# COMMENTS

*Comments are short papers which criticize or correct papers of other authors previously published in the* **Physical Review**. *Each Comment should state clearly to which paper it refers and must be accompanied by a brief abstract. The same publication schedule as for regular articles is followed, and page proofs are sent to authors.*

## Comment on "Relationship between McQuarrie and Helfand equations for the determination of shear viscosity from equilibrium molecular dynamics"

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In a recent paper, Chialvo, Cummings, and Evans [Phys. Rev. E **47**, 1702 (1993)] attempt to relate single-particle and collective expressions, due, respectively, to McQuarrie [*Statistical Mechanics* (Harper and Row, New York, 1976)] and Helfand [Phys. Rev. **119**, 1 (1960)] for the calculation of shear viscosities in molecular dynamics simulations. We point out that their analysis does not correspond to the simulation algorithm they actually use, that the system-size dependence they derive and the extrapolation procedure they propose are incorrect, and that they have established no relation between their analysis and the shear viscosity. Our own analysis explains the simulation results in terms of the artificial way that periodic box boundary crossings are handled. We find no support for a link between the McQuarrie formula and any valid statistical mechanical expression for the shear viscosity.

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In recent papers, Chialvo and Debenedetti [1] and Chialvo, Cummings, and Evans [2] discuss the relationship between the commonly-accepted Einstein relation for shear viscosity

$$\eta_{\mathrm{Helf}} = \lim_{t\to\infty} \frac{1}{2Vk_BT}\frac{\mathrm{d}}{\mathrm{d}t}\left\langle \left[\sum_{i=1}^{N} p_{xi}(t)z_i(t) - p_{xi}(0)z_i(0)\right]^2 \right\rangle \tag{1}$$

due to Helfand [3], and an expression

$$\eta_{\mathrm{McQ}} = \lim_{t\to\infty} \frac{1}{2Vk_BT}\frac{\mathrm{d}}{\mathrm{d}t}\left\langle \sum_{i=1}^{N} [p_{xi}(t)z_i(t) - p_{xi}(0)z_i(0)]^2 \right\rangle, \tag{2}$$

which appears in McQuarrie's book on statistical mechanics [4]. In both these expressions, $N$ is the number of particles, $V$ is the system volume, $T$ the temperature, and $k_B$ is Boltzmann's constant. $p_{xi}(t)$ is the $x$ component of momentum of atom $i$ at time $t$, and $z_i(t)$ is its $z$-coordinate. In Ref. [2] the authors claim to have established the equivalence of these two expressions, backing up this claim with simulation evidence.

In a previous Comment [5] we have analyzed the simulation algorithm first described in Ref. [1], pointing out differences between the Lennard-Jones fluid shear viscosities simulated in this way, and the accepted values for the same state point. Our analysis showed that the apparent Einstein relation seen by these authors could be associated with a single-particle correlation function arising from the way their algorithm handled periodic boundary crossings. We tested our analysis using an exactly soluble model: a system of independent atoms obeying Brownian dynamics with a prescribed diffusion coefficient. The analysis expresses the "viscosity" of this system exactly in terms of *static* quantities:

$$\eta_{\mathrm{McQ}} = 0.31L\rho\sqrt{mk_BT},$$

where $\rho$ is the density and $L$ the box size (we assume a cubic box throughout). This diverges with increasing $L$, in proportion to $L$, i.e., it goes as $N^{1/3}$ for fixed $\rho$ and $T$. It is not a transport coefficient. The above expression was confirmed very accurately by Brownian dynamics simulations. For the Lennard-Jones system, the same dependence on $L$, $\rho$, and $T$ comes out of our analysis, although the numerical prefactor must be evaluated approximately. It is, however, again dominated by a term which does not involve time correlations, i.e., a static, not a dynamic, quantity. It is clearly not related to the shear viscosity.

In a more recent paper [2], Chialvo, Cummings, and Evans note the divergence of their simulation results with increasing system size. Their analysis leads to $\eta_{\mathrm{McQ}} - \eta_{\mathrm{Helf}} \propto N^{2/3}$; they plot $\eta_{\mathrm{McQ}}$ against $N^{2/3}$ and linearly extrapolate to $N \to 0$ to obtain results "within 8–16 %" of the accepted values.

We have repeated the simulations of Ref. [2], and extended them to larger system size. The state point is $T^* \equiv kT/\varepsilon = 2.75$, $\rho^* \equiv \rho\sigma^3 = 0.7$ ($\varepsilon$ and $\sigma$ being the

 

Lennard-Jones well depth and diameter, respectively), first studied in detail by Holian and Evans [6], and the potential cutoff is $r_c = 2.38\sigma$. Run lengths were of order $t^*_{\rm run} \equiv t_{\rm run}\sqrt{\varepsilon/m\sigma^2} = 150$–$300$ (typically $5 \times 10^4$ – $7.5 \times 10^4$ steps of 0.003–0.004 reduced units each). We used the algorithm described unambiguously in Ref. [1] and in the flow diagram of Fig. 6 of Ref. [2], to calculate $\eta_{\rm McQ}$. Excellent statistics were obtained for the appropriate single-particle mean-squared displacement expressions, with the slope well established after approximately $t^* = 0.2$. $\eta_{\rm McQ}$ was calculated from the gradient in the region $0.5 < t^* < 1.5$.

For $N = 108$, 256, 500, 864, 1024, 2048, and 4000, our results are, in reduced units, $\eta^*_{\rm McQ} = 2.11$, 2.82, 3.52, 4.27, 4.54, 5.80, and 7.29, respectively. These are plotted as functions of $N^{1/3}$ and $N^{2/3}$ in Figs. 1 and 2. Our results for the first four system sizes match very closely those in Fig. 2 of Ref. [2]. All the results clearly conform to $\eta_{\rm McQ} \propto N^{1/3}$, not to the system-size dependence of Ref. [2]. In fact, close inspection of Fig. 2 of Ref. [2] reveals the curvature in the data points: the linear extrapolation of that paper is incorrect. The $N \to 0$ limit of $\eta_{\rm McQ}$, is zero; the $N \to \infty$ limit is infinity.

Virtually none of the analysis which appears in the main text of Ref. [2] is directly connected to the simulation methods described therein. The formal manipulations of the paper, including the discussion of system-size effects, do not refer to periodic boundary conditions in any way. In Appendix B of Ref. [2], the authors describe their method, and argue that appropriate variables are defined in the BPBC ("before applying periodic boundary corrections") convention: these are used in their simulations. However, they do not provide any evidence to justify this claim. The only rigorous result they obtain relates the ensemble average of the time derivative of their dynamical variable, $\dot{G}^{\rm BPBC}$, to the pressure tensor, a *static* quantity. Any dynamical variable whose ensemble average vanishes could be added to $\dot{G}^{\rm BPBC}$ without changing this result. Thus, there is no reason to believe that this variable can be used to calculate the shear viscosity. As shown above, the simulation results and the theory of Ref. [2] differ significantly: none of the simulation results in that paper can be used to substantiate the theoretical derivation.

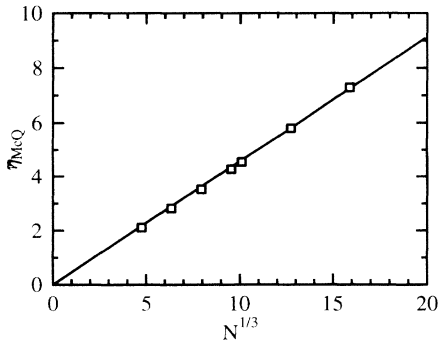


FIG. 1. "Viscosity" calculated by the "McQuarrie" prescription plotted as a function of $N^{1/3}$. Error bars are smaller than the symbol sizes. The straight line shows the expected scaling.

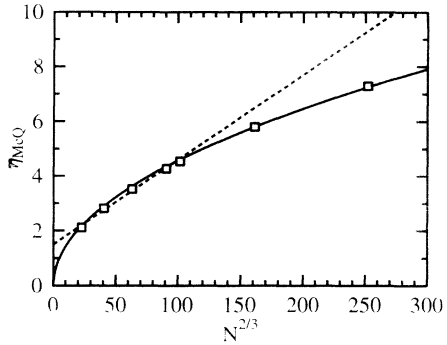


FIG. 2. "Viscosity" calculated by the "McQuarrie" prescription plotted as a function of $N^{2/3}$. Error bars are smaller than the symbol sizes. The curve shows the expected scaling, and the dashed line shows the linear fit to the first four points, as used in Ref. [2].

By contrast, our analysis [5] is based directly on the algorithm actually used by Chialvo *et al.* We relate, rigorously (in the limit of small simulation time step), the BPBC variables to single-particle coordinates and velocities in the unfolded system, i.e., to which no periodic boundary corrections are applied. These quantities smoothly evolve according to the classical equations of motion, and are well behaved in the thermodynamic limit. Our result [5] is

$$\eta_{\rm McQ} = \frac{L^2\rho}{kT}\int_0^\infty {\rm d}t\ \langle p_{xi}(t)p_{xi}(0)\dot{n}_{zi}(t)\dot{n}_{zi}(0)\rangle\,. \qquad (3)$$

Here $\dot{n}_{zi}(t) = v_{zi}(t)\sum_b \delta[z_i(t) - z_b]$, where we sum over the positions $z_b$ of all the box boundaries. This equation is exact. Only one term in the sum over boundaries need be retained if (as is always the case here) we may neglect particles diffusing a distance $L$ between one boundary and another in a time comparable with, or shorter than, the velocity decorrelation time. Then translational invariance and the definition of the Dirac $\delta$ function $\delta(x)$ give

$$\eta_{\rm McQ} = \frac{L\rho}{kT}\int_0^\infty {\rm d}t\ \langle p_{xi}(t)p_{xi}(0)v_{zi}(t)v_{zi}(0)\delta(\Delta z_i(t))\rangle\,,$$

where $\Delta z_i(t) = z_i(t) - z_i(0)$, the $z$ displacement calculated *without* applying any periodic boundary corrections. The ensemble average $\langle p_{xi}(t)p_{xi}(0)v_{zi}(t)v_{zi}(0)\delta(\Delta z_i(t))\rangle$ is an intensive quantity, and will be subject to only small $(\mathcal{O}(1/N))$ corrections from its value in the thermodynamic limit $N \to \infty$. This function describes crossings and recrossings of a single box boundary (or indeed any plane of constant $z$); we analyzed it in detail in Ref. [5], using methods familiar from chemical barrier-crossing problems [7]. The prefactor $L$ arises only from the prescription of Chialvo *et al.*; it is not in any way related to deviations of proper ensemble averages from their thermodynamic limiting values. The result $\eta_{\rm McQ} \propto L \propto N^{1/3}$ is exact (subject to the above proviso concerning multiple box boundary crossings) and

is confirmed by our simulations.

Finally, we comment on the formal manipulations of Refs. [1,2], which lead to the claimed equivalence between the Helfand and McQuarrie forms. These raise entirely different questions from the above discussion of the BPBC algorithm. We maintain that the authors have failed to prove that the McQuarrie expression is related to the shear viscosity in any way. This is because their derivation uses unbounded variables [like the coordinate $z_i(t)$] in ensemble averages without considering the consequences of taking the thermodynamic limit of infinite system size. These can be nontrivial, since averages involving these quantities are undefined in the absence of system boundary walls. In the standard derivation of statistical mechanical expressions for transport coefficients in unbounded systems [8], care is taken with the order of the large-wavelength (low wave number) and long-time (low frequency) limits, and the existence of a transport coefficient is closely linked to a specific conservation law, which is absent for the McQuarrie variables. Alternatively, one may consider a system bounded by real walls a distance $L$ apart, and consider the limit $L \to \infty$. Again, transportlike behavior depends upon the existence of an appropriate conservation law. This is discussed in detail elsewhere [9], and we simply note here that the McQuarrie expression fails dramatically in this case. We conclude that the McQuarrie formula is not a statistical mechanical expression for the shear viscosity, and that neither the theory nor the simulation results of Refs. [1,2] can be taken to support such a proposition.

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