

A technique for the calculation of mass, energy, and momentum densities at planes in molecular dynamics simulations

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(Received 26 December 1995; accepted 10 April 1996)

We present a new technique for the evaluation of hydrodynamic densities (for example mass, energy or momentum densities) at planes in molecular dynamics simulations. This technique employs an easily computed expression for the density at a plane that is formally exact, unlike other expressions such as histogram approximations. We present simple examples of applications of this procedure to the calculation of mass and momentum densities, and hence the streaming velocity, at planes in a fluid undergoing planar Poiseuille flow, and show how the temperature profile can be obtained by the same procedure. © 1996 American Institute of Physics. [S0021-9606(96)51423-6]

I. INTRODUCTION

In recent publications^{1,2} it has been shown how thermodynamic fluxes such as the pressure tensor and heat flux vector in a planar geometry can be computed in molecular dynamics simulations using formally exact expressions derived from the continuity equations. Quantities computed using these expressions have the advantages that they do not suffer from the smoothing effects of histogram approximations, they do not require evaluation of the troublesome O_{ij} infinite series differential operator, and they do not assume a functional form for the property of interest, as would be the case, for example, in least squares estimations of polynomial or Fourier series fit coefficients. In this work, we show how the hydrodynamic densities such as the mass, energy, and momentum density, can be calculated using similar methods.

II. THEORY AND RESULTS

We will derive an expression for the mass density as an example. The microscopic expression for the instantaneous mass density is given by

$$\rho(\mathbf{r}, t) = \sum_i m_i \delta[\mathbf{r} - \mathbf{r}_i(t)]. \quad (1)$$

We require an easily computed, exact expression for the time-averaged density. Because of the delta function localization of the mass, we cannot exactly evaluate the time average of the three-dimensional density. Instead, we average over the $x-z$ plane and evaluate the variation of the density in the y direction. That is,

$$\rho(y) = \frac{1}{\tau A} \int_0^\tau ds \int dx dz \rho(\mathbf{r}, s), \quad (2)$$

where A is the area of the plane and τ is the time interval over which we average. After averaging the delta function in

Eq. (1) over the $x-z$ plane, the remaining one-dimensional delta function can be rewritten in terms of a sum of delta functions in time as

$$\delta[y - y_i(t)] = \sum_\alpha \frac{\delta(t - t_\alpha)}{|\dot{y}_i(t_\alpha)|}, \quad (3)$$

where the t_α represent the times at which particle i crosses the plane located at y , and \dot{y}_i is the y component of the velocity of particle i . Evaluating the time average [Eq. (2)] of the density [Eq. (1)], using Eq. (3), we obtain

$$\rho(y) = \frac{1}{\tau A} \sum_i \sum_\alpha \frac{m_i}{|\dot{y}_i(t_\alpha)|} \quad (4)$$

for the time average of the mass density at y averaged over the $x-z$ plane. The computation of Eq. (4) is achieved by simply summing the quantity on the right-hand side over the number of times any particle crosses the plane located at y . The y component of the velocity of particle i at the precise time of the plane crossing is evaluated by solving for t_α using a Newton-Raphson scheme and then interpolating the velocity. The result [Eq. (4)] is analogous to those given previously for the kinetic parts of the pressure tensor and heat flux vector^{1,2} although the generality of these results was not previously recognized. For the special case of a hard particle-wall interaction, the analogous equation for the pressure at the wall has been known for some time, since it follows from the intuitive definition of pressure in terms of the momentum transferred to the wall (see Ref. 3 and references therein).

We have used the new technique to compute the density profile for a single-component atomic liquid undergoing planar Poiseuille flow between two walls as described in our previous work.^{1,2} The simulation parameters for these experiments were as follows: All quantities are expressed in the standard dimensionless reduced units defined with respect to the Lennard-Jones potential parameters and the mass of an atom. The (periodic) wall was constructed from three layers of 72 atoms, tethered to lattice sites by a harmonic potential with force constant 150.15. The fluid between the walls comprised 360 atoms. The fluid density was 0.75, the wall separation was 5.1, and the wall density was 0.85. The wall tem-

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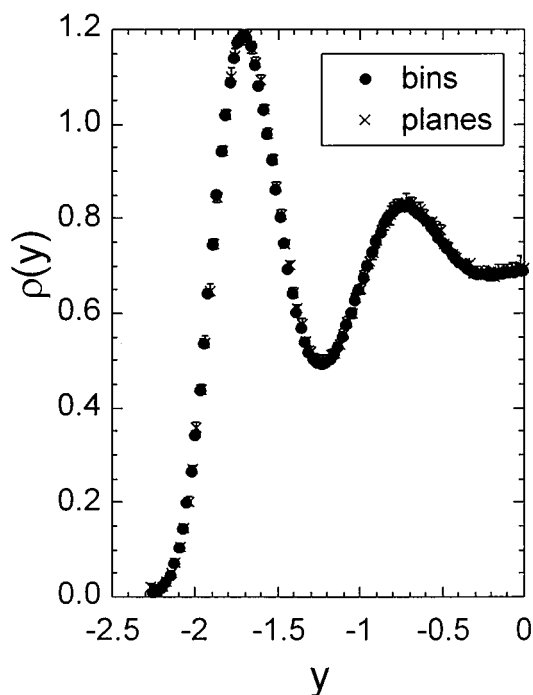


FIG. 1. Reduced number density as a function of position from the left-hand wall to the center of the channel at $y=0$. The results of calculations by the methods of bins (circles) and planes (crosses) are shown. Note that the error bars are approximately the same size as the symbols.

perature was maintained at 0.722 by a Gaussian constraint thermostat and heat was removed from the fluid by conduction to the walls. The flow was generated by an external field of 0.1, and results were collected over a period of 2×10^6 timesteps of length 0.001. Further details may be found in previous publications.^{1,2}

Figure 1 compares the mass density profiles obtained first by using the traditional histogram approximation (bins)^{1,2} and second, Eq. (4) (planes). The bin width was set at a value that gave a satisfactory compromise between statistical noise and resolution. The agreement between the two sets of results is excellent, verifying Eq. (4). At the bin width chosen for this comparison, the standard deviation in the binned density is typically 0.5 times the standard deviation in the planes density.

In principle, the bins (histogram) and planes techniques differ in that the bins technique involves averaging the data over a region of nonzero thickness in the y direction. This results in a loss of resolution, or the introduction of a systematic error due to smoothing, with a corresponding reduction in random error. In contrast, the planes technique does not average in the y direction. The statistical noise in the planes results is independent of the spacing of the planes, whereas the noise in the bins data can always be reduced at the expense of resolution, by increasing the bin width. Thus, we see that better resolution can only be achieved by reducing the bin width, giving a corresponding increase in the random error, when the histogram approach is applied. The major advantages of the planes method are therefore that the number of planes can be reduced with no loss of resolution

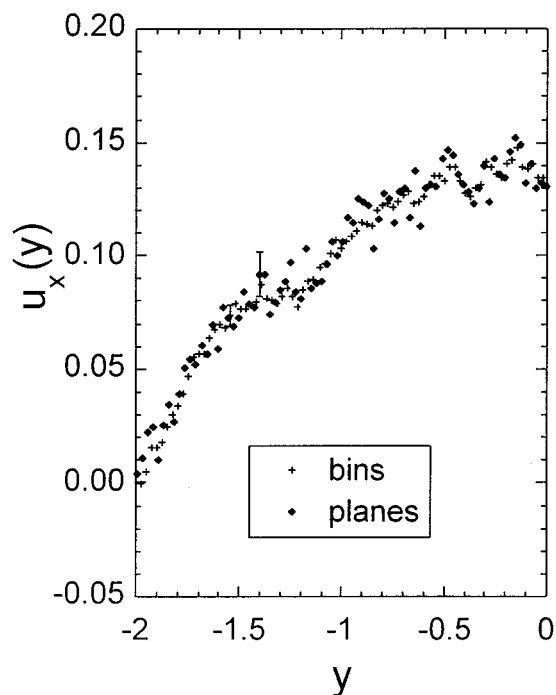


FIG. 2. Streaming velocity profile calculated by the method of planes (crosses) and by bins (squares) for the left half of the channel. Representative error bars are shown. The error bars for the bins data are approximately the same size as the symbols.

and that the maximum possible resolution is attainable without a divergent increase in random error. Consequently, the number of planes can be reduced for slowly varying quantities, resulting in a substantial increase in the computational efficiency.

It is straightforward to calculate the time average of the x component of the instantaneous momentum density vector $J_x(y, t) = \rho(y, t)u_x(y, t)$ averaged over the $x-z$ plane, using Eq. (3) and the microscopic expression for the momentum density

$$\mathbf{J}(\mathbf{r}, t) = \sum_i m_i \mathbf{v}_i \delta[\mathbf{r} - \mathbf{r}_i(t)] \quad (5)$$

giving

$$J_x(y) = \frac{1}{\tau A} \sum_i \sum_\alpha \frac{m_i v_{xi}}{|\dot{y}_i(t_\alpha)|} \quad (6)$$

for the time average. Here, v_{xi} is the x component of the laboratory velocity of particle i . The streaming velocity $u_x(y)$ can then be calculated as $J_x(y)/\rho(y)$, and an example of such a calculation is given in Fig. 2. The agreement between bins and planes results is once again excellent. It should be noted that the results obtained with Eqs. (4) and (6) are formally exact, in contrast to calculations that use a histogram approximation. Once again, as a consequence of the smoothing in the binned data, the random errors in the binned data are typically half of the random errors in the planes data.

Two significant features are immediately apparent in Fig. 2. First, we observe significant deviations from the ex-

pected quadratic velocity profile. These deviations result from the inhomogeneity of the fluid density near the walls. This will be discussed in more detail in a forthcoming paper. Second, the data from both methods become very scattered in the vicinity of the walls. This results from the very low density within one atomic diameter of the wall (see Fig. 1). Note also that the streaming velocity approaches zero at -2.0 , indicating that a stick boundary condition applies in this simulation. More discussion of these points can be found in Refs. 1 and 2.

Once the mass and momentum density profiles are known, it is a simple matter to obtain the shear stress profile in the steady state by integration of the momentum continuity equation, as has been shown previously.¹ This makes a separate evaluation of the shear stress profile unnecessary. Similarly, the heat flux vector profile can be obtained by integrating the heat continuity equation for the steady state if the internal energy, mass, and momentum density profiles are known.²

Similar methods can be used to calculate the temperature at a plane from the definition of the kinetic temperature in terms of the peculiar kinetic energy density and the number density

$$K(\mathbf{r}, t) = \frac{3}{2} k_B n(\mathbf{r}, t) T(\mathbf{r}, t), \quad (7)$$

where the peculiar kinetic energy density is evaluated using

$$K(y) = \frac{1}{\tau A} \sum_i \sum_\alpha \frac{m_i [v_{xi} - u_x(y_i)]^2}{2 |\dot{y}_i(t_\alpha)|} \quad (8)$$

and the number density is simply the mass density divided by the mass of a particle for a single component fluid.

III. CONCLUSION

In conclusion, we have introduced a new technique for the evaluation of hydrodynamic densities in molecular dynamics simulations with planar symmetry. This technique has the advantage of being formally exact, with no averaging in the direction normal to the planes, and the statistical noise in the density at a given plane is independent of the plane separation. The new technique is particularly well suited to the evaluation of streaming velocity and temperature profiles in a planar geometry, because it does not require an assumption of a functional form for the computed quantity, in contrast to least squares methods. The planes technique also offers the possibility of enhanced computational efficiency, because the plane separation can be increased as required with no loss of resolution, unlike the bin width in traditional binning methods.

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