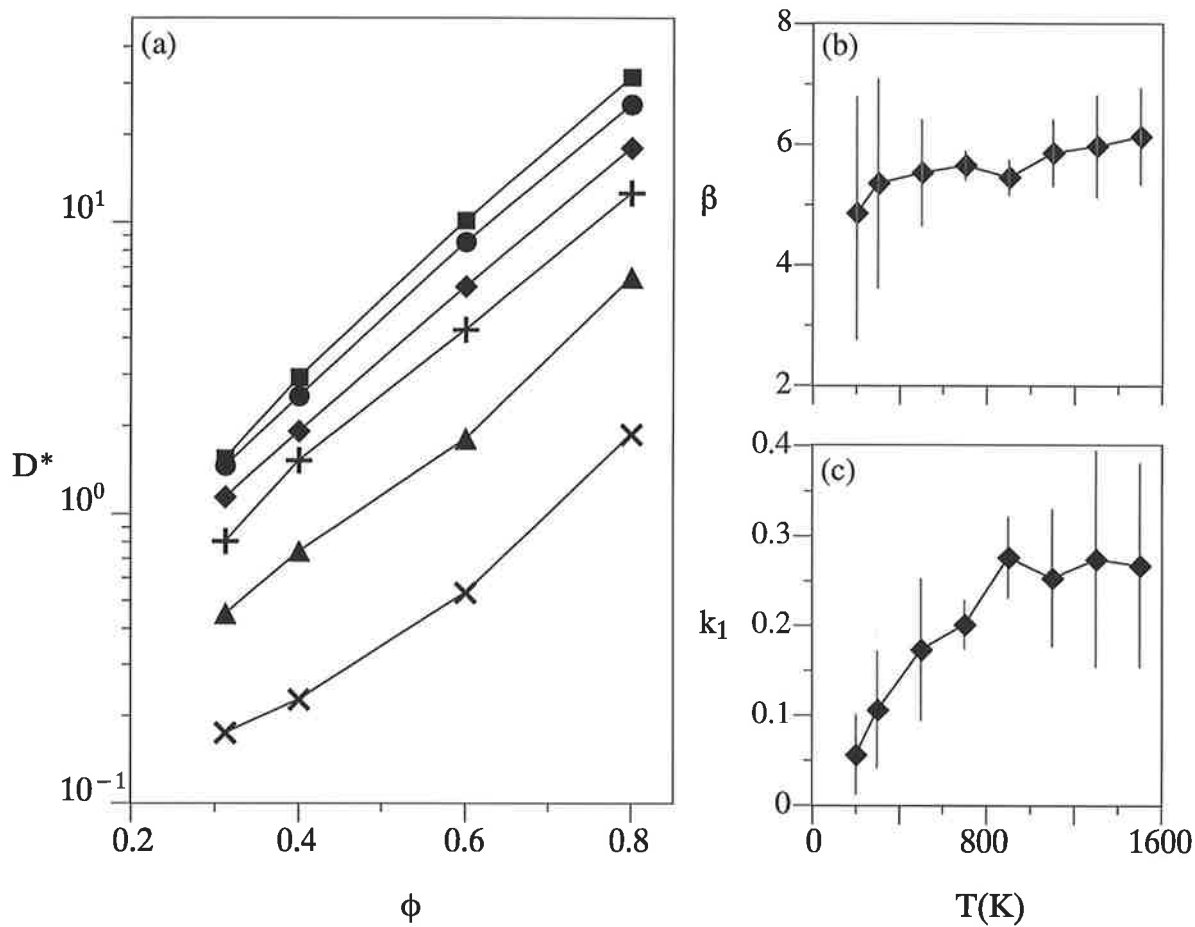


Figure 3.13. (a) Log–linear plot of effective diffusion coefficient for molecular fluid vs porosity: $T = 200$ K $\times$; $T = 300$ K $\blacktriangle$; $T = 500$ K $+$; $T = 700$ K $\blacklozenge$; $T = 1100$ K $\bullet$; $T = 1500$ K $\blacksquare$. (b) Variation of β –exponent with temperature (95% confidence bands shown). (c) Variation of k_1 –factor with temperature (95% confidence bands shown).

effective diffusion coefficient since it defines a negative area relative to that above the horizontal axis. As already stated, a long negative time–tail indicates a particle will eventually move in the opposite direction to its initial travels. This is precisely what happens when a particle enters a deadend pore – once it reaches the end of the deadend pore, it must turn around and travel back the way it came. The effect of the deadend pore space may be viewed from a different perspective. The ratio $\phi_e = D_e/D$ reflects the efficiency of the pore system in transporting fluid between two points in space. One measure of this efficiency is the time taken for a particle to travel between the two points. The time spent by a particle in the deadend pore space is lost time – the particle has effectively gone nowhere for some period of time. Equation (3–40) also accounts for

ordinary diffusion only; pore size effects have not been included. Reyes and Jensen (1985) investigated the effect of pore size and found Knudsen contributions may significantly affect the calculated diffusion coefficients (their Figure 9). As the pore system generation method used here unfortunately increases the effective pore size with porosity, the effective

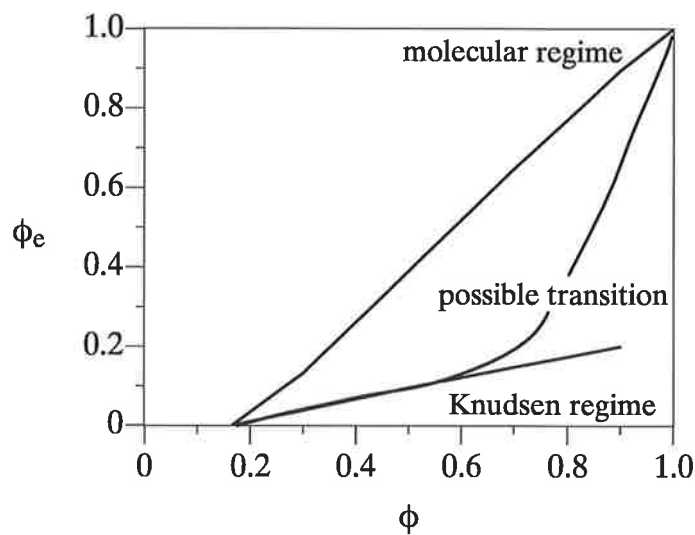


Figure 3.14. Example of possible transition between Knudsen and ordinary diffusion regimes when pore size increases with porosity.

diffusion coefficient will transition from a curve characteristic of Knudsen diffusion to one of ordinary diffusion as the porosity increases. Although no direct comparison may be made [they use a Bethe lattice which is fundamentally different from a cubic tessellation; Sahimi et al., 1990], Figure 3.14 indicates such a transition may be significant.

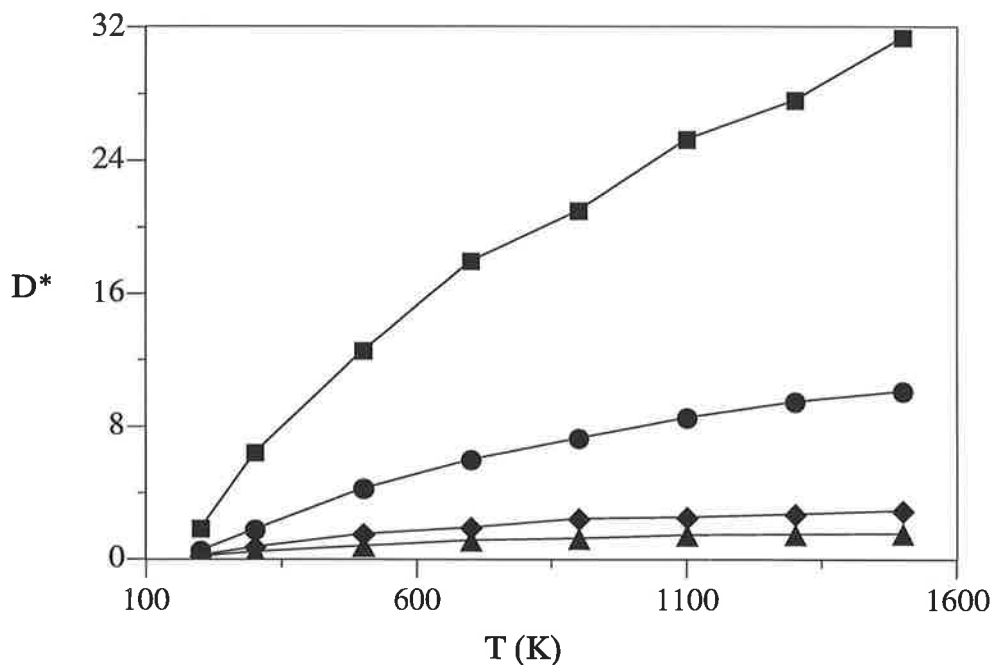


Figure 3.15. Effective diffusion coefficient of molecular fluid vs temperature: $\phi = 0.312$ $\blacktriangle$; $\phi = 0.4$ $\blacklozenge$; $\phi = 0.6$ $\bullet$; $\phi = 0.8$ $\blacksquare$.

The variation of the effective diffusion coefficient of the molecular fluid with temperature was also investigated – this variation for different porosities is shown in Figure 3.15. The plot of $\log -D_e$ against inverse temperature shown in Figure 3.16(a) indicates the effective diffusion coefficient at a given porosity ($0.312 < \phi \leq 0.8$) for $T \geq 200$ K varies as

$$D_e = k_2 e^{-\lambda/T} \quad (3-43)$$

where the variation of λ and k_2 with porosity are shown in Figure 3.16(b) and Figure 3.16(c) respectively. The pre-exponential factor appears to vary exponentially with porosity and thus verifies the form of equation (3-42). The exponent, λ , increases as the porosity increases from $\phi = 0.312$ to $\phi = 0.6$. Due to the errors associated with the fitting process, it is unclear if the exponent plateaus or decreases for $\phi > 0.6$.

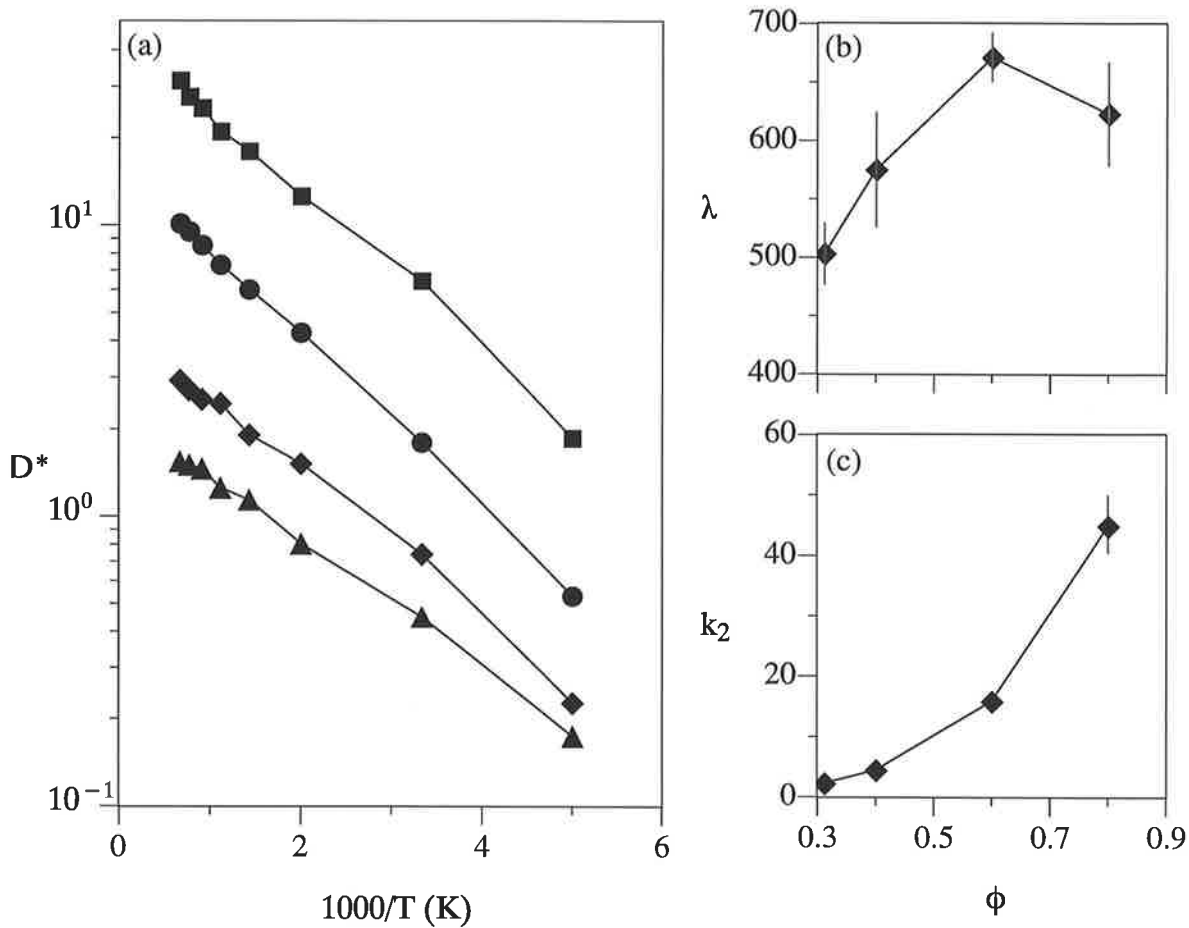


Figure 3.16. (a) Log-linear plot of effective diffusion coefficient for molecular fluid vs inverse temperature: $\phi = 0.312$ $\blacktriangle$; $\phi = 0.4$ $\blacklozenge$; $\phi = 0.6$ $\bullet$; $\phi = 0.8$ $\blacksquare$. (b) Variation of λ -exponent with porosity (95% confidence bands shown). (c) Variation of k_2 -factor with porosity (95% confidence bands shown).

The variation with temperature indicated by equation (3–43) is similar to that of liquids in the bulk phase [Reid et al., 1988] and is in marked contrast to that predicted by the kinetic theory of gases. For example, the ordinary diffusion coefficient of a gas varies with temperature as $T^{3/2}-T^2$ [Reid et al., 1988] whilst the Knudsen diffusivity is $T^{1/2}$ dependent [Present, 1958]. Although the exponential behavior may at first be surprising, the nature of the VACFs obtained in this work give a first hint that it is in fact reasonable. Figure 3.17 illustrates the changes that occur in the VACF as we move from the liquid to the gaseous state in the bulk phase. The VACF of a gas, Figure 3.17(c), is well approximated by an exponential function; infact, theory predicts this to be the case for a low density gas. The VACF of a liquid rapidly decays and displays either a positive, Figure 3.17(b), or negative, Figure 3.17(a), time–tail. Figure 3.8 indicates, for $\phi \leq 0.8$, that a gas within our porous solid is not dissimilar to a liquid in the bulk phase whilst it transitions to a behavior following the low density gas limit for $\phi = 0.95$ and $\phi = 0.99$. The above of course does not explain the fundamental basis for our temperature variation, but serves to indicate the behavior of a gas within our porous solid may be similar to that of a liquid in the bulk phase.

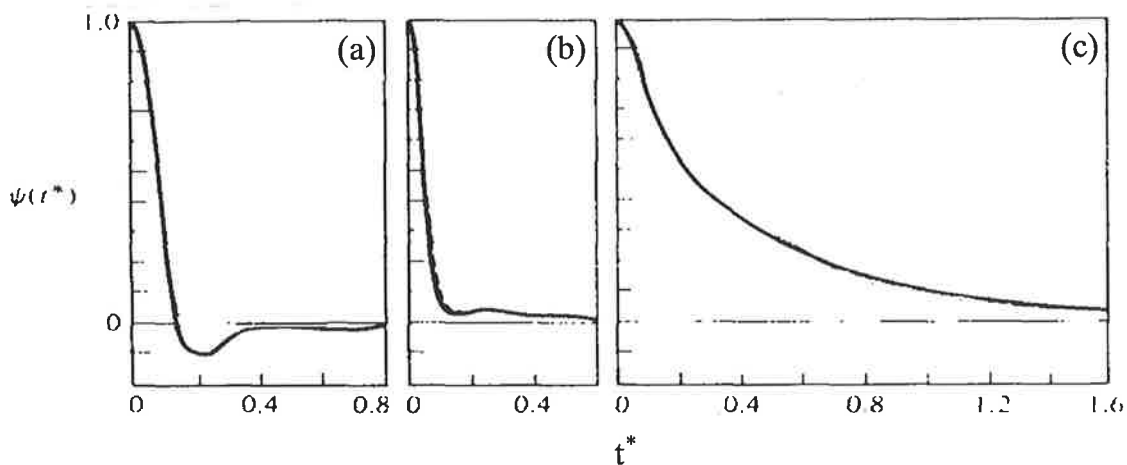


Figure 3.17. VACFs for a Lennard–Jones fluid within the bulk phase: (a) $\rho^* = 0.85$, $T^* = 0.76$ (liquid near triple point); (b) $\rho^* = 0.85$, $T^* = 4.64$; (c) $\rho^* = 0.3$, $T^* = 1.58$ (fluid at less than the critical density) [Boon and Yip, 1980].

If the effective diffusivity of a gas within a porous solid varies with temperature in a manner similar to that of a liquid, not a gas, in the bulk phase, then the common practice of normalizing an experimentally or numerically determined effective diffusivity with a gas diffusivity to yield a *temperature independent* tortuosity is in error. Use of such tortuosities will result in the incorrect estimation of diffusivities at temperatures other than that at which the original experiment took place.

3.3.3.6 Summary of Results

The new MD–percolation based technique described in §§3.3.1–2 was used to study the diffusion of an atomic gas (Ar) and a molecular gas (CO–like) within a microporous graphite medium under non–reactive conditions. The fundamental behavior of these systems was investigated by considering the mean square displacement (MSD), velocity autocorrelation function (VACF), and memory kernel (MK) associated with the VACF. The effective diffusivity of the molecular gas system was also investigated as a function of porosity and temperature. A summary of the main results follows:

- The MSD and VACF results are qualitatively reminiscent of past RW simulations on percolation clusters, and MD studies of the Lorentz gas.
- In general, diffusion of a gas particle within a porous solid occurs in three stages: super–diffusive at short times, anomalous (or sub–diffusive) at intermediate times, and Fickian at long times. All three stages are seen at lower porosities and temperatures, with the time spent in the anomalous regime decreasing as the porosity and/or temperature increases. At high enough porosities and/or temperatures, the anomalous regime does not occur at all (ie: the process transitions directly from super–diffusive to Fickian).
- The VACFs contain oscillatory components that diminish in magnitude and eventually disappear as temperature increases – this behavior reflects the fact that as the energy of a diffusing gas particle increases, so too does its ability to punch through the potential energy barriers associated with the pore system. Using the normal definition for tortuosity, this behavior implies that when the average gas particle energies are near to or less than the potential energy maxima, the tortuosity will be temperature dependent.
- The dependence of the effective diffusivity of a gas within a porous solid on temperature is similar to that of a liquid, not a gas, in the bulk phase – this means the common practice of normalizing an experimentally or numerically determined effective diffusivity with a gas diffusivity to yield a *temperature independent* tortuosity is in error. Use of such tortuosities will result in the incorrect estimation of diffusivities at temperatures other than that at which the original experiment took place.

Although application of the MD approach has been demonstrated, computational resource limitations prevented a full and rigorous study. Of particular concern was the

change of the MSD exponent, α , with porosity, and the variation of this exponent from that expected for a three dimensional random percolation problem. It is thought that the small number of realizations per configuration may be a possible source of this anomaly, but finite size effects may also be responsible. These concerns shall be addressed in a future study.

3.4 CONCLUDING REMARKS AND FUTURE WORK

In this chapter, a new discrete technique for the study of diffusion within porous solids was described and subsequently used to study the behavior of two gases (Ar and CO) within a model microporous graphite under non-reactive conditions. Many interesting behaviors of both fundamental and practical importance were revealed – a summary of these may be found in §3.3.3.6. In the immediate future, several key issues must be addressed such as finite size effects, and the accuracy of the method (ie: more realizations per condition are required). In order to explore suitability of Fick's law to describe diffusion within a porous solid, the average probability, $\langle P(\mathbf{r}, t) \rangle$, that a diffusing particle is at a position $\mathbf{r}$ at a time t is often considered where $r = |\mathbf{r}|$ [eg: O'Shaughnessy and Procaccia, 1985; Guyer, 1985; Havlin and Ben-Avraham, 1987; Sahimi, 1987; Roman et al., 1989; Giona and Roman, 1992] – this distribution will also be studied in the near future using the new approach described in this chapter. In the medium to long term, the molecular dynamic basis of this new technique offers considerable scope for extending it to the study of real complex fluid–solid systems, reaction, and the determination of other transport coefficients – issues associated with these extensions are briefly discussed in the following sections.

3.4.1 Application to Real Fluid–Solid Systems

As most porous solids of practical interest are characterized by multiple length scales of widely different orders, the MD approach cannot, at this stage, be used to generate effective properties for use in continuum models, nor can they be compared with

experiment*. On the other hand, the more macroscopic approaches of §§3.2.3 and 3.2.4 require, as input, the effective transport properties of the different phases that make up the porous solid (eg: the different macerals of a char) – these properties may be determined using the MD approach described in this chapter. If we wish to study real systems, two main issues must be addressed: (1) the molecular structure of the porous solid; and (2) the interaction potentials. These issues are briefly discussed in the following paragraphs.

The chemical composition and three dimensional structure of many real porous solids are not well known, and in light of their complexity, exact models are unlikely for some time. There is hope however! As crystalline materials like zeolites can be studied with relative ease using high resolution electron microscopy and diffractometry [Terasaki et al., 1984; Millward et al., 1985], extensive libraries of structural models have been available for some time [Price et al., 1994]. These models have been used in conjunction with MD techniques to study adsorption and diffusion within various zeolites [Yashonath 1991; Yashonath et al., 1991; El Amrani and Kolb, 1993], whilst reaction studies are presently underway [Demontis and Suffritti, 1994]. As they lack any regular atomic structure, amorphous solids such as polymers and coal have been more difficult to model. However, progress is also being made with these solids. Probable three dimensional models of polymers have been generated [Theodorou and Suter, 1985], and subsequently used in MD studies of diffusion [Muller–Plathe, 1992]. The widely varying chemical composition of coal, means modelling of its structure is particularly challenging. However, three dimensional molecular structures representative of individual macerals can now be generated [Faulon et al. 1993a; Carlson and Faulon, 1994] using computer–aided molecular modelling (CAMM) [Carlson, 1992] and computer–aided structural elucidation (CASE) [Smith, 1977; Faulon, 1991]. The

* Using a Fujitsu VP2200 (1 GFLOPS, 500 MBytes), simulation volumes of linear dimensions $L \approx 20-50\text{nm}$ were used in the study of Biggs and Agarwal (1994). An increase to $L \approx 350\text{nm}$ may be possible using the most powerful supercomputers of today [the highest configurations of the Fujitsu VPP550, Cray T3D, and Thinking Machines CM5 all have performance characteristics of: 100–300 GFLOPS, and 1000–3000 MBytes]. Most real porous solids are heterogeneous at macroscopic levels [ie: orders of μm ; eg: Gladden, 1993], whilst most experimental techniques yield properties averaged over tens of μm at least [eg: Gladden, 1993].

CASE–CAMM process as applied to coal [Faulon et al., 1992, 1993a] determines the number of molecular fragments and interfragment bonds of a coal maceral macromolecule by reconciling the “signature” of the macromolecule (defined by elemental analysis and NMR studies) with the sum of the “signatures” of the molecular fragments and interfragment bonds (defined by flash pyrolysis/gas chromatography/mass spectrometry studies). Once the number and type of fragments and interfragment bonds have been determined, possible non–isomorphic configurations can be generated under appropriate constraints (eg: bond lengths and angles) for subsequent energy minimization (via CAMM) and analysis. This process does not identify the exact chemical structure of a maceral, but rather yields a set of structures that are statistically equivalent to the maceral (in the sense that they match the elemental, molecular and NMR data of the maceral). The number of such structures is quite large, usually in the order of 10^5 to 10^6 . However, it has been demonstrated that at least for structural properties (density, porosity, pore size distribution), only a small sample (orders of ten) needs to be generated and subsequently analyzed [Faulon et al., 1993b, c, 1994]. This bodes well for MD studies of amorphous carbonaceous solids such as coal, char and coke.

As in this work, almost all molecular dynamic studies of fluid within porous media assume a rigid solid lattice. This simplification is often forced upon us by computational limitations, but is also a reasonable step when our interest is primarily limited to the gas behavior. Unfortunately, this assumption is not a good one when the diffusing gas molecules and pores are similar in size [Gusev et al., 1993; Gusev and Suter, 1993], whilst it also means no energy exchange may take place between the pore walls and impinging gas molecules – this prevents accurate treatment of the many phenomena directly affected by this energy exchange process such as absorption/desorption, chemisorption, non–catalytic and catalytic heterogeneous reactions, and surface diffusion [DePristo and Kara, 1990].

The simplest way of including gas–solid energy exchange is to solve the dynamical

equations for both the solid and gas atoms. Even today, however, this lattice dynamic/molecular dynamic (LD/MD) approach would require a considerable investment in computational resources, and would most definitely limit the size and complexity of the system that we may study. An alternative is to solve the dynamical equations only for those solid atoms which interact strongly with the gas (ie: those that are closest to the gas molecules). Using a generalized Langevin equation (GLE) approach, Adelman and Doll (1976) were the first to implement this philosophy in a realistic way [review of earlier attempts may be found in Tully, 1980a]. Briefly, following DePristo (1984), assuming harmonic interactions between the solid atoms*, the motion of the solid lattice may be described by

$$m_i \frac{d^2 \mathbf{r}_i}{dt^2} = - \sum_{j=1}^N \mathbf{K}_{ij} (\mathbf{r}_j - \mathbf{r}_{j0}) \quad (3-44)$$

where $\mathbf{K}_{ij}$ is the stiffness matrix of the solid atom pair $-ij$, and $\mathbf{r}_{j0}$ the equilibrium position vector of solid atom $-j$. Defining the mass weighted displacement coordinates as

$$\mathbf{u}_i = \sqrt{m_i} (\mathbf{r}_i - \mathbf{r}_{i0}) \quad (3-45)$$

and the frequency matrix by

$$\hat{\mathbf{K}}_{ij} = \frac{\mathbf{K}_{ij}}{\sqrt{m_i m_j}} \quad (3-46)$$

equation (3-44), when written for the whole solid lattice, becomes

$$\frac{d^2 \mathbf{u}}{dt^2} = - \hat{\mathbf{K}}^2 \mathbf{u} \quad (3-47)$$

Using the projector operator formalism of Zwanzig (1965) and Mori (1965), we may partition the solid atoms into two sets: the primary atoms which interact strongly with the impinging gas molecule, and the remainder which are termed secondary atoms. This process yields a system of Langevin equations for the motion of the primary atoms only

* This is an important restriction on the method [DePristo and Kara, 1990] – the primary zone may behave anharmonically when it interacts with the gas, but the secondary–secondary and secondary–primary interactions must be harmonic. The harmonic assumption is valid provided solid atom displacements are not too large – this could be a consideration at high temperatures typical of combustion. To the authors knowledge, this issue has received no attention in the GLE literature.

$$\begin{aligned} \frac{d^2 \mathbf{u}_p}{dt^2} = & -\hat{\mathbf{K}}_{pp}^2 \mathbf{u}_p(t) + \mathbf{A}(0)\mathbf{u}_p(t) - \mathbf{A}(t)\mathbf{u}_p(0) \\ & - \int_0^t \mathbf{A}(t-t') \frac{d\mathbf{u}_p}{dt'} dt' + \mathbf{r}(t) \end{aligned} \quad (3-48)$$

where $\mathbf{u}_p = \mathbf{P}\mathbf{u}$ and $\hat{\mathbf{K}}_{pp} = \mathbf{P}\hat{\mathbf{K}}\mathbf{P}$ are the primary atom subsets of $\mathbf{u}$ and $\hat{\mathbf{K}}$ respectively, and $\mathbf{P}$ the matrix that projects onto the primary lattice [see Adelman and Doll (1976) for details]. Interaction between the primary and secondary atoms (we are no longer interested in their motion; they are assumed to be at their equilibrium positions for force calculation purposes) is expressed via the friction kernel matrix, $\mathbf{A}$, which describes the dissipation of energy from the primary to the secondary atoms, and the random force vector, $\mathbf{r}$, which accounts for energy imparted to the primary atoms due to thermal fluctuations of the secondary. It turns out [Adelman and Doll, 1976] that we may simply add in the effect of the interacting gas atoms, $\mathbf{f}_{gp}$, to yield

$$\begin{aligned} \frac{d^2 \mathbf{u}_p}{dt^2} = & -\hat{\mathbf{K}}_{pp}^2 \mathbf{u}_p(t) + \mathbf{A}(0)\mathbf{u}_p(t) - \mathbf{A}(t)\mathbf{u}_p(0) \\ & - \int_0^t \mathbf{A}(t-t') \frac{d\mathbf{u}_p}{dt'} dt' + \mathbf{r}(t) + \mathbf{f}_{gp} \end{aligned} \quad (3-49)$$

This fact is extremely important as it means we may determine the friction kernel and random force independent of the gas–solid problem. Whilst this process results in a substantial reduction in the number of equations that must be solved for the solid, solution of the system of equations (3–49) is markedly more complex than that required for the original Newtonian equations – the many issues associated with this fact have been extensively discussed by DePristo and Kara (1990). Application of this approach has been primarily restricted to the study of metals [eg: DePristo and Kara, 1990], and some molecular solids such as GaAs [Lim et al., 1987]. To the author’s knowledge, it has not been applied to situations in which the surface is highly heterogeneous either chemically and/or geometrically.

If we are to apply the GLE approach to real porous solids, we must be able to determine

the friction kernel and random force. Formally, these are defined by

$$\mathbf{A}(t) = \hat{\mathbf{K}}_{ps}^2 \cos(\hat{\mathbf{K}}_{ss} t) \hat{\mathbf{K}}_{ss}^{-2} \hat{\mathbf{K}}_{sp}^{-2} \quad (3-50)$$

$$\mathbf{r}(t) = -\hat{\mathbf{K}}_{ps}^2 \cos(\hat{\mathbf{K}}_{ss} t) \mathbf{u}_s(0) - \hat{\mathbf{K}}_{ps}^2 \sin(\hat{\mathbf{K}}_{ss} t) \hat{\mathbf{K}}_{ss}^{-1} \dot{\mathbf{u}}_s(0) \quad (3-51)$$

where $\mathbf{u}_s = \mathbf{Q}\mathbf{u}$ and $\hat{\mathbf{K}}_{ss} = \mathbf{Q}\hat{\mathbf{K}}\mathbf{Q}$ are the secondary atom subsets of $\mathbf{u}$ and $\hat{\mathbf{K}}$ respectively, $\mathbf{Q} = \mathbf{I} - \mathbf{P}$ the matrix that projects onto the secondary lattice [details: Adelman and Doll, 1976], and $\hat{\mathbf{K}}_{sp} = \mathbf{Q}\hat{\mathbf{K}}\mathbf{P}$ and $\hat{\mathbf{K}}_{ps} = \mathbf{P}\hat{\mathbf{K}}\mathbf{Q}$ the cross-projections of $\hat{\mathbf{K}}$. For various reasons outlined by DePristo (1984), these are not normally used for simulation purposes. Rather, an integrable analytical form that captures the essential character of the system is assumed for the friction kernel

$$\mathbf{A}(t) = f(t, \mathbf{A}_1, \mathbf{A}_2, \dots, \mathbf{A}_n) \quad (3-52)$$

where $\mathbf{A}_i$ are parameter matrices determined by fitting this functional form to results obtained from LD simulations of the solid in question [DePristo, 1984], and/or experimental results [Tully, 1980b]. The random force need not be determined directly as it is related to the friction kernel via the second fluctuation–dissipation theorem [Kubo, 1966]. As availability of appropriate experimental data for complex solids is unlikely, a straight LD approach will most likely be required – the presence of $\hat{\mathbf{K}}_{sp}$ and $\hat{\mathbf{K}}_{ps}$ in equation (3–50) means a characteristic primary zone must be selected a priori. Whilst this does not represent a problem for ideal metal surfaces and simple molecular solids, lack of symmetry in complex molecular solid chemical structures typical of coal, char and polymers make selection of an appropriate primary zone difficult. Most existing models of such solids [eg: Theodorou and Suter, 1985; Faulon et al., 1993a] suggest a chemical structure made up of cross-linked macromolecules of $O(100-1000)$ constituent atoms. As the primary zone must be the same no matter where the gas molecule approaches the solid from, an appropriate definition could be the characteristic macromolecule. The size of the resultant primary zone would of course incur considerable computational penalties, and so reduction to a small fraction of the macromolecule at the expense of multiple primary zones might be advantageous.

Gas–gas, gas–solid and solid–solid interactions are described by potential energy surfaces. As the qualitative and quantitative nature of a potential energy surface (PES) for a given interaction depends upon all the intramolecular and intermolecular degrees of freedom associated with the interaction, full determination is, at this stage, limited to relatively simple systems [DePristo and Kara, 1990; Page and Lengsfeld, 1991]. Even if we could determine the full PES for any interaction of interest, the likely many–dimensional nature of the surface means it would be of limited use in MD calculations. It is for these reasons that almost all MD simulations utilize simple analytical representations of the PES. The most common [Allen and Tildesley, 1989] is the Lennard–Jones potential, equation (3–9), but more complex forms such as that of London–Eyring–Polanyi–Sato (LEPS) have been used when bond breakage is possible [eg: Diebold and Wolken, 1979] – the reader is referred to the many reviews for details [eg: Steele, 1974; Kihara and Ichimaru, 1978; Maitland et al., 1981; Murrell et al., 1984; Allen and Tildesley, 1989; Brenner and Garrison, 1989; DePristo and Kara, 1990; Simkin and Sheikhet, 1995]. Whilst these analytical potential functions have proven to be robust when used to study relatively simple systems (although they are still quite complex in the scheme of things), their use for the simulation of transport and reaction within solids such as polymers, coal and char is questionable – this represents a serious impediment to the use of MD for accurate study of transport and reaction within such complex solids [Car and Parrinello 1988; Parrinello, 1992]. In light of present computer technology, however, we will have to simply persist with use of analytical forms, with any conclusions being made tempered by the knowledge that the potentials used are *relatively* crude. In the longer term, *ab–initio* MD approaches such as that of Car and Parrinello (1985) will remove the need for explicit representation of the PES at all, and will permit more rigorous treatment of real fluid/porous solid systems under both reactive and non–reactive conditions. In the *ab–initio* MD approach of Car and Parrinello (1985), density–functional theory is used in conjunction with simulated annealing concepts [Kirkpatrick et al., 1983] to solve for the interatomic potentials as the MD simulation proceeds. Whilst this approach makes the actual MD simulation

computationally much more expensive when compared to the fully classical approach, it indirectly saves computer time as we only need to determine the various potential energy surfaces wherever the system samples them. Advances in computer speed and time integration algorithms [Tuckerman and Parrinello, 1994a, b] mean its application to systems such as polymers, coal and char will be possible in the not too distant future.

3.4.2 Calculation of Reaction Rates, and other Transport Coefficients

Discussion in the previous chapter clearly shows that although overall reaction schemes and associated rate expressions are available for char combustion, they are crude and generally unsatisfactory when we are interested in predicting the behavior of a specific char at a quantitative level. Transient kinetic techniques are now being successfully used to determine what are the most appropriate kinetic schemes for char reaction [eg: Kapteijn et al., 1992], the effect that various inorganics have on the reaction rates [eg: Freund, 1986], and the question of what is the reactive surface area [eg: Lizzio et al., 1990]. However, like experimental techniques used to study diffusion within porous solids (see §3.2.1), flawed conclusions can be drawn if technical pitfalls are not avoided, or results are improperly interpreted [Kapteijn et al., 1992]. Whilst the former can only be dealt with through vigilance and care, the previous chapter demonstrated that our interpretation of experimental results may be substantially improved by comparing them with those obtained from detailed mathematical models. As MD simulations give an unprecedented ability to “see” what is going on at the atomic level, it should offer an ideal counterpart to the transient kinetic technique.

It has been shown that surfaces of real solids at the microscopic level may be considered fractal in nature [Albano and Martín, 1989], and that the kinetics of reactions occurring on such surfaces cannot be modelled using classical approaches [Albano and Martín, 1989; Rastogi et al., 1991; Casties et al., 1993; Sahimi, 1994]. The reduced dimensional or fractal nature of the pore space of some solids have also been shown to be critical when modelling the kinetics of homogeneous reactions within such solids [Clément et al., 1989, 1990; López–Quintela and Buján–Núñez, 1991; Giona et al., 1992; Sahimi, 1994]. By

directly simulating the reaction–diffusion process with MD, these non–classical phenomena may be probed in detail exceeding that of any other technique, whilst in the longer term, *ab initio* molecular dynamics and realistic solid structure data (see §3.4.1) will permit accurate determination of parameters for non–classical rate expressions.

Reaction can be implemented in a number of ways. Perhaps the simplest is where two colliding hard spheres are assumed to react if the relative kinetic energy along their line of centers exceeds a critical level that is normally identified with the activation energy of the reaction being studied [Der and Fritzsche, 1985; Gorecki and Gryko, 1989]. This approach obviously only accounts for a single energy carrying mode, whilst it assumes that all interactions with an energy above the critical level will result in reaction [see Lee and DePristo (1986) for a good example of why these issues are important]. A more satisfactory and rigorous approach is to include the relevant degrees of freedom, and the potential energy surfaces that govern their interactions [eg: Persky and Broida, 1984; Bergsma et al., 1986; Edberg et al., 1987; Brown and Clarke, 1990; Wolken, 1978; Kara and DePristo, 1988]. As many of the details of this approach are unimportant here, the reader is referred to several recent reviews [Tully, 1981; Brenner and Garrison, 1989; DePristo and Kara, 1990; Brown, 1991]. It should be noted, however, that the main concern with implementing reaction in this way is the need to have an accurate picture of the relevant potential energy surfaces, and/or the most likely reaction paths – the various issues associated with this in relation to real systems are briefly discussed in §3.4.1.

Although the work undertaken in this chapter has been limited to the study of gas diffusion within porous solids, EMD can also be used to determine other transport coefficients such as the effective viscosity and thermal conductivity – both are likely to be affected by the presence of the pore space [eg: Butt, 1965]. Alternatively, discussion in the previous chapter shows that little is known about char thermal conductivity. Provided a good representation of the solid molecular structure can be obtained (see §3.4.1), MD may be used to address this issue. Infact, this may offer a way of improving

the process of structural elucidation described in the previous section – as properties like the thermal conductivity and specific heat are likely to be much more solid structure sensitive compared to geometric parameters such as porosity, comparison of MD determined values with those obtained from experiment will indicate suitability of the molecular structure used in the simulation.

Use of EMD in conjunction with Green–Kubo integral relationships has been the traditional path to determining transport properties from computer simulation [Allen and Tildesley, 1989]. It may not, however, be the best approach when we are interested in transport properties other than the diffusion coefficient, as the correlation functions used involve multiparticle properties (off–diagonal elements of pressure tensor for viscosity, components of energy flux for thermal conductivity) – this removes the possibility of averaging over the particles as we do for the velocity autocorrelation function [see equations (3–25)], and therefore substantially reduces the accuracy of the average. Although accuracy may be improved by increasing the number of time origins, this is computationally expensive [Evans and Morriss, 1984]. The weakness with this traditional approach is in the fact that the time correlation functions represent the average response to naturally occurring, and therefore small, fluctuations in the system properties [Allen and Tildesley, 1989]. In situations where long time–tails are observed (eg: gases within porous solids), this is particularly a problem as the signal–to–noise ratio is extremely poor – this may very well prevent an accurate determination of the transport coefficients at all [Evans and Morriss, 1984]. The obvious way around this problem is to perturb the system such that the signal–to–noise ratio is substantially improved, and then to measure the steady state response to this perturbation – this is the basis of nonequilibrium molecular dynamics (NEMD) [reviews: Evans and Morriss, 1984, 1990]. Although details are not important here, this method is particularly attractive when we wish to determine transport coefficients for situations in which the associated correlations functions have long time–tails – this means it could play a significant role in the study of transport within porous solids where even determination of the diffusion coefficient is hampered by this phenomena (see §3.3.3.3).

NOMENCLATURE

Latin (Note: vectors are bold lowercase, matrices bold uppercase)

A	friction kernel matrix
A_i	parameter matrices for friction kernel
D_e	effective diffusivity
D[*]	dimensionless diffusivity
d	Euclidean dimension of system
d_w	fractal dimension of random walk
d₁₂	desired bond length
f_{gp}	force vector acting on primary solid atoms due to gas molecules
f_i	force vector acting on atom—i
f_{i,p}	force vector acting on atom—i of molecule—p
f_r	random force
f_s	systematic force
f_t	total force
I	identity matrix
i	imaginary identity
K	memory function associated with velocity autocorrelation function
$\hat{K}$	frequency matrix
K_e	total kinetic energy of system
K_{ij}	stiffness matrix of solid atom pair—ij
$\hat{K}_{ij}$	frequency matrix of solid atom pair—ij
$\hat{K}_{pp}$	projection of frequency matrix onto primary solid atoms

$\hat{\mathbf{K}}_{ps}$	cross–projection of frequency matrix
$\hat{\mathbf{K}}_{ss}$	projection of frequency matrix onto secondary solid atoms
$\hat{\mathbf{K}}_{sp}$	cross–projection of frequency matrix
k_b	Boltzmann constant
k_1	pre–exponential factor for effective diffusivity scaling with porosity
k_2	pre–exponential factor for effective diffusivity scaling with temperature
L	linear dimension of simulation domain
ℓ	characteristic length of system
M	number of time origins over which MSD and VACF are averaged
M_d	total number of degrees–of–freedom of system
m_i	mass of atom–i
N	number of atoms
N_b	number of particles within cutoff radius
$\mathbf{n}_{i,p}$	Nosé–Hoover thermostat constraint vector acting on atom–i of molecule–p
$\mathbf{P}$	projection matrix
P	number of molecules
P_t	transmission probability
$\mathbf{Q}$	projection matrix
R^2	mean square displacement
$\mathbf{r}$	random force vector associated with GLE
r	distance
r^*	reduced distance

r_c	truncated interaction potential cutoff radius
$\mathbf{r}_i$	position vector of atom—i
$\mathbf{r}_{ij}$	displacement vector between atoms i—j
r_{ij}	magnitude of $\mathbf{r}_{ij}$
$\hat{\mathbf{r}}_{ij}$	unit vector along $\mathbf{r}_{ij}$
$\mathbf{r}_{io}$	equilibrium position vector of solid atom—i
$\mathbf{r}_{i,p}$	position vector of atom—i of molecule—p
$\mathbf{r}_{12,p}$	bond length vector of molecule—p
$r_{12,p}$	magnitude of $\mathbf{r}_{12,p}$
$\dot{\mathbf{r}}_{12,p}$	time rate—of—change of bond length vector of molecule—p
s	dummy time variable
T	temperature
T^*	reduced temperature
t	time
t^*	reduced time
t'	dummy time variable
t_o	time origin
$\mathbf{u}$	mass weighted displacement vector of all solid atoms
$\mathbf{u}_i$	mass weighted displacement vector of solid atom—i
u_{ij}	interaction potential acting between atoms i—j
$\bar{u}_{ij}$	truncated interaction potential acting between atoms i—j
u_f	external field interaction potential
u_n	n—body interaction potential

$\mathbf{u}_p$	projection of mass weighted displacement vector onto primary solid atoms
$\mathbf{u}_s$	projection of mass weighted displacement vector onto secondary solid atoms
$\dot{\mathbf{u}}_s$	time rate of change of $\mathbf{u}_s$
u_t	total interaction potential
$\mathbf{v}_i$	velocity vector of atom—i
$\mathbf{v}_{i,p}$	velocity vector of atom—i of molecule—p
Z	coordination number of lattice or tessellation

Greek

α	mean square displacement time scaling exponent
β	exponent for effective diffusivity scaling with porosity
β_p	critical exponent
γ_r	Fourier transform of random force
γ_t	Fourier transform of total force
ξ	correlation length
Δt	time step size
ε	Lennard—Jones interaction potential energy parameter
ϕ	porosity
ϕ_c	percolation threshold
ϕ_e	ratio of diffusivities
κ	tortuosity factor
λ	exponent for effective diffusivity scaling with temperature
λ_p	Lagrangian multiplier for bond constraint of molecule—p
ζ	Lagrangian multiplier for temperature constraint
ϱ^*	dimensionless density

σ	Lennard–Jones interaction potential length parameter
τ	Nosé–Hoover thermostat characteristic time constant
τ_A	sampling time for mean square displacement
τ_B	sampling time for velocity autocorrelation function
τ_c	correlation time
μ	critical exponent
ν	critical exponent
ψ_v	velocity autocorrelation function
ω	Fourier transform conjugate of time

Acronyms

CASE	computer–aided structural elucidation
CAMM	computer–aided molecular modelling
CPU	central processing unit
EMA	effective–medium approximation
EMD	equilibrium molecular dynamics
GLE	generalized Langevin equation
LD	lattice dynamics
LJ	Lennard–Jones
MC	Monte Carlo
MD	molecular dynamics
MK	memory kernel
MSD	mean square displacement
NEMD	nonequilibrium molecular dynamics
NH	Nosé–Hoover

NMR	nuclear magnetic resonance
NPT	mass–pressure–temperature
NVE	mass–volume–total energy
NVT	mass–volume–temperature
PDE	partial differential equation
PSRG	position–space renormalization group
RAN	[0:1] uniform random number
RFACF	random force autocorrelation function
RW	random walk
TFACF	total force autocorrelation function
VACF	velocity autocorrelation function
μ VT	chemical potential–volume–temperature

REFERENCES

1. Abbasi M.H, Evans J.W and Abramson I.S (1983): Diffusion of gases in porous solids: Monte Carlo simulations in the Knudsen and ordinary diffusion regimes, *AIChE Journal*, **29**, 617.
2. Adelman S.A and Doll J.D (1976): Generalized Langevin equation approach for atom/solid–surface scattering: General formulation for classical scattering off harmonic solids, *J. Chem. Phys.*, **64**, 2375.
3. Albano E and Márton H.O (1989): Adsorption isotherms on fractal substrata, *Phys. Rev. A*, **39**, 6003.
4. Alder B.J (1986): Molecular dynamics simulations, in *Molecular–Dynamics Simulation of Statistical–Mechanical Systems*, North–Holland, Amsterdam.
5. Alder B.J and Alley W.E (1978): Long–time correlation effects on displacement distributions, *J. Stat. Mech.*, **19**, 341.
6. Alder B.J and Wainwright T.E (1970): Decay of the velocity autocorrelation function, *Phys. Rev. A*, **1**, 18.
7. Alexander S and Orbach R (1982): Density of states on fractals: fractons, *J. Physique Lett.*, **43**, L625.
8. Alexandrowicz Z (1980): Critically branched chains and percolation clusters, *Phys. Lett. A*, **80**, 284.
9. Allen M.P and Tildesley D.J (1989): *Computer Simulation of Liquids*, Oxford University Press, Oxford.
10. Alley W.E and Alder B.J (1979): Modification of Fick’s law, *Phys. Rev. Lett.*, **43**, 653.
11. Andersen H.C (1983): Rattle: a ”velocity” version of the Shake algorithm for molecular dynamics calculations, *J. Comp. Phys.*, **52**, 24.
12. Baranyai A and Evans D.J (1990): New algorithm for constrained molecular–dynamics simulation of liquid benzene and naphthalene, *Mol. Phys.*, **70**, 53.

13. Barojas J, Levesque D and Quentrec B (1973): Simulation of diatomic homonuclear liquids, *Phys. Rev. A*, **7**, 1092.
14. Berendsen H.J.C (1986): Biological molecules and membranes, in *Molecular–Dynamics Simulation of Statistical–Mechanical Systems*, North–Holland, Amsterdam.
15. Berendsen H.J.C and van Gunsteren W.F (1986): Practical algorithms for dynamic simulations, in *Molecular–Dynamics Simulation of Statistical–Mechanical Systems*, North–Holland, Amsterdam.
16. Bergsma J.P, Edelsten P.M, Gertner B.J, Huber K.R, Reimers J.R, Wilson K.R and Wu S.M (1986): Dynamics of the A + BC reaction in solution, *Chem. Phys. Lett.*, **123**, 394.
17. Berne B.J and Harp G.D (1970): On the calculation of time correlation functions, *Adv. Chem. Phys.*, **17**, 63.
18. Bhatia S.K (1986): Stochastic theory of transport in inhomogeneous media, *Chem. Engng. Sci.*, **41**, 1311.
19. Biggs M and Agarwal P (1992): Mass diffusion of atomic fluids in random micropore spaces using equilibrium molecular dynamics, *Phys. Rev. A*, **46**, 3312.
20. Biggs M and Agarwal P (1994): Mass diffusion of diatomic fluids in random micropore spaces using equilibrium molecular dynamics, *Phys. Rev. E*, **49**, 531.
21. Boon J.P and Yip S (1980): *Molecular Hydrodynamics*, McGraw–Hill, New York.
22. Bradbury T.C (1968): *Theoretical Mechanics*, Wiley, New York.
23. Brenner D.W and Garrison B.J (1989): Gas–surface reactions: Molecular dynamics simulations of real systems, *Adv. Chem. Phys.*, **76**, 281.
24. Brown D and Clarke J.H.R (1984): A comparison of constant energy, constant temperature and constant pressure ensembles in molecular dynamics simulations of atomic liquids, *Mol. Phys.*, **51**, 1243.

25. Brown D and Clarke J.H.R (1990): A direct method of studying reaction rates by equilibrium molecular dynamics: Application to the kinetics of isomerization in liquid *n*–butane, *J. Chem. Phys.*, **92**, 3062.
26. Brown N.J (1991): Rate coefficient calculation for combustion modelling, in *Numerical Approaches to Combustion Modelling*, AIAA.
27. Bruin C (1972): Logarithmic terms in the diffusion coefficient for the Lorentz gas, *Phys. Rev. Lett.*, **29**, 1670.
28. Bruin C (1974): A computer experiment on diffusion in the Lorentz gas, *Physica*, **72**, 261.
29. Burganos V.N and Sotirchos S.V (1987): Diffusion in pore networks: Effective medium theory and smooth field approximation, *AIChE Journal*, **33**, 1678.
30. Burganos V.N and Sotirchos S.V (1988): Simulation of Knudsen diffusion in random networks of parallel pores, *Chem. Engng. Sci.*, **43**, 1685.
31. Burganos V.N and Sotirchos S.V (1989): Knudsen diffusion in parallel multidimensional or randomly orientated capillary structures, *Chem. Engng. Sci.*, **44**, 2451.
32. Butt J.B (1965): Thermal conductivity of porous catalysts, *AIChE Journal*, **11**, 106.
33. Car R and Parrinello M (1985): Unified approach for molecular dynamics and density–functional theory, *Phys. Rev. Lett.*, **55**, 2471.
34. Car R and Parrinello M (1988): Structural, dynamical, and electronic properties of amorphous silicon: An *ab initio* molecular–dynamics study, *Phys. Rev. Lett.*, **60**, 204.
35. Carlson G.A (1992): Computer simulation of the molecular structure of bituminous coal, *Energy Fuels*, **6**, 771.
36. Carlson G.A and Faulon J–L (1994): Applications of molecular modeling in coal research, *Am. Chem. Soc. Div. Fuel Chem. Preprints*, **39**, 18.

37. Casties A, Mai J and von Niessen W (1993): A Monte Carlo simulation of the CO oxidation on probabilistic fractals, *J. Chem. Phys.*, **99**, 3082.
38. Ciccotti G, Ferrario M and Ryckaert J–P (1982): Molecular dynamics of rigid systems in Cartesian coordinates: a general formulation, *Mol. Phys.*, **47**, 1253.
39. Clément E, Sander L.M and Kopelman R (1989): Steady–state diffusion–controlled $A + A \rightarrow 0$ reaction in Euclidean and fractal dimensions: Rate laws and particle self–ordering, *Phys. Rev. A*, **39**, 6472.
40. Clément E, Kopelman R and Sander L.M (1990): Bimolecular reaction $A + B \rightarrow 0$ at steady state on fractals: anomalous rate law and reactant self–organization, *Chem. Phys.*, **146**, 343.
41. Crowell A.D and Steele R.B (1961): Interaction potentials of simple nonpolar molecules with graphite, *J. Chem. Phys.*, **34**, 1347.
42. Cukier R.I and Freed K.F (1983): Diffusion controlled processes among stationary reactive sinks: Effective medium approach, *J. Chem. Phys.*, **78**, 2573.
43. Cunningham R.E and Williams R.J.J (1980): *Diffusion in Gases and Porous Media*, Plenum Press, New York.
44. Demontis P and Suffritti G.B (1994): Molecular dynamics studies on zeolites, in *Modeling of Structure and Reactivity in Zeolites*, Academic Press, London.
45. DePristo A.E (1984): Memory function parameterization in the GLE–ghost atom formalism: A microscopic approach, *Surface Sci.*, **141**, 40.
46. DePristo A.E and Kara A (1990): Molecule–surface scattering and reaction dynamics, *Adv. Chem. Phys.*, **77**, 163.
47. Der R and Fritzsche S (1985): Dynamical correlations and long–time tails in chemical reactions. A molecular dynamics study, *Chem. Phys. Lett.*, **121**, 177.
48. Diebold A.C and Wolken Jr. G (1979): The energetics of diatom/solid dissociative adsorption, *Surface Sci.*, **82**, 245.

49. Edberg R, Evans D.J and Morriss G.P (1986): Constrained molecular dynamics: Simulations of liquid alkanes with a new algorithm, *J. Chem. Phys.*, **84**, 6933.
50. Edberg R, Evans D.J and Morriss G.P (1987): Conformational kinetics in liquid butane by nonequilibrium molecular dynamics, *J. Chem. Phys.*, **87**, 5700.
51. El Amrani S and Kolb M (1993): Molecular dynamics simulations in zeolites: From deterministic to random motion, *J. Chem. Phys.*, **98**, 1509.
52. Epstein N (1989): On tortuosity and the tortuosity factor in flow and diffusion through porous media, *Chem. Engng. Sci.*, **44**, 777.
53. Evans D.J (1977): On the representation of orientation space, *Mol. Phys.*, **34**, 317.
54. Evans D.J (1983): Computer experiment for nonlinear thermodynamics of Couette flow, *J. Chem. Phys.*, **78**, 3297.
55. Evans D.J and Holian B.L (1985): The Nose–Hoover thermostat, *J. Chem. Phys.*, **83**, 4069.
56. Evans D.J and Morriss G.P (1984): Non–Newtonian molecular dynamics, *Comput. Phys. Rep.*, **1**, 297.
57. Evans D.J and Morriss G.P (1990): *Statistical Mechanics of Nonequilibrium Liquids*, Academic Press, London.
58. Evans D.J and Murad S (1977): Singularity free algorithm for molecular dynamics simulation of rigid polyatomics, *Mol. Phys.*, **34**, 327.
59. Evans J.W, Abbasi M.H and Sarin A (1980): A Monte Carlo simulation of the diffusion of gases in porous solids, *J. Chem. Phys.*, **72**, 2967.
60. Faulon J–L (1991): *Prediction, Elucidation, and Molecular Modeling: Algorithm and Application in Geochemistry*, PhD Thesis, Ecole des Mines, Paris.
61. Faulon J–L, Hatcher P.G and Wenzel K.A (1992): A computer assisted structural elucidation for coal macromolecules, *Am. Chem. Soc. Div. Fuel Chem. Preprints*, **37**, 900.

62. Faulon J–L, Hatcher P.G, Carlson G.A and Wenzel K.A (1993a): A computer–aided molecular model for high volatile bituminous coal, *Fuel Process. Technol.*, **34**, 277.
63. Faulon J–L, Carlson G.A, Mathews J.P and Hatcher P.G (1993b): Statistical evaluation of physical properties for coal macromolecules based on computer–generated structures, *Am. Chem. Soc. Div. Fuel Chem. Preprints*, **38**, 1275.
64. Faulon J–L, Carlson G.A, and Hatcher P.G (1993c): Statistical models for bituminous coal: A three–dimensional evaluation of structural and physical properties based on computer–generated structures, *Energy Fuels*, **7**, 1062.
65. Faulon J–L, Mathews J.P, Carlson G.A and Hatcher P.G (1994): Correlation between microporosity and fractal dimension of bituminous coal based on computer–generated models, *Energy Fuels*, **8**, 408.
66. Feng C and Stewart W.E (1973): Practical models for isothermal diffusion and flow of gases in porous solids, *Ind. Eng. Chem. Fund.*, **12**, 143.
67. Freund H (1986): Gasification of carbon by CO₂: a transient kinetics experiment, *Fuel*, **65**, 63.
68. Gavalas G.R and Kim S (1981): Periodic capillary models of diffusion in porous solids, *Chem. Engng. Sci.*, **36**, 1111.
69. Gear C.W (1971): *Numerical Initial Value Problems in Ordinary Differential Equations*, Prentice–Hall, Englewood Cliffs, New Jersey.
70. Gefen Y, Aharony A and Alexander S (1983): Anomalous diffusion on percolating clusters, *Phys. Rev. Lett.*, **50**, 77.
71. Gillan M.J (1986): A simulation model for hydrogen in palladium: I. Single particle dynamics, *J. Phys. C*, **19**, 6169.
72. Giona A.R, Giona M and Marrelli L (1992): Influence of pore–network topology on the reaction–diffusion kinetics in porous pellets, *Chem. Engng. Sci.*, **47**, 2623.

73. Giona M and Roman H.E (1992): A theory of transport phenomena in disordered systems, *Chem. Engng. Journal*, **49**, 1.
74. Gladden L.F (1993): Nuclear magnetic resonance studies of porous media, *Trans. IChemE*, **71**, 657.
75. Goldstein H (1981): *Classical Mechanics (2nd edition)*, Addison – Wesley, Reading.
76. Gorecki J and Gryko J (1989): Molecular dynamics simulation of a chemical reaction, *Comput. Phys. Commun.*, **54**, 245.
77. Grayson M and Eckroth D (1985): page 305, in volume 4, *Concise Encyclopedia of Chemical Technology*, Wiley, New York.
78. Gusev A.A, Arizzi S and Suter U.W (1993): Dynamics of light gases in rigid matrices of dense polymers, *J. Chem. Phys.*, **99**, 2221.
79. Gusev A.A and Suter U.W (1993): Dynamics of small molecules in dense polymers subject to thermal motion, *J. Chem. Phys.*, **99**.
80. Guyer R.A (1985): Diffusive motion on a fractal; $G_{nm}(t)$, *Phys. Rev. A*, **32**, 2324.
81. Hansen J.P (1986): Molecular – dynamics simulation of coulomb systems in two and three dimensions, in *Molecular – Dynamics Simulation of Statistical – Mechanical Systems*, North – Holland, Amsterdam.
82. Havlin S and Ben – Avraham D (1987): Diffusion in disordered media, *Adv. Phys.*, **36**, 695.
83. Havlin S and Bunde A (1991): *Fractals and Disordered Systems*, Springer – Verlag, Heidelberg.
84. Haynes Jr. H.W (1988): The experimental evaluation of catalyst effective diffusivity, *Catal. Rev. Sci. Eng.*, **30**, 563.
85. Heyes D.M (1992): Molecular dynamics simulations of liquid binary mixtures: Partial properties of mixing and transport coefficients, *J. Chem. Phys.*, **96**, 2217.

86. Hockney R.W (1970): The potential calculation and some applications, *Methods Comput. Phys.*, **9**, 136.
87. Hollewand M.P and Gladden L.F (1992a): Modelling of diffusion and reaction in porous catalysts using a random three – dimensional network model, *Chem. Engng. Sci.*, **47**, 1761.
88. Hollewand M.P and Gladden L.F (1992b): Representations of porous catalysts using random pore networks, *Chem. Engng. Sci.*, **47**, 2757.
89. Hoshen J and Kopelman R (1976): Percolation and cluster distribution. I. Cluster multiple labeling technique and critical concentration algorithm, *Phys. Rev. B*, **24**, 3438.
90. Hoover W.G (1985): Canonical dynamics: equilibrium phase – space distributions, *Phys. Rev. A*, **31**, 1695.
91. Hoover W.G, Ladd A.J.C and Moran B (1982): High – strain – rate plastic flow studied via nonequilibrium molecular dynamics, *Phys. Rev. Lett.*, **48**, 1818.
92. Jacobs D and Nakanishi H (1990): Autocorrelation functions for discrete random walks on disordered lattices, *Phys. Rev. A*, **41**, 706.
93. James C.P and Evans G.T (1987): Diffusion in the two – dimensional nonoverlapping Lorentz gas, *J. Chem. Phys.*, **87**, 4056.
94. Jerauld G.R, Hatfield J.C, Scriven L.E and Davis H.T (1984a): Percolation and conduction on Voronoi and triangular networks: a case study in topological disorder, *J. Phys. C*, **17**, 1519.
95. Jerauld G.R, Scriven L.E and Davis H.T (1984b): Percolation and conduction on the 3D Voronoi and regular networks: a second case study in topological disorder, *J. Phys. C*, **17**, 3429.
96. Johnson M.F and Stewart W.E (1965): Pore structure and gaseous diffusion in solid catalysts, *J. Catalysis*, **4**, 248.

97. Kapteijn F, Meijer R and Moulijn J.A (1992): Transient kinetic techniques for detailed insight in gas–solid reactions, *Energy Fuels*, **6**, 494.
98. Kara A and DePristo A.E (1988): Dynamics of dissociative chemisorption: N₂/W(110), *Surface Sci.*, **193**, 437.
99. Katz A.J and Thompson A.H (1987): Prediction of rock electrical conductivity from mercury injection measurements, *J. Geophys. Res.*, **92**, 599.
100. Kihara T and Ichimaru S (1978): *Intermolecular Forces*, John Wiley, Chichester.
101. Kirkpatrick S (1973): Percolation and conduction, *Rev. Mod. Phys.*, **45**, 574.
102. Kirkpatrick S, Gelatt Jr. C.D and Vecchi M. (1983): Optimization by simulated annealing, *Science*, **220**, 671.
103. Kubo R (1966): The fluctuation–dissipation theorem, *Rep. Prog. Phys.*, **29**, 255.
104. Kubo R, Toda M and Hashitsume N (1985): *Statistical Physics II: Nonequilibrium Statistical Physics*, Springer–Verlag, Berlin.
105. Lee C–Y and DePristo A.E (1986): Dissociation dynamics of H₂ on Ni(100), Ni(110), and Ni(111) surfaces, *J. Chem. Phys.*, **84**, 485.
106. Lim C, Tully J.C, Amirav A, Trevor P and Cardillo M.J (1987): Trajectory studies of hyperthermal Xe scattering from GaAs(110), *J. Chem. Phys.*, **87**, 1808.
107. Lizzio A.A, Jiang H, and Radovic L.R (1990): On the kinetics of carbon (char) gasification: Reconciling models with experiment, *Carbon*, **28**, 7.
108. López–Quintela M.A and Buján–Núñez M.C (1991): Computer simulation of partially diffusion–controlled reactions, *Chem. Phys.*, **157**, 307.
109. Lowe C.P and Masters A.J (1993): The long–time behavior of the velocity autocorrelation function in a Lorentz gas, *Physica A*, **195**, 149.
110. Maitland G.C, Rigby M, Smith B.E and Wakeham W.A (1981): *Intermolecular Forces: Their Origin and Determination*, Clarendon Press, Oxford.

111. McGreavy C, Andrade J.S and Rajagopal K (1992): Consistent evaluation of effective diffusion and reaction in pore networks, *Chem. Engng. Sci.*, **47**, 2751.
112. McQuarrie D.A (1976): *Statistical Mechanics*, Harper and Row, New York.
113. Melkote R.R and Jensen K.F (1989): Gas diffusion in random–fibre structures, *AIChE Journal*, **35**, 1942.
114. Memon M.K, Hockney R.W and Mitra S.K (1981): Molecular dynamics with constraints, *J. Comp. Phys.*, **43**, 345.
115. Millward G.R, Ramdas S and Thomas J.M (1985): On the direct imaging of offretite, cancrinite, chabazite and other related ABC–6 zeolites and their intergrowths, *Proc. Roy. Soc. London A*, **399**, 57.
116. Mori H (1965): Transport, collective motion, and Brownian motion, *Prog. Theor. Phys.*, **33**, 423.
117. Murrell J.N, Carter S, Farantos S.C, Huxley P and Varandas A.J.C (1984): *Molecular Potential Energy Functions*, John Wiley, Chirchester.
118. Muller–Plathe F (1992): Molecular dynamics simulation of gas transport in amorphous polypropylene, *J. Chem. Phys.*, **96**, 3200.
119. Murad S, Ravi P and Powles J.G (1993): A computer simulation study of fluids in model slit, tubular, and cubic micropores, *J. Chem. Phys.*, **98**, 9771.
120. Muralidhar R, Ramkrishna D, Nakanishi H and Jacobs D (1990): Anomalous diffusion: A dynamic perspective, *Physica A*, **167**, 539.
121. Muthukumar M (1982): Concentration dependence of diffusion controlled processes among static traps, *J. Phys. Chem.*, **76**, 2667.
122. Nakano Y and Evans J.W (1983): Monte Carlo simulation of diffusion of gases in a porous solid: Calculations for a new class of solids, *J. Chem. Phys.*, **78**, 2568.
123. Nicholson D and Parsonage N (1982): *Computer Simulation and the Statistical Mechanics of Adsorption*, Academic Press, New York.

124. Nosé S (1984): A unified formulation of the constant temperature molecular dynamics methods, *J. Chem. Phys.*, **81**, 511.
125. O'Shaughnessy B and Procaccia I (1985): Diffusion on fractals, *Phys. Rev. A*, **32**, 3073.
126. Page M and Lengsfeld III B.H (1991): Ab initio quantum chemistry for combustion, in *Numerical Approaches to Combustion Modelling*, AIAA.
127. Parrinello M (1992): *Ab initio* molecular dynamics, in *Molecular Dynamics Simulations*, Springer–Verlag, Berlin.
128. Pas M.F and Zwolinski B.J (1991): Computation of the transport coefficients of dense fluid neon, argon, krypton and xenon by molecular dynamics, *Mol. Phys.*, **73**, 471.
129. Persky A and Broida M (1984): Quasiclassical trajectory study of the reaction $O(^3P) + HCl \rightarrow OH + Cl$. The effects of vibrational excitation, rotational excitation, and isotopic substitution on the dynamics, *J. Chem. Phys.*, **81**, 4352.
130. Pierleoni C and Ryckaert J–P (1992): On the use of the Nosé–Hoover thermostat in the simulation of dynamic properties of a single chain molecule solvent, *Mol Phys*, **75**, 731.
131. Present R.D (1958): *Kinetic Theory of Gases*, McGraw–Hill, New York.
132. Price G.D, Wood I.G and Akporiaye D.E (1994): The prediction of zeolite structures, in *Modeling of Structure and Reactivity in Zeolites*, Academic Press, London.
133. Rammal R and Toulouse G (1983): Random walks on fractal structures and percolation clusters, *J. Physique Lett.*, **44**, L13.
134. Rastogi R.P, Das I and Pushkarna A (1991): Fractal–like kinetics in solid–gas reactions, *Chem. Phys. Lett.*, **186**, 1.
135. Reid R.C, Prausnitz J.M and Sherwood T.K (1988): *The Properties of Gases and Liquids*, McGraw–Hill, New York.

136. Reyes S and Jensen K.F (1985): Estimation of effective transport coefficients in porous solids based upon percolation concepts, *Chem. Engng. Sci.*, **40**, 1723.
137. Roman H.E, Bunde A and Havlin S (1989): Anomalous transport on random fractal structures: Stretched Gaussians, power-laws and logarithmic time dependences, *Ber. Bunsenges. Phys. Chem.*, **93**, 1205.
138. Ruthven D.M (1984): *Principles of Adsorption and Adsorption Processes*, John Wiley, New York.
139. Ryckaert J-P, Ciccotti G and Berendsen H.J.C (1977): Numerical integration of the Cartesian equations of motion of a system with constraints: molecular dynamics on n-alkanes, *J. Comp. Phys.*, **73**, 327.
140. Sahimi M (1987): Hydrodynamic dispersion near the percolation threshold: scaling and probability densities, *J. Phys. A*, **20**, L1293.
141. Sahimi M (1988): On the determination of transport properties of disordered systems, *Chem. Engng. Commun.*, **64**, 177.
142. Sahimi M (1990): Diffusion, absorption, and reaction in pillared clays. I. Rod-like molecules in a regular pore space, *J. Chem. Phys.*, **92**, 5107.
143. Sahimi M (1993): Flow phenomena in rocks: from continuum models to fractals, percolation, cellular automata, and simulated annealing, *Rev. Mod. Phys.*, **65**, 1393.
144. Sahimi M (1994): *Applications of Percolation Theory*, Taylor and Francis, London.
145. Sahimi M, Hughes B.D, Scriven L.E and Davis H.T (1983): Stochastic transport in disordered systems, *J. Chem. Phys.*, **78**, 6849.
146. Sahimi M, Gavalas G.R and Tsotsis T.T (1990): Statistical and continuum models of fluid-solid reactions in porous media, *Chem. Engng. Sci.*, **45**, 1443.
147. Sarmah S.K and Haynes Jr. H.W (1989): Effective diffusivity by pulse gas chromatography at elevated pressures, *AIChE Journal*, **35**, 1728.

148. Satterfield C.N (1970): *Mass Transfer in Heterogeneous Catalysis*, MIT Press, Cambridge, Massachusetts.
149. Satterfield C.N and Cadle P.J (1968): Diffusion in commercially manufactured pellet catalysts, *Ind. Engng. Chem. Proc. Des. Dev.*, **7**, 257.
150. Shah N and Ottino J.M (1986): Effective transport properties of disordered multi-phase composites: Application of real-space renormalization group theory, *Chem. Engng. Sci.*, **41**, 283.
151. Shah N and Ottino J.M (1987): Transport and reaction in evolving, disordered composites—I. Gasification of porous solids, *Chem. Engng. Sci.*, **42**, 63.
152. Simkin B.Y and Sheikhet I.I (1995): *Quantum Chemical and Statistical Theory of Solutions: A Computational Approach*, Ellis Horwood, London.
153. Smith D.H (1977): Computer-assisted structure elucidation, *Am. Chem. Soc. Symp. Series*, **54**.
154. Sotirchos S.V and Burganos V.N (1988): Analysis of multicomponent diffusion in pore networks, *AIChE Journal*, **34**, 1106.
155. Sotirchos S.V (1989): Multicomponent diffusion and convection in capillary structures, *AIChE Journal*, **35**, 1953.
156. Stauffer D and Aharony A (1992): *Introduction to Percolation Theory (2nd ed.)*, Taylor & Francis, London.
157. Steele W.A (1974): *The Interaction of Gases with Solid Surfaces*, Pergamon Press, Oxford.
158. Terasaki O, Thomas J.M and Ramdas S (1984): A new type of stacking fault in zeolites, *J. Chem. Soc. Commun.*, **4**, 216.
159. Theodorou D.N and Suter U.W (1985): Detailed molecular structure of a vinyl polymer glass, *Macromolecules*, **18**, 1467.

160. Tissen J.T.W.M and Janssen G.J.M (1990): Molecular–dynamics simulation of molten alkali carbonates, *Mol. Phys.*, **71**, 413.
161. Tomadakis M.M and Sotirchos S.V (1991a): Effective Knudsen diffusivities in structures of randomly overlapping fibres, *AIChE Journal*, **37**, 74.
162. Tomadakis M.M and Sotirchos S.V (1991b): Knudsen diffusivities and properties of structures of unidirectional fibres, *AIChE Journal*, **37**, 1175.
163. Tomadakis M.M and Sotirchos S.V (1993a): Ordinary and transition regime diffusion in random fiber structures, *AIChE Journal*, **39**, 397.
164. Tomadakis M.M and Sotirchos S.V (1993b): Effective diffusivities and conductivities of random dispersions of nonoverlapping and partially overlapping unidirectional fibers, *J. Chem. Phys.*, **99**, 9820.
165. Toukubo K, Nakanishi K and Watanabe N (1977): Molecular dynamics studies of Lennard–Jones liquid mixtures. II. Mass and size dependence in the behavior of one different particle, *J. Chem. Phys.*, **67**, 4162.
166. Tuckerman M.E and Parrinello M (1994a): Integrating the Car–Parrinello equations. I. Basic integration techniques, *J. Phys. Chem.*, **101**, 1302.
167. Tuckerman M.E and Parrinello M (1994b): Integrating the Car–Parrinello equations. II. Multiple time scale techniques, *J. Phys. Chem.*, **101**, 1316.
168. Tully J.C (1980a): Theories of the dynamics of inelastic and reactive processes at surfaces, *Ann. Rev. Phys. Chem.*, **31**, 319.
169. Tully J.C (1980b): Dynamics of gas–surface interactions: 3D generalized Langevin model applied to fcc and bcc surfaces, *J. Chem. Phys.*, **73**, 1975.
170. Tully J.C (1981): Dynamics of chemical processes at surfaces, *Acc. Chem. Res.*, **14**, 188.
171. Valix M.G, Trimm D.L, Smith I.W and Harris D.J (1992): Mass transfer effects in coal combustion, *Chem. Engng. Sci.*, **47**, 1607.

172. Verlet L (1967): Computer 'experiments' on classical fluids. I. Thermodynamical properties of Lennard–Jones molecules, *Phys. Rev.*, **159**, 98.
173. Wakao N and Smith J.M (1962): Diffusion in catalyst pellets, *Chem. Engng. Sci.*, **17**, 825.
174. Wang C.T and Smith J.M (1983): Tortuosity factors for diffusion in catalyst pellets, *AIChE Journal*, **29**, 132.
175. Winterfeld P.H (1981): *Percolation and Conduction Phenomena in Disordered Composite Media*, PhD Thesis, University of Minnesota.
176. Wolken Jr. G (1978): Model potential for reactions with solid surfaces: $\text{H}_2 + \text{Fe}(001)$, *J. Chem. Phys.*, **68**, 4338.
177. Woodcock L.V (1971): Isothermal molecular dynamics calculations for liquid salts, *Chem. Phys. Lett.*, **10**, 257.
178. Yashonath S (1991): A molecular dynamics study of cage–to–cage migration in sodium Y zeolite: role of surface–mediated diffusion, *J. Phys. Chem*, **95**, 5877.
179. Yashonath S, Demontis P and Klein M.L (1991): Temperature and concentration dependence of adsorption properties of methane in NaY: a molecular dynamics study, *J. Phys. Chem*, **95**, 5881.
180. Yip S (1986): Atomistic simulations in materials science, in *Molecular–Dynamics Simulation of Statistical–Mechanical Systems*, North–Holland, Amsterdam.
181. Zhang L and Seaton N.A (1994): The application of continuum equations to diffusion and reaction in pore networks, *Chem. Engng. Sci.*, **49**, 41.
182. Zwanzig R (1965): Time–correlation functions and transport coefficients in statistical mechanics, *Ann. Rev. Phys. Chem.*, **16**, 67.

CHAPTER 4

CONCLUSIONS AND PROSPECTS

4.1 CONCLUSIONS

Chapter 2 details a study in which a newly developed advanced single particle FBC model was successfully used to resolve several issues which have defied resolution by experiment alone. The newly developed model, which is perhaps the most advanced used to date, is based upon a transient, continuum, multicomponent mass and heat conservation formulation for both the porous char and surrounding boundary layer. Both the homogeneous $\text{CO}-\text{O}_2$, and heterogeneous $\text{C}-\text{O}_2$ and $\text{C}-\text{CO}_2$ reactions are included, with the primary CO/CO_2 product ratio being given by the Arrhenius expression of Tognotti et al. (1990). The mass fluxes are defined via the Dusty-gas model [Jackson, 1977], and percolation concepts [Stauffer and Aharony, 1992] are used to describe the effect that pore evolution has on char effective transport and reaction properties [Sahimi et al., 1990; Sahimi, 1994]. The model was solved using advanced finite element methods and iterative equation solvers that are particularly suited to distributed memory parallel architectures and vector processors [Winget and Hughes, 1985; Zienkiewicz and Zhu 1992; Shakib et al., 1989].

The primary conclusions reached are (a comprehensive summary of the results and conclusion drawn may be found in §2.3.6):

- Homogeneous reaction does occur within the boundary layer of a char *stationary* within an incipient fluidized bed, whilst it is also expected to occur for a *stationary* char resident within the emulsion phase of a bubbling fluidized bed with the extent of reaction diminishing as superficial gas velocity increases.
- The particle related CO/CO_2 product ratio can vary with temperature in a number of different ways depending upon various factors: (1) if boundary layer reaction is negligible (eg: when superficial gas velocity is high), then the ratio simply increases

with temperature; (2) if boundary layer reaction is significant and the char is small, then the ratio increases with temperature to a maximum where it then decreases with any further increase in temperature; and (3) if boundary layer reaction is significant and the char is both large and porous, then the ratio follows that found by Linjewile (1993) in his recent experiments. This last scenario arises from the interplay between the $\text{CO}-\text{O}_2$, $\text{C}-\text{O}_2$, and $\text{C}-\text{CO}_2$ reactions.

- It is tentatively postulated that the CO/CO_2 product ratio variation with char particle size can be either an increasing or decreasing function depending upon a host of factors in the same way that the ratio varies with temperature.
- The CO_2 gasification reaction can contribute to significant char conversion at higher FBC temperatures if the char is large (ie: the internal area available for CO_2 reaction is large).
- Peripheral disintegration can have a significant influence, especially at lower FBC temperatures, but the significance is strongly affected by the char's initial porosity, and the porosity at which the solid is considered to become unconsolidated (this is affected by char makeup, and FB forces on the char).

It was also found that boundary layer reaction affects the heat transfer coefficient, and that this has important consequences with regards the way the coefficient is determined and the correlations used to model it.

Chapter 3 details a new discrete technique for the study of diffusion within porous solids at the microscopic level. The molecular dynamic (MD) [Allen and Tildesley, 1989] and percolation [Stauffer and Aharony, 1992] basis of the new technique means many of the problems associated with the more conventional approaches [Sahimi et al., 1990] may be overcome, whilst it also offers an excellent basis for determining reactivity parameters and transport coefficients other than the diffusivity. By implementing the new technique on a vector supercomputer, it was used to study diffusion within two different gas/porous—graphite systems that may be considered prototypical of real combustion systems [Biggs and Agarwal, 1992, 1994]. Although conclusions of more fundamental

significance were also drawn (refer to §3.3.3.6 for a comprehensive summary), results and conclusions of particular concern to the coal combustion scientist are:

- The effective diffusion coefficient of a gas within a porous solid increases with temperature in a manner similar to a liquid in the bulk phase. This means that the ratio of diffusivities often used to describe the diffusivity of a gas within a porous solid is a function of temperature.
- The tortuosity, as normally defined, is temperature dependent.

4.2 PROSPECTS

4.2.1 Immediate Prospects

Throughout the text of Chapters 2 and 3, matters requiring further attention were highlighted. Those that may be dealt with in the short term are summarized here:

- A literature review (§2.2.1) has shown that despite its wide adoption, the isothermal assumption for a large char particle burning under FBC conditions is questionable. Although the results of the single particle study reported here did not reveal any real degree of non–isothermality, we were able to hypothesize conditions under which a char would be non–isothermal. A modelling study will be undertaken in the near future to seek confirmation of the hypothesized conditions, and the likely effect of ignoring non–isothermality under these conditions.
- It was found that the simplified, homogeneous film, shrinking core model used by Linjewile (1993) could not predict the high temperature minimum seen in the CO/CO₂ product ratio vs particle temperature curve experimentally determined by him because the overall reaction rate for the CO₂ gasification reaction was too small relative to that of the C–O₂ reaction. To test this, a study shall be undertaken in the near future in which the rate parameters of the simple model will be judiciously adjusted in an attempt to reproduce the experimentally observed CO/CO₂ ratio behaviour.

- Although the study of Chapter 3 revealed many interesting behaviors, the accuracy of the MD technique and the influence of finite size effects are unknown. By porting the original vectorized code to the CM-5, these concerns will be investigated in the near future.
- In order to explore the suitability of Fick's law for describing diffusion of a fluid within a porous solid, the average probability, $\langle P(r, t) \rangle$, that a diffusing particle is at a position $\mathbf{r}$ at a time t is often considered where $r = |\mathbf{r}|$ [eg: Havlin and Ben-Avraham, 1987]. Using the CM-5 code, this distribution for a fluid within a percolation system shall be investigated in the near future as a function of porosity and temperature.
- If Fick's law is not appropriate, then the diffusion process may be described by a non-classical diffusion equation; see §2.4.1. One particular theory that appears promising is that of Cushman (1991); equation (2-66). There are, however, many outstanding issues associated with application of this equation to real porous solids including how to determine the frequency and wavelength dependent diffusion coefficient. The MD approach of Chapter 3 and its nonequilibrium variant [Evans and Morriss, 1984, 1990] are excellent tools for exploring this and related issues. The CM-5 code will also be used to undertake this work in relation to percolation systems in the not too-distant future.

4.2.2 Longer Term Prospects

Whilst "simple" models such as that used by Linjewile (1993) will continue to be valuable engineering tools, it is anticipated that if we are to gain greater insight into many coal combustion phenomena, we will have to rely more and more upon detailed mathematical models that are solved on supercomputers. Both studies presented in this dissertation clearly demonstrate the value of this approach. The study reported in Chapter 2 is of an unprecedented scale (over 100 different FBC conditions considered), and it successfully addresses a number of key issues that have defied several past experimental attempts to resolve them. The new method of Chapter 3 revealed many

important behaviors that would otherwise be unobservable, and it offers an excellent platform for determining reactivity parameters and other transport coefficients.

Despite the many positive aspects of the work presented here, the concluding remarks of each chapter clearly show that obtaining quantitative results from either single particle models or the new technique of Chapter 3 will only be possible if we are able to: (1) gather extensive fundamental data on coal and how it behaves in an oxidizing and/or high temperature environment; (2) express this fundamental data in a form such that it is representative of the coal of interest, and useful for modelling purposes; and (3) develop models that represent the highly complex nature of the coal, and the processes that are going on within it during conversion. Although each of these are obviously non-trivial in their own right, the extensive discussions of §§2.4 and 3.4 show that many recent advances in both experiment and modelling offer hope.

In addition to avoiding the continuum and smooth field approximations, continuum percolation models such as that illustrated in Figure 1.1 offer a means by which we may naturally include the effect that the non-homogeneous structure of coal has on reaction, disintegration and transport phenomena. Each block of the tessellation would be identified with part of a maceral (or its derived feature in the char), mineral inclusion or pore. At a finer scale, the blocks may be associated with macromolecules, or even portions of these. In order to generate discrete models of coal or char, we may use quantitative microscopy techniques down to the μm level in conjunction with the reconstruction methods of Adler and others [Adler, 1992]; see §2.4.3. Below the μm level (where we are often looking at individual coal macerals or their derived features in the char) we may use the methods of Faulon and co-workers to generate a molecular structure as outlined in §3.4.1 which can then be utilized to define the pore space for a given species via the method of Gusev et al. (1993); see §2.4.3. The molecular structures of Faulon and co-workers may also be used in conjunction with the molecular dynamic technique of Chapter 3 as detailed in §3.4.1.

As solution of the continuum equations of reaction and diffusion on these discrete single

particle models is unlikely ever to be possible, alternatives must be sought. The most promising approach is lattice gas automata (§2.4.2) which has many features to recommend it: (1) the codes are extremely simple; (2) its vector and highly parallel nature means the scale of problems that may be solved will increase directly in line with computer technology; (3) it avoids round-off errors, and incurs no stability requirements; and (4) non-classical phenomena are revealed naturally. At present, we may explicitly simulate over a length scale range of 10^3 in 2D on a modest supercomputer (ie: 32 node CM-5), with this range increasing at a rate of more than one decade every 10 years.

In recent years, likely reaction paths, reactive surface area, effects of various inorganics on reaction rates, and reaction rate parameters have been determined via transient kinetic techniques [Kapteijn et al., 1992]. These studies are now being supported by MC simulations at the molecular level [Kyotani et al., 1993]. It is anticipated that once interaction parameters have been determined and/or sufficient computer power is available, MD methods will also be useful tools alongside transient kinetic techniques for studying reaction within coal and char; see §3.4.2 for a full discussion.

REFERENCES

1. Adler P.M (1992): *Porous Media: Geometry and Transports*, Butterworth–Heinemann, Boston.
2. Allen M.P and Tildesley D.J (1989): *Computer Simulation of Liquids*, Oxford University Press, Oxford.
3. Biggs M and Agarwal P (1992): Mass diffusion of atomic fluids in random micropore spaces using equilibrium molecular dynamics, *Phys. Rev. A*, **46**, 3312.
4. Biggs M and Agarwal P (1994): Mass diffusion of diatomic fluids in random micropore spaces using equilibrium molecular dynamics, *Phys. Rev. E*, **49**, 531.
5. Cushman J.H (1991): On diffusion in fractal porous media, *Water Resour. Res.*, **27**, 643.
6. Evans D.J and Morriss G.P (1984): Non–Newtonian molecular dynamics, *Comput. Phys. Rep.*, **1**, 297.
7. Evans D.J and Morriss G.P (1990): *Statistical Mechanics of Nonequilibrium Liquids*, Academic Press, London.
8. Gusev A.A, Arizzi S and Suter U.W (1993): Dynamics of light gases in rigid matrices of dense polymers, *J. Chem. Phys.*, **99**, 2221.
9. Havlin S and Ben–Avraham D (1987): Diffusion in disordered media, *Adv. Phys.*, **36**, 695.
10. Jackson R (1977): *Transport in Porous Catalysts*, Elsevier, Amsterdam.
11. Kapteijn F, Meijer R and Moulijn J.A (1992): Transient kinetic techniques for detailed insight in gas–solid reactions, *Energy Fuels*, **6**, 494.
12. Kyotani T, Leon y Leon C.A and Radovic L.R (1993): Simulation of carbon gasification kinetics using an edge recession model, *AIChE Journal*, **39**, 1178.
13. Linjewile T.M (1993): *Temperature of Burning Carbonaceous Particles in a Fluidized–bed Combustor*, Ph.D Thesis, University of Adelaide.

14. Sahimi M (1994): *Applications of Percolation Theory*, Taylor and Francis, London.
15. Sahimi M, Gavalas G.R and Tsotsis T.T (1990): Statistical and continuum models of fluid–solid reactions in porous media, *Chem. Engng. Sci.*, **45**, 1443.
16. Shakib F, Hughes T.J.R and Johan Z (1989): A multi–element group preconditioned GMRES algorithm for nonsymmetric systems arising in finite element analysis, *Comp. Meth. App. Mech. Engng.*, **75**, 1989.
17. Stauffer D and Aharony A (1992): *Introduction to Percolation Theory* (2nd ed.), Taylor & Francis, London.
18. Tognotti L, Longwell J.P and Sarofim A.F (1990): The products of the high temperature oxidation of a single char particle in an electrodynamic balance, 23rd *Symposium (International) on Combustion*, The Combustion Institute, Pittsburgh, 1207.
19. Winget J.M and Hughes T.J.R (1985): Solution algorithms for non–linear transient heat conduction analysis employing element–by–element iterative strategies, *Comp. Meth. App. Mech. Engng.*, **52**, 711.
20. Zienkiewicz O.C and Zhu J.Z (1992): The superconvergent patch recovery and a posteriori error estimates. Part I. The recovery technique, *Int. J. Num. Meth. Engng.*, **33**, 1331.