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

Ariel A. Chialvo and Peter T. Cummings
Department of Chemical Engineering, Thornton Hall, University of Virginia, Charlottesville, Virginia 22903-2442

Denis J. Evans
Research School of Chemistry, Australian National University, P.O. Box 4, Canberra, Australian Capital Territory 2601, Australia
(Received 27 February 1992)

A proof of the validity of the Chialvo-Debenedetti conjecture [Phys. Rev. A **43**, 4289 (1991)], the crucial element to achieve an equivalence between the McQuarrie [*Statistical Mechanics* (Harper & Row, New York, 1976)] and Helfand [Phys. Rev. **119**, 1 (1960)] shear-viscosity equations, is presented here. Some theoretical consequences of that validity are also discussed, such as the unification of most shear-viscosity expressions into one given by Andrews for first-order transport coefficients [J. Chem. Phys. **47**, 3161 (1967)]. The system-size dependence of the McQuarrie shear-viscosity values is analyzed and an extrapolation method is proposed and tested to determine the asymptotic values.

PACS number(s): 61.20.Ja, 61.20.Lc

INTRODUCTION

The theoretical equivalence between the Helfand [1] and McQuarrie [2] expressions, and consequently between the McQuarrie and Green-Kubo [2] formalisms, has been discussed recently by Chialvo and Debenedetti [3]. These authors have shown that the validity of McQuarrie's expression hinges upon "a plausible conjecture" which is supported by simulation results; however, Chialvo and Debenedetti were "not aware of a theoretical proof of its validity." The validity of the conjecture is not only the key to reduce the shear-viscosity calculation to a single-particle diffusionlike problem (as opposed to the original multiparticle counterpart), but also to obtain a unified expression whose form is neither purely mean-squared displacement [4] nor Green-Kubo (GK) [5].

In this work we first prove the theoretical validity of the conjecture (hereafter, not a conjecture), and then we derive some theoretical expressions based on this result which allow writing most shear-viscosity equations in a unified general expression similar to that derived, through a totally different approach, by Andrews [6] for first-order transport coefficients. Finally, we discuss the system-size dependence associated with the numerical determination of McQuarrie's shear viscosity owing to the finite size of the simulation box.

THEORETICAL BACKGROUND

Recently Chialvo and Debenedetti [3] compared two different methods of computing shear viscosity of a fluid using Einstein-like expressions. They began with Eq. (3.13) of Helfand's 1960 paper [1], namely,

$$\eta=\lim_{t\to\infty}\frac{1}{2kTV}\frac{d}{dt}\left\langle\sum_{i,j=1}^{N}p_{xi}(t)p_{xj}(0)[z_i(t)-z_j(0)]^2\right\rangle , \quad (1)$$

where η, t, T, V, and k denote shear viscosity, time, absolute temperature, volume, and Boltzmann constant, respectively. The symbols p_{xi} and z_i indicate the x component of the linear momentum and the z component of the position corresponding to particle i, respectively. They pointed out that McQuarrie [2] derived the following expression for the viscosity:

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

Helfand [1] also derived a third expression for the viscosity, namely,

$$\eta_H=\lim_{t\to\infty}\frac{1}{2kTV}\frac{d}{dt}\left\langle\left[\sum_{i=1}^{N}[p_{xi}(t)z_i(t)-p_{xi}(0)z_i(0)]\right]^2\right\rangle . \quad (3)$$

In Eqs. (1)–(3) $\langle\ \rangle$ denotes an equilibrium average in a zero momentum, $\sum_i p_i\equiv P=0$ ensemble. The reason why the total momentum must be zero is that if it is not zero, the velocity of the center of mass of the ensemble must be subtracted from the momenta appearing in Eqs. (1)–(3). This is because the pressure tensor only involves sums of peculiar momenta [7]. Since the required transport coefficient is macroscopic, it is also understood that the averages are to be taken in the thermodynamic limit. A convenient ensemble to use is the zero-momentum canonical ensemble, where

$$\langle B\rangle=\frac{\int B(\Gamma)\exp[-\beta H(\Gamma)]\delta(P)d\Gamma}{\int\exp[-\beta H(\Gamma)]\delta(P)d\Gamma} , \quad (4)$$

where $\beta=1/kT$, H is the system's Hamiltonian, δ ( ) is the Dirac delta function, and Γ denotes phase-space variables.

 ©1993 The American Physical Society

According to Ref. [3], the difference between the second and third expressions for the viscosity can be written as

$$\eta_H=\eta_{\mathrm{MQ}}-\lim_{t\to\infty}\frac{1}{kTV}\frac{d}{dt}\left\langle\sum_{\substack{i,j=1\\(i\neq j)}}[p_{xi}(t)z_i(t)p_{xj}(0)z_j(0)]\right\rangle$$

$$\equiv\eta_{\mathrm{MQ}}-\lim_{t\to\infty}\frac{N}{kTV}\frac{d}{dt}f(t)\ , \tag{5}$$

where $f(t)$ is expected to be intensive in the thermodynamic limit. Then $\eta_H=\eta_{\mathrm{MQ}}$ is achieved if $\lim_{t\to\infty}df(t)/dt=0$, which is the Chialvo-Debenedetti conjecture. Here we prove that $\lim_{t\to\infty}f(t)=0$, which ensures that $\lim_{t\to\infty}df(t)/dt=0$, thus proving the Chialvo-Debenedetti conjecture. Then we check the correctness of our proof by calculating $f(0)$.

Without loss of generality we can write $f(t)$ as

$$f(t)=\left\langle\sum_{j\neq1}^{N}[p_{x1}(t)z_1(t)p_{xj}(0)z_j(0)]\right\rangle\equiv\langle c(t)\rangle\ . \tag{6}$$

For systems that are mixing we can express the long-time behavior of $f(t)$ as [8]

$$\lim_{t\to\infty}f(t)=\langle p_{x1}(t)z_1(t)\rangle\left\langle\sum_{j\neq1}^{N}p_{xj}(0)z_j(0)\right\rangle$$

$$=\langle p_{x1}(0)z_1(0)\rangle\left\langle\sum_{j\neq1}^{N}p_{xj}(0)z_j(0)\right\rangle=0\ , \tag{7}$$

since by stationarity in an ensemble average $\langle p_{x1}(t)z_1(t)\rangle=\langle p_{x1}(0)z_1(0)\rangle$. Equation (7) is a statement of the fact that the phase variable $p_{x1}(t)z_1(t)$, is not a conserved quantity and is uncorrelated at sufficiently long times with the sum $\sum_j p_{xj}(0)z_j(0)$ taken over the other $N-1$ particles. Even though momentum is conserved, both terms on the right-hand side of Eq. (7) are zero since at equilibrium the momentum and coordinates of a particle are independent, i.e.,

$$\langle p_{x1}(0)z_1(0)\rangle=\langle p_{x1}(0)\rangle\langle z_1(0)\rangle=\frac{P_x}{N}\langle z_1(0)\rangle=0\ , \tag{8}$$

$$\sum_{j\neq1}^{N}\langle p_{xj}(0)z_j(0)\rangle=(N-1)\langle p_{x2}(0)\rangle\langle z_2(0)\rangle$$

$$=(N-1)\langle z_2(0)\rangle\frac{P_x}{N}=0\ . \tag{9}$$

Thus Eqs. (7)–(9) guarantee the correctness of the Chialvo-Debenedetti conjecture. Note that evidence for the validity of the mixing assumption in Eq. (7) is provided by our simulations since the limiting behavior of the conjecture function in Fig. 1 and Table I is consistent with Eq. (7).

It is enlightening to consider the zero time values of $f(t)$ and $df(t)/dt$. Again, since by Eq. (4) at equilibrium, the coordinates and the momenta are independent, we have

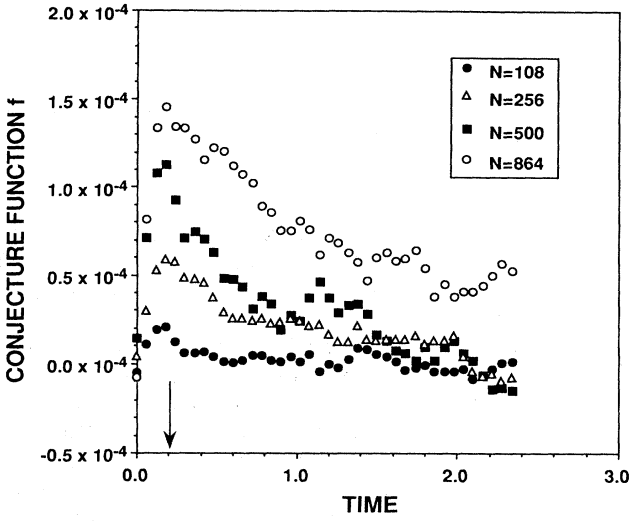

FIG. 1. Time dependence of the conjecture function $f(t)\Delta^2/(m^2\sigma^4)$ as defined by Eq. (6), parametric in N. Arrow indicates the location of $t_{\max}$.

$$f(0)=\left\langle\sum_{j\neq1}^{N}[p_{x1}(0)z_1(0)p_{xj}(0)z_j(0)]\right\rangle$$

$$=\sum_{j\neq1}^{N}\langle p_{x1}(0)p_{xj}(0)\rangle\langle z_1(0)z_j(0)\rangle$$

$$=(N-1)\langle p_{x1}(0)p_{x2}(0)\rangle\langle z_1(0)z_2(0)\rangle\ . \tag{10}$$

We will now consider the two ensemble averages separately. The momentum average can be written, taking into account the zero total momentum and the law of equipartition of energy, as

$$\langle p_{x1}(0)p_{x2}(0)\rangle=\frac{1}{N-1}\left\langle\sum_{j\neq i}^{N}p_{x1}(0)p_{xi}(0)\right\rangle$$

$$=\frac{1}{N-1}\left\langle\sum_{j=1}^{N}p_{x1}(0)p_{xj}(0)\right\rangle$$

$$-\frac{1}{N-1}\langle p_{x1}^2\rangle$$

$$=-\frac{mkT}{N-1}\ . \tag{11}$$

In the thermodynamic limit the coordinate average can

TABLE I. Comparison between simulation results and theoretical values of $Nf(0)\Delta^2/(m^2\sigma^2)$, where $f(0)$ is the first term of Eq. (15) and Δ is the dimensional time-step size, for a Lennard-Jones fluid at $kT/\varepsilon=2.75$ and $\rho\sigma^3=0.7$

System size	Simulation value	Theoretical value
108	−0.020 34	−0.019 22
500	−0.244 26	−0.247 21
864	−0.611 32	−0.615 13

be factorized as

$$\langle z_1(0)z_2(0)\rangle = \langle z_{\text{c.m.}}\rangle^2 , \tag{12}$$

where $z_{\text{c.m.}} = N^{-1}\sum_i z_i(t)$, and by substituting Eqs. (11) and (12) in (10) we find that

$$f(0) = -mkT\langle z_{\text{c.m}}\rangle^2 . \tag{13}$$

Equation (13) is an exact result derived from "first principles" and from the condition that $\sum_i p_i \equiv P = 0$. Our derivation of (13) also relies on the fact that the system's center of mass is at rest.

The latter is trivially satisfied by continuum systems. In computer simulations employing periodic boundary conditions (PBC's), there is an ambiguity in the definition of the position of the center of mass. Under PBC's one can compute $z_{\text{c.m.}} = N^{-1}\sum_i z_i(t)$ by performing the sum over the N particles which lie, at any time t, in the primitive cell. This PBC convention is often referred to as the *imaged* PBC convention (IPBC). Under IPBC's $z_{\text{c.m.}}(t)$ is not independent of time. One can also compute $z_{\text{c.m.}}(t)$ by using IPBC's at some time, say, $t=0$, and then following the N particles as they diffuse towards infinity throughout space. This convention is referred to as the infinite checkerboard, or unfolded PBC (UPBC). Under UPBC's $z_{\text{c.m.}}(t) = z_{\text{c.m.}}(0)$ for all times t. Finally, one can compute $z_{\text{c.m.}}(0)$ by using IPBC's at $t=0$, and $z_{\text{c.m.}}(t)$ in which all N particles are inside the primitive cell at time $(t-\Delta t)$, but some of them could have crossed the boundary at time t (the configuration before applying PBC's). This situation is referred to as the condition before applying PBC's (BPBC's). Under BPBC's, $z_{\text{c.m.}}(t)$ is dependent on time similarly to the IPBC case.

The change of the location of the center of mass at time t under BPBC's or IPBC's is

$$\Delta z_{\text{c.m.}}(t) = \frac{L}{N}\sum_i \{\Theta(-z_i(t)-0.5L) - \Theta(z_i(t)-0.5L)\} \tag{14}$$

(with similar expressions for $\Delta x_{\text{c.m.}}$ and $\Delta y_{\text{c.m.}}$) where $\Theta(\ )$ denotes the Heaviside function [i.e., $\Theta(x)=0$ if $x<0$ and $\Theta(x)=1$ if $x>0$], L the size of the simulation box, and N the number of particles. For the sake of simplicity we locate the origin at the center of the (cubic) simulation box. Thus under IPBC's, in order to satisfy simultaneously the conditions of zero linear momentum and center of mass at rest for periodic systems, the time averages given by Eqs. (1)–(12) must be taken over the molecular trajectories relative to the system's instantaneous center of mass (or to a fixed point in the relative-to-center of mass axes) unless the microscopic quantities involved are pairwise additive (certainly, not always the case). If an asterisk denotes the use of coordinates relative to the instantaneous center of mass, $z^*(t) = z(t) - z_{\text{c.m.}}(t)$, then under IPBC's or BPBC's $\langle z^*_{\text{c.m.}}(t)\rangle = \langle z(t)\rangle - \langle z_{\text{c.m.}}(t)\rangle = 0$ at any time. In this case, after recalling Eq. (12) and the definition of $z^*(t)$, Eq. (13) reduces to

$$f^*(0) = -mkT[\langle z\rangle^2 - \langle z_{\text{c.m.}}\rangle^2] = 0 , \tag{15}$$

i.e., there is a net contribution due to the motion of the system's center of mass.

For continuum (i.e., nonperiodic) systems and for periodic systems under the UPBC convention, $f(0)$ depends on the location of the origin of coordinates. If the origin is chosen at $t=0$ to coincide with the position of the center of mass, then $f(0) = f^*(0) = 0$. If the system's coordinates range from 0 to $L = (N/\rho)^{1/3}$, where ρ is the number density, then $z_{\text{c.m.}}(0) = L/2$ and $f(0) = -0.25mkT(N/\rho)^{2/3}$. If the system's coordinates range from $-0.5L$ to $0.5L$, $z_{\text{c.m.}}(0) = 0$ and $f(0) = 0$.

With respect to $df(t)/dt$ at $t=0$, it is easy to show that this slope is also zero. We will come back to this point in the discussion section.

THEORETICAL IMPLICATIONS OF THE CHIALVO- DEBENEDETTI CONJECTURE (REF. [9])

According to Eq. (7) we can immediately recast McQuarrie's shear-viscosity equation as

$$\eta_{\text{MQ}} = \lim_{t\to\infty} \frac{-1}{kTV}\frac{d}{dt}\langle X(t)\cdot X(0)\rangle , \tag{16}$$

with

$$X(t) = (\chi_1, \chi_2, \ldots, \chi_N), \quad \chi_i = p_{xi}z_i , \tag{17}$$

where the centered dot denotes the scalar product of two N arrays. By solving the time derivative we obtain

$$\eta_{\text{MQ}} = \lim_{t\to\infty} \frac{-1}{kTV}\langle J(t)\cdot X(0)\rangle , \tag{18}$$

with

$$J = (j_1, j_2, \ldots, j_N) , \quad j_i = \frac{d\chi_i}{dt} = p_{xi}p_{zi} + z_i f_{xi} , \tag{19}$$

where f_{xi} is the force on molecule i in the x direction and J is related to the xz component of the pressure tensor as follows:

$$J_p^{xz} = \sum_{i=1}^{N} j_i(t) = \frac{d}{dt}\sum_{i=1}^{N}\chi_i(t) . \tag{20}$$

Equation (18) is similar to a more general expression derived by Andrews [6] for first-order transport coefficients.

Note that Eq. (7) makes it possible to express most shear-viscosity equations whose forms are neither purely mean-squared displacement nor Green-Kubo in the unified form given by Eq. (18). For example, starting from Erpenbeck's reworking of the Green-Kubo expression [4],

$$\eta = \lim_{t\to\infty}\frac{1}{kTV}\left\langle J_p^{xz}(0)\int_0^t J_p^{xz}(s)ds\right\rangle , \tag{21}$$

after invoking Eq. (20), we obtain

$$\eta = \lim_{t\to\infty}\frac{1}{kTV}\left\langle J_p^{xz}(0)\sum_{j=1}^{N}[p_{xj}(t)z_j(t) - p_{xj}(0)z_j(0)]\right\rangle . \tag{22}$$

Recalling the properties of correlation functions [10],

$$\left\langle A(t)\frac{dA}{dt}(t)\right\rangle=0$$

and

$$\left\langle A(t)\frac{dA}{dt}(0)\right\rangle=-\left\langle A(0)\frac{dA}{dt}(t)\right\rangle , \tag{23}$$

where in principle $A(t)$ should be a fluctuation quantity (see Appendix A for details), we obtain from Eq. (22)

$$\begin{aligned}\eta&=\lim_{t\to\infty}\frac{-1}{kTV}\left\langle J_p^{xz}(t)\sum_{j=1}^{N}p_{xj}(0)z_j(0)\right\rangle\\&=\lim_{t\to\infty}\frac{-1}{kTV}\left\langle\frac{d}{dt}\sum_{i=1}^{N}p_{xi}(t)z_i(t)\sum_{j=1}^{N}p_{xj}(0)z_j(0)\right\rangle\\&=\lim_{t\to\infty}\frac{-1}{kTV}\frac{d}{dt}\left\langle\sum_{i=1}^{N}p_{xi}(t)z_i(t)\sum_{j=1}^{N}p_{xj}(0)z_j(0)\right\rangle ,\end{aligned} \tag{24}$$

and after invoking Eq. (7) we obtain

$$\begin{aligned}\eta&=\lim_{t\to\infty}\frac{-1}{kTV}\frac{d}{dt}\langle X(t)\cdot X(0)\rangle\\&=\lim_{t\to\infty}\frac{-1}{kTV}\langle J(t)\cdot X(0)\rangle .\end{aligned} \tag{25}$$

Second, starting from Hoheisel and Vogelsang's mean-squared-displacement integral expression [5],

$$\eta=\lim_{t\to\infty}\frac{1}{2VkT}\frac{d}{dt}\left\langle\left[\int_0^t J_p^{xz}(s)ds\right]^2\right\rangle , \tag{26}$$

we obtain, upon carrying out the differentiation,

$$\eta=\lim_{t\to\infty}\frac{1}{kTV}\left\langle J_p^{xz}(t)\sum_{j=1}^{N}[p_{xj}(t)z_j(t)-p_{xj}(0)z_j(0)]\right\rangle , \tag{27}$$

which, upon invoking the first identity in (23), reduces identically to Eq. (18).

NUMERICAL COMPUTATION OF $Nf(t)$

To study the numerical behavior of the conjecture function $f(t)$ we performed molecular-dynamics NVT MD simulations of truncated Lennard-Jones (LJ) spheres (cutoff radius $r_c=2.38\sigma$) at the state condition of $kT/\varepsilon=2.75$ and $\rho\sigma^3=0.7$ for $N=108$, 256, 500, and 864 particles. The calculation of the ensemble average indicated in Eq. (6) was performed over ν independent time origins ($t=0$) to avoid any correlation of time origin, and over the six permutations of $r_\alpha p_{\beta\neq\alpha}$ ($\alpha,\beta=x,y,z$) to improve the statistics. In fact, each simulation was divided into $\nu=100$ independent subruns, i.e., each experiment was obtained from a portion of phase-space trajectory generated in the simulation with no overlapping among those portions. The displacement of $r_\alpha p_{\beta\neq\alpha}$ ($\alpha,\beta=x,y,z$) was determined by taking the periodic boundary conditions into account correctly using what we referred to as the BPBC approach in Appendix B. The time average of the time derivative of the $r_\alpha p_\beta$ displacement in the BPBC convention gives directly the correct expression for the pressure tensor—Eqs. (11)–(13) in Ref. [17]—because it takes care implicitly of the periodic boundary conditions. This is described more fully in Appendix B.

The accuracy of our simulation results was tested by comparing the theoretical values of $f(0)$ given by the first term of Eq. (15) with the corresponding simulation values for $108\le N\le 864$, as shown in Table I. The time evolution of the conjecture function $f(t)$ obtained under the BPBC convention for the four system sizes is given in Fig. 1. The common feature of these curves is that $f(t)$ shows a narrow correlation zone, where $df/dt\approx\text{const}>0$, followed by a wider decorrelation zone where $df/dt\approx\text{const}<0$. For a fixed number of independent experiments (ν), the size of the correlation and the width of the decorrelation zones increase with N. Note that while $f(t)\approx 0$ and $df/dt\approx 0$ for $N\le 108$ in the interval $0\le t\le 2.5\sigma\sqrt{m/\varepsilon}$, for $N\ge 500$ these functions do not totally decorrelate even at $t\approx 2.5\sigma\sqrt{m/\varepsilon}$ (σ and ε are the Lennard-Jones size and energy parameters, and m is the mass of an atom).

The above behavior is consistent with the fact that $f(t)$ is just a difference of two time correlation functions, i.e.,

$$\begin{aligned}f(t)=N^{-1}&\left\langle\sum_{i=1}^{N}p_{xi}(t)z_i(t)\sum_{j=1}^{N}p_{xj}(0)z_j(0)\right\rangle\\&-\langle p_{x1}(t)z_1(t)p_{x1}(0)z_1(0)\rangle ,\end{aligned} \tag{28}$$

where

$$\begin{aligned}&f(0)=0 , \quad \left.\frac{df(t)}{dt}\right|_{t=0}=0 ,\\&\lim_{t\to\infty}f(t)=0 , \quad \lim_{t\to\infty}\frac{df(t)}{dt}=0 .\end{aligned} \tag{29}$$

Note also that $f(t)$ shows a maximum

$$\begin{aligned}\left.\frac{df(t)}{dt}\right|_{t=t_{\max}}=-\Bigg\langle&[p_{x1}(t)p_{z1}(t)+f_{x1}(t)z_1(t)]\\&\times\left[\sum_{j\neq 1}p_{xj}(0)z_j(0)\right]\Bigg\rangle=0 ,\end{aligned} \tag{30}$$

where in deriving Eq. (30) we have recalled Eq. (23). Although the value of $f(t_{\max})$ is a strong function of N, $t_{\max}$ is independent of N. This is suggested by Eq. (30) and confirmed by the simulation results of Fig. 1, where $t_{\max}\approx 0.2\sigma\sqrt{m/\varepsilon}$.

DISCUSSION AND CONCLUSIONS

The behavior shown by $f(t)$ in Fig. 1 suggests that the time at which we can assume $f(t)\approx 0$ and $df/dt\approx 0$ at fixed ν depends strongly on the system size N. This can be interpreted by analyzing the variance in $f(t)_T$ [11],

$$\begin{aligned}\langle(\delta f_T)^2\rangle&\equiv\langle c^2(t)\rangle-\langle f_T\rangle^2\\&\approx\frac{2\tau_f}{\nu T}\langle\delta f_T^2(0)\rangle , \quad \delta f_T=c(t)-f_T ,\end{aligned} \tag{31}$$

where the subscript T indicates the coarse-grain average over the interval T, $\nu=T_{\text{run}}/T$ is the number of experi-

ments (time origins), and τ_f is the characteristic decay time of the fluctuations in $c(t)$,

$$\tau_f = 2\langle \delta f_T^2(0)\rangle^{-1} \int_0^\infty \langle \delta f_T(t)\delta f_T(0)\rangle dt \ . \tag{32}$$

Now, according to the definition of $f(t)$ the exact value of the time correlation function involved in Eq. (31) has the N dependence

$$\langle \delta f_T^2(0)\rangle \sim N^{7/3} \tag{33}$$

so that

$$\langle \delta f_T^2(t)\rangle \sim \frac{\tau_f N^{7/3}}{\mathcal{R}T} \ . \tag{34}$$

Equation (34) reveals that the accuracy of the simulated values of $Nf(t)$ at constant T is inversely proportional to $N^{5/3}/\mathcal{R}$, i.e., the root-mean-square error of $Nf(t)$ decreases asymptotically either with decreasing N or increasing $\mathcal{R}$. For example, if we need $\mathcal{R}=100$ to achieve a required accuracy in $Nf(t)$ when $N=108$, the same accuracy will be obtained with $\mathcal{R}=102\,400$ when $N=864$, i.e., a prohibitively long simulation. Equation (34) also suggests that the leading N dependence of η_{MQ} at fixed $\mathcal{R}$ and T is given by the N dependence of the conjecture function $Nf(t)$.

It is reasonable to require that $T<T_r$, the sound traversal time of the simulation, which corresponds to the time taken for a sound wave to travel across the simulation box. This implies that T is limited by the size of the simulation box. Thus in practice we can decrease $\langle \delta f_T^2(t)\rangle$ more efficiently by reducing N. In fact, at constant $\mathcal{R}$, T, and τ_f, the smallest deviation from $f(t)\approx 0$ and $df/dt \approx 0$ is attained in the $N=0$ limit,

$$(\text{smallest deviation}) \Longleftrightarrow \lim_{N\to 0} \langle \delta f_T^2(0)\rangle \ , \tag{35}$$

where $\Longleftrightarrow$ denotes implication, so that by recalling Eq. (5) we have

$$\eta_H(N) - \eta_{MQ}(N) \sim \frac{N^{0.5}}{V}\langle \delta f_T^2(0)\rangle^{0.5} \sim N^{2/3} \quad \text{for } (\mathcal{R},T)=\text{const} \tag{36}$$

and consequently,

$$\lim_{N\to 0}\eta_H(N)_{\mathcal{R}T} = \lim_{N\to 0}\eta_{MQ}(N)_{\mathcal{R}T} = \lim_{N\to 0}\left[\eta_{MQ}(N)_{\mathcal{R}T} + \frac{N^{0.5}}{V}\langle \delta f_T^2(0)\rangle^{0.5}\right]_{\mathcal{R}T} , \tag{37}$$

which indicates that the calculated McQuarrie shear viscosity of a system at fixed $\mathcal{R}$ and T is equal to Helfand's value in the $N=0$ limit. Note that in order to apply the thermodynamic limit to Eq. (5) we must consider $\mathcal{R}$ and T as functions of the system size N (see Fig. 1), i.e.,

$$\eta_H(N) - \eta_{MQ}(N) \sim \frac{N^{0.5}}{V}\langle \delta f_T^2(0)\rangle^{0.5} \sim N^{-1} \Longrightarrow \mathcal{R}T \sim N^{5/6} \ . \tag{38}$$

Thus, according to Eqs. (5) and (34), we have that

$$\lim_{N\to 0}\eta_H(N) = \lim_{N\to 0}\eta_{MQ}(N) \quad \text{with } \mathcal{R}T=\text{const} \tag{39}$$

and

$$\lim_{N\to \infty}\eta_H(N) = \lim_{N\to \infty}\eta_{MQ}(N) \quad \text{with } \mathcal{R}T \sim N^{5/6} \ . \tag{40}$$

However, the extrapolation of $\eta_{MQ}(N)$ given by Eq. (40) is impractical because the strong N dependence of $\mathcal{R}T$ [see Eq. (38)] makes the simulations prohibitively expensive. [A third alternative could be the analysis of the N dependence for each term of Eq. (38), but this is beyond the scope of this paper.]

Results for $\eta_{MQ}(N)$ and the extrapolation given by Eq. (37) are shown in Fig. 2 at two state conditions. Interestingly, the extrapolated η_{MQ} values agree within 8–16% with the corresponding nonequilibrium molecular-dynamics (NEMD) results [12].

The unification of the shear viscosity expressions as given by Eq. (18) hinges upon the condition of thermodynamic limit as well as the requirement that the limiting time t must be much greater than the time required for the ensemble average of the corresponding autocorrelations to decay sufficiently to zero. Those conditions cannot be taken for granted in equilibrium computer simulation owing to the finite system size, which imposes the use of periodic boundary conditions, and consequently that the limiting time t must be smaller than the "sound traversal time" [11]. In summary, although theoretically correct, the "computer-simulation" equivalence of the shear-viscosity expressions that reduces to the Andrews

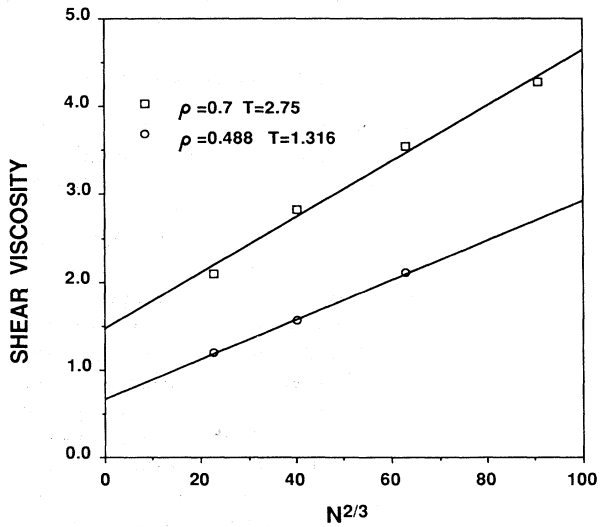

FIG. 2. System-size dependence of McQuarrie's shear-viscosity ($\eta\sigma^2/\sqrt{m\,\varepsilon}$) results for a LJ fluid at two state conditions: $kT/\varepsilon=2.75$, $\rho\sigma^3=0.7$ ($r_c/\sigma=2.38$), and $kT/\varepsilon=1.316$, $\rho\sigma^3=0.488$ ($r_c/\sigma=2.50$).

form [Eq. (18)] is mostly unknown and definitely deserves additional study.

ACKNOWLEDGMENTS

A.A.C. and P.T.C. gratefully acknowledge support of this research by the Division of Chemical Sciences, Office of Basic Energy Sciences, U.S. Department of Energy. The reported simulations were performed on a Cray Y-MP/832 supercomputer located at the Pittsburgh Supercomputing Center (CPWSCB), through Grant No. CBT910039P.

APPENDIX A

Given a dynamical property $A(t)$, we can define its fluctuation as

$$\alpha(t)=A(t)-\langle A(t)\rangle \ , \tag{A1}$$

where the angular brackets indicate time (ensemble) average. The fluctuation $\alpha(t)$ has the property [10]

$$\frac{d}{dt}\langle \alpha(t)\alpha(t+s)\rangle=0 \ , \tag{A2}$$

so that

$$\langle \alpha(t)\dot{\alpha}(0)\rangle=-\langle \alpha(0)\dot{\alpha}(t)\rangle \ , \tag{A3}$$

and then

$$\langle \alpha(t)\dot{\alpha}(t)\rangle=0 \quad \text{with } \dot{\alpha}(t)=\frac{d\alpha(t)}{dt} \ . \tag{A4}$$

Now, if $\langle \dot{A}(t)\rangle=0$, where $\dot{A}(t)=dA(t)/dt$, then

$$\begin{aligned}\langle \alpha(t)\dot{\alpha}(t)\rangle &=\langle [A(t)-\langle A(t)\rangle][\dot{A}(t)-\langle \dot{A}(t)\rangle]\rangle \\ &=0 \\ &=\langle A(t)\dot{A}(t)\rangle-\langle A(t)\rangle\langle \dot{A}(t)\rangle \\ &=0 \ ,\end{aligned} \tag{A5}$$

or, finally,

$$\langle A(t)\dot{A}(t)\rangle=\langle A(t)\rangle\langle \dot{A}(t)\rangle=0 \ . \tag{A6}$$

In summary, the condition $\langle \dot{A}(t)\rangle=0$ constrains the dynamic behavior of $\alpha(t)$ so that properties (A2)–(A4) apply also to the behavior of $A(t)$. This is an important result, as we will illustrate below. For instance, for $A(t)=\sum_i z_i(t)p_{yi}(t)$ we have that

$$\begin{aligned}\langle \dot{A}(t)\rangle &=\left\langle \sum_i [z_i(t)f_{yi}(t)+p_{zi}(t)p_{yi}(t)/m] \right\rangle \\ &=\begin{cases}0 & \text{if } z\neq y \\ \frac{1}{3}PV & \text{if } z=y \ ,\end{cases}\end{aligned} \tag{A7}$$

with $f_{yi}=dp_{yi}/dt$, provided that $\sum_i p_{\alpha i}(t)=0$ ($\alpha=x,y,z$) [9], i.e., the system should also be at rest. Then the autocorrelation expression associate with the GK shear-viscosity equation is

$$\begin{aligned}\langle \dot{\alpha}(t)\dot{\alpha}(0)\rangle &=\left\langle \left\{ \left[\sum_i z_i(t)f_{yi}(t)+p_{zi}(t)p_{yi}(t)/m \right]-\left\langle \sum_i z_i(t)f_{yi}(t)+p_{zi}(t)p_{yi}(t)/m \right\rangle \right\} \right. \\ &\quad \left. \times \left\{ \left[\sum_i z_i(0)f_{yi}(0)+p_{zi}(0)p_{yi}(0)/m \right]-\left\langle \sum_i z_i(0)f_{yi}(0)+p_{zi}(0)p_{yi}(0)/m \right\rangle \right\} \right\rangle \\ &=\left\langle \left[\sum_i z_i(t)f_{yi}(t)+p_{zi}(t)p_{yi}(t)/m \right] \left[\sum_i z_i(0)f_{yi}(0)+p_{zi}(0)p_{yi}(0)/m \right] \right\rangle \\ &=\langle \dot{A}(t)\dot{A}(0)\rangle \ .\end{aligned}$$

APPENDIX B

Here we present details on the calculation of the shear-viscosity generalized displacement in a simulation box centered at (0,0,0), and subject to periodic boundary conditions as well as minimum image criterion. The dynamic microscopic properties associated with the shear viscosity are the off-diagonal elements of the tensorial quantity

$$\mathsf{G}(t)\equiv \sum_{i=1}^{N} \mathbf{r}_i(t)\mathbf{v}_i(t) \ , \tag{B1}$$

where $\mathbf{r}_i$ and $\mathbf{v}_i$ are the position and velocity of particle i, respectively. For a finite, periodic system as is used in molecular simulations, some confusion arises about what is the appropriate quantity $\mathbf{r}_i(t)$ to be used in Eq. (B1). There are three possibilities. Computationally, we calculate $\mathsf{G}(t+\Delta t)$ from the relationship

$$\mathsf{G}(t+\Delta t)=\mathsf{G}(t)+\Delta\mathsf{G} \ , \tag{B2}$$

where the displacement $\Delta\mathsf{G}$ of $\mathsf{G}(t)$ between time steps t and $(t+\Delta t)$ is given by

$$\Delta\mathsf{G}=\sum_{i=1}^{N} \mathbf{r}_i(t+\Delta t)\mathbf{v}_i(t+\Delta t)-\sum_{i=1}^{N} \mathbf{r}_i(t)\mathbf{v}_i(t) \ . \tag{B3}$$

Three definitions for $\mathsf{G}(t)$ are possible depending on the choice of $\mathbf{r}_i(t)$: $\mathsf{G}^u(t)$, corresponding to the use of the

unfolded (UPBC) positions $\mathbf{r}_i^u(t+\Delta t)$ and $\mathbf{r}_i^u(t)$ [13]; $G^{PBC}(t)$, corresponding to the use of $\mathbf{r}_i^{PBC}(t+\Delta t)$ and $\mathbf{r}_i^{PBC}(t)$ in Eq. (B3) (IPBC), where $\mathbf{r}_i^{PBC}(t)$ is the image of molecule i determined by periodic boundary conditions and located inside the central simulation cell; and $G^{BPBC}(t)$, corresponding to the use of $\mathbf{r}_i^{BPBC}(t+\Delta t)$ and $\mathbf{r}_i^{PBC}(t)$ in Eq. (B3) (BPBC). These three cases are depicted in Figs. 4–6, respectively.

In the remainder of this appendix, we argue that the correct definition for $G(t)$ to be used in the simulation of finite-sized periodic system is $G^{BPBC}(t)$. We do so by showing that only the time derivative of $G^{BPBC}(t)$ yields the correct virial theorem and that the time derivatives of $G^u(t)$ and $G^{PBC}(t)$ are both zero at large times. One practical computational consequence is that $G^u(t)$ and $G^{PBC}(t)$ asymptote to constants as $t\to\infty$ while $G^{BPBC}(t)$ is linear in t as $t\to\infty$. Numerical computations are used to confirm this behavior (see Fig. 3).

Let us begin by considering $G^u(t)$,

$$G^u(t)\equiv\sum_{i=1}^{N}\mathbf{r}_i^u(t)\mathbf{v}_i(t)\ . \tag{B4}$$

We will assume, without loss of generality, that all the molecules in the summation in Eq. (B4) are located in the central simulation cell at time $t=0$. That is, if $\mathbf{n}_i(t)$ is the simulation cell in which molecule i is located at time t, then

$$\mathbf{n}_i(0)=\mathbf{0}=(0,0,0)\ . \tag{B5}$$

At any time the unfolded position $\mathbf{r}_i^u(t)$ of particle i is related to the position $\mathbf{r}_i^{PBC}(t)$ of the image of particle i inside the central simulation cell by

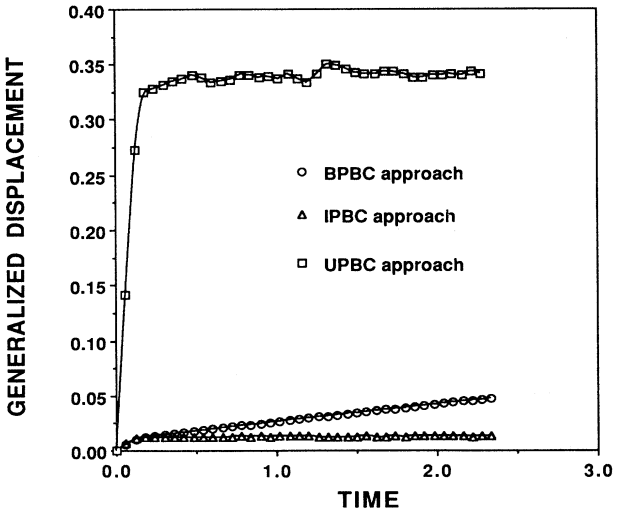

FIG. 3. Time dependence of McQuarrie's shear-viscosity generalized displacement [in $\Delta^2/(m^2\sigma^4)$ units] for a LJ fluid at the state conditions $kT/\varepsilon=2.75$, $\rho\sigma^3=0.7$ ($r_c/\sigma=2.38$). The curves correspond to the displacement of the off-diagonal elements of the tensor $G^u(t)=\sum_{i=1}^{N}\mathbf{r}_1^u(t)\mathbf{v}_i(t)$, $G^{PBC}(t)=\sum_{i=1}^{N}\mathbf{r}_i^{PBC}(t)\mathbf{v}_i(t)$, and $G^{BPBC}(t)=\sum_{i=1}^{N}\mathbf{r}_i^{BPBC}(t)\mathbf{v}_i(t)$.

$$\mathbf{r}_i^{PBC}(t)=\mathbf{r}_i^u(t)-\mathbf{n}_i(t)L\ , \tag{B6}$$

where $\mathbf{n}_i(t)$ is a simple cubic lattice vector whose elements are integers. The relationship between $\mathbf{r}_i^{BPBC}(t)$ and $\mathbf{r}_i^{PBC}(t)$, the positions of particle i before and after applying periodic boundary conditions, is given in terms of the "crossing function" $\boldsymbol{\phi}_i(t)$, viz.,

$$\mathbf{r}_i^{PBC}(t)=\mathbf{r}_i^{BPBC}(t)-L\boldsymbol{\phi}_i(t)\ , \tag{B7}$$

where, for a central simulation cell centered at (0,0,0),

$$\begin{aligned}\boldsymbol{\phi}_{ix}(t)&=\Theta(x_i(t)-0.5L)-\Theta(-x_i(t)-0.5L)\ ,\\ \boldsymbol{\phi}_{iy}(t)&=\Theta(y_i(t)-0.5L)-\Theta(-y_i(t)-0.5L)\ ,\\ \boldsymbol{\phi}_{iz}(t)&=\Theta(z_i(t)-0.5L)-\Theta(-z_i(t)-0.5L)\ .\end{aligned} \tag{B8}$$

In Eqs. (B8), $\Theta(a)$ is the Heaviside function,

$$\Theta(a)=\begin{cases}0 \Longleftarrow a<0\\ 1 \Longleftarrow a>0\ .\end{cases} \tag{B9}$$

Then, by using (B6) and (B7), $G^u(t)$ can be written, in addition to (B4), in the two equivalent forms

$$G^u(t)=\sum_{i=1}^{N}\{\mathbf{r}_i^{BPBC}(t)+[\mathbf{n}_i(t)-\boldsymbol{\phi}_i(t)]L\}\mathbf{v}_i(t) \tag{B10}$$

and

$$G^u(t)=\sum_{i=1}^{N}\{\mathbf{r}_i^{PBC}(t)+\mathbf{n}_i(t)L\}\mathbf{v}_i(t)\ . \tag{B11}$$

Using similar arguments used in the derivation of the virial theorem [14,15], the time average of the time derivative of $G^u(t)$, $\overline{\dot{G}^u(t)}$, is zero,

$$\overline{\dot{G}^u(t)}=\overline{\dot{G}^{PBC}(t)}+L\overline{\frac{d}{dt}\sum_{i=1}^{N}\mathbf{n}_i(t)\mathbf{v}_i(t)}=0\ . \tag{B12}$$

This can be seen by writing explicitly

$$\begin{aligned}\overline{\dot{G}^u(t)}&=\lim_{T\to\infty}\frac{1}{T}\sum_{i=1}^{N}\int_0^T d(\mathbf{r}_i^u\mathbf{v}_i)\\ &=\lim_{T\to\infty}\frac{1}{T}[\mathbf{r}_i^u\mathbf{v}_i(T)-\mathbf{r}_i^u\mathbf{v}_i(0)]\ .\end{aligned} \tag{B13}$$

The velocities of the molecules are finite because the system's kinetic energy is bounded, i.e.,

$$|\mathbf{v}_i(t)|\le(2K/m)^{0.5} \tag{B14}$$

where K is the total kinetic energy and the time dependence of the positional displacement is

$$|\mathbf{r}_i^u(t)|\sim t^{0.5}\ . \tag{B15}$$

Consequently,

$$\lim_{T\to\infty}\frac{1}{T}[\mathbf{r}_i^u\mathbf{v}_i(T)-\mathbf{r}_i^u\mathbf{v}_i(0)]<(2K/m)^{0.5}\lim_{T\to\infty}T^{-1/2}=0\ . \tag{B16}$$

The first term on the right-hand side (rhs) of the (B12) is also zero because, in addition to (B14), $|\mathbf{r}_i|\le+0.5L$, so that the argument leading to Eq. (B16) will apply with

the only change being that the $T^{-1/2}$ will be replaced by T^{-1}. Thus we obtain

$$\overline{\dot{G}^{\mathrm{PBC}}(t)} = -L\overline{\frac{d}{dt}\sum_{i=1}^{N}\mathbf{n}_i(t)\mathbf{v}_i(t)} = 0 \ . \tag{B17}$$

Then, by taking the time derivative of (B10) and recalling (B11), (B12), and (B17), we obtain

$$\overline{\dot{G}^{\mathrm{BPBC}}(t)} = L\overline{\frac{d}{dt}\sum_{i=1}^{N}\boldsymbol{\phi}_i(t)\mathbf{v}_i(t)} \ , \tag{B18}$$

which is the tensorial form of the virial theorem for a periodic system, as we demonstrate below.

According to (B8), the left-hand side of (B18) can be written as

$$\begin{aligned}\overline{\dot{G}^{\mathrm{BPBC}}(t)} &= \overline{\frac{d}{dt}\sum_{i=1}^{N}\mathbf{r}_i^{\mathrm{BPBC}}(t)\mathbf{v}_i(t)} \\ &= \overline{\sum_{i=1}^{N}[\mathbf{v}_i(t)\mathbf{v}_i(t)+\mathbf{r}_i^{\mathrm{BPBC}}(t)\mathbf{f}_i(t)/m]} \ ,\end{aligned} \tag{B19}$$

with

$$\dot{\mathbf{r}}_i^{\mathrm{BPBC}}(t) = \frac{d}{dt}\{\mathbf{r}_i^{u}(t)-L[\mathbf{n}_i(t)-\boldsymbol{\phi}_i(t)]\} = \dot{\mathbf{r}}_i^{u}(t) = \mathbf{v}_i \ , \tag{B20}$$

since $\dot{\mathbf{n}}_i(t)=\dot{\boldsymbol{\phi}}_i(t)$.

The rhs of (B18) requires some additional analysis and, for the sake of clarity, we will study the xy element of that tensor, i.e.,

$$\overline{\dot{G}_{xy}^{\mathrm{BPBC}}(t)} = L\overline{\sum_{i=1}^{N}\dot{\phi}_{ix}(t)v_{yi}(t)} + L\overline{\sum_{i=1}^{N}\phi_{ix}(t)f_{yi}(t)/m} \ . \tag{B21}$$

According to the definition of the "crossing function" and the identity for the Dirac δ function [16],

$$\delta(s-a)-\delta(-s-a) = 2|a|\delta(s^2-a^2) \ , \tag{B22}$$

we obtain

$$\dot{\phi}_{ix} = \delta(x_i^2-0.25L^2)Lv_{xi} \ . \tag{B23}$$

Then, invoking another identity for the δ function [16],

$$\delta(x^2-0.25L^2) = \delta(t-t_{\mathrm{PBC}})\Big/\left|\left[\frac{d(x^2)}{dt}\right]_{t_{\mathrm{PBC}}}\right| \ , \tag{B24}$$

the first term on the rhs of (B21) becomes

$$\begin{aligned}L^2\overline{\sum_{i=1}^{N}v_{yi}v_{xi}\delta[x_i^2-0.25L^2]} &= \lim_{T\to\infty}\frac{L^2}{T}\int_0^T\sum_{i=1}^{N}v_{yi}v_{xi}\frac{\delta(t-t_{\mathrm{PBC}})}{L|v_{xi}|}dt \\ &= \lim_{T\to\infty}\frac{L}{T}\int_0^T\sum_{i=1}^{N}v_{yi}\mathrm{sgn}(v_{xi})\delta[t-t_{\mathrm{PBC}}]dt \\ &= \lim_{T\to\infty}\frac{L}{T}\sum_{t_{\mathrm{PBC}}}\sum_{i}^{N}v_{yi}\mathrm{sgn}[n_{xi}(t_{\mathrm{PBC}})] = 0 \ ,\end{aligned} \tag{B25}$$

where sgn() denotes the sign function. Likewise, the second term on the rhs of (B21) becomes

$$\begin{aligned}L\overline{\sum_{i=1}^{N}\{\Theta(x_i-0.5L)-\Theta(-x_i-0.5L)\}f_{yi}} &= PL\oint_{A_{xz}}(\hat{\mathbf{v}}_x\cdot\hat{\mathbf{v}}_y)dA = PV\delta_{xy} \ ,\end{aligned} \tag{B26}$$

with A the area of a face of the simulation box, V the system volume, P the system pressure, δ_{xy} the Kronecker delta, and $\hat{\mathbf{v}}_\alpha$ a unit vector in the α direction. Note that the rhs of (B26) represents an alternative expression [to the rhs of (B19)] to determine the pressure tensor. Combining (B26) and (B21) then leads to

$$\overline{\dot{G}_{xy}^{\mathrm{BPBC}}(t)} = PV\delta_{xy} \tag{B27}$$

so that

$$P = (1/3V)\mathrm{Tr}\overline{\dot{G}^{\mathrm{BPBC}}(t)} \ , \tag{B28}$$

where Tr denotes trace of the tensor. Thus the only

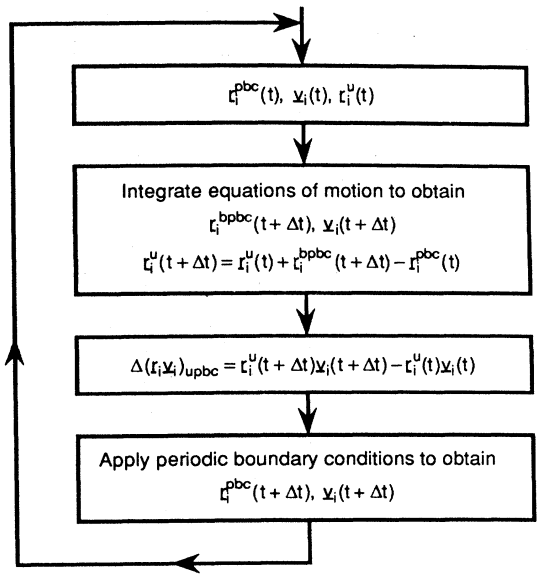

FIG. 4. Standard molecular-dynamics loop for one time step when using UPBC.

position-velocity tensor expression suitable to define the correct pressure tensor of a periodic system is the one involving the BPBC convention. In such a situation, the impulsive contribution of linear momentum due to the application of periodic boundary conditions plays the role of "external field" (what the rigid walls do in Clausius's virial theorem [14]). Note that the infinite checkerboard (UPBC) case corresponds to a zero "external field" situation [Eq. (B12)].

In summary, the displacements of the tensor $\mathsf{G}(t)$ [Eqs. (B1)] in the three conventions are related to one another as follows (Fig. 4):

$$\begin{aligned}(\Delta\mathbf{r}_i\mathbf{v}_i)_{\mathrm{UPBC}}&=\mathbf{r}_i^u(t+\Delta t)\mathbf{v}_i(t+\Delta t)-\mathbf{r}_i^u(t)\mathbf{v}_i(t)\\&=[\mathbf{r}_i^{\mathrm{PBC}}(t+\Delta t)+L\mathbf{n}_i(t+\Delta t)]\mathbf{v}_i(t+\Delta t)-[\mathbf{r}_i^{\mathrm{PBC}}(t)+L\mathbf{n}_i(t)]\mathbf{v}_i(t)\\&=(\Delta\mathbf{r}_i\mathbf{v}_i)_{\mathrm{IPBC}}+L[\mathbf{n}_i(t+\Delta t)\mathbf{v}_i(t+\Delta t)-\mathbf{n}_i(t)\mathbf{v}_i(t)]\ ,\end{aligned}\tag{B29}$$

where (Fig. 5)

$$(\Delta\mathbf{r}_i\mathbf{v}_i)_{\mathrm{IPBC}}=\mathbf{r}_i^{\mathrm{PBC}}(t+\Delta t)\mathbf{v}_i(t+\Delta t)-\mathbf{r}_i^{\mathrm{PBC}}(t)\mathbf{v}_i(t)\ .\tag{B30}$$

If particle i does not leave the current cell, $\mathbf{n}_i(t+\Delta t)=\mathbf{n}_i(t)$, so that (B29) becomes

$$(\Delta\mathbf{r}_i\mathbf{v}_i)_{\mathrm{UPBC}}=(\Delta\mathbf{r}_i\mathbf{v}_i)_{\mathrm{IPBC}}+L\mathbf{n}_i(t+\Delta t)[\mathbf{v}_i(t+\Delta t)-\mathbf{v}_i(t)]\tag{B31}$$

Otherwise, $\mathbf{n}_i(t)=\mathbf{n}_i(t+\Delta t)+\mathbf{n}_i^{\mathrm{imag}}$ with $\mathbf{n}^{\mathrm{imag}}=\{n_x,n_y,n_z\}$ and $n_\alpha=0,\pm1$ ($\alpha=x,y,z$), so that (B29) now reads

$$\begin{aligned}(\Delta\mathbf{r}_i\mathbf{v}_i)_{\mathrm{UPBC}}&=(\Delta\mathbf{r}_i\mathbf{v}_i)_{\mathrm{IPBC}}+L\mathbf{n}_i(t+\Delta t)\mathbf{v}_i(t+\Delta t)-L[\mathbf{n}_i(t+\Delta t)+\mathbf{n}^{\mathrm{imag}}(t)]\mathbf{v}_i(t)\\&=(\Delta\mathbf{r}_i\mathbf{v}_i)_{\mathrm{BPBC}}+L\mathbf{n}_i(t+\Delta t)[\mathbf{v}_i(t+\Delta t)-\mathbf{v}_i(t)]\end{aligned}\tag{B32}$$

with (Fig. 6)

$$(\Delta\mathbf{r}_i\mathbf{v}_i)_{\mathrm{BPBC}}=(\Delta\mathbf{r}_i\mathbf{v}_i)_{\mathrm{IPBC}}-L\mathbf{n}^{\mathrm{imag}}(t)\mathbf{v}_i(t)\ .\tag{B33}$$

Note that $\mathbf{n}^{\mathrm{imag}}$ in (B33) is simply $-\phi_i$ [compare Eqs. (B7) and (B33)].

Recently, Ladd [17] defined the displacement function $W(t)$ [his Eq. (11) with $m=1$] as

$$W(t)\equiv\sum_i\mathbf{r}_i\cdot\mathbf{v}_i\tag{B34}$$

for all particles *in* the simulation box. Equation (B34) is then identical to the trace of $\mathsf{G}^{\mathrm{PBC}}(t)$, i.e., it is under IPBC convention. Consequently, the time average of $\dot{W}(t)$, i.e., $\bar{\dot{W}}$, is [cf. Eqs. (B17) and (12) of Ref. [17]]

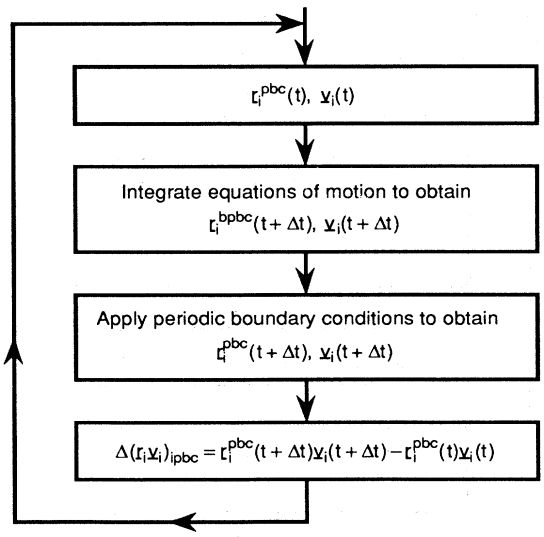

FIG. 5. Standard molecular-dynamics loop for one time step when using IPBC.

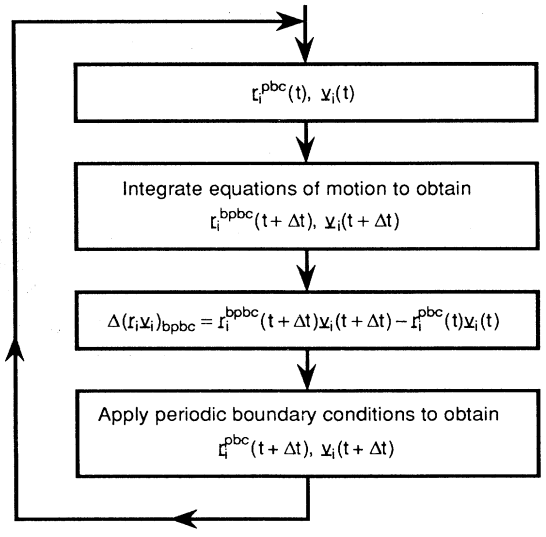

FIG. 6. Standard molecular-dynamics loop for one time step when using BPBC.

$$\overline{\dot{W}}=\mathrm{Tr}\overline{\dot{\mathbf{G}}^{\mathrm{PBC}}}=0\ . \tag{B35}$$

At this point Ladd introduced *ad hoc* the imaging function $-L\mathbf{n}F_i$ (where $\mathbf{n}$ is a unit vector outward normal to the face of the simulation box) to account for the flux of momentum crossing the boundaries due to the application of the PBC. The time average of the imaging function is just $-3PV$. By using the BPBC approach [see (B33)] not only do we derive rigorously Ladd's imaging function [(B16)–(B26)], where his vector $\mathbf{n}$ is our crossing function ϕ_i, but also take care implicitly of the periodic boundary conditions in the calculation of the shear-viscosity generalized displacement.

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

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

[3] A. A. Chialvo and P. G. Debenedetti, Phys. Rev. A **43**, 4289 (1991).

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

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

[6] F. C. Andrews, J. Chem. Phys. **47**, 3161 (1967), see Eqs. (40) and (41).

[7] D. J. Evans and G. P. Morriss, *Statistical Mechanics of Nonequilibrium Liquids* (Academic, New York, 1990).

[8] D. Ronis and I. Oppenheim, Physica **86A**, 475 (1977).

[9] A. A. Chialvo and P. G. Debenedetti (unpublished).

[10] S. A. Rice and P. Gray, *The Statistical Mechanics of Simple Liquids* (Wiley, New York, 1965), Sec. 7.3.B and Eq. (7.3.47).

[11] D. Frenkel, in *Simple Systems at Very High Density,* Vol. 186 of *NATO Advanced Study Institute, Series B: Physics,* edited by A. Polian, P. Loubeyre, and N. Boccara (Plenum, New York, 1989), p. 411.

[12] P. T. Cummings (unpublished).

[13] M. P. Allen and D. J. Tildesley, *Computer Simulation of Liquids* (Clarendon, Oxford, 1987).

[14] M. R. Clausius, C. R. Acad. Sci. Paris **70**, 1314 (1987).

[15] J. J. Erpenbeck and W. W. Wood, in *Modern Theoretical Chemistry. Statistical Mechanics,* edited by B. J. Berne (Plenum, New York, 1977), Vol. V, Part B.

[16] Yu. B. Rumer and M. Sh. Ryvkin, *Thermodynamics, Statistical Physics, and Kinetics,* English translation (Mir, Moscow, 1980), pp. 579–580.

[17] A. 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, Dordrecht, 1990).