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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 "Use of the McQuarrie equation for the computation of shear viscosity via equilibrium molecular dynamics"

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In a recent paper, Chialvo and Debenedetti [Phys. Rev. A **43**, 4289 (1991)] consider 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 an error in the discussion of origin independence in this paper, and show that the prescriptions set out in it are not related to the shear viscosity.

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In a recent paper, Chialvo and Debenedetti [1] discuss the relationship between the commonly accepted Einstein relation for shear viscosity

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

due to Helfand [2], and an expression

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

which appears in McQuarrie's book on statistical mechanics [3]. In both these expressions, V is the system volume, T the temperature, and k is Boltzmann constant. $p_{xi}(t)$ is the x component of the momentum of atom i at time t, and $z_i(t)$ is its z coordinate. McQuarrie left the proof of Eq. (2) as an exercise for the reader. Chialvo and Debenedetti conjecture that the two expressions are equivalent, although they do not attempt to prove this. They provide simulation evidence that the difference between η_{Helf} and η_{McQ} is small. If true, this would be a significant discovery, since the statistics of calculating single-particle expressions such as Eq. (2) are far superior to those for collective quantities such as Eq. (1). It would also be a remarkable theoretical development, linking the motion of a single particle to a conservation law for a collective quantity, namely the transverse momentum density. This paper has started to attract interest [4], although, to our knowledge, the McQuarrie formula is not currently in common use.

The aims of this comment are fourfold: (i) to point out an error in the argument presented by Chialvo and Debenedetti regarding the origin dependence of the McQuarrie expression; (ii) to emphasize the absence of a link between the single-particle variables and the conservation law for transverse momentum; (iii) to confirm that the values of "shear viscosity" calculated by Chialvo and Debenedetti by molecular dynamics are incorrect; (iv) to present an analysis which shows that the values calculated this way are not intimately connected with any transport coefficient. We aim to show that the McQuarrie expression, as implemented by Chialvo and Debenedetti, cannot be used to calculate the viscosity. We do not address the conjecture that the Helfand and McQuarrie forms might be equivalent, but it seems likely that, as implemented by Chialvo and Debenedetti, the Helfand expression is also incorrect. As usually implemented, however, it is exactly equivalent to the standard Green-Kubo expression, and is correct.

Chialvo and Debenedetti attempt to argue that the long-time limit of the McQuarrie form is independent of

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a translation of coordinates. To do this they transform it into

$$\eta_{\mathrm{McQ}} = -\lim_{t\to\infty} \frac{1}{VkT}\left\langle \left(\sum_{i=1}^{N} F_{xi}(t) z_i(t) + \frac{p_{xi}(t)p_{zi}(t)}{m}\right)\left(\sum_{j=1}^{N} p_{xj}(0) z_j(0)\right)\delta_{ij}\right\rangle .$$

Here m is the atomic mass. The Kronecker delta δ_{ij} allows the formal conversion of a single sum into a double one, over both i and j. However, in their equation (3.6) they equate this to

$$-\lim_{t\to\infty} \frac{1}{VkT}\left\langle J_p^{xz}(t)\left(\sum_{j=1}^{N} p_{xj}(0) z_j(0)\right)\delta_{ij}\right\rangle$$

with $J_p^{xz}(t) \equiv \sum_{i=1}^{N} p_{xi}(t)p_{zi}(t)/m + F_{xi}(t)z_i(t)$. In other words, they retain the Kronecker delta δ_{ij}, while at the same time having summed separately over the index i to define the quantity $J_p^{xz}(t)$. This error renders the proof of translational invariance void.

The ability to perform the summations over both i and j is crucial to the argument linking the Einstein relation with a transport coefficient and a conservation law in this case. The discussion is most conveniently summarized [5, 6] using spatially Fourier-transformed variables, because then the large-system (thermodynamic) and long-time limits may be taken in a controlled way, in the correct order, respectively, as $k \to 0$ and $t \to \infty$. Expressions linking a time correlation function integral (a Green-Kubo relation) and an Einstein relation

$$\eta = \lim_{t\to\infty}(2VkT)^{-1}\tfrac{d}{dt}\ \langle \Delta A(t)^2\rangle \qquad \text{(Einstein)} \qquad (3a)$$

$$= (VkT)^{-1}\int_0^\infty dt\ \left\langle \dot{A}(t)\dot{A}(0)\right\rangle \qquad \text{(Green-Kubo)}, \qquad (3b)$$

where the dot denotes time differentiation and $\Delta A(t) = \int_0^t dt' \dot{A}(t')$, arise *directly* from a microscopic conservation relation of the kind $\dot{\alpha}(k,t) = -ikj_\alpha(k,t)$, where we take k to lie in the z direction for convenience, and where $j_\alpha(k,t)$ is well behaved in the low-k limit. This guarantees that $\alpha(k,t)$ is a slowly evolving variable at low k. Equations (3a) and (3b) follow, with $A(t) = \lim_{k\to 0}\alpha(k,t)/(-ik)$ and $\dot{A}(t) = \lim_{k\to 0}\dot{\alpha}(k,t)/(-ik) = \lim_{k\to 0} j_\alpha(k,t)$. This is the procedure by which the large-system limit is correctly taken before the long-time limit in Eqs. (3a) and (3b); this is essential in order to avoid reaching the conclusion that the transport coefficient vanishes. In the case of shear viscosity, we have $\alpha(k,t) = p_x(k,t) \equiv \sum_{i=1}^{N} p_{xi}(t)\exp\{-ikz_i(t)\}$, the *collective* momentum density, and $j_\alpha(k,t) = P_{zx}(k,t)$, the zx component of the k-dependent pressure tensor. The proof that $\dot{p}_x(k,t) = -ikP_{zx}(k,t)$, and the precise form of $P_{zx}(k,t)$, are given in standard references [5, 6]. Then,

$$A(t) = \sum_{i=1}^{N} p_{xi}(t) z_i(t)\,, \qquad (4)$$

$$\dot{A}(t) = \sum_{i=1}^{N}\frac{p_{xi}(t)p_{zi}(t)}{m} + \sum_{i=1}^{N}\sum_{j>i}^{N} F_{xij} z_{ij}\,, \qquad (5)$$

where F_{xij} is the x component of the force between i and j (assumed pairwise additive) and $z_{ij} = z_i - z_j$ is the interatomic separation. $\dot{A}$, and its time integral $\Delta A(t)$, are clearly independent of the origin of coordinates. This relies on the double summation, and momentum conservation in the form of Newton's third law $F_{xij} = -F_{xji}$:

$$\sum_{i=1}^{N} F_{xi} z_i = \sum_{i=1}^{N}\sum_{j\neq i}^{N} F_{xij} z_i = \tfrac{1}{2}\sum_{i=1}^{N}\sum_{j\neq i}^{N} F_{xij} z_{ij}.$$

This derivation does not go through for the single-particle variables. The McQuarrie form of the Einstein relation, Eq. (2), takes the form of Eq. (3a) with $A_i(t) = p_{xi}(t)z_i(t)$ replacing $A(t)$, and an additional factor of N [to replace the sum in Eq. (2)]. No link of the form $\dot{A}_i(t) = \lim_{k\to 0}\dot{\alpha}_i(k,t)/(-ik)$ has been demonstrated in this case, nor does it seem obvious where one is to come from. The single-particle $\dot{A}_i$ variable is not translationally invariant.

This origin dependence is important. In simulations employing periodic boundary conditions, $\dot{A}$ in Eq. (5) is computed with all pair sums calculated in the minimum image convention. $\Delta A(t)$ is computed [7, 8] as the time integral $\Delta A(t) = \int_0^t dt' \dot{A}(t')$, and is also origin independent. [It is a subtlety of periodic boundaries that this is *not* equivalent to simply writing $\Delta A(t) \equiv A(t) - A(0)$, using Eq. (4) for $A(t)$.] In this way, the mathematical equivalence of the Einstein [Eq. (3a)] and Green-Kubo [Eq. (3b)] prescriptions is preserved, and the time evolution of $\Delta A(t)$ is independent of the absolute position of the box boundaries: nothing happens to $\Delta A(t)$, defined in this way, as a consequence of a particle crossing a box boundary. The single-particle $\Delta A_i(t)$ cannot be written in origin-independent form like this: as we have seen, the double summation over i and j is essential. Instead, Chialvo and Debenedetti do something quite different, involving explicit effects of box boundary crossings, for both single-particle and collective cases, and this different prescription leads to erroneous results.

To see this, write $A_i(t) = p_{xi}(t)z_i(t)$ where $z_i(t)$ is a coordinate located in the simulation box at time $t = 0$, but then allowed to vary smoothly, throughout the infinite checkerboard system modeled in the simulation, without imposing periodic boundary conditions. Then $\Delta A_i(t) = \int_0^t dt' \dot{A}_i(t') = A_i(t) - A_i(0)$ may be used in an Einstein relation. Averaging over initial conditions gives a quantity $\langle \Delta A_i(t)^2\rangle$ which increases linearly with t. However this does *not* give the shear viscosity; it is in fact a simple exercise to show that the gradient gives $\rho m D$ where D is the diffusion coefficient. This is *not* the procedure Chialvo and Debenedetti adopt. Define also $A_i'(t) = p_{xi}(t)z_i'(t)$ where now $z_i'(t)$ is the periodically imaged coordinate, defined to lie in a specified range, e.g., $-L/2 \le z_i'(t) \le L/2$, at all times (L is the box length). We can relate this to $z_i(t)$ by

$$z_i'(t) = z_i(t) - n_{zi}(t)L\,,$$

where $n_{zi}(t)$ is a staircase function (an infinite series of unit step functions) giving the integer z label of the box in which the freely diffusing particle i resides at time t.

$A'_i(t)$ is bounded, so clearly $\langle \Delta A'_i(t)^2 \rangle$ does not increase with t at large t: this also is not a route to η. The time derivatives $\dot{A}'_i(t)$ and $\dot{A}_i(t)$ are related by

$$\dot{A}'_i(t) = \dot{A}_i(t) - \dot{p}_{xi}(t) n_{zi}(t) L - p_{xi}(t) \dot{n}_{zi}(t) L.$$

$A'_i(t)$ suffers a step-function discontinuity whenever particle i crosses a box boundary. Its time derivative $\dot{A}'_i(t)$ contains both step-function (from n_{zi}) and δ-function (from $\dot{n}_{zi}$) discontinuities when this occurs. In their paper, following their Eq. (3.11), Chialvo and Debenedetti describe their prescription for handling periodic boundaries. It is easy to see that this corresponds to using a variable whose time derivative is identical with $\dot{A}'_i(t)$, but from which the δ function term is dropped:

$$\dot{A}_i^{\mathrm{CD}}(t) \equiv \dot{A}_i(t) - \dot{p}_{xi}(t) n_{zi}(t) L \tag{6a}$$

$$\equiv \dot{A}'_i(t) + p_{xi}(t) \dot{n}_{zi}(t) L. \tag{6b}$$

To see this, simply integrate Eq. (6b) over one time step from t_n to t_{n+1}. If no boundary crossing occurs in this time step, the change $\int_{t_n}^{t_{n+1}} dt\ \dot{A}_i^{\mathrm{CD}}(t)$ is identical with $A'_i(t_{n+1}) - A'_i(t_n)$, and this is consistent with instruction (a) of the original paper, together with the imposition of periodic boundary corrections in instruction (b) of the previous step. If a boundary crossing *does* occur, the step discontinuity in A'_i is correctly removed at the moment of crossing [as per instructions (b) and (c) of the original paper] by the extra term in $p_{xi}\dot{n}_{zi}L$, and hence does not contribute to the accumulated change ΔA_i^{CD}. The only difference is that, in the algorithm, the periodic imaging operation is postponed until the end of the time step, rather than being performed at the exact moment of boundary crossing. This unavoidably introduces an (algorithm discretization) error, but this vanishes as $\delta t = t_{n+1} - t_n \to 0$, and so is insignificant. The time integral $\Delta A_i^{\mathrm{CD}}(t) \equiv \int_0^t dt' \dot{A}_i^{\mathrm{CD}}(t')$ is used in the "McQuarrie" expression. Note that $\dot{A}_i^{\mathrm{CD}}(t)$ suffers a step-function discontinuity whenever a boundary crossing occurs. The same applies to its collective counterpart, obtained by summing over i, and used in the prescription that Chialvo and Debenedetti call "Helfand." This is quite different from the behavior of variables used in the Green-Kubo expression, and from the Helfand expression using the time-integrated form for $\Delta A(t)$: these variables change smoothly with time. No justification has been presented for associating the variable $\dot{A}_i^{\mathrm{CD}}(t)$ with any transport coefficient, and below we show that there is none. First, however, we check Chialvo and Debenedetti's simulation results.

We have repeated the molecular-dynamics (MD) simulations of Ref. [1] at the state point $T^* \equiv kT/\varepsilon = 2.75$, $\rho^* \equiv \rho\sigma^3 = 0.7$, ($\varepsilon$ and σ being the Lennard-Jones well depth and diameter, respectively) first studied in detail by Holian and Evans [9], but using precisely the potential, system size $N = 108$, and simulation parameters of Chialvo and Debenedetti. We have calculated η by Helfand's expression, with time-integrated $\Delta A(t)$, by the equivalent Green-Kubo expression, and by nonequilibrium molecular dynamics [9]. We have also evaluated η_{McQ} and η_{Helf} by the Chialvo and Debenedetti prescriptions. Run lengths were $t^*_{\mathrm{run}} \equiv t_{\mathrm{run}}\sqrt{\varepsilon/m\sigma^2} = 150$ for equilibrium MD (5×10^5 steps of 0.003 units each), and $t^*_{\mathrm{run}} = 200$–2000 for nonequilibrium MD, depending on shear rate. Our results appear in Table I, and typical mean-squared displacement curves are shown in Fig. 1. We have succeeded in reproducing the values of Chialvo and Debenedetti of η_{McQ} and η_{Helf}. Our results for η, however, do not agree with theirs, corresponding instead, rather closely, with those of Holian and Evans. The discrepancy, a factor of approximately 1.7, is therefore *not* attributable to differences in potential truncation as Chialvo and Debenedetti suggest: it is a consequence of their method. Other simulations at different state points (not reported here) bear out the view that there is not a close connection between η_{McQ} (or η_{Helf}) and η; moreover η_{McQ} and η_{Helf} grow quite noticeably with increasing system size, whereas η does not.

Secondly, we have carried out Brownian-dynamics (BD) simulations in periodic boundary conditions. This entails the numerical solution of the Langevin equation for $N = 108$ independent, freely diffusing atoms in three dimensions [10]. The only input parameters are the temperature T, diffusion coefficient D, particle mass m, and the box dimensions. η_{McQ} was calculated exactly as in the molecular-dynamics simulations. A typical mean-square displacement curve, for $T^* = 2.75, \rho^* = 0.7$, and with the correct diffusion coefficient $D^* \equiv D\sqrt{m/\varepsilon\sigma^2} = 0.26$ [11–13], is shown in the figure. This curve agrees surprisingly well with the MD result: the short-time behavior is accurately reproduced, and the long-time gradient is correct within 14%. More surprising (see the table) are the consequences of varying D, T, and ρ (hence L):

TABLE I. Results of equilibrium and nonequilibrium molecular-dynamics simulations, and of Brownian-dynamics simulations. For each state point (ρ^*, T^*) we tabulate the diffusion coefficient D^* (measured in MD, input as a parameter in BD), and the viscosity as measured conventionally, η^*, and by the "McQuarrie" prescription, η^*_{McQ}. The nonequilibrium results have been extrapolated to zero shear rate. All results are in Lennard-Jones reduced units.

Method	ρ^*	T^*	D^*	η^*	η^*_{McQ}	$\eta_{\mathrm{McQ}}/L\rho\sqrt{mkT}$
MD(eq)	0.7	2.75	0.26	1.18	2.11	0.34
MD(ne)	0.7	2.75		1.27		
BD	0.7	2.75	0.26		1.88	0.30
BD	0.7	5.5	0.26		2.68	0.30
BD	0.7	2.75	1.04		1.86	0.30
BD	5.6	2.75	0.26		7.69	0.31

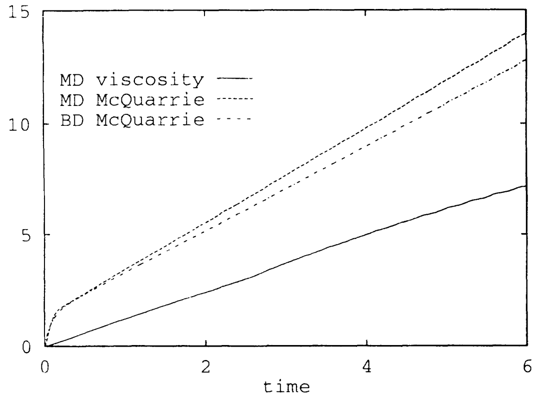

FIG. 1. Viscosity mean-squared displacements $(2VkT)^{-1}\langle \Delta A(t)^2\rangle$ [see Eq. (3a)] as calculated by the conventional method in a molecular-dynamics simulation (solid line), by the Chialvo and Debenedetti "McQuarrie" prescription in molecular dynamics (dashed line) and by the same prescription in Brownian-dynamics (dashed-dotted line), at the Holian-Evans state point. Variables are in Lennard-Jones reduced units.

$\eta_{\rm McQ}$ (BD) is *independent* of D, and conforms quite well to the empirical formula

$$\eta_{\rm McQ} \approx 0.3L\rho\sqrt{mkT} \qquad \text{(BD)} \tag{7}$$

over a wide range of parameters. This suggests that the BD values of $\eta_{\rm McQ}$ have little to do with any dynamical properties, certainly not the viscosity, and that the same may be true of the MD results.

To understand this, we present an analysis of the time evolution of the Chialvo and Debenedetti variable $\dot{A}_i^{\rm CD}(t)$. We have

$$\eta_{\rm McQ} = \frac{\rho}{kT}\int_0^\infty dt\, \left\langle \dot{A}_i^{\rm CD}(t)\dot{A}_i^{\rm CD}(0)\right\rangle .$$

It is convenient to start from Eq. (6b), define $\dot{\mathcal{A}}_i(t) = p_{xi}(t)\dot{n}_{zi}(t)L$, and write $\dot{A}_i^{\rm CD}(t) = \dot{A}'_i(t) + \dot{\mathcal{A}}_i(t)$. Since A'_i is bounded, the infinite time integrals of $\langle \dot{A}'_i(t)\dot{A}'_i(0)\rangle$, and both the cross terms between $\dot{A}'_i$ and $\dot{\mathcal{A}}_i$, will be identically zero. Thus

$$\eta_{\rm McQ} = \frac{\rho}{kT}\int_0^\infty dt\, \left\langle \dot{\mathcal{A}}_i(t)\dot{\mathcal{A}}_i(0)\right\rangle$$
$$= \frac{L^2\rho}{kT}\int_0^\infty dt\, \langle p_{xi}(t)p_{xi}(0)\dot{n}_{zi}(t)\dot{n}_{zi}(0)\rangle . \tag{8}$$

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. However, the maximum time $t_{\rm max}$ out to which correlations are studied by Chialvo and Debenedetti is *short* ($t^*_{\rm max} = 8$) compared with the time $t_{\rm box} \approx L^2/2D$ (here $t^*_{\rm box} \approx 50$) required for an atom to diffuse the length of the simulation box. Moreover [because of the decay of the $p_{xi}(t)$ correlations] the integrand in Eq. (8) will fall to zero in a time of order $t_v = mD/kT$, the velocity correlation time (here, $t^*_v \approx 0.1$). Hence we may restrict our interest to crossings and recrossings of a *single* boundary, and we write $\dot{n}_{zi}(t) = v_{zi}(t)\delta(z_i(t))$, placing the boundary at the origin for convenience.

There is a static, $t = 0$, contribution to the integral of Eq. (8). Here we may rigorously factorize the x and z parts, and write

$$\eta_{\rm McQ}(\text{static}) = \frac{L^2\rho}{kT}\int_0^\varepsilon dt\, \langle p_{xi}(t)p_{xi}(0)\rangle\, \langle \dot{n}_{zi}(t)\dot{n}_{zi}(0)\rangle$$
$$= L^2\rho m \int_0^\varepsilon dt\, \langle \dot{n}_{zi}(t)\dot{n}_{zi}(0)\rangle , \tag{9}$$

where ε is a small positive time, and we use $\langle p_{xi}^2\rangle = mkT$. This is handled by standard methods for barrier crossings [14]:

$$\eta_{\rm McQ}(\text{static}) = L^2\rho m\, \langle \Delta n_{zi}(\varepsilon)\dot{n}_{zi}(0)\rangle$$
$$= L^2\rho m\, \langle \Delta n_{zi}(\varepsilon)v_{zi}(0)\delta(z_i(0))\rangle .$$

The δ function localizes the atom at the boundary. Atoms may depart in either direction: $\Delta n_{zi}(\varepsilon)$ will be $+1$ if $v_{zi}(0)$ is positive and -1 if it is negative. Thus

$$\eta_{\rm McQ}(\text{static}) = L^2\rho m\, \langle |v_{zi}(0)|\delta(z_i(0))\rangle .$$

We separate configurational and velocity averages, write $\langle \delta(z_i(0))\rangle = L^{-1}$ and $\langle |v_{zi}|\rangle = \sqrt{kT/2\pi m}$, to give

$$\eta_{\rm McQ}(\text{static}) = L\rho\sqrt{mkT/2\pi} = 0.40L\rho\sqrt{mkT} . \tag{10}$$

For the Holian-Evans state point, $T^* = 2.75$, $\rho^* = 0.7$, $L^* = 5.363$, and $\eta^*_{\rm McQ}(\text{static}) = 2.48$, overestimating the value quoted by Chialvo and Debenedetti by about 14%. This is an exact result, and it turns out to be the dominant contribution to $\eta_{\rm McQ}$; evidently it has nothing to do with shear viscosity, nor indeed the details of the interatomic potential. The divergent dependence on system size ($\propto L$) also shows that the result cannot be related to a statistical mechanical property in the thermodynamic limit.

Note that, although this term arises at short times in our analysis, this is only because we have split $\dot{A}_i^{\rm CD}(t)$ into $\dot{A}'_i(t)$ and $\dot{\mathcal{A}}_i(t)$. The terms involving $\dot{A}'_i(t)$ will appear in the evolution of $\langle \Delta A_i^{\rm CD}(t)^2\rangle$ at short times, but they will all cancel exactly within a time of order t_v. Our analysis simply gives the limiting gradient at long times, through Eq. (8).

To analyze the remaining, dynamic, contribution to the integral of Eq. (8), we make the Gaussian approximation [5]. This is exact at short and long times, and in error by only a few percent in between. We use it here to give a guide to the expected results. Within this approximation we may immediately factorize:

$$\eta_{\rm McQ}(\text{dynamic}) \approx \frac{L^2\rho}{kT}\int_\varepsilon^\infty dt \langle p_{xi}(t)p_{xi}(0)\rangle\langle \dot{n}_{zi}(t)\dot{n}_{zi}(0)\rangle$$
$$= \frac{L^2\rho}{kT}\int_\varepsilon^\infty dt \langle p_{xi}(t)p_{xi}(0)\rangle$$
$$\times\langle v_{zi}(t)v_{zi}(0)\delta(z_i(t))\delta(z_i(0))\rangle . \tag{11}$$

We may use origin independence to average over initial z coordinates, giving

$$\eta_{\mathrm{McQ}}(\text{dynamic}) = \frac{L\rho}{kT}\int_{\epsilon}^{\infty} dt\ \langle p_{xi}(t)p_{xi}(0)\rangle \times \langle v_{zi}(t)v_{zi}(0)\delta(\Delta z_i(t))\rangle$$

where $\Delta z_i(t) = z_i(t) - z_i(0)$. Now insert the integral representation of the delta function $\delta(\Delta z_i(t)) = (2\pi)^{-1}\int_{-\infty}^{\infty} dk\ \exp\{ik\Delta z_i(t)\}$ to give

$$\eta_{\mathrm{McQ}}(\text{dynamic}) = \frac{L\rho}{2\pi kT}\int_{\epsilon}^{\infty} dt\ \langle p_{xi}(t)p_{xi}(0)\rangle \times \int_{-\infty}^{\infty} dk\ \left\langle v_{zi}(t)v_{zi}(0)e^{ik\Delta z_i(t)}\right\rangle .$$

The second average is proportional to the double time derivative of the intermediate scattering function

$$\eta_{\mathrm{McQ}}(\text{dynamic}) = -\frac{L\rho}{2\pi kT}\int_{\epsilon}^{\infty} dt\ \langle p_{xi}(t)p_{xi}(0)\rangle \times \int_{-\infty}^{\infty} dk\ k^{-2}\ddot{I}_s(k,t)$$

where $I_s(k,t) = \langle\exp\{ik\Delta z_i(t)\}\rangle$. In turn, within the Gaussian approximation, this may be expressed in terms of the velocity autocorrelation function. Define for convenience $C_v(t) = \langle v_{zi}(t)v_{zi}(0)\rangle$, $C_v^{(1)}(t) = \int_0^t dt'\ C_v(t')$, and $C_v^{(2)}(t) = \int_0^t dt'\ C_v^{(1)}(t')$. We have $\langle p_{xi}(t)p_{xi}(0)\rangle = m^2C_v(t)$, $C_v^{(2)}(t) = \langle\Delta z_i(t)^2\rangle/2$, and $I_s(k,t) \approx \exp\{-k^2C_v^{(2)}(t)\}$. Thus we may write

$$\eta_{\mathrm{McQ}}(\text{dynamic}) = -\frac{L\rho m^2}{2\pi kT}\int_{\epsilon}^{\infty} dt\ C_v(t)\int_{-\infty}^{\infty} dk\ \left[k^2C_v^{(1)}(t)^2 - C_v(t)\right]e^{-k^2C_v^{(2)}(t)}. \tag{12}$$

Performing the integrals over k gives

$$\eta_{\mathrm{McQ}}(\text{dynamic}) = -L\rho\sqrt{\frac{mkT}{2\pi}}\left\{\left(\frac{m}{kT}\right)^{3/2}\int_{\epsilon}^{\infty} dt\ \frac{C_v(t)}{\sqrt{2C_v^{(2)}(t)}} \times \left[\frac{C_v^{(1)}(t)^2}{2C_v^{(2)}(t)} - C_v(t)\right]\right\}. \tag{13}$$

The term in curly brackets is a pure number. It may be evaluated for a simple Brownian motion model, $C_v(t) = (kT/m)\exp\{-t/t_v\}$, where it gives

$$\begin{aligned}\eta_{\mathrm{McQ}}(\text{dynamic}) &\approx -0.22L\rho\sqrt{mkT/2\pi}\\ &= -0.09L\rho\sqrt{mkT}\quad(\text{BD}).\end{aligned} \tag{14}$$

This, then, is a negative correction of about 20% to the static part, Eq. (10), and it is independent of t_v (hence, D). The overall result is

$$\eta_{\mathrm{McQ}} \approx 0.78L\rho\sqrt{mkT/2\pi} = 0.31L\rho\sqrt{mkT}\quad(\text{BD}).$$

This explains the Brownian-dynamics results, Eq. (7), entirely in terms of static quantities. A more accurate estimate of $\eta_{\mathrm{McQ}}(\text{dynamic})$ can be made from $C_v(t)$, as calculated in the MD simulation, by performing the integral of Eq. (13) numerically. This will be accurate apart from non-Gaussian corrections. The result, at the Holian-Evans state point, is

$$\begin{aligned}\eta_{\mathrm{McQ}}(\text{dynamic}) &\approx -0.19L\rho\sqrt{mkT/2\pi}\\ &= -0.08L\rho\sqrt{mkT}\quad(\text{MD})\end{aligned} \tag{15}$$

so the overall estimate is

$$\eta_{\mathrm{McQ}} \approx 0.81L\rho\sqrt{mkT/2\pi} = 0.32L\rho\sqrt{mkT}\quad(\text{MD}).$$

In reduced units this is $\eta^*_{\mathrm{McQ}} = 2.01$, in good agreement with the values calculated by Chialvo and Debenedetti, and confirmed in the table.

In conclusion, we have shown that the McQuarrie expression, as implemented by Chialvo and Debenedetti, is not a suitable route to the shear viscosity in computer simulations; indeed it seems not to be related to transport at all. Our analysis indicates that it is poorly behaved in the thermodynamic limit (proportional to box length L). Within a Brownian motion model, the result is quite well determined by static quantities, and is unrelated to the details of the intermolecular potential; a more accurate estimate (within the Gaussian approximation) may be made with a knowledge of the velocity autocorrelation function. The problem lies with the definition of the dynamical variable used in this expression, and the way periodic boundaries are handled. For the single-particle case, there seems to be no better alternative, and we believe that there is no single-particle route to this collective transport coefficient. We have not proved anything regarding the Helfand expression, but it seems likely that this also is incorrect, if periodic boundaries are handled in this way. The formal Helfand expression, with $\Delta A(t)$ calculated by time-integrating the pressure tensor, is mathematically equivalent to the conventional Green-Kubo expression, and is correct.

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