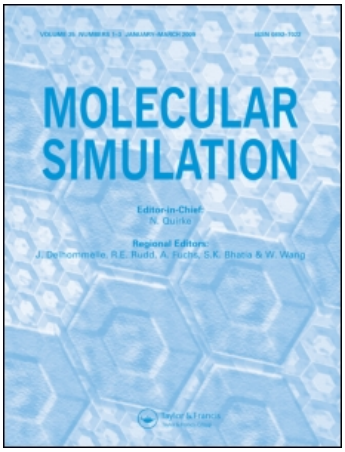

Molecular Simulation
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713644482

Mass and Energy Transport Through Slit Pores: Application to Planar Poiseuille Flow

B. D. Todd[a]; Denis J. Evans[a]
[a] Research School of Chemistry, Australian National University, Canberra, Australia

To cite this Article Todd, B. D. and Evans, Denis J.(1996) 'Mass and Energy Transport Through Slit Pores: Application to Planar Poiseuille Flow', Molecular Simulation, 17: 4, 317 — 332
To link to this Article: DOI: 10.1080/08927029608024115
URL: http://dx.doi.org/10.1080/08927029608024115

Molecular Simulation, 1996, Vol. 17, pp. 317–332
Reprints available directly from the publisher
Photocopying permitted by license only

MASS AND ENERGY TRANSPORT THROUGH SLIT PORES: APPLICATION TO PLANAR POISEUILLE FLOW

B. D. TODD and DENIS J. EVANS

Research School of Chemistry, Australian National University, GPO Box 414, Canberra, ACT 2601, Australia

(Received November 1995; accepted April 1996)

We develop a simple, efficient and general statistical mechanical technique for calculating the pressure tensor and the heat flux vector in atomic fluids. The method is applied to the case of planar Poiseuille flow through a narrow slit pore and the results indicate that our technique is accurate and relatively efficient. A second method to calculate shear stress is derived from the momentum continuity equation. This mesoscopic method again is seen to be accurate with good computational efficiency.

We also find that the commonly used approximation to the Irving-Kirkwood expression for the heat flux and the pressure tensor (where the Irving-Kirkwood O_{ij} operator is set equal to unity-the so-called IK1 approximation), leads to incorrect results for highly inhomogeneous fluids. In such cases the pressure tensor and heat flux vector display spurious oscillations.

We calculate the spatially dependent viscosity across a narrow pore and find that it exhibits real but weak oscillations, a consequence of oscillations in the number density. Finally we point out that if the heat flux vector is coupled to the gradient of the square of the strain rate tensor such an effect will only affect the shape of the temperature profile. For planar Poiseuille flow, the temperature profile should deviate from the classical quartic form and include an additional quadratic component. The actual magnitude and shape of the heat flux vector remain exactly as they would if such a coupling did not exist.

Keywords: NEMD; inhomogeneous fluid; slit pore; transport properties; Poiseuille flow

1. INTRODUCTION

Atomistic computer simulation studies of inhomogeneous nonequilibrium fluids, such as fluids flowing through microporous media, have only seriously been investigated over last few years [1–9]. This has coincided with recent advances in experimental work, in which the properties of ultra-thin layers

of fluid sandwiched between solid surfaces have been investigated [10–12]. The theoretical and experimental techniques available for this study and the consequent analysis of the results are far from complete, and further progress remains to be made in this field. However, the first exact nonequilibrium molecular dynamics (NEMD) techniques to calculate the pressure tensor and heat flux vector for highly inhomogeneous fluids have recently been developed [13,14] and applied to the case of planar Poiseuille flow in narrow pores. From a knowledge of the streaming velocity, density, stress tensor, heat flux and temperature one is able to then calculate spatially dependent transport coefficients which characterise the fluid.

The use of nonequilibrium molecular dynamics to simulate both Couette and Poiseuille flow in microporous media has been attempted previously. Bitsanis *et al.* [2], using the reservoir method developed by Ashurst and Hoover [15,16], where a liquid is sheared between two semi-infinite reservoirs, studied the effects of strong inhomogeneities on the transport properties of a Lennard-Jones fluid. They calculated effective viscosities of the fluid by using a local average density model (LADM), which is in effect an harmonic average of the local viscosities within the pore. The LADM model assumes that the local transport coefficients are those of the homogeneous fluid at a mean density obtained by averaging the local density over a molecular volume. They were able to show that the strong density profile of the fluid causes significant changes to the shear stress and the effective shear viscosity for Couette flow, compared with a homogeneous fluid at the same average density and temperature. However, they did not attempt to derive spatially dependent viscosities.

In a follow up to their initial work, Bitsanis *et al.* [3,4] extended their model to include the cases of planar Poiseuille flow and squeezing flow. They were able to show that the effective viscosity of a confined fluid experiencing squeezing flow is significantly higher than the bulk fluid viscosity, in agreement with experiment [10]. They also showed the dependence of effective viscosity on pore width, demonstrating that it oscillates as a function of pore width. However, once again they did not attempt to calculate the spatially dependent viscosity.

One of the most interesting studies done on molecular dynamics simulations of boundary driven Couette flow was carried out by Liem *et al.* [17]. They showed that the velocity profile was not the simple linear profile predicted by the Navier-Stokes equations, and was best approximated by a fifth order polynomial. They also showed that the temperature profile deviated from the classical prediction of a second order polynomial. Furthermore,

they calculated a position dependent viscosity by taking the ratio of the constant shear stress to the strain rate, and found that it varied across the channel, being a minimum at the centre of the fluid and a maximum at the walls, an effect they attributed primarily to the large variation of the temperature within the fluid. Todd *et al.* [13] have also found a similar trend with the position dependent viscosities for the case of Poiseuille flow. However, whereas Todd *et al.* measured significant oscillations in the viscosity profile close to the walls. Liem *et al.* did not have sufficient spatial resolution to observe this.

Of further interest in the work of Liem *et al.* is the deviation in the temperature profile of the fluid from the classical Navier-Stokes solution. One explanation they give for this is the incorrect assumption of a constant thermal conductivity and viscosity. This may well be part of the reason, but the work of Baranyai *et al.* [18], Todd *et al.* [19] and Todd and Evans [20] suggests there may be another reason. Baranyai *et al.* [18] postulated that in addition to the normal Fourier law, which couples the heat flux vector to the gradient of the temperature, there is an additional cross coupling to the gradient of the square of the strain rate tensor. Todd and Evans [20] further showed that for planar Poiseuille flow the inclusion of a cross coupling term in the energy continuity equation results in a heat flux which is unchanged from that which would be predicted by the usual Navier-Stokes energy balance equation. If the coupling does exist it would affect the shape of the temperature profile, changing it from being purely quartic, as predicted by classical Navier-Stokes theory, to a quartic plus quadratic profile.

Very little work has been carried out on the heat flux and thermal conductivity of fluids confined within narrow pores. Mareschal *et al.* [8], using stochastic boundary conditions, simulated a nonequilibrium fluid of constant heat flux, and were thus able to derive the thermal conductivity by taking the ratio of the heat flux to the gradient of the temperature. They tested this against theoretical values given by a first-order Chapman-Enskog solution and found good agreement. Murad *et al.* [21] have studied the anisotropic thermal conductivity of a fluid in a system of microscopic slit pores, and find that such fluids exhibit strong anisotropy, particularly when the walls are almost impermeable.

Todd *et al.* [14] have recently derived a new statistical mechanical technique to calculate the heat flux vector for a highly inhomogeneous fluid. This technique is very efficient. They applied their method to the case of Poiseuille flow and were able for the first time to calculate the heat flux

vector as a function of position within a pore. However they were unable to obtain reliable estimates of the thermal conductivity of the fluids studied due to the difficulty in making highly accurate temperature measurements. Work is continuing on this task, with the hope of obtaining spatially dependent thermal conductivities for highly inhomogeneous fluids.

Very little work has been carried out on the theory of position dependent transport coefficients. Pozhar and Gubbins [22,23] have proposed a theory, based on functional perturbation theory, to describe the dynamical behaviour of dense inhomogeneous fluids, and are able to calculate spatially dependent viscosities and thermal conductivities. This theory has recently been tested against NEMD simulations for Poiseuille flow and the results show favourable agreement [24].

There is some confusion over how to calculate the stress tensor for an inhomogeneous nonequilibrium fluid. For instance, Thompson and Robbins [25] calculated the shear stress for a Lennard-Jones fluid undergoing Couette flow and found that it exhibited oscillations correlated with the density oscillations. They said this cannot be understood in terms of the macroscopic equations of hydrodynamics because these are derived assuming that quantities are averaged over scales larger than the mean free path. This is certainly true for the case of the Navier-Stokes equations, but is not the case for the momentum continuity equation. A direct integration of the latter for Couette flow will yield a constant value for the shear stress. Although Thompson and Robbins do not indicate how they calculated the shear stress, we suspect that they used an approximation to the Irving-Kirkwood expression for the pressure tensor (which we call here the IK1 approximation) [13]. The use of the IK1 expressions for the pressure tensor and heat flux vector are valid for homogeneous fluids, but break down when the fluid is strongly inhomogeneous. Recent work, in which the shear stress has been calculated correctly via nonequilibrium statistical mechanics [13], has shown that the IK1 approximation breaks down in a highly inhomogeneous fluid, and that when the shear stress is calculated by this approximation it exhibits oscillations similar to those which have been reported in the literature. However, these oscillations are spurious; they are merely a consequence of ignoring the higher order terms of the full Irving-Kirkwood expression. In the case of Poiseuille flow, there are real oscillations which are observed in the shear stress [13,20,24], but the use of the IK1 approximation masks these real effects with much larger artificial oscillations. Peters and Tildesley [26] calculated the normal pressure and the shear stress for fluid mixtures undergoing Couette flow. They observe spurious behaviour in both functions, which is inconsistent with the conditions for mechanical stability in this system.

2. METHOD

2.1. Pressure Tensor

The pressure tensor of an atomic fluid, **P**, is often defined as the infinitesimal force, $d\mathbf{F}$, felt 'across' an infinitesimal area, $d\mathbf{A}$, which moves with the local streaming velocity, $\mathbf{u}(\mathbf{r},t)$, of the fluid, $d\mathbf{F} = -d\mathbf{A}.\mathbf{P}$.

The Irving-Kirkwood expression is obtained from the 'hydrodynamic route' [27,28]

$$\mathbf{P}(\mathbf{r},t) = \frac{1}{V}\left[\sum_i m_i[\mathbf{v}_i(t)-\mathbf{u}(\mathbf{r}_i,t)][\mathbf{v}_i(t)-\mathbf{u}(\mathbf{r}_i,t)] + \frac{1}{2}\sum \mathbf{r}_{ij}(t)O_{ij}(t)\mathbf{F}_{ij}(t)|_{\mathbf{r}_i(t)=\mathbf{r}}\right] \tag{1}$$

where V is the volume of the system, $\mathbf{v}_i$ is the total particle velocity, $\mathbf{u}$ is the streaming velocity of the fluid, $\mathbf{F}_{ij}$ is the force on atom i due to atom j, and O_{ij} is the differential operator,

$$O_{ij} = 1 - \frac{1}{2!}\mathbf{r}_{ij}.\frac{\partial}{\partial \mathbf{r}} + \cdots\cdots + \frac{1}{n!}\left[-\mathbf{r}_{ij}.\frac{\partial}{\partial \mathbf{r}}\right]^{n-1} + \cdots \tag{2}$$

In homogeneous fluids the gradient operator $\partial/\partial\mathbf{r} = \mathbf{0}$, and the IK1 approximation for the O_{ij} operator is exact [13]. For inhomogeneous fluids the IK1 approximation is reasonably accurate provided that the characteristic length scale which describes inhomogeneities is much longer than the range of the intermolecular potential. The difference been the full IK and the approximate IK1 expressions for the configurational component of the pressure tensor may be seen more readily by noting their instantaneous **k**-space expressions. The IK expression is given as

$$\mathbf{P}^U_{IK}(\mathbf{k}) = -\frac{1}{2}\sum_{ij}\mathbf{r}_{ij}\mathbf{F}_{ij}\left(\frac{1-e^{i\mathbf{k}.\mathbf{r}_{ij}}}{-i\mathbf{k}.\mathbf{r}_{ij}}\right)e^{i\mathbf{k}.\mathbf{r}_i}, \tag{3}$$

whereas the simpler IK1 approximation is

$$\mathbf{P}^U_{IK1}(\mathbf{k}) = -\frac{1}{2}\sum_{ij}\mathbf{r}_{ij}\mathbf{F}_{ij}e^{i\mathbf{k}.\mathbf{r}_i}. \tag{4}$$

There have been numerous equilibrium calculations of the pressure tensor in the liquid-gas interface, thereby enabling a determination of the surface tension of fluids, *e.g.* [29–33]. In the case of an equilibrium planar interface with surface area A, the full Irving-Kirkwood definition of the pressure tensor leads to the following expressions for the transverse and normal components of $\mathbf{P}$ respectively [29,31]:

$$P_T(z) = \rho(z)kT - \frac{1}{4A}\left[\sum_{i<j} \frac{x_{ij}^2 + y_{ij}^2}{r_{ij}} \phi'(r_{ij}) \frac{1}{|z_{ij}|} \Theta\left(\frac{z - z_i}{z_{ij}}\right)\Theta\left(\frac{z_j - z}{z_{ij}}\right)\right] \quad (5a)$$

$$P_N(z) = \rho(z)kT - \frac{1}{2A}\left[\sum_{i<j} \frac{z_{ij}^2}{r_{ij}} \phi'(r_{ij}) \frac{1}{|z_{ij}|} \Theta\left(\frac{z - z_i}{z_{ij}}\right)\Theta\left(\frac{z_j - z}{z_{ij}}\right)\right] \quad (5b)$$

where in this planar geometry x and y are parallel to the surface and z is perpendicular, $\rho(z)$ is the local density at z, $\phi(\mathbf{r}_{ij})$ is the intermolecular potential, $\Theta(x)$ is the Heaviside step function, and $\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j$. Note: $P_T = P_{xx} = P_{yy}$ and $P_N = P_{zz}$. However, as they stand these equations are not valid for a nonequlibrium system.

By Fourier transforming the momentum continuity equation of hydrodynamics, using the definitions of the microscopic density and momentum density, and considering a 3 dimensional system with planar geometry, such that inhomogeneity is assumed only in the y direction, and finally by inverse Fourier transforming the final expressions, one may obtain, respectively, the following statistical mechanical equations for the configurational and kinetic components of the pressure tensor at a planar surface anywhere within the fluid [13],

$$P_{\alpha y}^U(y) = \frac{1}{4A}\sum_{ij} F_{\alpha ij}[\mathrm{sgn}(y_i - y) - \mathrm{sgn}(y_j - y)]$$

$$= \frac{1}{4A}\sum_{ij} F_{\alpha ij}[\Theta(y_i - y)\Theta(y - y_j) - \Theta(y_j - y)\Theta(y - y_i)] \quad (6)$$

$$P_{\alpha y}^K(y,t) = \frac{1}{2A}\sum_i p_{\alpha i}(t)\frac{d}{dt}\mathrm{sgn}[y_i(t) - y]$$

$$= \frac{1}{A}\sum_{t_{i,m}}\sum_i p_{\alpha i}(t_{i,m})\delta(t_{i,m} - t)\mathrm{sgn}[p_{yi}(t_{i,m})] \quad (7)$$

Here A is the cross sectional area of the plane in the $x-z$ direction, $p_{\alpha i}$ is the α-component of the peculiar momentum of particle i, and it is noted that particle i crosses a plane at a set of times $\{t_{i,m}; i=1,..,N;\ m=1,2,....\}$. Equation (7) can be more readily used in computer simulation by taking the time average over the observation time τ

$$P^K_{\alpha y}(y) = \lim_{\tau\to\infty} \frac{1}{A\tau} \sum_{0<t_{i,m}<\tau} \sum_i p_{\alpha i}(t_{i,m}) \mathrm{sgn}[p_{yi}(t_{i,m})] \tag{8}$$

The above derivation shows for the first time the logical connection between the Irving-Kirkwood microscopic mass and momentum densities, and the mechanical definition of pressure as being a force that 'acts across an area'. This derivation also avoids the dubious mathematical operations of making Taylor series expansions of differences of delta functions, which was used in the original Irving-Kirkwood derivation of (1,2). We refer the reader to reference [13] for a full derivation and a more complete discussion of these expressions, including their relation to the well known ambiguity in the definition of the pressure tensor. Eqns. (6–8) will be referred to as 'Method of Planes' or MOP expressions for the pressure tensor.

A further route to the stress P_{xy} is obtained by a direct integration of the momentum continuity equation of hydrodynamics [13]. This so called 'mesoscopic' route gives the shear stress for planar Poiseuille flow as

$$P_{xy}(y) = F_e \int_0^y dy'\, n(y') \tag{9}$$

where F_e is the force applied to each atom which drives the flow (*e.g.* gravity), and $n(y)$ is the number density. We call this integration of the momentum continuity equation the IMC method. Equation (9) is valid even for fluids subject to many-body interparticle interactions.

2.2. Heat Flux Vector

The full Irving-Kirkwood expression for the heat flux vector is [27,28]

$$J_q(\mathbf{r}) = \frac{1}{V} \Big\langle \sum_{ij} (\mathbf{v}_i(t) - \mathbf{u}(\mathbf{r},t)) U_i(t) - \frac{1}{2} \sum_{ij} \mathbf{r}_{ij}(t) (\mathbf{v}_i(t) - \mathbf{u}(\mathbf{r},t)) . \mathbf{F}_{ij}(t) O_{ij}(t) | \mathbf{r}_i(t) = \mathbf{r} \Big\rangle \tag{10}$$

where U_i is the contribution of particle i to the internal energy of the fluid, and the other variables are as previously defined. In the derivation of this equation it is assumed that the streaming velocity does not vary significantly over the range of the interatomic forces.

In an analogous way we can, starting from the hydrodynamic continuity equation for the local energy density of the liquid, obtain MOP expressions for the configurational and kinetic components of the heat flux vector vector respectively [14],

$$J_{qy}^{U}(y,t) = -\frac{1}{4A}\sum_i\sum_j(\mathbf{v}_i-\mathbf{u}(y))\cdot\mathbf{F}_{ij}(\mathrm{sgn}(y-y_i)-\mathrm{sgn}(y-y_j)) \tag{11}$$

$$J_{qy}^{K}(y) = \lim_{\tau\to\infty}\frac{1}{A\tau}\sum_{0<t_{i,m}<\tau}\sum_i U_i\,\mathrm{sgn}[c_{yi}(t_{i,m})] \tag{12}$$

where c_{yi} is the y-component of the peculiar velocity of particle i.

The mesoscopic analogue of these expressions for the heat flux is found by integrating the hydrodynamic continuity equation for the specific internal energy, which for the special case of planar Poiseuille flow becomes [14]

$$J_{qy}(y) = -\int_0^y dy'\,P_{xy}(y')\gamma(y') \tag{13}$$

where $\gamma(y)$ is the strain rate defined as

$$\gamma(y) = \frac{\partial u_x(y)}{\partial y} \tag{14}$$

We call the calculation of the heat flux vector by integrating the energy continuity equation (*i.e.*, eqn.13) the IEC method. Again this expression is valid for fluids subject to many-body forces.

3. RESULTS AND DISCUSSION

Figure 1 shows the geometry of the system studied. The details of these simulations may be found in references [13,14,20] and the reader is referred to them for details. All fluid and wall particles were WCA atoms and the walls were fixed in place by a combination of harmonic restoring forces and a constraint mechanism. The wall atoms were also thermostatted to remove

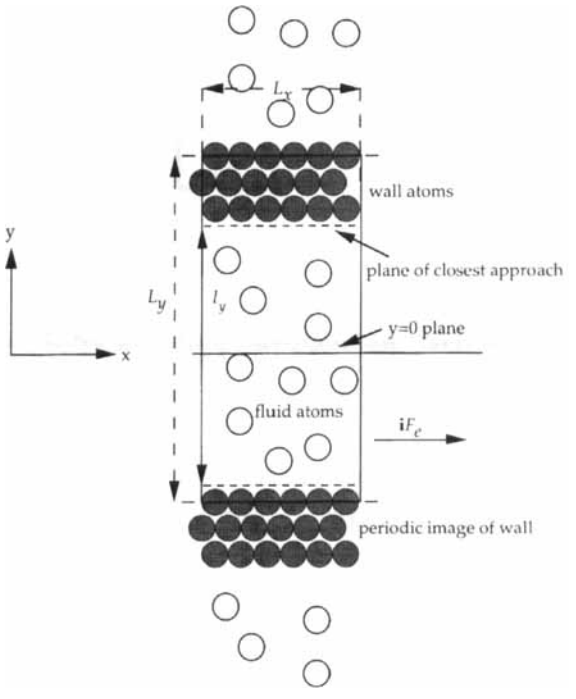

FIGURE 1 Simulation geometry for planar Poiseuille flow. The z-axis is normal to the page.

the viscous heat produced by the shearing motion in the bulk of the fluid. The fluid atoms satisfy Newton's equations of motion for particles interacting both with other fluid atoms and, if they are sufficiently close to the walls, with wall atoms. The system is fully periodic in all three dimensions.

Figure 2 shows the IK1 and MOP pressure P_{yy} as a function of position in a pore of width 25σ. It also shows the pressure calculated on the left wall, defined as the total y component of force per unit area exerted on the wall atoms by fluid particles. As is clearly seen, spurious oscillations are observed in the IK1 results close to the walls, whereas we know that for mechanically stable nonequilibrium steady state, P_{yy} must be constant across the entire fluid. The IK1 values of P_{yy} in fact correlate with the density profile, as is seen in Figure 3. These oscillations in P_{yy} are not real effects; they are caused entirely by the failure to account for the higher order O_{ij} terms in the full IK1 expansion for the pressure tensor. P_{yy} calculated via MOP does however display the correct mechanical behaviour: it is completely constant across the entire pore, and this value agrees very well with P_{yy} calculated at the wall, as indeed it must.

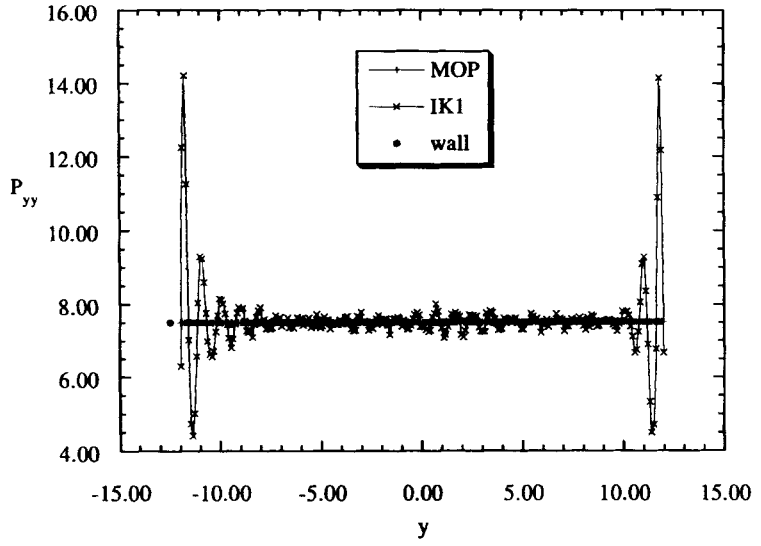

FIGURE 2 P_{yy} calculated by IK1 and MoP for a pore of width 25σ, mean density $\bar{n} = 0.8362$, and mean temperature $\bar{T} = 0.97$.

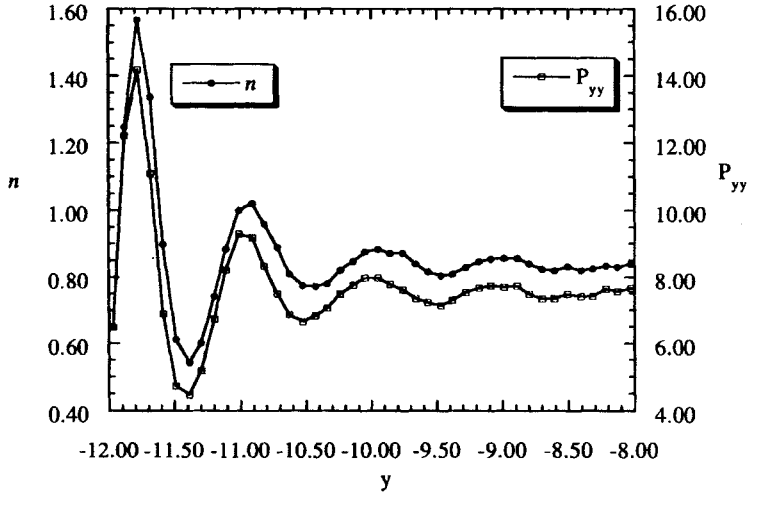

FIGURE 3 Correlation between P_{yy}(IK1) and $n(y)$ for the system of Figure 2.

In Figure 4 we display P_{xy}, again calculated by IK1 and MOP. Again a similar behaviour is observed: the IK1 values display spurious oscillations near the walls, whereas those calculated by MOP display an almost linear

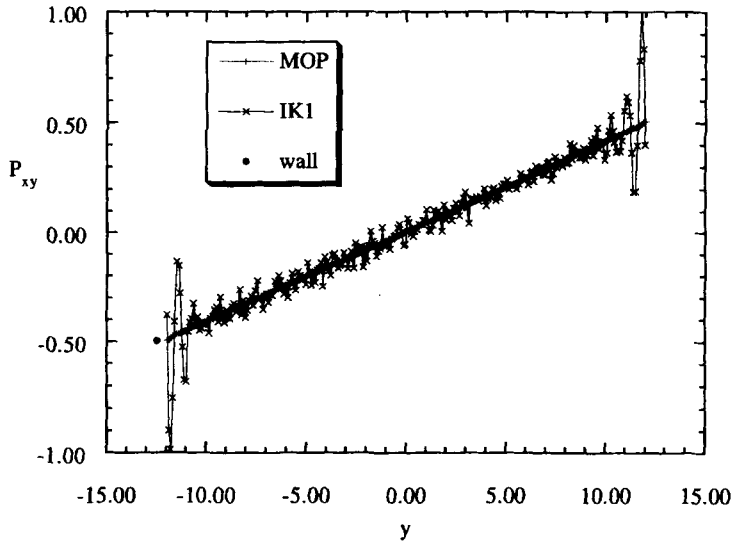

FIGURE 4 P_{xy} calculated by IK1, MoP and at the walls for the system of Figure 2.

behaviour. Once again P_{xy} calculated at the left wall agrees very well with the MOP results.

In Figure 5 P_{xy} is displayed for a pore of 10σ. This time P_{xy} has been calculated by the MOP and IMC techniques. Both independent methods produce identical results within the estimated statistical uncertainty. Clearly, P_{xy} is not purely linear but displays oscillations close to the walls. These oscillations are real effects and are not to be confused with the spurious oscillations observed for the IK1 results of Figure 4.

If we define the viscosity as

$$\eta(y) = -\frac{\langle P_{xy}(y) \rangle}{\langle \gamma(y) \rangle} \tag{15}$$

we can then calculate the spatially inhomogeneous viscosity profiles as a function of position across the pore. In calculating $\gamma(y)$ we have assumed a symmetric parabolic profile for the streaming velocity [13].

The viscosity profile is displayed in Figure 6 for a pore of width 10σ. Clearly the viscosity for such an highly inhomogeneous fluid is not constant but is a strongly oscillating function of position. These osillations are caused by oscillations in the shear stress $-P_{xy}$, since $\gamma(y)$ is assumed here to be linear. It is worth pointing out that if the IK1 values of P_{xy} were used the

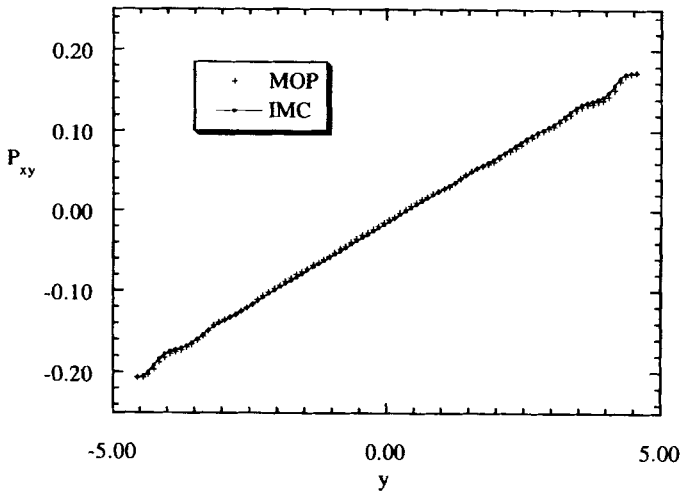

FIGURE 5 P_{xy} calculated MOP and IMC for a pore of width 10σ; $\bar{n} = 0.84$, $\bar{T} = 0.91$.

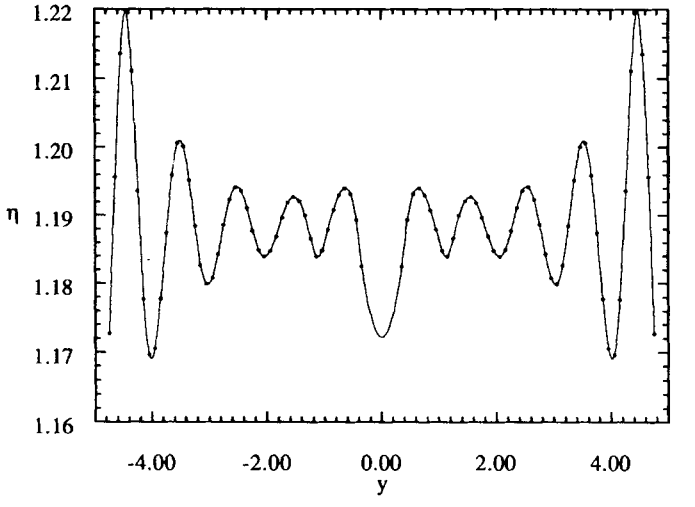

FIGURE 6 Viscosity for a pore of width 10σ; $\bar{n} = 0.71$, $\bar{T} = 0.9$.

viscosity profiles would show oscillations with much larger amplitudes due to spurious oscillations caused by ignoring the higher order terms in the O_{ij} expansion, and would obviously be incorrect.

In Figure 7 we display the heat flux vector for a pore of width 50σ, calculated by the IK1 and MOP techniques. Once again we see that for a

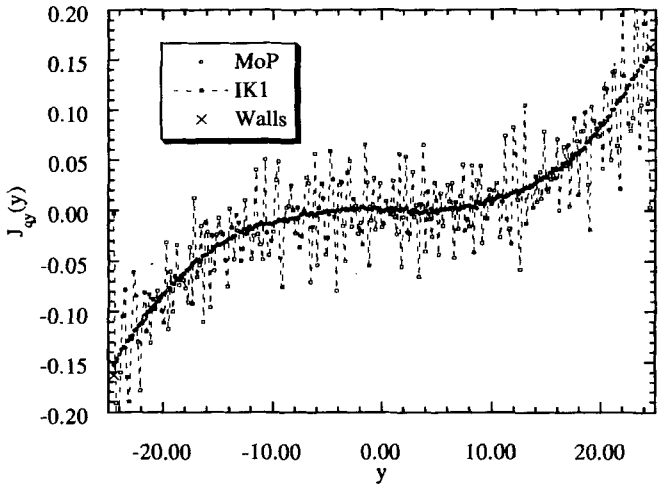

FIGURE 7 $J_{qy}(y)$ calculated by MoP and IK1 for a pore of width 50σ; $\bar{n} = 0.84$, $\bar{T} = 0.9$. Also shown is the value of the heat flux at the walls.

given run length the MOP results are more accurate. Also shown is the heat flux calculated at the wall, defined as

$$\langle J_{qy}(y_{\text{wall}})\rangle = \frac{1}{A}\langle K_w \alpha\rangle \tag{16}$$

were K_w is the kinetic energy of the wall atoms, α is the thermostat multiplier, and the angle brackets indicate a time average [14]. In Figure 8 we compare the heat flux for the MOP and IEC methods and find once again excellent agreement.

Finally we make a comment on the shape of the heat flux vector. Classical hydrodynamics, in the form of the Navier-Stokes energy balance equation, predicts for planar Poiseuille flow a temperature profile which should be purely quartic. If the heat flux vector is defined by the constitutive Fourier relation $\mathbf{J}_q = -\lambda_{NS}\nabla T$, where λ_{NS} is the Navier-Stokes thermal conductivity, it is clear that it should have a cubic profile, which it does, as displayed by Figure 8. However, Baranyai *et al.* [18] postulated that the heat flux is also coupled to the gradient of the square of the strain rate tensor, which for our geometry would imply a constitutive relation of the form

$$J_q(y) = -\lambda\frac{\partial T(y)}{\partial y} - \xi\frac{\partial \gamma^2(y)}{\partial y}, \tag{17}$$

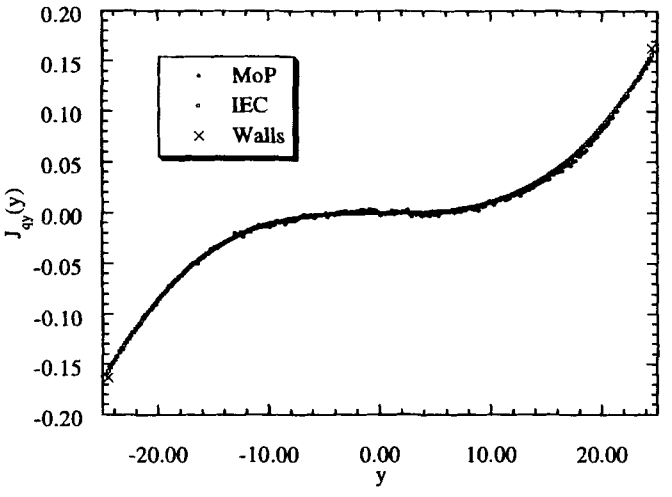

FIGURE 8 $J_{qy}(y)$ calculated by MoP and IEC for the system of Figure 7.

where ξ is the cross coupling coefficient. Since $\gamma(y)$ is linear for planar Poiseuille flow, the second term on the right hand side of (17) might be expected to introduce a linear term into the heat flux equation. However, we do not observe this linear term, and the heat flux is purely cubic. Baranyai *et al.* [18] also showed that the introduction of the cross coupling term in (17) changes the shape of the temperature profile from the purely quartic prediction of classical Navier-Stokes theory, to a quartic plus parabolic term. Todd and Evans [20] then showed that the gradient of the parabolic term (*i.e.*, the first term on the right hand side of (17)) exactly cancels the linear term introduced by the cross coupling term, thus leaving the heat flux vector purely cubic. In other words, for the case of planar Poiseuille flow, the existence of a cross coupling between the heat flux vector and the gradient of the square of the strain rate tensor does not change the shape or magnitude of the heat flux vector from what would ordinarily be predicted by classical hydrodynamics. The only evidence for this coupling is to be found in the shape of the temperature profile, which should contain an additional quadratic component. We are currently attempting to observe this term for planar Poiseuille flow.

4. CONCLUSION

We showed that for a highly inhomogeneous fluid the Irving-Kirkwood O_{ij} operator must be included in the Irving-Kirkwood expressions for the

pressure tensor and heat flux vector. Setting $O_{ij} = 1$ (as is commonly done) leads to incorrect values for these quantities. This has important consequences for the case of flows through pores, in which strong density oscillations near the walls will cause anomalous oscillations in the IK1 expressions for $\mathbf{P}$ and $\mathbf{J}_q$.

We have derived exact expressions for the pressure tensor and heat flux vector which include an infinite summation of the O_{ij} term. As they stand, the expressions are valid for planar flow, but could be generalised for other geometries. For the case of planar Poiseuille flow we have compared our MOP calculations of the stress and heat flux with direct integrations of the momentum and energy continuity equations of hydrodynamics. The agreement between both methods is excellent.

Finally we point out that a possible coupling of the heat flux vector to the gradient of the square of the strain rate tensor is compatible with the observable shape and magnitude of the heat flux. Although no evidence for its existence is evident in the heat flux vector itself, the effect should add a parabolic term to the normally quartic temperature profile. These measurements are extremely difficult to make, due to the high degree of statistical accuracy required.

References

[1] Snook, I. K. and Van Megan, W. (1980) "Solvation forces in simple dense fluids. I", *J. Chem. Phys.*, **72**(5), 2907.

[2] Bitsanis, I., Magda, J. J., Tirell, M. and Davis, H. T. (1987) "Molecular dynamics of flow in micropores", *J. Chem. Phys.*, **87**(3), 1733.

[3] Bitsanis, I., Vanderlick, T. K., Tirrell, M. and Davis, H. T. (1988) "A tractable molecular theory of flow in strongly inhomogeneous fluids", *J. Chem. Phys.*, **89**(5), 3152.

[4] Bitsanis, I., Somers, S. A., Davis, H. T. and Tirrell, M. (1990) "Microscopic dynamics of flow in molecularly narrow pores", *J. Chem. Phys.*, **93**(5), 3427.

[5] Somers, S. A. and Davis, H. T. (1992) "Microscopic dynamics of fluids confined between smooth and atomically structured solid surfaces", *J. Chem. Phys.*, **96**(7) 5389.

[6] Vanderlick, T. K. and Davis, H. T. (1987) "Self-diffusion in fluids in microporous fluids", *J. Chem. Phys.*, **87**(3), 1791.

[7] Davis, H. T. (1987) "Kinetic theory of inhomogeneous fluid: Tracer diffusion", *J. Chem. Phys.*, **86**(3), 1474.

[8] Mareschal, M., Kestemont, E., Baras, F., Clementi, E. and Nicolis, G. (1987) "Nonequilibrium states by molecular dynamics transport coefficients in constrained fluids", *Phys. Rev. A*, **35**(9), 3883.

[9] Lupkowski, M. and van Swol, F. (1991) "Ultrathin films under shear", *J. Chem. Phys.*, **95**(3), 1995.

[10] Chan, D. Y. C. and Horn, R. G. (1985) "The drainage of thin liquid films between solid surfaces", *J. Chem. Phys.*, **83**(10), 5311.

[11] Gee, M. L., McGuiggan, P. M., Israelachvili, J. N. and Homola, A. M. (1990) "Liquid to solid like transitions of molecularly thin films under shear", *J. Chem. Phys.*, **93**(3), 1895.

[12] Georges, J. M., Millot, S., Loubet, J. L. and Tonck, A. (1993) "Drainage of thin films between relatively smooth surfaces". *J. Chem. Phys.*, **98**(9), 7345.

[13] Todd, B. D., Evans, D. J. and Daivis, P. J. (1995) "The pressure tensor for inhomogeneous fluids", *Phys. Rev. E*, **52**(2), 1627.
[14] Todd, B. D., Davis, P. J. and Evans, D. J. (1995) "Heat flux vector in highly inhomogeneous nonequilibrium fluids", *Phys. Rev. E*, **51**(5), 4362.
[15] Ashurst, W. T. and Hoover, W. G. (1973) "Argon shear viscosity via a Lennard-Jones potential with equilibrium and nonequilibrium molecular dynamics", *Phys. Rev. Lett.*, **31**, 206.
[16] Ashurst, W. T. and Hoover, W. G. (1975) "Dense-fluid shear viscosity via nonequilibrium molecular dynamics", *Phys. Rev.*, **A11**(2), 658.
[17] Liem, S. Y., Brown, D. and Clarke, J. H. R. (1992) "Investigation of the homogeneous-shear nonequilibrium molecular dynamics method", *Phys. Rev.*, **A45**(6), 3706.
[18] Baranyai, A., Evans, D. J. and Daivis, P. J. (1992) "Isothermal shear-induced heat flow", *Phys. Rev.*, **A46**(12), 7593.
[19] Todd, B. D., Evans, D. J. and Daivis, P. J. unpublished.
[20] Todd, B. D. and Evans, D. J. (1995) "The heat flux vector for highly inhomogeneous nonequilibrium fluids in very narrow pores", *J. Chem. Phys.*, **103**(22), 9804.
[21] Murad, S., Ravi, P. and Powles, J. G. (1993) "Anisotropic thermal conductivity of a fluid in a system of microscopic slit pores", *Phys. Rev.*, **E48**(5), 4110.
[22] Pozhar, L. A. and Gubbins, K. E. (1991) "Dense inhomogeneous fluids: Functional perturbation theory, the generalized Langevin equation and kinetic theory", *J. Chem. Phys.*, **94**(2), 1367.
[23] Pozhar, L. A. and Gubbins, K. E. (1993) "Transport theory of dense, strongly inhomogeneous fluids", *J. Chem. Phys.*, **99**(8), 8970.
[24] Akhmatskaya, E. V., Todd, B D., Daivis, P. J., Evans, D. J., Gubbins, K. E. and Pozhar, L. A. "A study of viscosity inhomogeneity in porous media", unpublished.
[25] Thompson, P. A. and Robbins, M. O. (1990) "Shear flow near solids: Epitaxial order and flow boundary conditions", *Phys. Rev.*, **A41**(12), 6830.
[26] Peters, G. H. and Tildesley, D. J. (1995) "Computer simulation of the rheology of grafted chains under shear", *Phys. Rev.*, **E52**(2), 1882.
[27] Irving, J. H. and Kirkwood, J. G. (1950) "The statistical mechanical theory of transport processes. IV. The equations of hydrodynamics", *J. Chem. Phys.*, **18**(6), 817.
[28] Evans, D. J. and Morriss, G. P. (1990) "Statistical Mechanics of Nonequilibrium Liquids", Academic Press, London.
[29] Rao, M. and Berne, B. J. (1979) "On the location of surface of tension in the planar surface between liquid and vapour", *Mol. Phys.*, **37**(2), 455.
[30] Hemingway, S. J., Henderson, J. R. and Rowlinson, J. S. (1981) "The density profile and surface tension of a drop", *Faraday Symp., Chem. Soc.*, **16**, 33.
[31] Walton, J. P. R. B., Tildesley, D. J., Rowlinson, J. S. and Henderson, J. R. (1983) "The pressure tensor at the planar surface of a liquid", *Mol. Phys.*, **48**(6), 1357.
[32] Lee, D. J., Telo da Gamma, M. M. and Gubbins, K. E. (1984) "The vapour-liqiud interface for a Lennard-Jones model of argon-krypton mixtures", *Mol. Phys.*, **53**(5), 1113.
[33] Haye, M. J. and Bruin, C. (1994) "Molecular dynamics study of the curvature correction to the surface tension", *J. Chem. Phys.*, **100**(1), 556.