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The Theory of Dissipative
Processes in Gases

by

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NOTE:- The author of the thesis has published one article during the course of the work. This article was submitted for publication on 28th October, 1963, and appeared in the Journal of Chemical Physics 40, 3166 (1964). A further note on this work by the author has been accepted for publication by the Journal and will appear under "Comments on".

ABSTRACT.

A special ensemble, called a fluctuation ensemble, is discussed and the corresponding phase space distribution function is rigorously defined. The special subensemble is obtained by choosing, from the grand ensemble, at a specified time, $t=0$ say, those configurations in which a molecule is at a given point \underline{x}_1 , moving with a specified velocity \underline{v}_1 . In a dilute gas, it is shown that the fluctuation ensemble contains configurations which are realized when a molecule is injected or allowed to diffuse into a gas originally, i.e. at time $t=0$, in equilibrium. The one particle velocity distribution function corresponding to the special subensemble is rigorously defined, and is divided into two separate contributions - one associated with the motion of the distinguished molecule, and the other with the rest. A general subensemble in which the distinguished molecule has a specified distribution at time $t=0$ is also discussed, and the one particle velocity distribution functions rigorously defined. These functions are then connected with those of the special sub-ensemble.

The distribution functions are obtained for a general subensemble in which the velocity of the distinguished molecule is specified at time $t=0$. The velocity distribution functions associated with the motion of this distinguished molecule are obtained for a general molecular model from forward and backward Boltzmann equations, and, in

particular, for Maxwellian molecules. The distribution function associated with the motion of the other molecules for the Maxwellian molecular model is also calculated.

The Kubo-type transport coefficients of thermal conduction and viscosity are evaluated, from the above distribution functions, for Maxwellian molecules forming a dilute gas, using a method developed by Green, and, as expected, the values obtained are those given by the Chapman-Enskog method. The exact mean-free-path coefficients are obtained by using the distribution function associated with the motion of the distinguished molecule, and are compared with the exact transport coefficients as given by the Kubo method.

The corresponding general and special subensembles of the grand ensemble of non-equilibrium are discussed, and the corresponding distribution functions rigorously defined. It is shown, as in the equilibrium case, that in dilute gases this special subensemble is equivalent to considering a system in which a molecule is distinguished at time $t=0$ by its position and velocity, and is surrounded by a gas in a "steady" state of non-equilibrium at time $t=0$. The distribution functions, corresponding to those of the equilibrium case, are found using forward and backward Boltzmann equations for a general molecular model, and, in particular, discussed for Maxwellian molecules. An experimental procedure which involves the injection or

diffusion of radioactive particles into a gas, is suggested as a method of confirming the results.

The distribution functions are used to define various mean accelerations in a gas, in both equilibrium and non-equilibrium, as suggested by the statistical theory of fluids developed by Kirkwood. These mean accelerations are evaluated for Maxwellian molecules. In the equilibrium case, a "forward" mean acceleration is shown to be equivalent to that defined by O'Toole and Dahler. The equivalence of all the definitions of mean accelerations involved in kinetic theory is precisely discussed, and it is shown rigorously that the definition used in the thesis, and so by O'Toole and Dahler, is not equivalent to that defined by Kirkwood.