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

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To date, the calculation of shear viscosity for soft-core fluids via equilibrium molecular dynamics has been done almost exclusively using the Green-Kubo formalism. The alternative mean-squared displacement approach has not been used, except for hard-sphere fluids, in which case the expression proposed by Helfand [Phys. Rev. **119**, 1 (1960)] has invariably been selected. When written in the form given by McQuarrie [*Statistical Mechanics* (Harper & Row, New York, 1976), Chap. 21], however, the mean-squared displacement approach offers significant computational advantages over both its Green-Kubo and Helfand counterparts. In order to achieve comparable statistical significance, the number of experiments needed when using the Green-Kubo or Helfand formalisms is more than an order of magnitude higher than for the McQuarrie expression. For pairwise-additive systems with zero linear momentum, the McQuarrie method yields frame-independent shear viscosities. The hitherto unexplored McQuarrie implementation of the mean-squared displacement approach to shear-viscosity calculation thus appears superior to alternative methods currently in use.

I. INTRODUCTION

Twenty years after the first report on shear viscosity calculation via molecular dynamics,[1] important questions remain regarding the evaluation of this property for soft-core potential fluids.[2] These include the effects of potential truncation and shifting,[2,3] anomalies in the sample-size (N) dependence,[2,4,5] and the effect of the long-time tail on the cross and potential contributions to the stress autocorrelation function.[2,6,7] These questions are also important in the case of viscosity calculations via nonequilibrium molecular dynamics,[3,8] since agreement between equilibrium and nonequilibrium results is often used as a consistency test.[3,8,9]

Alder, Gass, and Wainwright's hard-sphere,[1] as well as Michels and Trappeniers's square-well calculations[10] employed a mean-squared-displacement approach for the calculation of shear viscosity. This choice was motivated by the fact that the evaluation of stress autocorrelations is not straightforward for hard spheres, which experience δ-function forces upon collision.[1] Most viscosity calculations for soft-core fluids via equilibrium molecular dynamics have employed the Green-Kubo (GK) approach (see, for example, Refs. 3–5, 8, and 9). Although the theoretical equivalence between the mean-squared-displacement and GK formalisms in the thermodynamic limit is well known,[11–13] their relative computational and numerical merits have not been explored to date. This is surprising, especially in light of the significant computational advantages which one of the possible implementations of the mean-squared-displacement formalism possesses, as will be shown in this paper.

The mean-squared-displacement equation for shear viscosity can be written in at least two forms: one given by Helfand,[12] and the other by McQuarrie.[11] The latter form has never, to the best of our knowledge, been used in simulation work. Furthermore, the theoretical equivalence between the Helfand and McQuarrie expressions has not been discussed to date. In this paper, we first address this theoretical equivalence, and derive the constraints under which it applies. Subsequently, we discuss the implementation of the McQuarrie formalism for viscosity calculations in periodic systems, and derive the conditions which must be satisfied in order for the method to yield results which are invariant under coordinate translation.

Finally, we investigate the relative merits of the GK and mean-squared-displacement formalisms (the latter in both its Helfand and McQuarrie implementations) by performing viscosity calculations in the course of *NVE* and *NVT* equilibrium-molecular-dynamics simulations of a Lennard-Jones fluid.

II. THEORETICAL EQUIVALENCE BETWEEN DIFFERENT DISPLACEMENT EQUATIONS

The mean-squared-displacement expression for the shear viscosity can be written in (at least) three different ways. The equations are equivalent in the thermodynamic limit, but have quite different numerical implications. To see this, we first write

$$\eta=\frac{1}{2kTV}\left[\frac{d}{dt}\left\langle\sum_{i,j=1}^{N}p_{xi}(t)p_{xj}(0)[z_i(t)-z_j(0)]^2\right\rangle\right]_{\text{large } t}, \tag{2.1}$$

$$\eta=\frac{1}{2kTV}\left[\frac{d}{dt}\left\langle\sum_{i=1}^{N}[p_{xi}(t)z_i(t)-p_{xi}(0)z_i(0)]^2\right\rangle\right]_{\text{large } t}, \tag{2.2}$$

$$\eta=\frac{1}{2kTV}\left[\frac{d}{dt}\left\langle\left[\sum_{i=1}^{N}[p_{xi}(t)z_i(t)-p_{xi}(0)z_i(0)]\right]^2\right\rangle\right]_{\text{large } t}, \tag{2.3}$$

where the time derivative is to be taken at long times, $p_{xi}(t)$ and $z_i(t)$ denote the x component of the linear momentum and the z component of the position vector of particle i at time t, and the angle brackets indicate canonical ensemble averaging,[12] including the six possible $\alpha\beta$ permutations ($\alpha\neq\beta=x,y,z$). Equation (2.1) (with t^{-1} replacing d/dt) is Eq. (3.13) in Ref. 12 and Eq. (21.304) in Ref. 11. Starting from this relationship, Helfand[12] arrived at Eq. (2.3) and McQuarrie[11] to Eq. (2.2). We do not rederive Eq. (2.1) here: the interested reader can consult the above references.[11,12] Rather, we focus here on the theoretical and computational relationship between these expressions.

Expanding the argument in Eq. (2.1) we obtain

$$\begin{aligned}\left\langle\sum_{i,j=1}^{N}p_{xi}(t)p_{xj}(0)[z_i(t)-z_j(0)]^2\right\rangle &=\left\langle\sum_{i,j=1}^{N}p_{xi}(t)p_{xj}(0)z_i^2(t)\right\rangle+\left\langle\sum_{i,j=1}^{N}p_{xi}(t)p_{xj}(0)z_j^2(0)\right\rangle\\ &\quad-2\left\langle\sum_{i,j=1}^{N}p_{xi}(t)p_{xj}(0)z_i(t)z_j(0)\right\rangle .\end{aligned} \tag{2.4}$$

The first term on the right-hand side can be transformed as follows:[12]

$$\begin{aligned}\left\langle\sum_{i,j=1}^{N}p_{xi}(t)p_{xj}(0)z_i^2(t)\right\rangle &=\left\langle\sum_{i=1}^{N}p_{xi}(t)z_i^2(t)\sum_{j=1}^{N}p_{xj}(0)\right\rangle\\ &=\left\langle\sum_{i=1}^{N}p_{xi}(t)z_i^2(t)\sum_{j=1}^{N}p_{xj}(t)\right\rangle\\ &=\left\langle\sum_{i,j=1}^{N}p_{xi}(t)z_i^2(t)p_{xj}(t)\right\rangle\\ &=\left\langle\sum_{i=1}^{N}p_{xi}^2(t)z_i^2(t)\right\rangle+\left\langle\sum_{i\neq j=1}^{N}p_{xi}(t)p_{xj}(t)z_i^2(t)\right\rangle ,\end{aligned} \tag{2.5}$$

where we have used conservation of linear momentum.[12] The assumption of constant linear momentum in a canonical system needs to be carefully considered. A canonical ensemble is composed of closed systems bounded by rigid diathermal walls. The linear momentum of the walls can be strictly imposed, for example, by requiring that they be at rest, in which case it is zero. However, the particles' total linear momentum is not strictly conserved. According to Helfand,[12] "Since total momentum is not strictly conserved due to wall interactions we have assumed above that the correlation of the deviations with the other factors are either small or short lived." This approximation introduces an error of order δ/L, where δ is the effective range of intermolecular interactions (<10 Å), and L is the characteristic length of the container. It underlies all of Helfand's original derivations as well as the present treatment. Although isothermality and conservation of linear momentum can both be rigorously imposed in simulations (Sec. III), this should not obscure the fact that the theoretical viscosity expressions assume the simultaneous validity of these two conditions, a situation which is not strictly possible in real systems.

The second term on the right-hand side of Eq. (2.4), similarly, becomes

$$\left\langle\sum_{i,j=1}^{N}p_{xi}(t)p_{xj}(0)z_j^2(0)\right\rangle =\left\langle\sum_{i=1}^{N}p_{xi}^2(0)z_i^2(0)\right\rangle+\left\langle\sum_{i\neq j=1}^{N}p_{xi}(0)p_{xj}(0)z_j^2(0)\right\rangle \tag{2.6}$$

and, for the third quantity in Eq. (2.4), we write

$$\begin{aligned}\left\langle\sum_{i,j=1}^{N}p_{xi}(t)p_{xj}(0)z_i(t)z_j(0)\right\rangle &=\left\langle\sum_{i=1}^{N}p_{xi}(t)p_{xi}(0)z_i(t)z_i(0)\right\rangle\\ &\quad+\left\langle\sum_{i\neq j=1}^{N}p_{xi}(t)p_{xj}(0)z_i(t)z_j(0)\right\rangle .\end{aligned} \tag{2.7}$$

The argument in Eq. (2.1) therefore reads

$$\begin{aligned}\left\langle\sum_{i,j=1}^{N}p_{xi}(t)p_{xj}(0)[z_i(t)-z_j(0)]^2\right\rangle &=\left\langle\sum_{i=1}^{N}p_{xi}^2(t)z_i^2(t)\right\rangle+\left\langle\sum_{i\neq j=1}^{N}p_{xi}(t)p_{xj}(t)z_i^2(t)\right\rangle\\ &\quad+\left\langle\sum_{i=1}^{N}p_{xi}^2(0)z_i^2(0)\right\rangle+\left\langle\sum_{i\neq j=1}^{N}p_{xi}(0)p_{xj}(0)z_j^2(0)\right\rangle\\ &\quad-2\left\langle\sum_{i=1}^{N}p_{xi}(t)p_{xi}(0)z_i(t)z_i(0)\right\rangle-2\left\langle\sum_{i\neq j=1}^{N}p_{xi}(t)p_{xj}(0)z_i(t)z_j(0)\right\rangle .\end{aligned} \tag{2.8}$$

Expanding the argument in Eq. (2.2) we obtain, without any transformation,

$$\left\langle \sum_{i=1}^{N} [p_{xi}(t)z_i(t)-p_{xi}(0)z_i(0)]^2 \right\rangle = \left\langle \sum_{i=1}^{N} p_{xi}^2(t)z_i^2(t) \right\rangle + \left\langle \sum_{i=1}^{N} p_{xi}^2(0)z_i^2(0) \right\rangle - 2\left\langle \sum_{i=1}^{N} p_{xi}(t)p_{xi}(0)z_i(t)z_i(0) \right\rangle \tag{2.9}$$

and, invoking conservation of linear momentum,[12] as was done in Eq. (2.5), we obtain, for the argument in Helfand's expression [i.e., Eq. (2.3)],

$$\begin{aligned}\left\langle \left[\sum_{i=1}^{N} [p_{xi}(t)z_i(t)-p_{xi}(0)z_i(0)] \right]^2 \right\rangle = {} & \left\langle \sum_{i=1}^{N} p_{xi}^2(t)z_i^2(t) \right\rangle + \left\langle \sum_{i\neq j=1}^{N} p_{xi}(t)p_{xj}(t)z_i(t)z_j(t) \right\rangle \\ & + \left\langle \sum_{i=1}^{N} p_{xi}^2(0)z_i^2(0) \right\rangle + \left\langle \sum_{i\neq j=1}^{N} p_{xi}(0)p_{xj}(0)z_i(0)z_j(0) \right\rangle \\ & - 2\left\langle \sum_{i=1}^{N} p_{xi}(t)p_{xi}(0)z_i(t)z_i(0) \right\rangle - 2\left\langle \sum_{i\neq j=1}^{N} p_{xi}(t)p_{xj}(0)z_i(t)z_j(0) \right\rangle .\end{aligned} \tag{2.10}$$

The equivalence of the Helfand and McQuarrie expressions [Eqs. (2.3) and (2.2), respectively] means that their time-dependent contributions grow at the same rate with respect to time in the long-time limit. Comparing Eqs. (2.9) and (2.10), and noting that $\langle \sum_{i=1}^{N} p_{xi}^2(t)z_i^2(t) \rangle$ and $\langle \sum_{i\neq j=1}^{N} p_{xi}(t)p_{xj}(t)z_i(t)z_j(t) \rangle$ are constant in a stationary (equilibrium) ensemble, we can write

$$\eta_H = \eta_{\text{MQ}} - \frac{1}{kTV} \left[\frac{d}{dt} \left[\left\langle \sum_{i\neq j=1} [p_{xi}(t)p_{xj}(0)z_i(t)z_j(0)] \right\rangle \right] \right]_{\text{large } t} , \tag{2.11}$$

where the subscripts denote the Helfand and McQuarrie expressions. It follows that the equivalence of Helfand and McQuarrie expressions depends on the following condition:

$$\left[\frac{d}{dt} \left[\left\langle \sum_{i\neq j=1}^{N} [p_{xi}(t)p_{xj}(0)z_i(t)z_j(0)] \right\rangle \right] \right]_{\text{large } t} = 0 . \tag{2.12}$$

Equation (2.12) is a plausible conjecture. Although we will show in Sec. IV that this conjecture is fully supported by simulation results, we are not aware of a theoretical proof of its validity.

The presence of an additional term in the Helfand expression introduces fluctuations, whose numerical implications will be discussed in Sec. IV. Its absence from the McQuarrie formula represents a very important simplification, insofar as it reduces the computation of the shear viscosity to a one-particle problem,

$$\eta = \frac{N}{2kTV} \left[\frac{d}{dt} \left\langle [p_{xi}(t)z_i(t)-p_{xi}(0)z_i(0)]^2 \right\rangle \right]_{\text{large } t} . \tag{2.13}$$

At present, however, the validity of Eq. (2.13) rests on plausibility arguments [i.e., Eq. (2.12)]. Though consistent with numerical (simulation) tests, the validity of such arguments is yet to be established theoretically.

III. NUMERICAL COMPUTATION OF DISPLACEMENT FORMULAS IN PERIODIC SYSTEMS

We now discuss the suitability of mean-squared-displacement formulas for the numerical computation of viscosity in periodic systems. Specifically, we focus our attention on the McQuarrie form. As pointed out by Allen and Tildesley,[14] the direct computation of the displacement of a quantity is always, in principle, more convenient than its indirect evaluation via time integration of the corresponding autocorrelation function, i.e.,

$$\lim_{t\to\infty} 0.5\frac{d}{dt}\langle [\varphi(t)-\varphi(0)]^2 \rangle = \lim_{t\to\infty} \int_0^t \langle \dot{\varphi}(s)\dot{\varphi}(0) \rangle ds . \tag{3.1}$$

The correct computer implementation of the left-hand side (lhs) of Eq. (3.1) for periodic systems is clearly straightforward for $\varphi(t)=\mathbf{r}(t)$, where $\mathbf{r}$ denotes the position of a particle. In this case, care must be taken to use the continuous function of time unaffected by periodic boundary conditions, commonly referred to as "unfolded" positions,[15] i.e., the integral of the velocity. Note in particular that when $\varphi(t)=\mathbf{r}(t)$, the lhs of Eq. (3.1) is invariant under coordinate translation. In the case of shear viscosity, the calculation of the lhs of Eq. (3.1) is not, in principle, as straightforward. Indeed, for viscosity, $\varphi(t)$ is a sum of terms having the form $r_x p_y(t)$ (or any permutation thereof), and the lhs of Eq. (3.1) becomes frame dependent, since it contains products of absolute positions and velocities. This was initially pointed out by Hoheisel and Vogelsang[9] as well as by Schoen,[16] who proposed an integral form of the lhs of Eq. (3.1) (i.e., a non-GK integral form) precisely to avoid a supposed dependence of the computed viscosity on the choice of reference frame. Specifically, these authors wrote

$$\lim_{t\to\infty}\frac{d}{dt}\langle[\varphi(t)-\varphi(0)]^2\rangle=\lim_{t\to\infty}\frac{d}{dt}\left\langle\left[\int_0^t\dot{\varphi}(s)ds\right]^2\right\rangle . \tag{3.2}$$

Note that $\dot{\varphi}(s)$ is simply a sum over all particles of terms of the form $p_{xi}p_{zi}/m+z_iF_{xi}$ (or any of the six equivalent permutations thereof). For pairwise-additive forces, this becomes $p_{xi}p_{zi}/m+\sum_{j\neq i}(z_i-z_j)F_{xij}$, where F_{xij} is the x component of the force on i due to j. Therefore the integrand of Eq. (3.2) is frame independent.

We now show that the long-time limit of the time derivative of the shear viscosity generalized displacement, i.e.,

$$\lim_{t\to\infty}\frac{d}{dt}\left\langle\sum_{i=1}^{N}[x_i(t)p_{yi}(t)-x_i(0)p_{yi}(0)]^2\right\rangle \tag{3.3}$$

is invariant upon coordinate translation for a pairwise additive system with $\sum_i p_{\alpha i}=0$ $(\alpha=x,y,z)$. To this end, we consider the McQuarrie form and write

$$\eta=-\frac{1}{kTV}\left[\frac{d}{dt}\left[\left\langle\sum_{i=1}^{N}p_{xi}(t)p_{xi}(0)z_i(t)z_i(0)\right\rangle\right]\right]_{\text{large }t} . \tag{3.4}$$

Taking into account that the summation contains no $i\neq j$-terms, it can be written as

$$\eta=-\frac{1}{kTV}\left\{\frac{d}{dt}\left[\left\langle\left[\sum_{i=1}^{N}p_{xi}(t)z_i(t)\right]\left[\sum_{j=1}^{N}p_{xj}(0)z_j(0)\right]\delta_{ij}\right\rangle\right]\right\}_{\text{large }t} , \tag{3.5}$$

where δ_{ij} is Kronecker's delta. Carrying out the differentiation, to which only time-dependent terms contribute, we have

$$\begin{aligned}\eta&=-\frac{1}{kTV}\left[\left\langle\left[\sum_{i=1}^{N}F_{xi}(t)z_i(t)+\frac{p_{xi}(t)p_{zi}(t)}{m}\right]\left[\sum_{j=1}^{N}p_{xj}(0)z_j(0)\right]\delta_{ij}\right\rangle\right]_{\text{large }t}\\&=-\frac{1}{kTV}\left[\left\langle J_p^{xz}(t)\left[\sum_{j=1}^{N}p_{xj}(0)z_j(0)\right]\delta_{ij}\right\rangle\right]_{\text{large }t}\end{aligned} \tag{3.6}$$

where we have defined

$$J_p^{xz}(t)=\sum_{i=1}^{N}\frac{p_{xi}(t)p_{zi}(t)}{m}+z_i(t)F_{xi}(t) . \tag{3.7}$$

Consider now a translation of the origin such that $r_\alpha\rightarrow r_\alpha+\Delta_{r\alpha}$ $(\alpha=x,y,z)$. Then

$$\begin{aligned}&\left\langle J_p^{xz}(t)\left[\sum_{j=1}^{N}p_{xj}(0)z_j(0)\right]\delta_{ij}\right\rangle_{\text{new}}\\&\quad=\left\langle J_p^{xz}(t)\left[\sum_{j=1}^{N}p_{xj}(0)z_j(0)\right]\delta_{ij}\right\rangle_{\text{old}}\\&\quad\quad+\Delta_{r\alpha}\left\langle J_p^{xz}(t)\left[\sum_{j=1}^{N}p_{xj}(0)\right]\delta_{ij}\right\rangle ,\end{aligned} \tag{3.8}$$

where the last term in Eq. (3.8) is zero for a system in which $\sum_i p_{\alpha i}=0$ $(\alpha=x,y,z)$, and we have used the fact that $J_p^{\alpha\beta}(t)(\alpha,\beta=x,y,z)$ is frame invariant for pairwise-additive systems. Then, as long as zero total linear momentum is imposed at the outset (system at rest), and the thermostating procedure conserves momentum (see below), the rate of increase (but not the actual value) of the displacement-explicit expression for a pairwise-additive system is independent of the choice of coordinates in the long-time limit. Literature statements regarding the unsuitability of mean-squared-displacement expressions for viscosity calculations in periodic systems[9] are therefore incorrect. This assertion will be substantiated below through simulation results.

The proper implementation of the viscosity generalized displacement in periodic systems will now be discussed. According to Eq. (3.2), the displacement can be written either as such, or in integral form. For the latter, the relevant quantity is

$$\sum_{i=1}^{N}\int_0^t\left[\frac{p_{xi}p_{yi}}{m}+x_iF_{yi}\right]dt=\sum_{i=1}^{N}\int_{x_ip_{yi}(0)}^{x_ip_{yi}(t)}d(x_ip_{yi}) , \tag{3.9}$$

where the integrand on the lhs of (3.9) is simply an off-diagonal element of the pressure tensor. Then the integral can be easily calculated numerically

$$\sum_{i=1}^{N}\int_0^t\left[\frac{p_{xi}p_{yi}}{m}+x_iF_{yi}\right]dt\cong h\sum_{l=1}^{n}\sum_{i=1}^{N}J_{pi}^{xy}(l) , \tag{3.10}$$

with h, the integration time step, $n=t/h$, and

$$J_{pi}^{xy}=\frac{p_{xi}p_{yi}}{m}+x_iF_{yi} . \tag{3.11}$$

Just as with the calculation of the virial, the positions included in J_{pi}^{xy} are those of the molecules located in the bounded region of space where the simulation takes place and not those of their periodic replicas.[17]

Alternatively, if the displacement is not transformed into an integral, one simply writes

(a) $x_i(t_{n+1})p_{yi}(t_{n+1})-x_i(0)p_{yi}(0)$

$\equiv\delta(t_{n+1})=\delta(t_n)-x_i(t_n)p_{yi}(t_n)+x_i(t_{n+1})p_{yi}(t_{n+1})$,

(b) apply periodic boundary conditions,

(c) $x_i(t_n)p_{yi}(t_n) = x_i(t_{n+1})p_{yi}(t_{n+1})$,

where (a) and (c) are not equations but machine instructions.

Finally, we discuss the generation of canonical ensemble averages subject to the zero total linear momentum constraint. This can be easily achieved by using the momentum scaling method[18] to keep the system's temperature constant, provided velocities are initially assigned such that the total linear momentum is zero. In that case, one has

$$p_{xi}(t_{n+1}) = p_{xi}(t_n)\left[\left[\sum_i p_i^2(t_n)\right]/3mNkT\right]^{1/2} \tag{3.12}$$

and

$$\sum_i p_{xi}(t_{n+1}) = \left[\left[\sum_i p_i^2(t_n)\right]/3mNkT\right]^{1/2} \sum_i p_{xi}(t_n) \ , \tag{3.13}$$

so that if $\sum_i p_i(t_n)$ vanishes, so will $\sum_i p_i(t_{n+1})$. In Eqs. (3.12) and (3.13), $p_i^2 = p_{xi}^2 + p_{yi}^2 + p_{zi}^2$.

IV. NUMERICAL RESULTS: TEST RUNS AND DISCUSSION

NVT simulations of truncated Lennard-Jones (LJ) spheres were used to compare the relative numerical and computational merits of the different mean-squared-displacement forms of the shear viscosity equations, i.e., Eqs. (2.2) and (2.3), and of their GK counterpart. For this purpose we chose the supercritical condition $T=2.75$ and $\rho=0.7$ (in σ,ε units), already used by Holian and Evans for a modified LJ potential.[3] Additional simulations were also performed at $T=1.75$, $\rho=0.7$.

The ensemble averages indicated in Eqs. (2.2) and (2.3) were performed over initial times and over the six possible permutations of $r_\alpha p_{\beta\neq\alpha}$ (with $\alpha,\beta=x,y,z$). The averaging over time origins was done by partitioning the total run into five to ten independent subruns, each containing 10^2–2×10^3 origins, separated by a time gap of 20 time steps, i.e., about 6(500–20 000) elements in the ensemble [6 components times (5–10 subruns) times time origins]. The statistical uncertainties quoted below were obtained by calculating the spread among subrun viscosities. The mean viscosity was calculated from the slope of the mean-squared-displacement line. The GK integrands were evaluated using the same number of uncorrelated experiments that were used with the Helfand formula, and the corresponding integrals were evaluated with a cutoff of ~500–800 time steps, beyond which they showed no sensitivity to the time cutoff.

We analyzed the numerical equivalence between the mean-squared-displacement and GK expressions via *NVT* and *NVE* molecular-dynamics simulation for a system size $N=108$, using two different potential cutoffs. To avoid possible sources of ambiguity, all simulations were started from an initial fcc configuration, while initial velocity components were randomly assigned from a uniform distribution corresponding to the desired temperature. Equilibration lasted about 2000 time steps (time step size, 0.003 in units of $\sigma/\sqrt{\varepsilon/m}$). Details about the algorithm have been discussed elsewhere.[19,20] The resulting shear viscosity values are presented in Table I.

Note that all simulations have been performed with the same system size ($N=108$) to eliminate any possible size-dependent effects on the calculated shear viscosity values. Although the internal consistency of our results is evident from Table I, the shear viscosities calculated in this work (~2.1) differ appreciably from those obtained by Holian and Evans[3] at the same conditions (~1.4). These authors used a different potential (cubic-spline-modified LJ). Little is known at present about the effects of truncation and shifting upon simulated time-dependent properties.[21] Our results suggest that these effects can be significant.

The comparison of runs 3 and 4 shows that the magnitude of the fluctuations in the calculated viscosities for the various subruns about the mean (i.e., the statistical uncertainty) is more than an order of magnitude higher for the Helfand than for the McQuarrie method. The comparison of runs 1, 2, and 4 shows that, in order to achieve comparable accuracy, the number of required

TABLE I. Shear-viscosity results for Lennard-Jones spheres. All simulations are *NVT* ($N=108$), at $T=2.75$, $\rho=0.7$, except where otherwise noted.

Run	No. of expts.[a]	Cutoff (σ)	Method	η ($\sqrt{m\varepsilon}/\sigma^2$)[b]
1	(2000)(5)(6)	2.38	Green-Kubo	2.03±0.18
2	(100)(5)(6)	2.38	McQuarrie	2.18±0.10
3	(2000)(10)(6)	2.38	McQuarrie	2.14±0.06
4	(2000)(10)(6)	2.38	Helfand	2.27±0.7
5	(100)(5)(6)	1.488	McQuarrie	2.23±0.11
6[c]	(100)(5)(6)	2.38	McQuarrie	2.12±0.07
7[d]	(100)(5)(6)	2.38	McQuarrie	1.73±0.08
8[d]	(2000)(5)(6)	2.38	Green-Kubo	1.82±0.20

[a] (Time origins) times (subruns) times (components). The gap is 20 time steps between origins in all cases.

[b] Standard deviation of subruns about the mean. Viscosity in the units shown in parentheses.

[c] *NVE* simulation with $\langle T \rangle = 2.857$.

[d] *NVT* simulation; $T=1.75$, $\rho=0.7$.

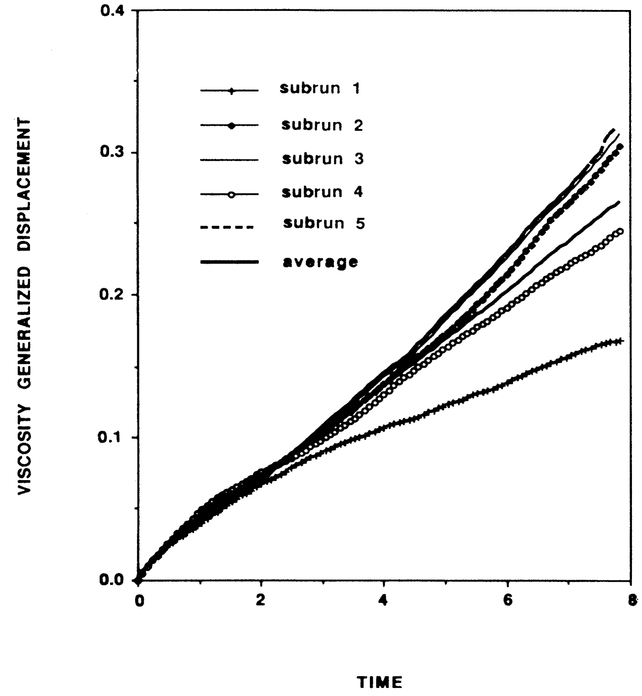

FIG. 1. Evolution of the viscosity generalized displacement for Helfand's expression [Eq. (2.3)]. $N=108$ Lennard-Jones spheres, $\rho=0.7$, $T=2.75$. Experiments per subrun $=12\,000$; gap $=20\Delta$. For the sake of convenience in the numerical integration of the equations of motion, we use p times Δ as the momentum, where p is given in the usual m,ε,σ units. Time is in units of $\sigma/\sqrt{\varepsilon/m}$.

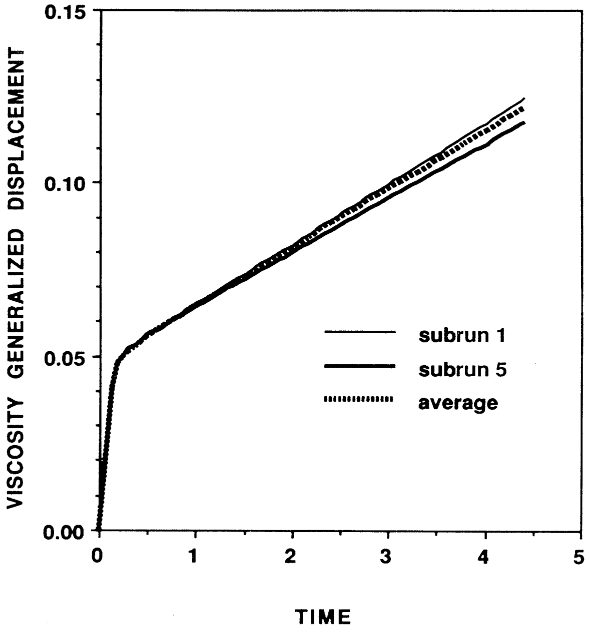

FIG. 2. Evolution of the viscosity generalized displacement for McQuarrie's expression [Eq. (2.2)]. Counterpart of Fig. 1, but with 600 experiments per subrun. Subruns 2, 3, and 4 fall entirely between 1 and 5.

(time origins times subruns) is more than an order of magnitude higher for the GK and Helfand expressions than for the McQuarrie formula. Neither the cutoff (runs 2,5) nor the choice of ensemble (runs 2,6) have statistically significant effects on the computed shear viscosity. Even after a 20-fold reduction in the number of time origins, the statistical uncertainties associated with the McQuarrie formula are smaller than those resulting from a Green-Kubo calculation (runs 7,8:1,2).

The superiority of the McQuarrie formula is not unexpected in light of Eq. (2.11) and the ensuing discussion. In fact, we found that despite the observation that each of the independent subruns produced a well-defined long-time slope (correlation coefficient ~0.99) the standard deviation about this mean was always significantly higher for the Helfand than for the McQuarrie calculations. This is illustrated in Figs. 1 and 2. Note in particular that the number of experiments per sub-runs is 12 000 in Fig. 1 and 600 in Fig. 2.

Finally, Fig. 3 shows the evolution of the argument of Eq. (2.12) in the course of a typical simulation ($N=108$, $\rho=0.7$, $T=2.75$, 5 subruns, 1200 experiments per subrun). Similar behavior was observed for other conditions and system sizes. The conjecture [i.e., the validity of Eq. (2.12) and hence of McQuarrie's formula] is thus supported by simulation results. Note, however, that although the argument of Eq. (2.12) does not grow with time, its fluctuations are significant (at least for the system sizes investigated here). This is consistent with the different behavior shown in Figs. 1 and 2 for the arguments of the Helfand and McQuarrie expressions.

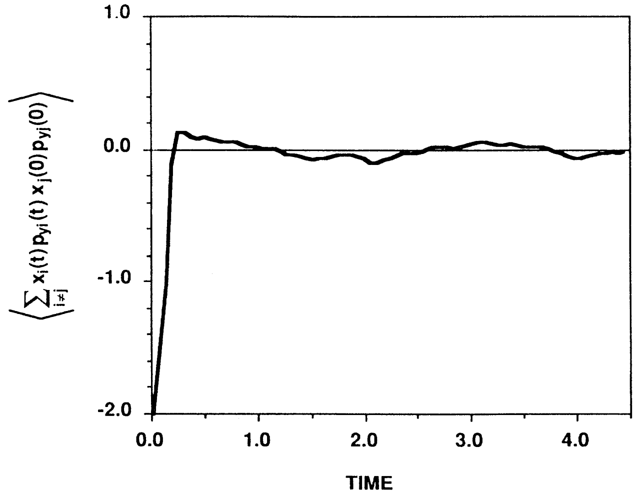

FIG. 3. Evolution of the argument of expression (2.12) (conjecture) for the same system and conditions of Fig. 2, after five subruns of 1200 experiments each.

V. CONCLUSIONS

The McQuarrie form of the mean-squared-displacement expression for the calculation of shear viscosity offers significant computational advantages with respect to both the Helfand form and the Green-Kubo method within the context of equilibrium molecular dynamics. The validity of the McQuarrie expression hinges upon a conjecture which is supported by simulation results but has not yet been proved rigorously. The Helfand expression contains a term, not present in the McQuarrie equation, which, although it does not (according to the conjecture) contribute to the viscosity in the long-time limit, gives rise to significant noise.

The McQuarrie form represents a considerable simplification with respect to its Helfand counterpart in that it reduces the calculation of shear viscosity to a single-particle diffusionlike problem. In molecular-dynamics calculations with periodic systems, it leads to frame-independent results provided the linear momentum is zero, and the forces are pairwise additive.

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[1] B. J. Alder, D. M. Gass, and T. E. Wainwright, J. Chem. Phys. **53**, 3813 (1970).

[2] J. J. Erpenbeck, Phys. Rev. A **38**, 6255 (1988).

[3] B. L. Holian and D. J. Evans, J. Chem. Phys. **78**, 5147 (1983).

[4] D. Levesque, L. Verlet, and J. Kürkijarvi, Phys. Rev. A **7**, 1690 (1973).

[5] D. Levesque and L. Verlet, Mol. Phys. **61**, 143 (1987).

[6] D. J. Evans, J. Stat. Phys. **22**, 81 (1980).

[7] J. J. Erpenbeck and W. W. Wood, J. Stat. Phys. **24**, 455 (1981).

[8] G. Marechal, J. P. Ryckaert, and A. Bellemans, Mol. Phys. **61**, 33 (1987).

[9] C. Hoheisel and R. Vogelsang, Comput. Phys. Rep. **8** (1988), and references therein.

[10] J. P. J. Michels and N. J. Trappeniers, Physica A **107**, 299 (1981).

[11] D. McQuarrie, *Statistical Mechanics* (Harper & Row, New York, 1976), Chap. 21.

[12] E. Helfand, Phys. Rev. **119**, 1 (1960).

[13] J. P. Hansen and I. R. McDonald, *Theory of Simple Liquids,* 2nd ed. (Academic, London, 1986), Chap. 8.

[14] M. P. Allen and D. J. Tildesley, *Computer Simulation of Liquids* (Clarendon, Oxford, 1987), Sec. 6.5.5, p. 205.

[15] M. P. Allen and D. J. Tildesley, *Computer Simulation of Liquids* (Ref. 14), p. 60.

[16] M. Schoen, Ph.D. thesis, Ruhr Universtät, Bochum, 1986.

[17] A. J. C. Ladd, in *Computer Modeling of Fluids, Polymers and Solids,* Vol. 293 of *NATO Advanced Study Institute Series C: Physics,* edited by C. R. A. Catlow, S. C. Parker, and M. P. Allen (Kluwer Academic, Dordrecht, 1990), Secs. 6 and 11, pp. 55–82.

[18] J. M. Haile and S. Gupta, J. Chem. Phys. **79**, 3067 (1983).

[19] A. A. Chialvo and P. G. Debenedetti, Comput. Phys. Commun. **60**, 215 (1990).

[20] A. A. Chialvo, D. L. Heath, and P. G. Debenedetti, J. Chem. Phys. **91**, 7818 (1989).

[21] J. G. Powles, Physica A **126**, 289 (1984).