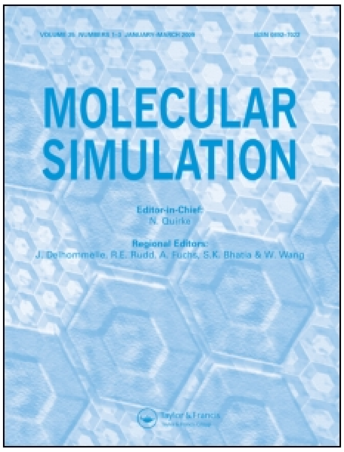

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Some Notes on David Nicholson's Contributions to Modelling Adsorption

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SOME NOTES ON DAVID NICHOLSON'S CONTRIBUTIONS TO MODELLING ADSORPTION

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During his career David has built up a very large number of scientific contacts throughout the world. Many of these became friends and collaborators. Imperial College was, of course, a good place to start from: R.M. Barrer was from New Zealand and John Petropoulos from Greece. Subsequently, he collaborated with scientists from other European Union countries, especially from France and Germany as well as more researchers from Greece. He also made many contacts in the US. A very important example was the sabbatical he had with W.A. Steele at Penn State, where he made his first big incursion into intermolecular forces. He also had very useful exchanges of visits with K.E. Gubbins, which led to joint work. More recently he developed working relationships with scientists from Japan and from South Korea. The scientific value of these contacts may be gauged from the large number of his publications, which involve researchers from these countries as co-authors. However, I am sure the readiness with which overseas researchers participated was in part also due to the friendly and helpful manner with which David received them here.

His early work at Imperial College (with R.M. Barrer and R. Ash) was on transient gas flow through single capillaries, and took account of slip flow and of adsorption effects (1963) [1]. It involved both experimental and theoretical work, and gave him an interest in such topics, which has remained until this day. It also started a long and fruitful collaboration with John Petropoulos (and subsequently with other members of the Greek group), when they considered two-phase flow and sorption–desorption hysteresis (1968) [2] and went on to consider three-dimensional networks of pores with unequal radii. This work was of interest industrially as a way of determining the pore size distribution and structure of porous solids.

Main-frame computers were by now reasonably accessible, and David was keen to use them for studies of physisorption. Previously, Grand Canonical Ensemble Monte Carlo (GCEMC) simulations of chemisorption, involving only molecules restricted to monolayer lattice sites, had been done by others. In collaboration with L.A. Rowley and N.G. Parsonage a GCEMC method suitable for a non-uniform three-dimensional system [3,4] was developed. The first GCEMC method of any kind had been reported by Norman and Filinov in the USSR. The Imperial College program was applied to Lennard–Jones argon on a continuum graphite surface and reproduced many of the isotherm and isosteric heat features which had been previously found by experimentalists and attributed to defects (1976). At this stage it was thought that in order to make further progress it would probably be necessary obtain better intermolecular potentials. For the graphite surface a graphite/fluid potential due to W.A. Steele, which took account of the symmetry of the graphite c-plane was adopted. Surprisingly, it was found that this change led to less good agreement for the adsorption isotherm than had been obtained using the previous simple 9-3 potential (1977) [5].

With the introduction of models with structured walls the possibility that the adsorbed layer would be either commensurate or incommensurate with the substrate arose. According to the substrate and the adsorbate either type was found to occur experimentally on single surfaces. He compared the behaviour of argon and nitrogen, which adsorb on graphite in the incommensurate and commensurate manner, respectively. For argon it was easily possible to obtain a simple hysteresis "loop", whereas the evidence for a "loop" was very much weaker with nitrogen as the adsorbate [6].

At this stage he also started to make more use of molecular dynamics. With T. Demi he used equilibrium molecular dynamics to compute the self-diffusion rate in a model micropore system which resembled linked zeolite cages (1991) [7]. Subsequently, he (with R. Cracknell and N. Quirke, 1995) employed non-equilibrium molecular dynamics in making direct molecular dynamics simulations down a chemical potential gradient, for which the flux had both cooperative viscous and purely diffusive components. This procedure uses both stochastic and dynamic steps. In spite of the chemical potential gradient being extremely high (much higher than is likely to be encountered) linearity is found between flux and gradient [8].

A further development of the GCEMC technique was that of "rotational insertion bias", which was a considerable advance towards overcoming of the problem of the very low acceptancy rate for the insertion of non-spherical particles. This technique was first used on the simulation of water and subsequently for lamellar bilayers involving nonionic surfactants (with Cracknell and Parsonage, 1992) [9].

With the great industrial interest in possible new processes for the separation of gases, he (with N. Quirke) was soon extending his MD studies into the use of activated carbons for the binary mixtures of simple hydrocarbons (1993). Again, he (with S. Tennison and R. Cracknell, 1996) [10] and with K. Gubbins (1996) [11] studied adsorption and its possible selectivity for mixtures of carbon dioxide with methane and nitrogen and with methane, respectively.

The newly synthesised zeolite silicalite and some related AlPO4 materials and their adsorption properties also attracted his attention (with R. Pellenq and A. Boutin, 1994–95). In the course of this work it was necessary to obtain interatomic potentials for the constituent atoms or ions. There had always been a major problem in the calculation of the energies of zeolite structures and of adsorption systems involving them arising from the value, which should be used for the polarisability of the oxygen ions. Widely different estimates for the polarisability had been made according to the partial charge, which was assumed to reside on the ions. A new method of determining the polarisability of ions in their actual environment had been recently developed by Moretti, based on Auger-electron spectroscopic data. Pellenq and Nicholson used this method to obtain the polarisabilities for O ions in 12 common, important zeolites, confirming the wide range of values for the polarisability. Interestingly, when such polarisability values were inserted in a "state of the art" potential which they had previously proposed, predictions of the adsorption isotherm of argon on silicalite at 77 K, for which a "stepped" curve is found, their calculated results agreed well with experiment below the "step", but not above the "step" (1993) [12,13].

Recently in collaboration with Gale and others he has studied the energetics of possible calcium ion positions in chabazite with low Al/Si ratios. The problem of the potential functions required for this work was solved by high level *ab-initio* computations. The calcium ion positions found to be optimum were in good agreement with the corresponding X-ray diffraction results (with J. Gale and T. Grey, 1999) [14].

Carbon nanotubes have also attracted attention. Adsorption in these "tubes" had previously been studied by K. Gubbins (1995), and it is now intended to study flow of fluid through the tubes. As a preliminary for this work their phonon spectra has recently been calculated (with V. Sokhan and N. Quirke, 2000) [15].

If I were to pick out one characteristic of his work it would be the care in choosing the potentials. In many cases the time he devoted to this process would be comparable to that needed for the actual simulations. This has probably been an important contributory factor to the high success rate he has undoubtedly had in his work.

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