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## Response to “Comment on ‘Molecular simulation and continuum mechanics study of simple fluids in nonisothermal planar Couette flows’” [J. Chem. Phys. 111, 10730 (1999)] **FREE**


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
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# Response to “Comment on ‘Molecular simulation and continuum mechanics study of simple fluids in nonisothermal planar Couette flows’” [J. Chem. Phys. 111, 10730 (1999)]

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In this letter we address some of the issues raised by Todd *et al.* in their comment regarding our paper;<sup>1</sup> we appreciate the efforts put in by Todd *et al.* to provide an alternate interpretation of our results. In the following we only discuss a few points where we are in disagreement with the explanations provided by Todd *et al.*, most of which stem from the different objectives of our work compared to the objectives of homogeneous shear simulations.

Our statement “Transport coefficients are significantly affected by the thermostat” is intended to mean that, for shear flow of confined fluids, the transport coefficients that one simulates depend on whether the sheared fluid is artificially forced to remain at a constant temperature or not (i.e., whether the sheared fluid is thermostated or not). We have no doubt that, once a fluid is constrained to remain at a constant temperature, most thermostats will yield the same results.

As stated in our original paper,<sup>1</sup> the different viscosity-shear rate behavior exhibited by the two methods in Fig. 4 is a result of the “isochoric increase in temperature and hence pressure in the system” for the case where only the walls were held at a constant temperature. As stated by us<sup>1</sup> and also in the comment by Todd *et al.*, the results in Fig. 4 of our paper were presented for the sole purpose of comparison with previous literature and to point out that temperature gradients in the sheared fluid lead to significantly different flow behavior. If our goal was to determine bulk rheological properties, we would have resorted to a different methodology; that, however, was not the case in our study. We have a fundamentally different view on the matter of comparing results of simulations of confined fluids (with either thermostated confined fluid simulations or homogeneous shear simulations) at the same state point. Reiterating statements from our original paper,<sup>1</sup> we believe that, for a confined fluid, the familiar concept of a state point from bulk thermodynamics must be modified to incorporate additional information, such as the thickness of the gap between the surfaces, temperature, and nature of confining walls, etc. These

variables are absent from a bulk, homogeneous system.

Todd *et al.* state that “Such comparisons obviate the need to perform (TSB) (thermostat sliding boundary) simulations” suggesting that TSB methods should be abandoned and HS (homogeneous shear) methods should be used instead. They state that TSB methods should not be criticized just because they use a thermostat but also because of their density inhomogeneities. Although we agree that TSB methods should not be implemented (because of the use of a thermostat for the sheared fluid), it is our opinion that density inhomogeneities represent an essential feature of confined systems. Thus, for investigations of shear flow of confined fluids (e.g., for applications such as lubrication or for investigation of boundary conditions such as slip or no-slip at the polymer melt-wall interface), an appropriate technique to use is shear flow simulation of confined fluids where only the walls are held at a constant temperature.

Todd *et al.* have quoted a statement from a paper by Liem *et al.*<sup>2</sup> which we believe is completely consistent with our arguments. We would like to point out that, even today, most shear flow simulations are conducted at shear rates that are not physically realizable in the laboratory. (As a sidenote, we would also like to note that one of the biggest challenges faced by experimental rheologists in achieving high shear rates is precisely the control of viscous heating.) In light of these issues, it is entirely appropriate to investigate the conditions (shear rates) under which the act of thermostating the sheared fluid will yield unphysical results.

We differ on the issue of thermal conductivity and would like to point out that our statements are clearly correct from a macroscopic, experimental point of view. Although a connection can be made between thermal conductivity and a microscopic correlation function, thereby establishing some equivalence between the two, thermal conductivity as originally defined by Fourier is a macroscopic, experimentally measurable quantity and is the phenomenological coefficient in the relationship (Fourier’s law of heat conduction) between heat flux and temperature gradient.<sup>3</sup> Our assertion of

infinite thermal conductivity is based on the energy balance equation as follows. For a system at steady state (and neglecting the temperature dependence of viscosity  $\mu$  and thermal conductivity  $k$ ), the energy balance equation for our flow geometry (walls normal to the  $z$  axis, confined fluid flows in the  $x$  direction under simple shear) reduces to<sup>3</sup>

$$k \frac{\delta^2 T}{\delta z^2} + \mu \left( \frac{\delta V_x}{\delta z} \right)^2 = 0, \quad (1)$$

subject to the boundary conditions:

$$z=0, \quad T=T_{\text{wall}}, \quad (2)$$

$$z=H, \quad T=T_{\text{wall}}. \quad (3)$$

If the second term in the differential equation vanishes, the equation yields a flat temperature profile in the flow channel (i.e., no temperature rise due to viscous heating). Since we have a velocity gradient in the flow system and also a finite viscosity (nonzero component  $\tau_{zx}$  of the stress tensor), the only way the second term could vanish would be if the thermal conductivity ( $k$ ) was infinite.

Indeed, if a real fluid were to be sheared in the laboratory at the shear rates typically used in simulations, it would experience both a significant temperature rise (and a temperature gradient) and a heat flux. In this context, simulating a sheared fluid that does not exhibit a temperature gradient (at these shear rates which are very high compared to laboratory shear rates) is equivalent to simulating a fluid with infinite thermal conductivity. This point is further illustrated here by presenting estimates of viscous heating effects for a real fluid for a couple of situations relevant to this discussion. For this back-of-the-envelope type calculation, we will assume constant values of viscosity and thermal conductivity (the temperature dependence of these coefficients can be taken into account by using perturbation-type analysis, as shown in our paper, or, even better, by resorting to a numerical method; we have also ignored any possible shear rate dependence of viscosity and thermal conductivity).

Estimation of viscous heating effects, Case A: Consider the case where the fluid in our simulations represents Argon.

For Argon, at a temperature of 300 K, we have:<sup>4</sup> Viscosity,  $\mu=2.29 \times 10^{-5}$  Pa s and thermal conductivity,  $k=0.0177$  W/m K. Using these values of transport coefficients a solution of the energy balance equation predicts a temperature rise of about 210 K at a reduced shear rate of 0.4 (Lennard-Jones parameters for Argon<sup>3</sup> were also used for converting from reduced units to real units).

Estimation of viscous heating effects, Case B: Consider a simple Newtonian fluid, namely water being sheared in a typical Couette rheometer. For water at a temperature of 294 K, we have:<sup>5</sup> Viscosity,  $\mu=9.82 \times 10^{-4}$  Pa s and thermal conductivity,  $k=0.5988$  W/m K. For a typical Couette rheometer, the gap thickness is about 1 mm. Once again, using these values, a solution of energy balance equation predicts a temperature rise of 20 500 K at a shear rate of  $10^7 \text{ s}^{-1}$  (this shear rate is still one or two orders of magnitude lower than the lowest shear rates that can be meaningfully simulated today). This tremendous temperature rise, of course, invalidates our assumptions of constant viscosity and thermal conductivity, but nevertheless indicates the importance of considering the effects of viscous heating. We would also like to point out that the viscous heating effects illustrated above (for both simulation and experimental situations) would in general be even more pronounced for shear flow of lubricants (e.g., long alkanes) because of their higher viscosity and lower thermal conductivity values.

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<sup>1</sup>R. Khare, J. de Pablo, and A. Yethiraj, *J. Chem. Phys.* **107**, 2589 (1997).

<sup>2</sup>S. Y. Liem, D. Brown, and J. H. R. Clarke, *Phys. Rev. A* **45**, 3706 (1992).

<sup>3</sup>R. B. Bird, W. E. Stewart, and E. N. Lightfoot, *Transport Phenomena* (Wiley, New York, 1960).

<sup>4</sup>*Perry's Chemical Engineer's Handbook*, 6th ed., edited by R. H. Perry, D. W. Green, and J. O. Maloney (McGraw-Hill, New York, 1984).

<sup>5</sup>W. L. McCabe, J. C. Smith, and P. Harriott, *Unit Operations of Chemical Engineering* (McGraw-Hill, New York, 1993).