

COMMENTS

Comment on “Molecular simulation and continuum mechanics study of simple fluids in nonisothermal planar Couette flows”**[J. Chem. Phys. 107, 2589 (1997)]**B. D. Todd^{a)}*Computer Simulation and Physical Applications Group, School of Information Technology, Swinburne University of Technology, PO Box 218, Hawthorn, Victoria 3122, Australia*

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In their paper, Khare, de Pablo, and Yethiraj¹ have compared the results of simulations of planar Couette flow of simple fluids with and without a thermostat acting on the fluid. In particular, they considered an atomic fluid sandwiched between parallel atomic walls and looked at the cases where (1) no homogeneous thermostat is applied to the fluid and viscous heat is removed by conduction of heat to the walls [sliding boundary, (SB), method] and (2) a homogeneous thermostat is applied to the fluid and to the walls (TSB). They found discrepancies in the shear viscosity calculated for both results and concluded that it is preferable to perform simulations by the SB method.

We agree with the authors' conclusions that the TSB method is inappropriate, and in this Comment suggest an alternative way of analyzing their results, in which the *local* properties of the fluid are considered explicitly. Our intention is to point out that TSB methods are an inadequate simulation technique to use, and indeed can be almost entirely bypassed by a judicious use of standard homogeneous shear (HS) techniques.

First, in their paper Khare *et al.* have stated that the transport properties of fluids are sensitive to the use of a thermostat. It is important to clarify what the authors mean in their statement that “transport coefficients are significantly affected by the thermostat.” In the case of simple fluids it is of course *not* the thermostat itself that significantly affects the transport coefficients.² In fact a wide variety of thermostats have been used in the calculation of the transport coefficients of simple fluids. That these transport coefficients agree with one another demonstrates the insensitivity of thermophysical properties to the thermostatting mechanism.² Thus, it is not the thermostat in itself which creates discrepancies between the SB and TSB simulations, but rather the particular way in which Khare *et al.* have analyzed their

simulation data. In what follows, we suggest an alternative way to interpret their data.

As an example, consider their Fig. 4, in which they plot viscosity as a function of the square root of the strain rate for both the SB and TSB methods. Not surprisingly they find that their SB results demonstrate unphysical shear thickening at high strain rates, while the TSB results demonstrate shear thinning as expected. The authors did not give any explanation of this behavior, apart from stating that “viscous heating becomes significant.” We appreciate that the authors performed such comparisons in an attempt to demonstrate how previous workers in the field have analyzed their own TSB results. However, we suggest that it is actually inappropriate to compare these two “viscosities” on the same plot as they are not at equivalent thermodynamic state points. Previous workers may not have fully appreciated that in the SB case the temperature and density are not constant but vary throughout the fluid. What these workers are actually plotting—particularly for the SB case—is an *effective* fluid viscosity, which is *not* a material property of the fluid. If Khare *et al.* had calculated *local* viscosities (i.e., at a number of temperatures, densities, and strain rates in small regions throughout the fluid) in the SB method and then compared these with TSB viscosities calculated at *equivalent* local state points, they would have found better agreement between the two sets of results even at higher strain rates. Thus, the anomalies labeled as “viscous heating effects” are entirely due to the way in which the analysis and interpretation of the simulation data is performed.

The TSB method should not be criticized just because it uses a thermostat; it should be criticized because the system is not truly homogeneous and is thus complex to characterize. It was precisely because of this deficiency that HS methods were developed in the first place. The major difference between the *local* properties of an SB simulation with those

of a *thermodynamically equivalent* HS system is the absence of a heat flux in the latter. Existing evidence suggests that the heat flux has a negligible effect on the shear viscosity,³ even in the nonlinear regime. In the absence of nonlocal transport phenomena (that would exist near the fluid–wall interface, for example) the *local* viscosity calculated by both methods will be close to identical! Such comparisons obviate the need to perform TSB simulations. Only when inhomogeneity in the fluid causes significant nonlocal behavior can one expect measurable differences between the local properties of an SB simulation and corresponding HS values. This, for example, would be expected to be the case for the shear viscosity $\eta(\mathbf{r})$, where \mathbf{r} is located near the fluid–wall interface. Nonlocal effects would become important now, and the usual definition of the local viscosity ($-P_{yx}(\mathbf{r})/\dot{\gamma}(\mathbf{r})$) would be in error. In such cases a nonlocal generalization of the linear constitutive relation relating stress to strain rate is required.^{4,5}

A good example of a comparison of *local* fluid properties was in fact undertaken by Liem *et al.*,³ in which they found excellent agreement between the HS and SB algorithms up to the largest shear rates for which their SB techniques were stable, ($\dot{\gamma} \sim 0.5$). Liem *et al.* acknowledged the equivalence of their calculated thermodynamic properties and transport coefficients for *both* HS and SB methods at *all* the strain rates they studied. We quote from Liem *et al.*: “It would seem from this that a fluid shearing with heat being removed at a rate *which is naturally realizable* (their italics³) either through conduction or homogeneously behaves in much the same way.” Whether there is disagreement between the HS and SB material properties of the fluid at shear rates that are higher than the maximum shear rates which are physically realizable is an unphysical question which by definition cannot be answered.

In several parts of their paper the authors state that thermostating a sheared fluid such that its entire mass is at a constant temperature corresponds to a fluid with infinite thermal conductivity. This, they claim, is the case for both HS and TSB methods. We point out that this is not correct from a microscopic perspective. Indeed, we have previously used HS methods to calculate the strain rate dependent thermal conductivity *tensor* of shearing fluids.^{6,7} These calculations resulted in finite values of the thermal conductivity which agreed with equilibrium Green–Kubo results in the linear limit.

Finally, we wish to draw attention to some other general points which are relevant for those interested in performing simulations of confined fluids under shear:

- The authors suggested that large statistical uncertainties in the fluid’s shear stress make a direct calculation of this property impractical. In actual fact, this is no longer a problem. We have recently performed precisely these types of calculations^{8–10} which are exact, efficient, and demonstrate excellent statistical accuracy. Calculating the wall shear stress suffices for planar Couette flow, but would be inappropriate for more complex flows, such as Poiseuille flow, in which the fluid stress is not constant and must be calculated directly.

- The authors performed computations of the viscosity under conditions of constant normal stress $\langle P_{zz} \rangle$. We are aware that they correctly computed the normal stress of the fluid by simply calculating that of the wall and equating the two, even though this is not actually stated in their paper. We point out that a *direct* evaluation of the fluid stresses is nontrivial since the standard expression for the pressure tensor, $\langle \mathbf{P} \rangle = (1/V) \langle \sum_i^{N_{\text{fluid}}} m_i [\mathbf{v}_i - \mathbf{u}(\mathbf{r}_i)] [\mathbf{v}_i - \mathbf{u}(\mathbf{r}_i)] + \sum_{i=1}^{N_{\text{fluid}}-1} \sum_{j>i}^{N_{\text{fluid}}} \mathbf{r}_{ij} \mathbf{F}_{ij} \rangle$, which is valid for bulk fluids, is incorrect for highly inhomogeneous fluids, such as those confined to narrow pores.^{8,11,12} Despite this, a direct calculation is certainly feasible, and as stated above demonstrates excellent statistical accuracy.

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