Comment on "Reversing the perturbation in nonequilibrium molecular dynamics: An easy way to calculate the shear viscosity of fluids"

Christopher P. Calderon and Wm. T. Ashurst*
Combustion Research Facility, Sandia National Laboratories, Livermore, California 94551-0969
(Received 20 August 2001; published 26 July 2002)

Müller-Plathe [Phys. Rev. E **59**, 4894 (1999)] gives a velocity exchange method that creates a shear momentum flux. Measurement of the mean velocity gradient allows the determination of the shear viscosity. Low gradients are achieved when the time interval between exchanges is large (low frequency). We show that low frequency does not produce a steady shear flow while a weaker, but continuous exchange, does have a steady flow.

DOI: 10.1103/PhysRevE.66.013201 PACS number(s): 66.20.+d, 61.20.Ja, 02.70.−c

Müller-Plathe (MP) has presented a velocity exchange method by which either shear viscosity [1] or thermal conductivity [2] may be calculated in a molecular dynamics simulation. In this method the flux is created by the exchange while the resulting gradient is measured. This is the reverse of the usual procedure, but it may be advantageous in calculating thermal conductivity of complex molecules. Here we will discuss only the shear flow scheme: a selected pair of atoms, separated by a known distance in y, exchange their x component of velocity and thereby cause a flux of momentum P_{xy}. The selected atom pair have the extreme x velocity values within their respective spatial region. This process is repeated every W time steps (W is the parameter that determines the exchange frequency). The system response is the establishment of a mean velocity gradient between the atom pair. Consider a periodic system divided into m bins in the y direction. At the exchange time the atom in the first bin with the most negative x velocity exchanges its x velocity with the atom in bin $m/2+1$ which has the most positive x velocity. The resulting mean velocity is periodic in y with a negative (positive) gradient in the lower (upper) half of the system.

MP presents mean velocity profiles with values of $W=3$, 15, 60, 300, and 1200 [1]. The two lower values result in nonlinear velocity gradients. Our concern is in the larger values of W and how the system behaves between the exchanges. Note that an upper limit on W, which corresponds to a lower limit on the flux, is the level of thermal noise within the system. We find that large values of W ($=320$) produce an unsteady shear flow, and thus a possible complication in the extrapolation of results to low gradient values when the transport coefficient has a rate dependence [3].

To illustrate the unsteady nature, we examine the potential part of the shear viscosity in a very dense fluid where the kinetic contribution is small. In an equilibrium system the pair distribution function is isotropic and only depends upon the atom separation. When this isotropic distribution is distorted by the shearing motion then a term with the symmetry of shearing motion is established and it is this term that determines the potential part of the shear stress. Thus, the pair distribution function in a shear flow may be expanded in spherical harmonics [4,5] and the first order approximation of the potential contribution to viscosity is dependent on a term with the symmetry of xy/r^2 when the x component of velocity has a gradient in the y direction. Hence we examine the temporal behavior of xy/r^2 versus r for all pairs of atoms. Using $W=320$ we break the time interval between exchanges into eight subintervals of 40 time steps each and gather the pairwise probability of xy/r^2 within each subinterval, the total number of exchanges is 330. We do find a nonsteady nature in this shear distribution function and a corresponding nonsteady nature in the mean velocity gradient when it is also broken into subinterval averages, see Fig. 1. We have used a Lennard-Jones (LJ) potential with a cutoff of 2.5σ, the reduced temperature is 0.72 and the reduced density is 0.844. The number of atoms is 1500, the y width is 25.2σ, and the other two dimensions are 8.4σ. The total number of time steps is 10^5 with $dt=0.007$. We speculate that the temperature profiles that are not parabolic in nature, see Fig. 4(a) in MP, are created by the pulses of heat genera-

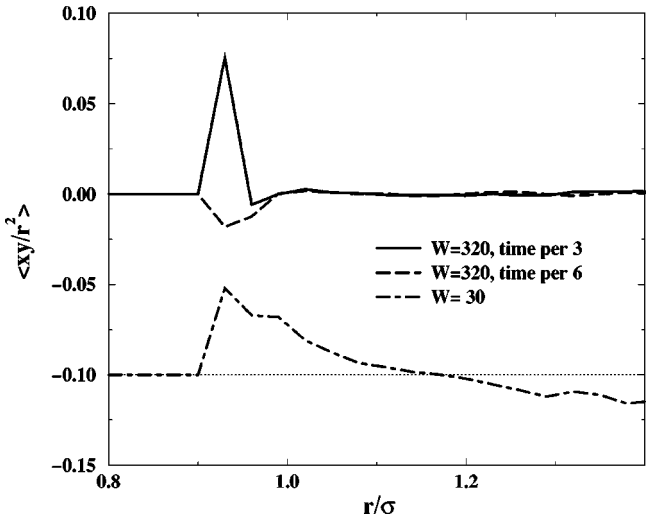

FIG. 1. The shear pair distribution function has a temporal dependence with respect to the exchange time of $W=320$ time steps (there are eight periods between exchanges, periods 3 and 6 are shown). A higher frequency of exchange, $W=30$, and a more steady flow, increases the radial extent of the positive correlation (the curve is displaced by 0.1 for clarity and the time average is over all time periods).

*Email address: ashurs@ca.sandia.gov

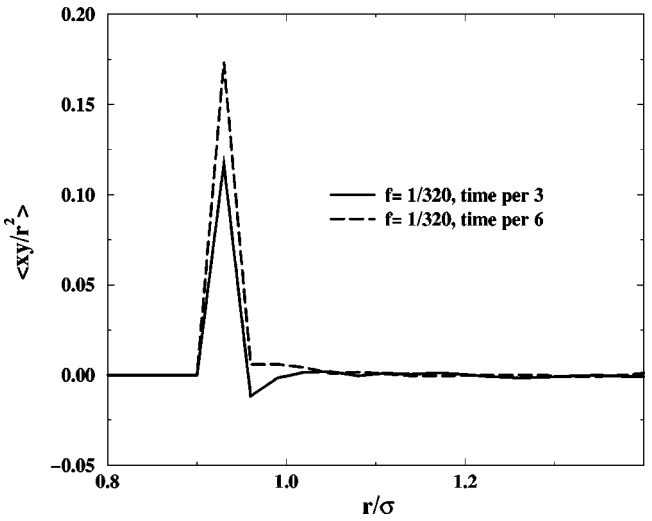

FIG. 2. The shear pair distribution function with a continuous velocity exchange, with the fraction $f=1/320$ of the velocity exchanged every time step, does not have the temporal dependence seen in Fig. 1 (the same time periods are shown in both figures).

tion that will occur in the low frequency exchange simulations.

It is possible to make a more steady shearing system with the exchange concept and to do that we have also computed a system in which only a fraction of the velocity is exchanged at every step. Let the selected atom pair have velocities v_1, v_2 before the exchange and v_1', v_2' after the exchange. Using $v_1'=(1-f)v_1+fv_2$ and $v_2'=fv_1+(1-f)v_2$ with $f=1$ produces the original full exchange method and this exchange is done at an interval of W time steps. Our modification is to set $f=1/W$ and do the exchange at *every* step. On each step the atom pair that have the extreme velocities may be different, but we find that the magnitude of the velocity difference shows little variation from step to step (implying that the velocity distribution is quite steady). With this continuous-exchange method we find that the shear distribution function does not indicate any temporal changes as in the first method, see Fig. 2 where the fraction value is $f=1/320$. Linear momentum is conserved, but not total energy energy in this continuous method, and so we have used a Gaussian control of mean temperature in both methods given here (see also MP). Another way which maintains the advantages of the original scheme (and suggested by Müller-Plathe [5]), is the simple remedy of reducing the desired velocity difference in selecting the atom pair. Hence, linear momentum, system energy, and the exchange frequency may be held constant while obtaining viscosities at various levels of strain rate. We have not done this but expect that results similar to that seen in our continuous method would be obtained.

Bounds on the exchange frequency which maintain a steady shear flow may be estimated in two ways: the Maxwell relaxation time $\tau_M=\eta/G$, where G is the high frequency shear modulus [6,7] and η is the shear viscosity, provides one estimate and linear response theory provides another. Using linear response theory the decay of a weak perturbation that produces shearing motion may be equated to the decay of the stress autocorrelation in an equilibrium system [8]. For the LJ state point of interest here the autocorrelation decays to zero in two time units [3], and with a time step of 0.007, this implies that an exchange with $W>286$ will produce periods of no mean shear before the next exchange occurs, as seen in Fig. 1. In addition to using these estimates one can gather information with respect to the exchange time, as was done in generating Fig. 1, and determine an exchange frequency with the desired response for the state point of interest.

This work was supported by the United States Department of Energy through the Office of Basic Energy Sciences, Division of Chemical Sciences.

[1] F. Müller-Plathe, Phys. Rev. E **59**, 4894 (1999).
[2] F. Müller-Plathe, J. Chem. Phys. **106**, 6082 (1997).
[3] M. Ferrario, G. Ciccotti, B. L. Holian, and J.-P. Ryckaert, Phys. Rev. A **44**, 6936 (1991).
[4] G. Marcelli, B. D. Todd, and R. J. Sadus, Phys. Rev. E **63**, 021204 (2001).
[5] F. Müller-Plathe (private communication); P. Bordat and F. Müller-Plathe, J. Chem. Phys. **116**, 3362 (2002).
[6] W. T. Ashurst and W. G. Hoover, Phys. Rev. A **11**, 658 (1975).
[7] S. Hess and D. J. Evans, Phys. Rev. E **64**, 011207 (2001).
[8] J.-P. Ryckaert, A. Bellemans, G. Ciccotti, and G. V. Paolini, Phys. Rev. A **39**, 259 (1989).