

## General Discussion

**Dr. R. M. Lynden-Bell** (*University of Cambridge*) asked: Has Dr. Woodcock any explanation for the remarkable difference between  $\eta_{\parallel}^s$  near the walls with hard and soft walls?

**Dr. L. V. Woodcock** (*Bradford University*) replied:  $\eta_{\parallel}^s(z)$  is the shear viscosity profile for flow in the transverse direction; it corresponds to transfer of momentum in the longitudinal direction or, alternatively, to a parallel stress flux. The foremost observation about the shear viscosity profiles for both hard and cohesive walls is that the effect of a smooth wall on the viscosity profile is rather feeble whatever the wall potential. Whether the effective shear viscosity increases or decreases in the immediate vicinity of the wall seems to depend in a rather obscure way on a subtle interplay between enhanced stress fluctuations and a less rapid decay of the time correlation, which, however, may have a negative tail. The equilibrium stress fluctuations are roughly the same for both wall-particle potentials. The effect of 'switching on' the cohesive wall-molecule potential seems to be to tighten up the structure of the first layer, now adsorbed, at the wall, as evidenced by the sharp peaks in  $\rho(z)$ . One consequence of this seems to be a longer relaxation time for the decay of fluctuations in the parallel stress.

In response to a question concerning recent evidence for non-Newtonian behaviour of liquids in very narrow pores at relatively low shear rates, **Dr. Woodcock** commented: The experimental work to which I referred measures the resistance to flow of films of otherwise Newtonian liquids (*e.g.* hexadecane) 1–6 molecules thick confined between atomically smooth mica plates, reported recently by van Alsten and Granick at the University of Illinois.<sup>1</sup> In a personal communication they have informed me that very recent experiments show non-Newtonian shear thinning to occur for 4–6 layers of simple hydrocarbon liquids at shear rates as low as  $10^2 \text{ s}^{-1}$ .

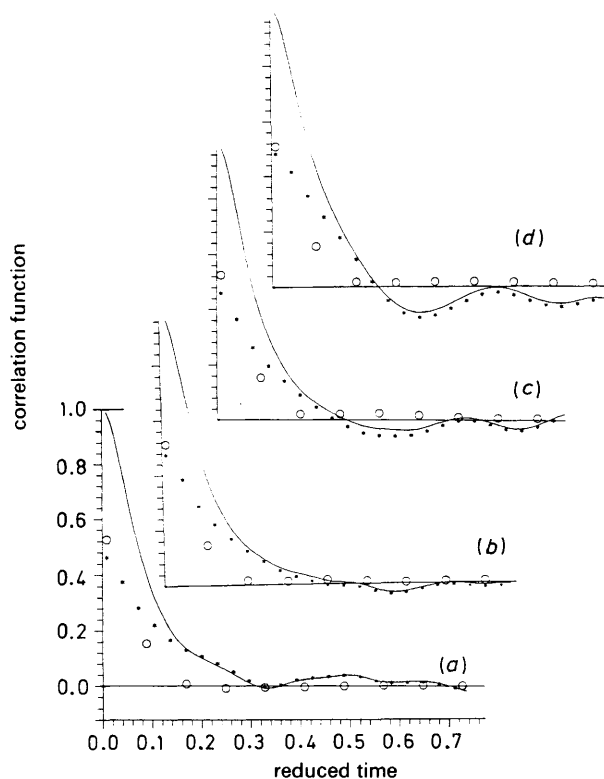
This observation supports our decision to approach the interfacial viscosity problem initially by EMD rather than NEMD; there is no theory for the extrapolation to low shear of NEMD data, so, for the pore system, one does not know that the NEMD results are in the linear region.

<sup>1</sup> J. van Alsten and S. Granick, *Phys. Rev. Lett.*, 1988, **61**, 2570.

**Dr. J. H. R. Clarke** (UMIST) asked: Are the forms of the stress correlation functions different in the cases of the confined and bulk fluid? Your data would suggest that this is the case: the confined and bulk fluid shear viscosities appear to be within a factor of 2, but the mean-squared shear stress for the confined case was found to be an order of magnitude larger than in the bulk. Do the confined fluid correlation functions show more rapid decay—or perhaps have less prominent long-time tails?

**Dr. Woodcock** replied: Dr. Clarke rightly observes from our data that confinement must have affected the shapes of the normalised stress autocorrelation functions, because the five- to six-fold increase in  $\langle S^2 \rangle$  is not matched by quite such large increases in the effective viscosities. The point is interesting and best understood by looking at spatially resolved stress correlation functions for individual strips, calculated as described in our paper but not actually presented.

Fig. 1 shows normalised correlation functions of reduced time for the  $8.4\sigma$  pore hard-wall system resolved into eight



**Fig. 1** Normalised correlation functions of reduced time for one  $8.4\sigma$  pore hard-wall system: (O) autocorrelation, (\*) cross-correlation, (—) total; (a) strip 1, (b) strip 2, (c) strip 3, (d) strip 4

strips (or 'bins'); since the pore is symmetric about its centre in the  $z$ -direction we need only look at four strips ranging from strip 1 nearest to the wall to strip 4 of the central region. The correlation functions shown in this figure are for the transverse shear viscosity ( $\eta_{\perp}^s$ ) or stress, corresponding to parallel flow. As Dr. Clarke suggests, the correlation functions do indeed decay somewhat more rapidly (*cf.* Fig. 2 of our paper), but there appears to be a more prominent negative tail induced in the central region, and which disappears at the wall.

**Prof. D. J. Tildesley** (*University of Southampton*) asked: In defining the profile of viscosity we are dealing with molecules at time zero which are in layer  $i$  and which at a time  $t$  are in layer  $j$ . Is there a unique way of deciding if this correlation should contribute to the viscosity of layer  $i$  or  $j$ ?

**Dr. Woodcock** responded: One can calculate a time correlation function going forward or backward in time; it is the same. The correlation  $S_i(t_1)S_j(t_2)$  contributes to the correlation 'bin' of  $Z_i(t_1)$  going forward in time, by definition, whereas it would contribute to the correlation 'bin' containing  $Z_j(t_2)$  going backwards in time. Since all the correlations are symmetric even functions of time, the question of 'which bin?' does not arise. In practice, of course, we only count forward correlations. The same applies to cross-correlations  $S_i(t_1)S_j(t_2)$ ; in the mathematical sense I think you implied, therefore, the profile is unique.

In a more general sense there is no unique definition of a viscosity profile, because there are many different conceivable ways of resolving the stress of a system of interacting particles spatially. The profile we have defined and calculated in this work is a self-consistent resolution of the total stress

time-correlation function based on the spatial division of the pair stress  $S_{ij}$  equally at  $r_i$  and  $r_j$ .

A possibly useful practical ratio to note in this context may be the ratio of the time to diffuse one 'bin-width' to the stress relaxation time. For a bin-width equal to  $\sigma$ , this ratio is *ca.* 10 for a triple-point LJ liquid.

**Prof. Tildesley** continued: Trouton's law is an empirical relationship between the shear and elongational viscosity for Newtonian fluids. Do we expect this relationship to hold for molecules in a narrow pore?

**Dr. Woodcock** answered: Trouton's law essentially says there is only one independent material constant for momentum transfer in the deformation of an otherwise isotropic, homogeneous, incompressible, Newtonian fluid. Trouton's value 3 for the ratio  $\eta^e/\eta^s$  actually arises from the peculiar definition of elongation rate ( $\dot{\epsilon}$ ) for a pure uniaxial extension; for planar elongation (fixed width)  $\dot{\epsilon}$  is equivalent to  $\dot{\gamma}$  for pure shear, and for biaxial elongation (such as squeezing of two finite plates)  $\dot{\epsilon}$  is usually defined so that Trouton's constant is 4. Whatever the case, no new viscosity coefficient is involved.

Trouton's rule does not hold for fluids which are anisotropic, or flows which are anisotropic; this includes liquid crystals, many polymers, crystalline solids or colloidal crystals, and indeed all non-Newtonian fluids which are associated with shear-induced normal stress differences. In these cases Trouton's ratio ( $\eta^e/\eta^s$ ) is a measure of the degree of anisotropy in non-linear extensional flow.

Accordingly, we do not expect Trouton's rule to hold for the elongational viscosity profiles in the vicinity of the pore walls, or for the net effective elongational viscosity of a liquid in a narrow pore, because of the anisotropy induced into the local stress fluctuations by the presence of the confining walls.

A simple microscopic way of seeing it (using the convention that  $Z$  is perpendicular and  $X$  and  $Y$  are parallel) is that the fluctuations  $\langle \Delta X_{ij}^2 \rangle$ ,  $\langle \Delta Z_{ij}^2 \rangle$ ,  $\langle \Delta X_{ij} \Delta Y_{ij} \rangle$  and  $\langle \Delta X_{ij} \Delta Z_{ij} \rangle$  are no longer equivalent; hence there are four different viscosity coefficient profiles for linear incompressible flow in a narrow pore or at a solid surface.

**Dr. J. Yarwood** (*University of Durham*) said: I have three points for Dr. Woodcock. What is the role of the elongational viscosity in the interpretation of the microscopic dynamics of (say) a lubricant molecule? Is the 'flow' property of such a material only dependent on the shear viscosity? (as is usually assumed to be the case when reorientational relaxation times are interpreted using the Stokes–Einstein–Kivelston approach). If not, why not? Under what conditions is liquid 'elongation' likely to occur?

**Dr. Woodcock** replied: In response to your first question, I do not think a single transport coefficient tells us very much about microscopic dynamics; molecular dynamics determine the constitutive rheological coefficients, which, in turn, determine the macroscopic fluid dynamics, not the other way round.

Responding to your second point, if by flow property you mean the fluid mechanics, then, for an isotropic homogeneous Newtonian liquid in the linear response domain, there is only one independent transport coefficient for incompressible viscous flow; Trouton's law applies for any elongation flow components. The fluid mechanics is only dependent on the shear viscosity in this case.

If, on the other hand, the lubricant is in a non-linear flow, an anisotropic compressible flow, or in a highly confined

space, for example as in a real lubrication process, Trouton's ratio can increase by orders of magnitude and elongational viscosity effects may become predominant.

Turning to your final point, liquid elongation occurs to some extent when it is subjected to any general deformation. Planar elongation is, in fact, equivalent to pure shear. Uniaxial and biaxial elongations occur in, for example, entrance and exit flows at orifices to pipes *etc.*, drainage under gravity, jets and sprays from a nozzle, pumping and mixing operations. For non-Newtonian flows with a high Trouton ratio, *e.g.* polymer melts in fibre spinning, the elongational viscosity may be the total controlling factor.

In the context of the present meeting I might add that flow through natural porous media generally involves tortuous paths, into and out of narrow channels of complex and variable dimensions; here we can expect a substantial dependence of the overall flow rate on the effective elongational viscosities, particularly when the interfacial effects are large.

**Prof. R. D. Noble** (*University of Colorado*) said: I would like to ask Prof. Gubbins if he would discuss his results in the supercritical region.

**Prof. K. E. Gubbins** (*Cornell University*) responded: Although no phase transitions are observed at supercritical temperatures, the adsorption behaviour is of interest because of the important practical applications of adsorbents at such state conditions. We have chosen to plot the excess adsorption (the average density of fluid in the pore minus the density of the bulk fluid at the same temperature and chemical potential), since this is of interest in connection with the storage of methane in porous media. When the pressure of the bulk gas is low, the adsorption excess rises rapidly with increasing pressure owing to strong adsorption by the narrow pores; thus the pores become filled with a relatively dense fluid even for modest pressures, and further increase of the bulk fluid pressure has less effect on the density in the pores, leading to a maximum in the adsorption excess at some particular value of the bulk pressure or density. As the temperature is lowered, this maximum in the adsorption becomes more pronounced, and shifts to lower values of the bulk pressure (density). The height and position of these maxima also depend on the pore width as shown in our Fig. 4. For small pore widths the maximum adsorption obtainable exhibits oscillations which arise from packing effects; a pore width of  $H^* = 4.9$ , for example, can accommodate four layers of methane molecules, but a slight reduction in the value of  $H^*$  will result in the loss of a whole layer of fluid molecules and a sudden drop in the adsorption. Further reduction in  $H^*$  will lead to a rise in adsorption per unit volume of pore (down to  $H^* \approx 3.9$ ), since the number of fluid molecules can remain approximately the same while the pore volume decreases. These oscillations have the same origin as those observed in experiments to study the force between solid walls as a function of the wall separation by Israelachvili and others. For sufficiently small pores (see our Fig. 4) the adsorption drops off rapidly to zero because the fluid–wall forces become repulsive. A more complete discussion of adsorption behaviour for these supercritical gases is given in ref. 1.

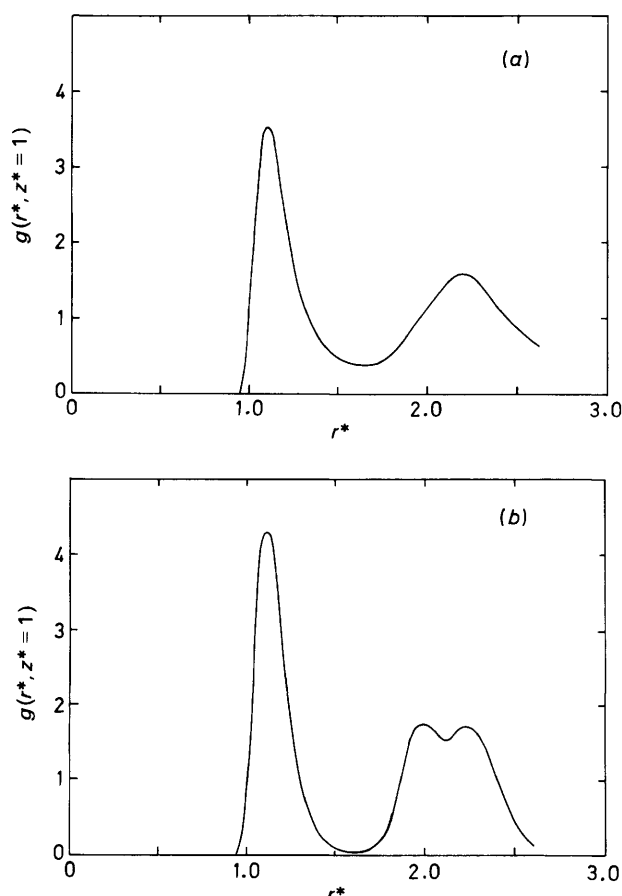
1 Z. Tan and K. E. Gubbins, *J. Phys. Chem.*, 1990, **94**, 6061.

**Dr. J. P. R. B. Walton** (*BP Research, Sunbury-on-Thames*) asked: I am interested in the quasi-two-dimensional freezing transition which you observe in the simulations of methane at  $T^* = 0.5$  in the  $H^* = 5$  slit. The isotherm calculated *via* GCMC (Fig. 5 of your paper) shows this occurring at

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$\mu^* = -8.5$ , with a (slight) jump in density from point C to point D. Fig. 7 of your paper shows single configurations in the layer on the wall from MD simulations at  $\mu^* = -9.0$  (a) and  $-8.0$  (b) (neither of which value, incidentally, corresponds to point C or D, in contradiction with the caption to Fig. 7), and an increase in density clearly takes place on increasing  $\mu^*$ . However, I find it hard to see whether any long-range order has really appeared in (b), and would perhaps hesitate before describing the snapshot in Fig. 7(b) as being representative of a 'regular crystal array' if for no other reason than the 'defects' in the 'lattice' which can be seen there. This uncertainty would be obviated by the calculation of, say, the in-layer pair correlation function, in which a transition to a solid phase would show up as the appearance of new peaks and new long-ranged behaviour. Do you plan to look at this for your system? Alternatively, if you have already done so, could you tell us what you have observed? Finally, do you expect the introduction of corrugations on the walls of the slit *via* the potential with laterally varying periodicity to have as much of an effect on the structure parallel to the wall as you have seen in the density profile for the smallest slit (your Fig. 1)?

**Prof. Gubbins** replied: Yes, we have calculated the pair correlation function  $g(r^*, z^* = 1)$  for molecules in the contact layer near the wall, and we find a sharp change in behaviour on going from point C to D of Fig. 5(a) of our paper. These results are shown here in Fig. 2, which shows additional long-range structure and a split peak near  $r^* = 2.1$  for points near D, which we take to be due to the formation of a solid-like



**Fig. 2** The pair correlation function from MD in the  $x, y$ -plane for the contact layer for  $H^* = 5$ ,  $T^* = 0.5$  (a) a point a little before C in Fig. 5(a) of our paper ( $\mu^* = -9.0$ ), and (b) a point a little beyond D in Fig. 5(a) ( $\mu^* = -8.0$ )

phase. We have also calculated diffusion coefficients in this region, and find that D suffers a pronounced decrease, by a factor of 50–100, on going from C to D. Thus we feel confident that a quasi-two-dimensional freezing transition occurs in the simulation. It is true that the chemical potentials chosen in Fig. 7 of our paper do not exactly correspond to the transition point, but to points either side of the transition; however, the snapshots shown are typical of states immediately on either side of the transition. Finally, we would expect the effect of lateral wall structure on the contact layer to be somewhat similar to that found for the density profile for the smallest slit.

**Prof. Tildesley** said: Below the two-dimensional triple point (56 K), methane on graphite forms islands of  $\sqrt{3} \times \sqrt{3}$  commensurate solid in coexistence with a two-dimensional gas. In the simulations of a structured surface pore is there any evidence of a commensurate structure in the plane of the surface?

The definition of a structured surface in Steele's expansion in reciprocal lattice vectors requires an origin for each plane. In narrow pores will the relevant positions of these origins on opposite walls affect the solid structure formed?

**Prof. Gubbins** responded: We have not yet completed our simulations at low temperatures with a structured surface, so we cannot answer this question about the commensurate phase. In narrow pores I would expect that the relative positions of the lattice origin for the two walls might well affect the solid structure formed for small pores.

**Prof. J. M. D. MacElroy** (University of Missouri-Rolla) said: We have recently<sup>1</sup> examined the modified Enskog theory of Davis<sup>2</sup> for a Lennard-Jones liquid in cylindrical pores with both structureless and atomically structured walls, and we found that this theory is quantitatively poor for the structured system owing to the omission of a mechanism for momentum interchange during collisions (interactions) with the wall. Does the kinetic theory which you provide in preliminary form in section 5 of your paper take into consideration this momentum interchange *via* collision operators for the particle-wall interactions?

- 1 J. M. D. MacElroy and S.-H. Suh, *Mol. Simul.*, 1989, **2**, 313.
- 2 H. T. Davis, *J. Chem. Phys.*, 1987, **86**, 1474.

**Dr. L. A. Pozhar** (Ukrainian Academy of Sciences) replied: Although eqn. (11) in our paper is not written explicitly for the fluid-wall case, it is exact at this stage and does not contain modified Enskog-like assumptions as does the theory of Davis. The term which is responsible for momentum exchange between the fluid molecules and the wall is implicitly contained in the first term on the right-hand side of eqn. (11). More detailed equations, which treat structured walls more explicitly, can be found in ref. 1.

- 1 L. A. Pozhar and K. E. Gubbins, *J. Chem. Phys.*, 1991, **94**, 1367.

**Dr. Walton** asked Prof. Gubbins: The self-diffusion coefficients in both the  $x$ - and  $z$ -direction which are given in Table 1 of your paper decrease as one goes from (i) the first inner layer of the  $H^* = 5$  slit to (ii) the  $H^* = 5$  contact layer to (iii) the  $H^* = 2.5$  contact layer. It is stated that the  $D_z$  values correlate well with the fraction  $f(t)$  of molecules which are still in a layer after a time  $t$  has elapsed. However, the plot of  $f(t)$  (your Fig. 8) shows that this decreases (at, say,  $t = 10$ ) upon moving from (i) the  $H^* = 5$  contact layer to (ii) the  $H^* = 2.5$



contact layer to (iii) the inner layer of the  $H^* = 5$  slit. I would have thought that a 'good correlation' between  $D_z$  and  $f$  would mean that  $D_z$  is inversely proportional to  $f$ , i.e. that curve (ii) should lie above curve (i) in Fig. 8. This appears to be the case at low values for  $t$ , although it is rather difficult to tell from the figure. Do you have any explanation of why, at large  $t$ , the molecules appear to be staying in the  $H^* = 5$  contact layer for longer (and yet have a higher  $D_z$ ) than those in the  $H^* = 2.5$  contact layer?

**Prof. Gubbins** responded: First, the value of  $D_z^*$  at  $H^* = 2.5$  given in our preprint was a misprint. The correct value is  $D_z^* = 0.03 \pm 0.01$ , about the same as the value for the contact layer at  $H^* = 5.0$ . Secondly, more recent simulations for other  $H^*$  values show that the half-life  $t_{1/2}^*$  (the time after which  $f = 0.5$ , i.e. after which 50% of the molecules have left a given layer) oscillates as  $H^*$  is varied, and we believe these oscillations are the reason why the curve for  $f$  in Fig. 8 for  $H^* = 2.5$  lies below that for the contact layer for  $H^* = 5$ . These oscillations in  $t_{1/2}^*$  with varying  $H^*$  are probably the result of packing effects. We observe that as  $H^*$  is increased  $t_{1/2}^*$  generally increases, but decreases sharply each time a new layer of molecules is adsorbed. We are in the process of investigating this behaviour further.

**Prof. R. D. Noble** asked: Can one simulate molecules in small pores by placing marbles in a cylinder and shaking it?

**Dr. Woodcock** said: It is clearly easier for human beings to do experiments with marbles, rather than atoms, on scales of time and distance more directly amenable to our senses. Such experiments could be most valuable if only we could show that a law of corresponding states exists between a molecular system in thermal equilibrium and a granular system in steady-state quasi-equilibrium.

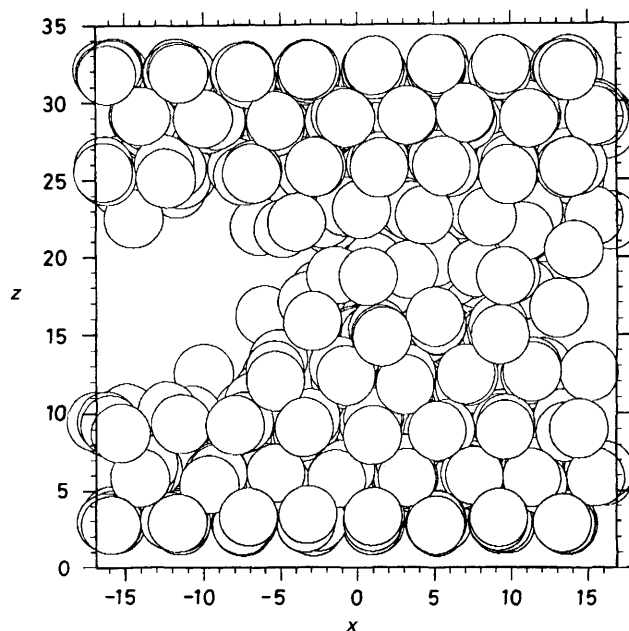
Coincidentally, we<sup>1</sup> have recently been examining the status of the equipartition principle, including the Maxwell-Boltzmann distribution law for granular systems using computer simulations of boxes of vibrating, slightly inelastic spheres (with essentially infinite heat capacity). This simple steady-state model tells us that granular systems do indeed obey thermal equilibrium distribution laws provided the amplitude of the vibration is much less than the size of the system (this corresponds to the 'thermodynamic limit'), irrespective of the frequency or direction of the perturbation.

I can therefore imagine all kinds of educational experiments, for example, two boxes of vibrating marbles connected by a pore. One must overcome gravity by going to very high kinetic energies, or doing the experiments in space of course. For research purposes, however, it's probably easier to do such 'experiments' with numbers using a computer.

1 T. Knight, *Thesis*, University of Bradford, to be submitted.

**Dr. Lynden-Bell** said: I have been doing some simulations recently<sup>1</sup> which may be relevant to larger pores, although they were intended to investigate the process of adhesion of two surface-premelted crystals. I see spontaneous formation of bridges when two multilayers of Lennard-Jones atoms at temperatures below, but near, the melting point were gradually brought closer and allowed to equilibrate at fixed separations. The multilayers were backed by a fixed substrate with the characteristics of the bulk crystal. Fig. 3 shows such a bridge.

1 R. M. Lynden-Bell, *Surf. Sci.*, 1991, **244**, 266.



**Fig. 3** A configuration from a simulation of two crystal surfaces showing spontaneous bridge formation at  $T/T_m = 0.76$ . The surfaces were formed by (100) planes of an f.c.c. lattice and were originally separated by 2.1 interlayer spacings. The configuration is viewed from a direction parallel to the surfaces, and there are periodic boundaries at the sides of the picture. At the top and bottom there is bulk substrate

**Prof. Gubbins** said: In a study of adsorption hysteresis in small pores<sup>1</sup> we observed bridging by the adsorbed fluid. In that case we used molecular-dynamics simulations to study the adsorption behaviour on increasing the pressure of the bulk gas for a fixed pore size. At a certain bulk pressure the layer of fluid adsorbed on the wall took on an unduloidal character, and at a slightly higher pressure a bridge of adsorbed fluid formed across the pore. The temperature was above the melting point in this case, but the phenomenon may well be similar to what Dr. Lynden-Bell observed.

1 G. S. Heffelfinger, F. van Swol and K. E. Gubbins, *J. Chem. Phys.*, 1988, **89**, 5202.

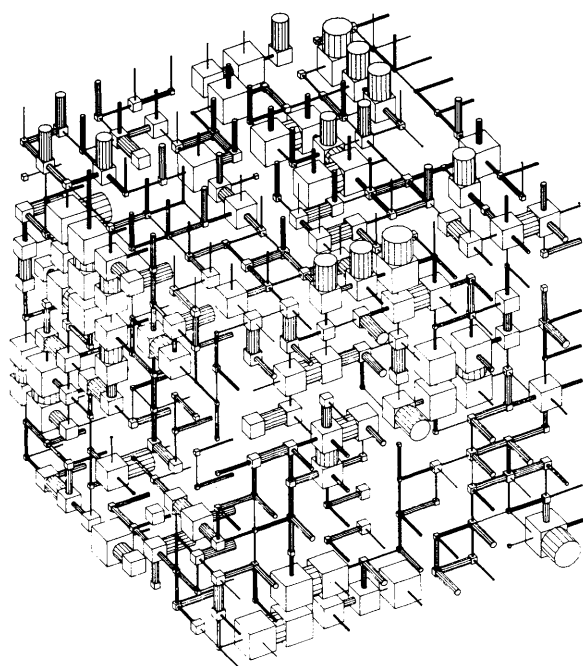
**Prof. Noble** asked: I would like to ask Dr. Petropoulos to discuss the physical basis for the result that the permeability can decrease as adsorption increases.

**Dr. J. H. Petropoulos** (*Democritus National Research Centre*) said: The effect of increasing adsorption on gas permeation through narrow pores is twofold. On the one hand, the number of gas molecules within the pores (under a given set of boundary conditions) increases, thus enhancing permeability. On the other hand, the mean diffusion path length of the said molecules (determined by gas-wall collisions under the conditions envisaged here) tends to decrease, thus reducing permeability. In practice, the former effect is usually preponderant ('normal' permeability behaviour); however, as shown here and in previous papers, the latter effect can prevail under suitable conditions in the weak adsorption region, thus giving rise to inversion of the aforementioned normal permeability behaviour. Experimental observations of such inversions to date are, in our view, sufficient to establish its reality beyond doubt; while the fact that a MD study by McElroy and Raghavan<sup>1</sup> of molecular diffusion of methane through a simulated aggregate of silica microspheres (similar to that described in the paper by the same authors here) did not reveal any such inversion, is attributable (*cf.* curve A1 of

Fig. 4 in our paper) to the combination of small effective width and length of the elementary pores therein.

- 1 J. M. D. MacElroy and K. Raghavan, *J. Chem. Phys.*, 1990, **93**, 2068.

**Dr. G. P. Matthews** (*Polytechnic Southwest, Plymouth*) said: I would like to raise a question which has arisen from a large-scale study, and which has a bearing on Dr. Petropoulos' study of diffusion in networked micropores. We have studied diffusion of alkanes through Clashac outcrop sandstone. A large range of pore-level properties (mercury porosimetry, porosity, pore/throat coordination number, tortuosity, permeability and primary drainage/secondary imbibition hysteresis) can be simulated with a model  $10 \times 10 \times 10$  array of pores and throats with a range of diameters from 1 to 200  $\mu\text{m}$  (Fig. 4).<sup>1</sup> Mesopores and micropores are absent



**Fig. 4** Model of Clashac outcrop sandstone formed by a  $10 \times 10 \times 10$  array of pores and throats

from the model, as evidenced by the fact that its surface area is a factor of 50 too low. The simulated tortuosity  $\tau$  of 2.9, which compares well with that calculated from conductivity measurements of brine-saturated rock, can be employed to calculate the diffusion  $D$  in the porous medium by means of Van Brakel's expression:<sup>2</sup>

$$\tau^2 = D_{12} \phi / D$$

where  $\phi$  is the porosity and  $D_{12}$  the diffusion in the bulk gas phase. We take experimental  $D_{12}$  values for methane and n-butane, and use the rigorous kinetic theory for isobutane which gives almost identical values of  $D_{12}$  for n-butane and isobutane because their masses are the same and their effective gas-phase collision diameters are almost identical (0.553 and 0.563 nm, respectively). If we now compare the simulation with our own experimentally determined values,<sup>3</sup> all in units of  $10^{-3} \text{ cm}^2 \text{ s}^{-1}$ ,

method	methane	n-butane	isobutane
simulation	3.17	1.40	1.39
experiment	3.19	1.55	2.23

we see that the methane and n-butane diffusion can be explained by the macropore network, but the isobutane diffusion cannot.

Can Dr. Petropoulos' work on networked micropores supply at least a qualitative explanation of this discrepancy?

- 1 M. Spearing and G. P. Matthews, *Transport in Porous Media*, 1991, **6**, 71.
- 2 J. Van Brakel, *Powder Technol.*, 1975, **11**, 205.
- 3 G. P. Matthews and M. C. Spearing, *Marine Petrol. Geol.*, in the press.

**Dr. Petropoulos** replied: Differences in the micropore transport of n-butane and isobutane are indeed to be expected on the basis of differences in the gas–solid interaction considered in our paper; but I would agree with Dr. Matthews that the consistency of his methane and n-butane data points to diffusion in macropores as the controlling mode of transport in his case. I would add that this conclusion may be drawn irrespective of the particular pore model assumed. This, in conjunction with the fact that no experimental value of  $D_{12}$  for isobutane was available, suggests that the most likely explanation of the anomaly shown by this gas is to be sought in the assumptions inherent in the theoretical estimation of  $D_{12}$ .

**Prof. D. J. Morantz** (*PIRA*) said: Several references have been made suggesting that the wall structure can be disregarded in considering flow properties of adjacent fluids. Surely this needs to be qualified? For example, Dr. Nicholson has already mentioned that molecular reflection off walls may either be specular or diffuse (for the case of 'rough' walls).

In the case of diffuse reflection this would imply sticky collisions, with the consequence that orientational changes could take place; such changes would involve entropic changes. These effects could perhaps have a bearing on the interesting discrepancies in the flow properties between isobutane and n-butane described by Dr. Matthews.

**Dr. Woodcock** responded: For a smooth wall, the shear stress arising from the wall–particle potentials does not fluctuate and does not therefore contribute to interfacial viscous resistance to shear flow irrespective of whether the wall collisions are diffuse or specular. A rough, or frictional, wall–particle collisional model would seem to be the minimum requirement in the Hamiltonian to obtain the 'diffuse' interactions required for hydrodynamic 'stick' conditions at the solid surface. There is no doubt that such solid-wall fine structure is an essential ingredient in any realistic model of flow properties at the interface. The method we advance, however, for interfacial viscosities, requires development and understanding in the beginning for simple idealised models. Prof. Tildesley has just introduced a most appropriate expression in this context: 'Hamiltonian surgery'. How can we understand and describe the effects of various wall structures on interfacial viscosities if we do not first know the effects of a wall without structure? This is a foremost application of MD simulations in research.

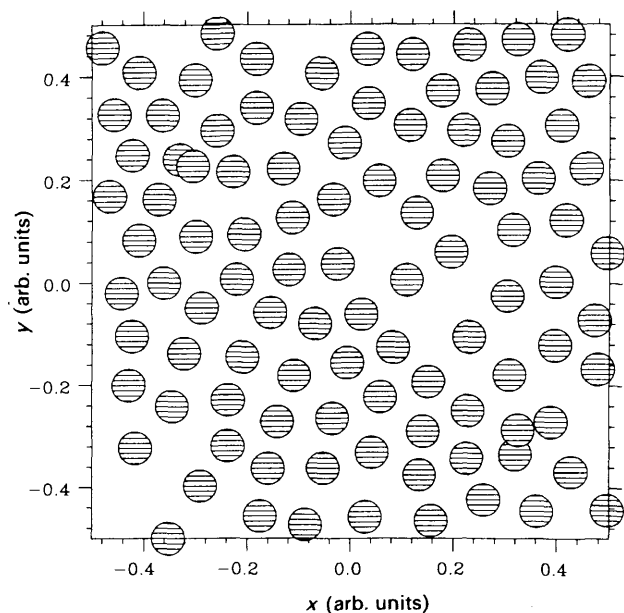
With regard to your second point, I am not sure what you mean by 'sticky collision'. Any diffuse scattering of translational or angular momenta at wall collisions for non-spherical molecules would presumably affect the thermodynamic properties of the interface. I am inclined to agree, therefore, that subtle changes in wall structure may indeed lead to substantially different effects on the interfacial rheology and fluid mechanics of various molecular geometries. These are fascinating questions for future computer simulations.

**Prof. Gubbins** also replied: Although we have not studied the effect of wall structure on flow properties of fluids, I know that such a study has been made recently by H. T. Davis and coworkers at the University of Minnesota, using molecular-dynamics simulation. I would certainly expect there to be a significant effect due to the structure.

**Dr. Petropoulos** concluded: I agree with Prof. Morantz that the effect of pore wall structure on fluid transport can be disregarded only up to a certain point (as indicated, for example, in *o*-xylene for the system treated therein). As far as the butane–isobutane data of Dr. Matthews are concerned, gas–wall collisions are not likely to play a significant role, as indicated in the relevant discussion (*v.s.*). However, considerations of ‘stickiness’ also apply to gas–gas collisions. On this basis, one may indeed expect some difference in the value of  $D_{12}$  for n-butane and isobutane, which (as indicated in the relevant discussion) appears to be the most likely explanation for the discrepancies observed by Dr. Matthews.

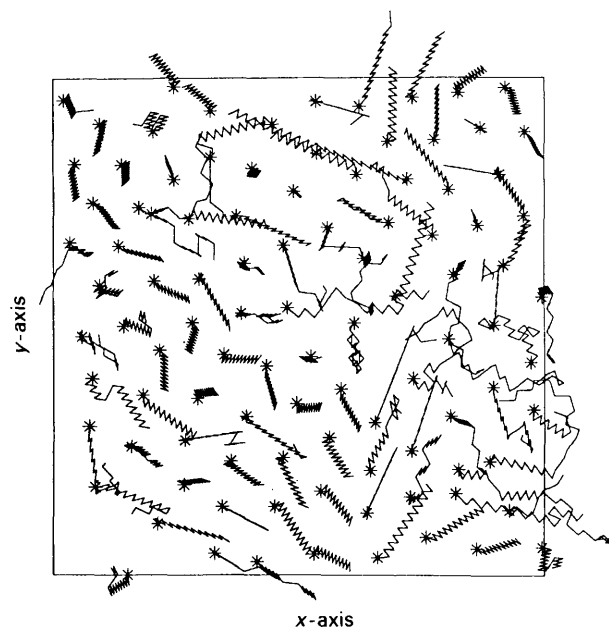
**Mr. J. I. Siepmann** (University of Cambridge) addressed Prof. Klein: I would like to draw your attention to recent Monte Carlo (MC) calculations of self-assembled monolayers by McDonald and myself.<sup>1</sup> The simulations are performed on a model that is similar to the one used by Hautman and Klein in their molecular dynamics (MD) studies of alkyl thiols.<sup>2</sup> In MD simulations, equilibrium averages are sampled by following the natural time evolution of a many-body system. In contrast, the MC technique allows for ‘unphysical’ moves in configuration space. Such moves may correspond to transformations that take place only over very long times in MD simulations. We use a novel MC sampling scheme, called configurational-bias MC, that enables us to sample configuration space very efficiently, since large-scale conformational changes are made to a trial molecule in a single attempt.<sup>3</sup>

The main difference between the simulations of Hautman and Klein and our own is that our simulations start from initial configurations where the headgroups are positioned on a randomly diluted square lattice. Hence they are not prejudiced towards a hexagonal arrangement of the chains.



**Fig. 5** Top view of a snapshot of the sulphur headgroup configuration from a simulation of  $\text{HS}(\text{CH}_2)_{19}\text{CH}_3$  at a surface area of  $21.4 \text{ Å}^2$  and  $T = 300 \text{ K}$

Despite the different initial conditions, the properties (*e.g.* the percentage of *gauche* defects, the average tilt angle of the chains or the density profile) of the monolayer system agree well with experimental results and the MD results.<sup>2</sup> However, there is one remarkable difference between the MD and MC results: the MC simulation does not result in configurations with a solid-like headgroup configuration (see Fig. 5), and the chains do not have a uniform tilt direction (see Fig. 6).



**Fig. 6** Top view of the chain conformations for the same configuration as in Fig. 5. The headgroups are marked by stars

Further work aimed at investigating the reasons for the discrepancies between the MD and MC results is in progress.

- 1 J. I. Siepmann and I. R. McDonald, in preparation.
- 2 J. Hautman and M. L. Klein, *J. Chem. Phys.*, 1989, **91**, 4994.
- 3 J. I. Siepmann and D. Frenkel, *Mol. Phys.*, submitted.

**Note added in proof:** Note that further MC calculations revealed that the initial configuration, the box shape and the range of the spherical potential cut-off have a by no means negligible influence on the simulation results. We find that under certain conditions the outcome of the MC simulations agrees much better with the findings of the MD simulations of Hautman and Klein. Furthermore, it should be pointed out that the problem of quasi-ergodicity cannot be neglected for this kind of system.

**Prof. M. L. Klein** (University of Pennsylvania) said: Our system size and box dimensions were chosen so as to mimic the structure within a domain of a typical self-assembled monolayer. Such a procedure indeed effectively encourages the head-groups to remain on a triangular lattice. Whether or not this is the global minimum energy state of our potential-model is not clear. Your calculations, carried out for a square box, necessarily frustrate the formation of a triangular lattice. Indeed, the resulting configuration from your Monte Carlo calculation are suggestive of a ‘liquid-like’ system. Perhaps the two calculations are investigating extreme limiting cases of a system exhibiting two-phase coexistence. The rectangular box employed by us has constrained the system to be ‘solid’, whereas the cubic box has frustrated the system and yields a ‘liquid’. Such a result is probably indicative of inadequacies in the potential model: the real system is neither liquid-like nor two-phased. Elsewhere,<sup>1</sup> we have shown that an all-atom



## GENERAL DISCUSSION

description of the alkane chain is vital to achieve a realistic chain packing density. Also, our knowledge of the head-group–substrate interactions is currently inadequate to parametrize a realistic potential. The differences between the two calculations will probably be less if the all-atom description is considered.

As a caution, let me remind the audience that if one wished to study solid argon *via* simulations it would be unwise to start from a random arrangement of atoms. For Lennard-Jones potentials, and pairwise additivity, the ground-state configuration (global minimum at  $T = 0$  K) is h.c.p. Simulation using a cubic box and very long runs will eventually yield an f.c.c. lattice.<sup>2,3</sup> While this is the correct structure, experimentally, it is the wrong one for the model! Thus, the boundary conditions can influence the results in even this simple example. For monolayers of long-chain (flexible) molecules these will probably be more subtle than the case of solid argon. The global minimum of a given model may not be the relevant structure. In our case, we decided to prejudice the system to have head-groups ordered on a triangular lattice, as indicated by published experimental data. This is akin to studying a Lennard-Jones solid (argon) starting from a system arranged initially on an f.c.c. lattice.

- 1 J. P. Bareman and M. L. Klein, *J. Phys. Chem.*, 1990, **94**, 5202.
- 2 S. Nosé and F. Yonezawa, *J. Chem. Phys.*, 1986, **84**, 1803.
- 3 H. Jonsson and H. C. Andersen, *Phys. Rev. Lett.*, 1988, **60**, 2295.

**Dr. J. Yarwood** asked Prof. Klein: How do the properties of the ‘tail’ groups in your simulation change when the charges on (say C and N atoms) are altered. So, for example, does the ferroelectric property of the alkyl cyanide depend on potential? For the alkyl alcohol material it seems to be very easy to probe the degree of hydrogen bonding in a real monolayer using vibrational spectroscopy. Has this been explored? What is the lifetime of a hydrogen-bond in the simulation and how does it compare with simulations of liquid water?

**Prof. Klein** replied: References to work on —OH terminated surfaces are given in our paper. There seems to be some evidence of time-dependent surface reconstruction in this case. Spectroscopic studies should indeed provide a valuable probe, and infrared (unpublished) work by Ulman (Kodak) and Nuzzo (AT&T) seems to be consistent with the types of structures that are seen in our MD simulations.

The question concerning whether the structure of our —CN terminated chains is reasonable or not remains to be determined by experiment. Of course, the final structure is very dependent on the choice of potential model (surface charges). It also depends on whether or not there is an even or odd number of CH<sub>2</sub> groups! What is really needed at this point is more experimental data. We have made specific predictions. The model could be refined further, but in the absence of definitive experiments would this be wise?

**Dr. R. K. Thomas** (Oxford University) said: Macroscopic wetting behaviour may not be a good criterion for judging behaviour at the molecular level because it may depend on larger-scale inhomogeneities of the surface. Thus, comparisons between the MD results on water molecules on the hydroxylated thiol surface, impressive though they are, and wetting results should not be regarded as a definite explanation of the wetting behaviour.

**Prof. Morantz** said: Concerning the slow transformation, from hydrophilic to hydrophobic character, of the OH

groups of the self-assembled monolayers of alkylthiols, my understanding is that Prof. Klein’s model achieves an initial metastable state in MD simulations which corresponds to the initial, rapidly established, non-equilibrium structures observed in real experiments.

If, then, in the real system it is possible to ascribe to some trigger the initiation of a slow transformation by an impurity (such as I believe that Dr. Thomas has indicated), where might such impurity reside: on the underlying support substrate, or within the upper OH-containing skin? If the impurity is, say, entrapped air, then how could this have been echoed in the MD model?

Is it through the imposition of a planar upper surface boundary; a constraint which the OH groups (neighbouring the upper skin) reject? Is this how the real and the simulated model correspond; alternatively, does the boundary constraint impose defects which mimic entrapped impurities?

**Prof. Klein** responded: Surface reconstruction of —OH terminated surfaces is a somewhat controversial topic. Some research groups indeed imply that such effects are due to surface impurities as you suggest. In the simulations we find evidence for the rapid formation (on the timescale of the simulation) of a ‘glassy’ two-dimensional hydrogen-bonded network. This network slowly (100 ps) ‘crystallises’ into a more ordered structure based, in part, on dimerized rows (akin to the surface reconstruction row dimerization seen on the free surface of silicon). The structure we have found in the MD simulation is sufficiently stable and compact that it is a likely candidate for the real —OH terminated surface.

You point about impurities influencing surface properties is well taken, and this probably has relevance to the remarks of Dr. Thomas concerning the wetting characteristics of silica surfaces.

**Prof. Tildesley** said: Many Langmuir–Blodgett films are permeable to a few parts per million of gas molecules. Yet the structures Prof. Klein has shown are structurally quite solid-like. Does he feel that grain boundaries play a key role in the permeability of the films?

One way to resolve the difficulty of locking in the starting structure in the MD simulation would be to use a constant-pressure technique and change the sides of the cell in the plane of the surface. This would not be possible for a structured surface and may be technically difficult for a smooth surface.

**Prof. Klein** replied: Diffusion of gas molecules in compact monolayers of long-chain molecules may be easier than one would first imagine. Calculations by Roe and coworkers (Cincinnati) on glassy alkane systems has identified a diffusion mechanism that involves the cooperative relaxation of local chain regions. Dislocations, grain boundaries, domain walls *etc.*, will provide natural ‘entry points’ for gas molecules in monolayers of long-chain molecules. In the case of self-assembled films such defects are very likely, since the coherence length of the domains is small.

Constant spreading pressure simulations for two-dimensional systems have been attempted by various workers. Harris and Rice<sup>1</sup> reported one such study. There are obvious difficulties associated with doing the calculation correctly, since the spreading pressure is determined by the integral of stress components [ $\pi_{zz}(z) = \frac{1}{2}(\pi_{xx}(z) + \pi_{yy}(z))$ ]. The formulation is clear, but whether or not a simulation is possible remains to be seen. It would be of extreme interest to

carry out such a study in view of the new data on Langmuir and Langmuir–Blodgett films.

1 J. Harris and S. A. Rice, *J. Chem. Phys.*, 1988, **89**, 5898.

**Dr. B. Vessal** (*University of Keele*) said: Could Prof. Klein explain briefly how the Ewald sum for a 2D system, was made, and what advantage does it have over the already-published method for doing the sum in two dimensions?

**Prof. Klein** answered: Indeed, 2D Ewald methods do exist in the literature. However, the particular problem considered in our paper suggested to us an approach that treats the  $x$ ,  $y$ -surface *via* ‘usual’ 2D Ewald methods and the  $z$ -direction (normal to the surface) *via* a Taylor series expansion *i.e.* the thickness of the ‘polar region’ is small. The details of our method will be published.<sup>1</sup>

1 J. Hautman and M. L. Klein, *Mol. Phys.*, 1991, submitted.

**Dr. A. R. Hillman** (*University of Bristol*) said: Could Dr. Fernandez explain the reasons for the choice of the interfacial profile models in Fig. 4 of her paper? Is there an obvious physical significance to these shapes, particularly those which incorporate a discontinuity?

**Dr. M. L. Fernandez** (*Imperial College, London*) said: The way in which the reflectivity profiles were fitted was by starting with the simplest possible model and progressively introducing more details according to the failures in the fitting.

None of the theoretical interfacial shapes available in the literature seemed to explain our reflectivity data, and that is why we had to search for an interfacial shape which would explain our NR measurements. In the paper we comment on the resemblance of our final model to that proposed by Brochard *et al.* for a polymer/solvent system, although they are by no means identical. It was clear during the data fitting that in order to explain the data satisfactorily one had to include a discontinuity on the dPMMA side of the interface, although its physical significance is not understood. Perhaps when we carry out measurements over a larger  $q$ -range we will be able to refine the shape of the discontinuity, and to ascertain its significance.

**Prof. P. Meares** (*University of Exeter*) said: In studying the penetration of organic solvent vapours into polymers one must distinguish the phenomena well above  $T_g$  of the polymer, where the concentration profile can be described at all times by Fick’s equation with a concentration-dependent diffusion coefficient and well below  $T_g$ , where so-called Case II transport occurs. In this a sharp boundary of penetrated and non-penetrated polymer is seen and it advances into the polymer at constant velocity, in contradiction with Fickian predictions. The time course of penetration is controlled by relaxation of swelling stresses in the unattacked polymer. Such time-dependences persist a few degrees above  $T_g$ . Could Dr. Fernandez tell us if the penetration of PMMA into SCPE occurring less than 4 K above  $T_g$  obeys Fick’s equation with  $D(c)$  at all times in her experiments?

**Dr. Fernandez** answered: We have not attempted to extract a diffusion coefficient from our interfacial profiles, but these are clearly non-Fickian. We believe that, as stated in the question, the process that is taking place in the first instances of the intermixing between these two species is one of swelling of the SCPE by the dPMMA owing to the very low and very high mobilities, respectively, of the diffusing polymers.

**Dr. Yarwood** said: I have three questions for Dr. Fernandez. First do you adjust your polymer chain length in order to affect the diffusion rate into the interfacial region? Secondly is there a possibility that (with neutrons of very short wavelength) you are only looking at part of the interface? (We examine the polymer/polymer unit surface using Raman spectroscopy with  $\lambda \approx 5000$  Å, so we define our ‘interface’ over a spatial range of *ca.* 1000 Å). So, finally, is the ‘interfacial’ region defined by the technique used?

**Dr. Fernandez** replied: With regard to your first point, yes. In this work we were interested in studying the diffusion behaviour between two polymers with very dissimilar mobilities. This was achieved by choosing SCPE with a high chlorine content, which greatly increases  $T_g$  of the polymer, and a relatively low molecular weight fraction of dPMMD.

Turning to your next point, the neutron reflection measurements in the present study see the whole of the interface, which is of the order of tens to a few hundreds of ångströms. If one tried to measure the same interface with a technique with a poorer resolution, such as stated in the question, one would not be able to do so because the whole of the interface would be smaller than the instrumental resolution.

In reply to your final question, the interfacial region is not defined by the technique used, but one could give different values for the magnitude of a particular interface when using different techniques. This might be due to the fact that each technique is sensitive to a particular aspect of the system, and therefore what one measures as the interface might vary according to the measurements taken. Another problem is that of defining what is the interface. It is possible that users of different techniques are implicitly using different definitions for the interface and therefore quoting different answers.

**Dr. Thomas** commented: Neutron reflectivity, by measuring the density profiles for each component in a mixture, defines the interface more precisely than does any other technique. Limitations may be the ‘roughness’ of a sample, which converts some of the specular reflection into non-specular scattering, and lack of resolution. Was the non-specular scattering of the polymer samples examined? What are the prospects of extending the measurements to values of  $k_{\max}$  higher than used in the paper?

**Dr. Fernandez** answered: Yes, the non-specular scattering of the polymer samples was examined at the ILL neutron facility in Grenoble by using a two-dimensional detector. Some non-specular scattered intensity was observed, but it was found to be very low and effectively negligible.

Neutron reflection measurements extended to higher  $k$  values would be very desirable, since they would allow one to refine the fitting parameters to a greater extent than has been done so far. We intend to make these measurements within the next few months.

**Prof. G. B. Suffritti** (*University of Sassari*) asked Dr. Baros: What are your thoughts on the molecular mechanism of diffusion of pyrene in membranes? Do you hypothesize surface diffusion or bulk diffusion?

**Dr. F. Baros** (*CNRS, Nancy*) replied: Because pyrene is highly hydrophobic, it moves inside the bilayer, quite far from the polar heads of the phospholipid chains, as already mentioned in our paper.

Concerning the diffusion of pyrene in the protein itself, we assume that it occurs only in the few phospholipids sur-



rounding the protein, because we do not observe any change in the ratio  $I(373)/I(393)$  of the fluorescence spectra of the probe when proteins are added to the bilayer. (This ratio give a good indication of the polarity of the medium in which pyrene migrates.)

**Dr. M. E. Cates** (*University of Cambridge*) asked: Could Dr. Hillman comment further on the effects of solvent penetration into the film, with regard to its rigidity and the treatment of the hydrodynamic layer?

**Dr. Hillman** replied: Dr. Cates raises an important and topical<sup>1</sup> issue, that of film rigidity. All the mobile species transport processes we discuss here were quantified using the Sauerbrey equation [eqn. (1) and ref. (24) of our paper], which relates measured frequency changes to film mass changes. This relationship holds for a rigidly coupled mass; non-rigidly coupled masses yield smaller frequency changes.

If the thickness (typically 300 nm in the experiments here)<sup>2</sup> and density of the hydrodynamic layer remain constant† immersion of the electrode simply results in a shift in absolute frequencies. Since we measure frequency changes associated with electrochemical processes, *e.g.* film oxidation/reduction, the baseline is not crucial.

Provided the above two constraints (on the polymer and solution phases, respectively) are satisfied, changes in film mobile species population and the presence of the hydrodynamic layer lead to additive mass changes.<sup>2</sup> If the film is non-rigid (or becomes so upon oxidation/reduction), extraction of film mass changes is non-trivial. If the solution kinematic viscosity changes, we have the problem of a shifting baseline. For film mass changes of the magnitude observed here, baseline drift was not a significant problem.

We have several pieces of evidence to support our simple approach, two circumstantial (for all three systems), and three unequivocal ones (specific to particular systems):

First, the films we have studied are all relatively dense, *i.e.* contain relatively little solvent, in the media employed for

their characterization. Intuitively, one might expect them to be rigid.

Secondly, comparisons between *in situ* electrochemical and frequency data, and between *in situ* and *ex situ* frequency data, are consistent with rigidity. The criterion here is consistency between coulometric and gravimetric assays of the electroactive material present.

Thirdly, this circumstantial evidence has been confirmed by some preliminary impedance measurements on the polybithiophene system.<sup>3</sup> The idea here is to obtain the complete frequency response of the crystal, rather than rely on the (single point) resonant frequency, and see whether the Q-factor is altered.<sup>4</sup> Despite the presence of solvent in PBT films in either oxidation state, we find them to be rigid.

Fourthly, ellipsometric estimates of film thickness and EQCM estimates of film mass give sensible densities for polythionine films; non-rigidity would yield unreasonable densities. This method of comparing ellipsometric and EQCM data to obtain film density has been demonstrated rather nicely for polyaniline by Gottesfeld *et al.*<sup>5</sup>

Fifthly, poly(vinylferrocene) presents the most interesting of the systems we have studied, as regards rigidity. Other workers<sup>6</sup> have used the impedance method to demonstrate rigidity in aqueous media (as used for the characterisation studies reported here). Contrastingly, in the solvent used for film deposition ( $\text{CH}_2\text{Cl}_2$ ), the oxidised (as deposited)  $\text{PVF}^+\text{ClO}_4^-$  film is non-rigid. The evidence for this is a frequency change during film deposition that is typically a factor of two smaller than expected on the basis of subsequent coulometry in aqueous media, and a comparison of *ex situ* data for clean and film-coated electrodes. We have recently reported this data in more detail elsewhere.<sup>7</sup>

- 1 R. Borjas and D. A. Buttry, *J. Electroanal. Chem.*, 1990, **280**, 73.
- 2 S. Bruckenstein and M. Shay, *Electrochim. Acta*, 1985, **30**, 1295.
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- 5 J. Rishpon, A. Redondo, C. Derouin and S. Gottesfeld, *J. Electroanal. Chem.*, 1990, **294**, 73.
- 6 P. T. Varineau and D. A. Buttry, *J. Phys. Chem.*, 1987, **91**, 1292.
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† In practice the requirement is sufficiently good temperature control over the time course of the experiment to prevent significant changes in the liquid kinematic viscosity.