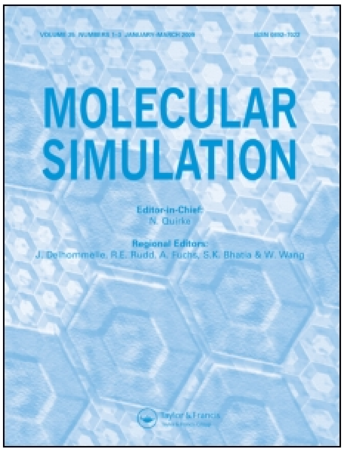

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A PIONEER IN THE STUDY OF POROUS MATERIALS: A SHORT APPRECIATION OF THE WORK OF DAVID NICHOLSON

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David Nicholson's long-standing interest in the properties of porous materials appears to date back to his PhD work on the thermal decomposition of oxalates, which he undertook at Salford with the late David Dollimore. He evidently saw the opportunity to bring some mathematical rigour to bear on this rather messy area of research by making one of the first attempts to model the relationship between the development of surface area and the kinetics of thermal decomposition [1].

Nicholson's introduction to the transport of gases through porous media came with his appointment to a BP post-doctoral fellowship at Imperial College, London. His early work with Richard Barrer [2] was concerned *inter alia* with the Knudsen flow (molecular streaming) regime. Particular aspects discussed at this stage included the properties of single capillaries and the effect of the length-to-width ratio on the Knudsen minimum. At this time, there was also a growing awareness of the importance of "surface flow", which Barrer and his co-workers had included as a component in their formalised treatment of the total flux.

There followed the highly successful collaboration [3,4] on gas permeability and network modelling with John Petropoulos and others at the Democritos Nuclear Research Centre, Athens. Nicholson and Petropoulos [5] used a rather general approach to calculate molecular trajectories by solving the equations of motion for molecules travelling in a potential field within slits and cylindrical pores. The flux was then obtained by statistically averaging the trajectories over momentum and space co-ordinates, cosine law reflection being assumed. This method gave the required Knudsen value for an infinitely repulsive wall, whereas the introduction of an attractive component resulted in the flux passing through a temperature minimum. It was concluded that simple Knudsen flow rarely occurs in real porous media. Various capillary network models were proposed by Nicholson and Petropoulos [4] to allow the effects of changing the pore size and connectivity and the role of capillary condensation to be taken into account [6]. Modelling the network properties was a demanding task [7] and it was fortunate that improved computing facilities were then beginning to become available.

Another timely development was David's close collaboration with Neville Parsonage. No doubt, other contributors to this *festschrift* will draw attention to the pioneering work of Nicholson and Parsonage in the computer simulation of adsorption systems [8]. Here, it is appropriate to refer to the simulation of molecular pore filling and transport through model pore structures. In this area, Nicholson has played a leading role by modelling the behaviour of fluids in micropores (pore width $<\sim 2\,\mathrm{nm}$). For example, his grand ensemble Monte Carlo simulation [9] of argon and nitrogen adsorption in model microporous graphite has provided new evidence for a cooperative mechanism of micropore filling. Also, in their simulation study of nitrogen adsorption in slit-shaped MgO pores, Nicholson *et al.* [10] obtained a wide variety of adsorption isotherms and heat curves, which were dependent on the slit width. There was clear evidence for the contribution of the quadrupole–quadrupole interactions between nitrogen molecules adsorbed on opposite walls to the filling of the larger micropores (i.e. supermicropore filling). Furthermore, Nicholson's work has drawn attention to the extreme sensitivity of the computed isotherms to small changes in the interaction potentials.

It is well known that adsorption isotherms are much easier to determine experimentally than differential enthalpies of adsorption. On the other hand, it is generally accepted that valuable information concerning the mechanisms of adsorption can be obtained by studying the energetics of adsorption. This approach was adopted by Nicholson and Quirke [11] in their recent simulation study of the role of the isosteric enthalpy, q_{st}, in micropore characterisation. It had already been found by Nicholson [12] that thermal disordering of a surface oxide structure appeared to have only a minor effect on the q_{st}—density curves for methane adsorption. It was tentatively concluded that surface structural disorder could not by itself account for the very steep decline in q_{st} which is often found experimentally. However, when the structural heterogeneity was modelled by introducing a distribution of slit pore widths, the simulated enthalpy curves were quite similar to those obtained experimentally.

In the recent work of Nicholson and Quirke [11], the role of the micropore size distribution in determining composite adsorption enthalpies and isotherms was explored in some detail. By skewing the distribution to include, or exclude, ultramicropores (i.e. pores of molecular dimensions), it was found that the enthalpy curves exhibited useful structural features, whereas the isotherms were all essentially Type I in the IUPAC classification. It was pointed out that the use of simulation to separate the adsorbate–adsorbate and adsorbate–adsorbent interactions is of particular value in the application of the energetics approach for studying physisorption mechanisms.

Mercury porosimetry has been widely used for many years for determining the pore size distribution of catalysts and other porous materials. It was already known that the technique was not entirely reliable, but before 1990, few attempts had been made to model the movement of mercury into and out of three-dimensional networks. With the support of the ICI Materials Group, a systematic computer modelling study was undertaken by Nicholson and others [12]. This work provided a critical appraisal of the experimental porosimetry data and revealed that the shape and location of a single intrusion curve does not by itself allow a reliable estimate to be made of the pore size distribution. However, it was possible to identify and interpret certain distinctive intrusion–extrusion features. The successful outcome of this project was to a large extent due to David's involvement and it illustrates the harmonious way in which industrial and academic scientists can collaborate.

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