

The University of Adelaide  
School of Chemical Engineering

Molecular Dynamics Study of Peptide  
Adsorption at Liquid/Solid Interfaces

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## ABSTRACT

Biomolecule adsorption at liquid/solid interfaces is ubiquitous in nature. The phenomenon also arises in a diverse range of traditional scientific and engineering applications; such as the physiological response to medical implants or the bio-fouling of process equipment. The same behaviour may also hold the key to the creation of self-assembling hierarchical materials for applications in the emerging field of bionanotechnology. A detailed understanding of biomolecule adsorption is essential to elucidating the behaviour of natural systems and realizing the technological potential of the process. Due to the difficulty in investigating the adsorption process experimentally molecular simulation is finding increasing application in the study of this phenomenon on a molecular scale. Molecular dynamics (MD) is a simulation protocol that is widely employed in study of biomolecules. This thesis reports the application of MD simulations to the adsorption of experimentally identified solid binding peptides at their targeted liquid/solid interfaces. In the first body of work reported here, the adsorption of gold and platinum binding peptides at their respective water/solid interfaces is elucidated in detail at the molecular level to propose an adsorption mechanism for peptide adsorption at strongly interacting liquid/solid interfaces. In a second study, the mechanism is extended to moderately interacting interfaces by considering adsorption of a graphite binding peptide at the water/graphite interface and a generalised model of peptide adsorption at liquid/solid interfaces. Attention is then given to quantifying the adsorption propensity through two routes. The first is *via* the free energy of adsorption, where it is demonstrated that a non-equilibrium MD method is able to predict the experimentally observed adsorption propensity for a series of graphite binding peptides. Finally, a more computationally efficient method for predicting the relative adsorption propensity of peptides based on the peptide-surface interaction energy is described. The parameter is shown to correlate well with the free energy of adsorption and is capable of ranking peptides in terms of binding propensity in line with experimental results.

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## DECLARATION

I certify that this work contains no material which has been accepted for the award of any other degree or diploma in my name, in any 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. In addition, I certify that no part of this work will, in the future, be used in a submission in my name, for any other degree or diploma in any university or other tertiary institution without the prior approval of the University of Adelaide and where applicable, any partner institution responsible for the joint-award of this degree.

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## LIST OF PUBLICATION PRODUCED FROM THIS THESIS

Chapter 3: M. J. Penna, M. Mijajlovic, M. J. Biggs, “Molecular-level understanding of protein adsorption at the interface between water and a strongly interacting uncharged solid surface.” *J. Am. Chem. Soc.*, **2014**, 136, 5323-5331 (Cover Article, ACS Editor’s Choice, JACS Spotlight).

Chapter 4: M. J. Penna, M. Mijajlovic, C. Tamerler, M. J. Biggs, “Molecular-level understanding of the adsorption mechanism of a graphite-binding peptide at the graphite/water interface.” *Soft Matter*, **2015**, 26, 5192-5203. (Cover Article).

Chapter 5: M. J. Penna, M. Mijajlovic, C. Tamerler, M. J. Biggs, “Free energies of adsorption of peptides at liquid/solid interfaces *via* nonequilibrium molecular dynamics: Semi quantitative comparison with experiment.” submitted to *Langmuir*.

Chapter 6: M. J. Penna, M. Mijajlovic, C. Tamerler, M. J. Biggs, “Prediction of relative peptide adsorption propensity using molecular dynamics.” submitted to *ACS Applied Materials and Interfaces*.

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