Einstein-Kubo-Helfand and McQuarrie relations for transport coefficients

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The formal equivalence of the Green-Kubo and Einstein-Kubo-Helfand (EKH) expressions for transport coefficients is well known. For finite systems subject to periodic boundary conditions, the EKH relations are ambiguous as to whether the toroidal or infinite-checkerboard descriptions should be used for the coordinates. We first describe qualitatively the application of both descriptions to the calculation of the self-diffusion and shear viscosity coefficients. We then show that the calculation of the self-diffusion coefficient using the infinite-checkerboard EKH relation is equivalent to the Green-Kubo calculation, while the toroidal calculation is not. For shear viscosity, we find that neither the toroidal nor infinite-checkerboard calculation from the EKH relation is equivalent to the Green-Kubo calculation, even though the formal theory presumably suggests that each is correct when the long-time limit is taken after the limit of large-system size. An alternative relation for the shear viscosity of finite periodic systems is derived from the Green-Kubo formula, consisting of the infinite-checkerboard expression plus correction terms having a fundamentally more complicated dependence on the coordinates and momenta. A simple qualitative analysis of the system-size dependence of the difference between the time-dependent Green-Kubo and the infinite-checkerboard EKH shear viscosities [$\eta(t;N)$ and $\eta_E^{(C)}(t;N)$, respectively] shows this difference to be of $O(N^{1/3})$ (N being the number of particles) at early times. Monte Carlo molecular dynamics calculations of $\eta_E^{(C)}(t;N)$ for an equimolar binary mixture of hard spheres (diameter ratio of 0.4 and mass ratio of 0.03) confirm these large differences at a few mean free times, but suggest a long-time plateau value having the magnitude of the Green-Kubo result, but the values at 70 mean free times do not approach $\eta(t;N)$ with increasing N. Finally, we consider the one-particle, EKH-like, McQuarrie expression for shear viscosity, showing that the Chialvo-Cummings-Evans [Phys. Rev. E **47**, 1702 (1993)] "proof" is defective. Moreover, we demonstrate through molecular dynamics calculations for the same hard-sphere mixture that the two-particle contribution to the time-dependent viscosity, which must vanish at long times for the McQuarrie formula to be valid, in fact contributes roughly 40% of the shear viscosity at a volume of $(5\sqrt{2}/2)\sum_a N_a\sigma_a^3$, where N_a is the number of particles of species a having diameter σ_a.

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I. INTRODUCTION

About 40 years ago, Green [1,2] and Kubo [3] introduced the method which bears their names for the calculation of transport coefficients as time integrals of time-correlation functions of certain microscopic currents. With the advent of computational physics and, in particular, the Monte Carlo and molecular dynamics methods, it became possible to apply the Green-Kubo (GK) method to systems of relatively few interacting particles to obtain estimates of the transport coefficients for particular interaction laws. These calculations led not only to the discovery of the long-time tails of the GK time-correlation functions and the divergence of the GK transport coefficients in two dimensions, but also, for the three-dimensional systems which concern us here, to numerous specific results for self-diffusion, mutual diffusion, bulk and shear viscosity, and thermal conductivity of model gases and liquids, forming an important basis for the understanding of both the theory and phenomenology of transport processes.

An alternative route to the transport coefficients is through generalizations of the Einstein relation for the self-diffusion coefficient in terms of the mean-squared displacement,

$$D=\lim_{t\to\infty}\frac{1}{6}\frac{d}{dt}\langle\Delta r^2(t)\rangle\ , \tag{1}$$

in which $\Delta r(t)$ is the displacement of a diffusing particle in time interval t. Kubo [3] first pointed out the existence of such generalizations and Helfand [4] derived expressions of this form for the coefficients of viscosity and thermal conduction, as well as self-diffusion. Helfand showed that his expressions were, in fact, double time integrals of the Green-Kubo time-correlation functions, up to terms of $o(1/t)$. Thus the Helfand theory constitutes an alternative route to the Green-Kubo relations and has been widely quoted in this regard; see, for example [5]. While these expressions for the transport coefficients are sometimes referred to as the Einstein expressions, here we use all three names, calling them the Einstein-Kubo-Helfand (EKH) relations.

A number of other authors [6–11] have discussed related expressions involving integrated forms of the GK microscopic currents in connection with molecular dynamics calculations of the transport coefficients, particularly for hard spheres for which many of the microscopic currents appearing in the Green-Kubo expressions are

singular. In fact, these hard-sphere calculations are not based on the EKH expressions, but instead are based on time correlations of the *time integrals of the microscopic currents* of Green and Kubo. This same integration of the microscopic currents has also been used for soft potentials [9,10]. Even for self-diffusion for which the Einstein relation, Eq. (1), has ostensibly been used by many workers to compute D, it should be recognized that typically these calculations use periodic boundary conditions and the displacement, $\Delta r(t)$, is actually calculated for the "infinite-checkerboard" or "unfolded" particle coordinates, a concept which most certainly lies outside the EKH theory. The point is that the so-called Einstein or Helfand calculations in the literature are simply modified Green-Kubo calculations; the EKH approach, except for self-diffusion, has not strictly speaking been attempted.

An exception is the recent calculation by Chialvo and Debenedetti [11] (CD) who attempted to compute the shear viscosity coefficient not only from one variant of the EKH expression but also from an expression given without proof by McQuarrie [5] as well as by Hoheisel and Vogelsang [10] who reference the doctoral thesis of Schoen. In fact, the procedure described by CD for the calculation of the EKH and the McQuarrie displacement functions [the analogs of $\Delta r_i(t)$ in the self-diffusion case] has been examined by Allen, Brown, and Masters [12] (ABM) who find the CD calculation to be incorrect, corresponding neither to the time integral of the GK microscopic current nor to the EKH displacement function. Moreover, they compare the CD results for the viscosity with those from the GK formula and from nonequilibrium molecular dynamics, finding the latter two results to be in reasonable agreement with each other, but differing substantially from the CD results. Thus it seems that a literal application of the EKH formulas for other than self-diffusion has not been reported for finite periodic systems.

Nonetheless, CD raise the possibility that, even though their particular calculations may not be correct, the EKH relations may have some special advantages in the evaluation of the viscosity coefficient, at least if the McQuarrie form is used, for they compare calculations using both approaches, finding agreement within their statistical uncertainties, with the McQuarrie formula having a large statistical advantage. This advantage arises from the fact that the McQuarrie formula expresses the shear viscosity in terms of a one-particle time-correlation function, for which one can, in a molecular dynamics calculation, obtain an estimate for each particle in the system, rather than the single estimate which one makes in the GK method. Moreover, Chialvo, Cummings, and Evans [13] (CCE) claim to *prove* the McQuarrie formula, holding out the promise that the shear viscosity might be calculated with a precision similar to that for the self-diffusion coefficient, which also is given by a one-particle time-correlation function. To support their proof, however, CCE use the same peculiar numerical techniques as CD to attempt to demonstrate that the two-particle time-correlation function, which is the difference between the EKH and McQuarrie formulas, vanishes.

The purpose of the present contribution is the clarification of the relationship of the EKH and the GK expressions, particular for the case of interest in the numerical calculation of transport coefficients, *viz.*, finite systems subject to periodic boundary conditions. After discussing the formal equivalence of these relations in Sec. II, we describe in Sec. III their application to periodic systems, subject to the interpretation of particle positions as toroidal coordinates, $\vec{r}_i(t)$, or as infinite-checkerboard coordinates, $\vec{R}_i(t)$. We show that the latter interpretation maintains this equivalence of GK and EKH methods in the case of self-diffusion but not in the case of shear viscosity. Indeed, we demonstrate that the time-dependent, infinite-checkerboard EKH viscosity has large $[O(N^{1/3})]$ differences with the GK result at short times. Using Monte Carlo, molecular dynamics calculations of the infinite-checkerboard EKH viscosity for a mixture of hard spheres, we investigate the differences with the GK viscosity for longer times and systems as large as 4000 particles, finding little to suggest that the EKH method can yield the correct shear viscosity. In Sec. IV, we consider the McQuarrie formula, demonstrating that the CCE proof is fallacious because the two-particle time-correlation function, whose long-time behavior is crucial, can be shown to vanish only to leading order in the system size [i.e., O (1)], not to the $O(1/N)$ accuracy which is required. We discuss briefly the numerical evidence presented by these authors in support of the McQuarrie relation. Finally we present the results of a numerical investigation of the McQuarrie formula for the same mixture of hard spheres which demonstrates rather clearly that not only the proof but the formula itself is invalid. We summarize our conclusions with respect to the calculation of the shear viscosity in Sec. V.

II. FORMAL EQUIVALENCE OF GK AND EKH FORMULAS

Consider the Green-Kubo relation for the generic transport coefficient μ for a one-component system of particles at temperature T and number density n,

$$\begin{aligned} \mu &= \lim_{t\to\infty} \mathrm{tlim}\mu(t;N) , \\ \mu(t;N) &= a_\mu \int_0^t ds \rho_\mu(s;N) , \\ \rho_\mu(t;N) &= \langle J_\mu(0) J_\mu(t) \rangle , \end{aligned} \tag{2}$$

in which tlim denotes the thermodynamic limit (fixed T and n), $J_\mu(t) \equiv J_\mu[\mathbf{x}^N(t)]$ is the microscopic current appropriate to transport coefficient μ at dynamical time t, and the $\langle\ \rangle$ denotes a canonical ensemble average over the initial ($t=0$) phase of the N particles at temperature T and volume $V=N/n$; that is, for a function of the phase $F(\mathbf{x}^N)$,

$$\langle F(\mathbf{x}^N) \rangle = \int d\mathbf{x}^N \rho_{NVT}(\mathbf{x}^N) F(\mathbf{x}^N) . \tag{3}$$

Here $\rho_{NVT}(\mathbf{x}^N)$ is the canonical distribution function in phase space, $\mathbf{x}^N$; if the particle positions and velocities are

$\vec{r}_i$ and $\vec{v}_i$, then

$$\rho_{NVT}(\mathbf{x}^N)=\exp[-\beta H_N(\mathbf{x}^N)]/Z_{NVT} ,$$
$$H_N=\tfrac{1}{2}m\sum_i v_i^2+\Phi_N(\mathbf{r}^N) , \tag{4}$$
$$Z_{NVT}=\int d\mathbf{x}^N\exp[-\beta H_N(\mathbf{x}^N)] ,$$

in which m is the particle mass, $\mathbf{x}^N=(\mathbf{r}^N,\mathbf{v}^N)$, $\mathbf{r}^N$ is the configuration, $(\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_N)$, $\mathbf{v}^N$ is the velocity, $(\vec{v}_1,\vec{v}_2,\ldots,\vec{v}_N)$, $\beta=1/k_BT$, k_B is the Boltzmann constant, H_N is the Hamiltonian, Φ_N is the potential energy of the system, and the i sum is over the N particles of the system.

The microscopic currents and the coefficients a_μ for the cases of self-diffusion D and shear viscosity η are given explicitly by

$$a_D=1 ,$$
$$J_D(t)=v_{xi}(t) , \tag{5}$$
$$a_\eta=\beta/V ,$$
$$J_\eta(t)=T_{xy}(t) ,$$

in which $\mathbf{T}(t)$ is the stress-volume tensor (called simply the stress tensor hereafter). For a system having potential energy given by a sum of central pair interactions,

$$\Phi_N(\mathbf{r}^N)=\frac{1}{2}\sum_{i,j\neq i}\phi(r_{ij}) ,$$
$$\vec{r}_{ij}=\vec{r}_i-\vec{r}_j \tag{6}$$

(in which r denotes the magnitude of $\vec{r}$), the stress tensor is

$$\mathbf{T}=\sum_i\left[m\vec{v}_i\vec{v}_i+\frac{1}{2}\sum_{j\neq i}\vec{r}_{ij}\vec{F}(\vec{r}_{ij})\right] , \tag{7}$$

where $\vec{F}(\vec{r})$ is the force on a particle at $\vec{r}$ due to a central particle, *viz.*,

$$\vec{F}(\vec{r})=-\hat{\mathbf{r}}\frac{d\phi(r)}{dr} , \tag{8}$$

in which $\hat{\mathbf{r}}$ is the unit vector in the direction of $\vec{r}$.

We write the EKH expressions in similar detail; again, for the transport coefficient μ, we have

$$\mu=\lim_{t\to\infty}\lim_{}\mu_E(t;N) ,$$
$$\mu_E(t;N)=\tfrac{1}{2}a_\mu\frac{d}{dt}S_\mu(t;N) ,$$
$$S_\mu(t;N)=\langle[\Delta G_\mu(t)]^2\rangle , \tag{9}$$
$$\Delta G_\mu(t)=G_\mu(t)-G_\mu(0) ,$$

and for self-diffusion and shear viscosity in particular [14],

$$G_D(t)=r_{xi}(t) ,$$
$$G_\eta(t)=m\sum_i r_{xi}(t)v_{yi}(t) . \tag{10}$$

We note in passing that our definition of the EKH transport coefficients contains the time derivative of the "mean-squared displacement" rather than a $1/t$ factor which is sometimes used.

The formal equivalence between Eqs. (2) and (9) is readily proven as follows. By inverting the order of integration and averaging in Eq. (2), we obtain

$$\mu(t;N)=a_\mu\langle J_\mu(0)\Delta G_\mu(t)\rangle , \tag{11}$$

by virtue of the fact that

$$\Delta G_\mu(t)=\int_0^t ds J_\mu(s) , \tag{12}$$

which follows from Newton's equations of motion,

$$\frac{d\vec{r}_i}{dt}=\vec{v}_i ,$$
$$m\frac{d\vec{v}_i}{dt}=\sum_{j\neq i}\vec{F}(\vec{r}_{ij})=-\sum_{j\neq i}\vec{F}(\vec{r}_{ji}) . \tag{13}$$

Moreover, one sees from Eqs. (9) and (12) that the EKH transport coefficient becomes, when the time derivative is taken inside the ensemble average,

$$\mu_E(t;N)=a_\mu\langle J_\mu(t)\Delta G_\mu(t)\rangle . \tag{14}$$

Transforming the right-hand side of this relation from an average over the phase at $t=0$ to the phase at time t, evaluating the Jacobian of the transformation through the Liouville theorem to be 1, using the time invariance of the distribution function along a trajectory, and, finally, recognizing the so-called time-reversal invariance of the dynamical trajectory, one proves for both self-diffusion and shear viscosity that

$$\mu_E(t;N)=\mu(t;N) , \tag{15}$$

so that the GK and EKH formulas are indeed formally equivalent. The equivalence is only formal because the dynamics of the fluid can be described by the simple Newtonian equations only for particles which are unaffected by boundary effects for the times in question. Specifically, when Newton's equations are supplemented by boundary conditions, Eq. (12) no longer holds in general. One additional observation with respect to the formal theory is important: Even though the functions G_μ are *not* invariant to translational changes in the origin of the coordinates, the ΔG_μ evidently are invariant by virtue of the translational invariance of J_μ and Eq. (12).

III. FINITE PERIODIC SYSTEMS

In the numerical estimation of statistical mechanical averages through Monte Carlo and molecular dynamics simulation, one needs to supplement the equations of motion with boundary conditions which stabilize the system at the desired thermodynamic state. To minimize finite-system effects, researchers usually choose periodic "boundary conditions" (PBC) whereby the potential energy, Eq. (6), is replaced by

$$\Phi_N(\mathbf{r}^N)=\frac{1}{2}\sum_{i,j}\sum_{\vec{\nu}}{}'\phi(|\vec{r}_{ij}+\vec{\nu}L|) , \tag{16}$$

in which we have assumed for simplicity a cubic system, $V=L^3$; the primed $\vec{\nu}$ sum is over all triples of signed integers, except that the $\vec{\nu}=0$ term is omitted when $j=i$.

Under the periodic boundary conditions, the analysis of Sec. II is no longer completely valid and the equivalence of the Green-Kubo and EKH formulations must be reexamined. Moreover, while either formulation presumably remains valid, provided one properly accounts for the approach to the thermodynamic limit, from the point of view of numerical calculations, the details of the approach to that limit can be of considerable importance. Our aim is to describe at least qualitatively the behavior of the various approaches and to suggest the best alternative.

In dealing with PBC, it is often important to distinguish two closely related descriptions of the system. In the *infinite-checkerboard form* (also called the "unfolded" form) of PBC, the positions of the particles $\vec{R}_i$ are no longer limited to the "primary" periodic cell but fill infinite space through "image" particles at $\vec{R}_i+\vec{\nu}L$ for all triples of signed integers $\vec{\nu}$. The $\vec{\nu}$ sum in Eq. (16) then adds together the interactions between each (of the N distinct) particle and the other particles in the checkerboard. The *toroidal form* of the periodic boundary conditions considers particles on a torus, with each $\vec{r}_i$ having components lying in the interval $(0,L]$. In this form, the ν sum in Eq. (16) adds together the interactions between each pair, including the contributions from multiple passages around the torus. For the purposes of the present discussion, the important distinction lies in the dynamics whereby $\vec{R}_i(t)$, unlike $\vec{r}_i(t)$, is the integral of the velocity, $\vec{v}_i(t)$, and is continuous in t. We have then the infinite-checkerboard equations of motion from Eq. (16),

$$\frac{d\vec{R}_i}{dt}=\vec{v}_i \ ,$$

$$m\frac{d\vec{v}_i}{dt}=\sum_j \sum_{\vec{\nu}}{}' \vec{F}(\vec{R}_{ij}+\vec{\nu}L) \tag{17}$$

$$=-\sum_j \sum_{\vec{\nu}}{}' \vec{F}(\vec{R}_{ji}+\vec{\nu}L) \ ,$$

rather than Eq. (13), with initial conditions $\vec{R}_i(0)=\vec{r}_i(0)$ and $\vec{v}_i(0)$. The toroidal coordinate $\vec{r}_i(t)$ is the position of the image of $\vec{R}_i(t)$ which lies in the primary cell at time t,

$$r_{\alpha i}(t)=R_{\alpha i}(t) \text{ modulo } L \ , \quad \alpha\in\{x,y,z\} \ .$$

Because the EKH functions G_μ, Eq. (10), depend explicitly on particle positions, the toroidal–infinite-checkerboard distinction is expected to have important implications for the EKH transport coefficients.

It is important to also be aware that, from the point of view of statistical mechanical averaging, there is no material distinction between the two descriptions because the canonical distribution function, Eq. (4), is defined only in the fixed volume, $0<r_{\alpha i}\le L$ for which $\vec{r}_i$ and $\vec{R}_i$ are the same. Nonetheless, in the case of time-correlation functions, which are averages of functions of particle positions as functions of time, it is obvious that both toroidal and infinite-checkerboard definitions of the time-correlation function are possible and need not be equal.

With the change of our focus from the formal theory of the previous section to finite systems and periodic boundary conditions, it is important to recognize that it may be numerically advantageous to adjust the precise form of the microscopic currents so that they have the character of fluctuations about a long time average [15,16]. The only condition to be imposed on such changes is that the macroscopic transport coefficient which results from taking the long-time limit of the large-system limit of $\mu(t;N)$, Eq. (2), should be unaltered. One such change to the formal expressions for the currents arises from the fact that under PBC the linear momentum, in addition to the total energy, survives as a constant of the motion, as can easily be proven from the equations of motion, Eq. (17). [By virtue of this conservation of momentum, the center of mass (c.m.) of the infinite-checkerboard coordinates moves with a fixed velocity, even though the c.m. of the toroidal coordinates undergoes an additional impulsive motion as particles cross the plane at $r_{\alpha i}=L$.] To understand the modifications for self-diffusion, we write the velocity autocorrelation function (VACF) explicitly as

$$\rho_D(t;N)=\int d\mathbf{x}^N v_{xi}v_{xi}(t)\rho_{NVT}(\mathbf{x}^N) \ , \tag{18}$$

and introduce δ functions in the conserved energy E and linear momentum $\vec{M}$ to obtain,

$$\rho_D(t;N)=\frac{1}{Z_{NVT}}\int d\vec{M}\int dE\,\exp(-\beta E) \times\int d\mathbf{x}^N v_{xi}v_{xi}(t)\Delta(\mathbf{x}^N;\vec{M},E) \ ,$$

$$\Delta(\mathbf{x}^N;\vec{M},E)=\delta[\vec{M}-\vec{p}_N(\mathbf{v}^N)]\delta[E-H_N(\mathbf{x}^N)] \ , \tag{19}$$

$$\vec{p}_N=m\sum_i \vec{v}_i \ .$$

But the phase integral in the first part of Eq. (19) is essentially the VACF in the "molecular dynamics" ensemble,

$$\rho_D^{NVE\vec{M}}(t;N)=\int d\mathbf{x}^N v_{xi}v_{xi}(t)\rho_{NVE\vec{M}}(\mathbf{x}^N) \ ,$$

$$\rho_{NVE\vec{M}}(\mathbf{x}^N)=\frac{\Delta(\mathbf{x}^N;\vec{M},E)}{Z_{NVE\vec{M}}} \ , \tag{20}$$

$$Z_{NVE\vec{M}}=\int d\mathbf{x}^N\Delta(\mathbf{x}^N;\vec{M},E) \ ,$$

so that

$$\rho_D(t;N)=\frac{1}{Z_{NVT}}\int d\vec{M}\int dE\,\exp(-\beta E) \times\rho_D^{NVE\vec{M}}(t;N)Z_{NVE\vec{M}} \ . \tag{21}$$

Assuming that the system is "mixing," it follows that at long times $v_{xi}(t)$ is uncorrelated with $v_{xi}(0)$ in the ensemble having fixed values of the constants of the motion, viz.,

$$\rho_D^{NVE\vec{M}}(t;N)\to\langle v_{xi}\rangle^2_{NVE\vec{M}} \ . \tag{22}$$

The average on the right-hand side can readily be evaluated so that

$$\rho_D^{NVE\vec{M}}(t;N)\to(M_x/Nm)^2 , \tag{23}$$

which we substitute into Eq. (21) to obtain

$$\rho_D(t;N)\to\frac{\langle v_{xi}^2\rangle}{N} ; \tag{24}$$

the VACF approaches a constant, albeit one which vanishes in the thermodynamic limit, and the infinite-system time-dependent self-diffusion coefficient $D(t;N)$ diverges in time.

From a theoretical point of view, this divergence is inconsequential in that the large-N limit is taken before the time limit [see Eq. (2)]. However, numerically it is expedient to redefine the microscopic currents for both self-diffusion and shear viscosity to obtain forms of the time-correlation functions which are better behaved for finite systems. For self-diffusion, one proceeds essentially by inspection, replacing $v_{xi}(t)$ by the velocity in the center-of-mass frame,

$$\begin{aligned} &J_D(t)=u_{xi}(t) , \\ &\vec{u}_i(t)=\vec{v}_i(t)-\frac{\vec{p}_N(\mathbf{v}^N)}{Nm} , \end{aligned} \tag{25}$$

from which one readily finds

$$\rho_D(t;N)\to 0 , \tag{26}$$

a result which is supported by numerical results for both hard disks [17] and hard spheres [18]. For the case of shear viscosity, the modified microscopic current follows from the calculation of the spatially averaged momentum flux across an element of surface which is moving with the velocity of the center of mass in a finite periodic system. Following Erpenbeck and Wood [19], we obtain the stress tensor,

$$\mathbf{T}=\sum_i\left[m\vec{u}_i\vec{u}_i+\frac{1}{2}\sum_j{\sum_{\vec{\nu}}}'(\vec{r}_{ij}+\vec{\nu}L)\vec{F}(\vec{r}_{ij}+\vec{\nu}L)\right] , \tag{27}$$

differing from Eq. (7) in the presence of both the velocity in the c.m. frame and the sum of the force term over all periodic images. While it may not be evident from the papers on the subject, we believe that the microscopic currents of Eqs. (25) and (27) have been used in most, if not all, of the numerical GK calculations of self-diffusion and viscosity in the literature, in as much as Eq. (27) reduces to Eq. (7), subject to the so-called "minimum-image convention" for an interaction potential having a range $<L/2$. In any case, for finite periodic systems, we view these equations as defining the GK theory for self-diffusion and shear viscosity, without explicitly notating the differences between the modified quantities and those of the formal theory of the previous section.

First, we note that the GK calculation, as specified in Eq. (2), is independent of the choice of toroidal or infinite-checkerboard coordinates because the microscopic currents, Eqs. (25) and (27), depend either only on the velocities or on *sums over all images* of functions of the differences in particle positions and these are independent of the toroidal-checkerboard distinction. Thus the time-dependent GK transport coefficient, $\mu(t;N)$, defined by Eq. (2), continues to be given by Eq. (11), in which $\Delta G_\mu(t)$ is now *defined* by Eq. (12) rather than Eq. (10).

We distinguish the GK from the EKH transport coefficients defined through the EKH functions $G_\mu(t)$ of Eq. (10), modified by replacing particle velocities and positions by particle velocities and positions in the c.m. (of the $\vec{R}_i$) frame of reference, defining $\vec{q}_i$ and $\vec{Q}_i$ to be the toroidal and infinite-checkerboard positions, respectively,

$$\begin{aligned} &\vec{Q}_i(t)=\vec{R}_i(t)-\vec{v}_0 t , \\ &q_{\alpha i}(t)=Q_{\alpha i}(t) \text{ modulo } L , \quad \alpha\in\{x,y,z\} , \\ &\vec{u}_i(t)=\vec{v}_i(t)-\vec{v}_0 , \\ &\vec{v}_0=\frac{1}{N}\sum_i\vec{v}_i(t) , \end{aligned} \tag{28}$$

yielding the EKH functions,

$$\begin{aligned} &G_D^{(C)}(t)=Q_{xi}(t) , \\ &G_D^{(T)}(t)=q_{xi}(t) , \\ &G_\eta^{(C)}(t)=\sum_i mQ_{xi}(t)u_{yi}(t) , \\ &G_\eta^{(T)}(t)=\sum_i mq_{xi}(t)u_{yi}(t) , \end{aligned} \tag{29}$$

and then the EKH mean-squared displacements, defined in analogy with the third part of Eq. (9) to be

$$S_\mu^{(\alpha)}(t;N)=\langle[\Delta G_\mu^{(\alpha)}(t)]^2\rangle , \quad \alpha\in\{T,C\} . \tag{30}$$

We obtain, then, two distinct sets of EKH time-dependent transport coefficients when we differentiate as in the second part of Eq. (9),

$$\begin{aligned} \mu_E^{(\alpha)}(t;N)&=\tfrac{1}{2}a_\mu\frac{d}{dt}S_\mu^{(\alpha)}(t;N) , \quad \alpha\in\{T,C\} \\ &=a_\mu\langle J_\mu^{(\alpha)}(t)\Delta G_\mu^{(\alpha)}(t)\rangle , \quad \alpha\in\{T,C\} , \\ J_\mu^{(\alpha)}(t)&\equiv\frac{d}{dt}G_\mu^{(\alpha)}(t) , \quad \alpha\in\{T,C\} , \end{aligned} \tag{31}$$

in place of Eq. (14). Moreover, these are to be distinguished from the various other quantities analogous to Eqs. (11) and (14),

$$\begin{aligned} &a_\mu\langle J_\mu(0)\Delta G_\mu^{(\alpha)}(t)\rangle , \\ &a_\mu\langle J_\mu(t)\Delta G_\mu^{(\alpha)}(t)\rangle , \end{aligned}$$

which contain the GK microscopic currents. Both these forms consist of a composition of GK and EKH functions and are not considered further in this paper.

It is important to be aware that the distinction we draw here between the GK and EKH formalisms has typically not been made in the past. In a study of the shear viscosity of hard spheres [8], for example, we referred to the mean-squared displacement $\langle[\Delta G_\eta(t)]^2\rangle$, based on

Eq. (12), as an "Einstein function," even though under the current notation this quantity remains one aspect of the GK formalism which will be discussed below. Our aim is not to question to the correctness of earlier calculations but to develop notation sufficient for the discussion of the problem at hand.

Consider first the toroidal form $S_\mu^{(T)}(t;N)$. Because $G_\mu^{(T)}$ contains only the coordinates $\vec{q}_i$ which are bounded in time and velocities $\vec{u}_i$, one can readily establish the long-time bound, $a_\mu S_\mu^{(T)}=O(N^{2/3})$. Consequently, the time derivative of $S_\mu^{(T)}(t;N)$ is expected to vanish at long times and cannot be expected to yield the transport coefficient. Nonetheless, one might argue that for times up to the decay time of the autocorrelation function, $\rho_\mu(t;N)$ (exclusive of its long-time-tail contribution), the bulk of the particles in the system, i.e., all but the $O(N^{2/3})$ near the "boundary" of the primary periodic cell, will not experience the boundary conditions and can, one argues, be expected to yield time correlations as in an infinite system. In Fig. 1 we illustrate the supposed determination of the transport coefficient from $S_\mu^{(T)}$ by plotting the hypothetical quantity,

$$\frac{a_\mu S_\mu^{(T)}(t;N)}{2\mu}=\frac{1-e^{-\alpha(N)t/t_h}}{\alpha(N)}-\frac{1-e^{-\beta t/t_h}}{\beta}\ ,$$
$$\alpha(N)=(N_h/N)^{2/3}\ , \qquad (32)$$
$$\beta=2$$

(where N_h and t_h are constants which scale the number of particles and the time, respectively) as a function of time for three values of N. Even though this function doubtlessly ignores important features of the true toroidal functions, it approaches $(\beta-\alpha)/\alpha\beta=O(N^{2/3})$ at long times, grows quadradically with t at short times, and approaches $t/t_h-(1-e^{-\beta t/t_h})/\beta$ for finite t and large N which is essentially linear with unit slope for $t\gg t_h/\beta$. A plateau in the slope should elongate in time with increasing N, even though for all N the slope vanishes at long times. To determine the transport coefficient, one would need to evaluate the large N limit of this plateau value, a task which might well be expected to require calculations over several orders of magnitude in N but which might, on the basis of the argument, at least be theoretically possible.

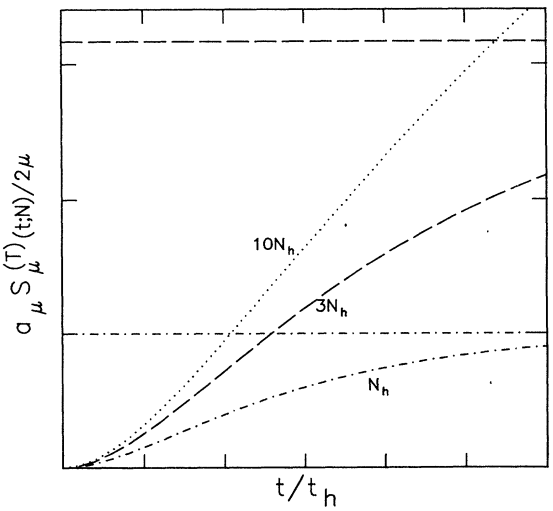

FIG. 1. Qualitative sketch of the conjectured behavior, Eq. (32), of the scaled Einstein-Kubo-Helfand mean-squared displacement, $S_\mu^{(T)}(t)$, for generic transport property μ from the toroidal version of periodic boundary conditions, as a function of time t for three different system sizes. Each curve approaches an N-dependent asymptote, indicated for the two smaller systems by the horizontal broken lines. The transport coefficient would be obtained from the large-system limit of the slope of the curves in the linear region (near two units in t) which lengthens with increasing N.

The infinite-checkerboard EKH functions would seem to provide a more favorable route because of the absence of both obvious long-time bounds on $S_\mu^{(C)}(t;N)$ and unphysical δ functions in the time derivative of the particle positions. In the case of self-diffusion, the infinite-checkerboard $S_D^{(C)}(t;N)$ becomes linear in the time in that $\langle \Delta Q_{xi}^2(t)\rangle$ becomes proportional to t at long time, as shown by a number of molecular dynamics calculations [14,17,18], demonstrating that each particle *diffuses* through the infinite checkerboard, at least if the number of particles is not so small that collisionless trajectories occur with appreciable probability in the canonical ensemble. The slope of this line is an estimate of the self-diffusion coefficient which typically has a weak dependence on N.

We now show that the infinite-checkerboard approach through $S_D^{(C)}(t;N)$ is equivalent to the GK calculation. While the above derivation of Eq. (15) no longer holds, one can extend the proof as follows: Consider $D_E^{(C)}(t;N)$ from Eq. (31), substituting from the first of Eq. (29), to obtain

$$D_E^{(C)}(t;N)=\langle u_{xi}(t)[Q_{xi}(t)-Q_{xi}(0)]\rangle\ , \qquad (33)$$

in which $\vec{Q}_i(0)\equiv\vec{q}_i(0)$ lies within the primary cell. Explicitly

$$D_E^{(C)}(t;N)=\int d\mathbf{v}^N\int_L d\mathbf{r}^N e^{-\beta H_N(\mathbf{x}^N)}u_{xi}(t)\times[Q_{xi}(t)-q_{xi}]/Z_{NVT}\ , \qquad (34)$$
$$\int_L d\mathbf{r}^N\equiv\prod_{i=1}^N\int_0^L dr_{xi}\int_0^L dr_{yi}\int_0^L dr_{zi}\ .$$

We transform the variables of integration from the toroidal phase $\mathbf{x}^N(0)$ at time 0 to the toroidal phase $\mathbf{x}^N(t)$ at time t, noting that the Jacobian for the transformation is 1 and that the Boltzmann factor is invariant, to obtain

$$D_E^{(C)}(t;N)=\int d\mathbf{v}^N(t)\int_L d\mathbf{r}^N(t)e^{-\beta H_N\mathbf{x}^N(t)]}u_{xi}(t)\times[Q_{xi}(t)-q_{xi}(0)]/Z_{NVT}\ . \qquad (35)$$

Next we transform to interaction over the phase with velocities reversed, $\mathbf{y}^N=[\mathbf{v}'^N,\mathbf{r}'^N]=[-\mathbf{v}^N(t),\mathbf{r}^N(t)]$, with the Boltzmann factor again remaining invariant:

$$D_E^{(C)}(t;N)=-\int d\mathbf{v}'^N\int_L d\mathbf{r}'^N e^{-\beta H_N[y^N]}u'_{xi}$$
$$\times[Q_{xi}(t)-q_{xi}(0)]/Z_{NVT}\ . \quad (36)$$

We evaluate the displacement term under these transformations as follows: Write $\vec{Q}_i(t)=\vec{q}_i(t)+\vec{\nu}_i(t)L$ to define the translation vector $\vec{\nu}_i(t)$ relating the toroidal and infinite-checkerboard coordinates. Thus

$$\begin{aligned}\Delta\vec{Q}_i(t)&\equiv\vec{Q}_i(t)-\vec{q}_i(0)\\&=\vec{q}_i(t)-[\vec{q}_i(0)-\vec{\nu}_i(t)L]\\&=\vec{q}'_i-[\vec{q}_i(0)-\vec{\nu}_i(t)L]\ .\end{aligned} \quad (37)$$

But from time-reversal invariance, the trajectory of i through the phase $\mathbf{y}^N$ retraces its trajectory through $\mathbf{x}^N$, translated by $-\vec{\nu}_i(t)L$, i.e., $\vec{q}_i(0)-\vec{\nu}_i(t)L=\vec{Q}'_i(t)$. Therefore,

$$\Delta\vec{Q}_i(t)=-[\vec{Q}'_i(t)-\vec{q}'_i] \quad (38)$$

and, substituting into Eq. (36) and recognizing that $\Delta G_D=\Delta G_D^{(C)}$, we obtain

$$D_E^{(C)}(t;N)=D(t;N) \quad (39)$$

[in which the right-hand side continues to be defined in the context of PBC through Eqs. (2), (11), (12), as previously noted] so that Eq. (15) holds for the infinite-checkerboard description of self-diffusion.

Thus we see that the infinite-checkerboard version of the EKH relation can be used to calculate the self-diffusion coefficient, being equivalent to the GK method. Clearly the infinite-checkerboard form, $D_E^{(C)}(t;N)$, can be expected to behave more favorably than $D_E^{(T)}(t;N)$ with respect to both long times at finite N and large N at large but finite t.

Before discussing the calculation of the shear viscosity from the EKH functions, $S_\eta^{(T)}$ or $S_\eta^{(C)}$, it is useful to consider the "proper" displacement function for shear viscosity under periodic boundary conditions, i.e., the integral, Eq. (12), of the GK current. Thus we consider

$$\Delta G_\eta(t)=\int_0^t ds\, J_\eta(s) \quad (40)$$

in which J_η is obtained from an off-diagonal element of Eq. (27). Replacing $\vec{r}_{ij}$ by the equally valid $\vec{Q}_{ij}$ in this equation and integrating by parts using the equations of motion, Eq. (17), we obtain

$$\begin{aligned}\Delta G_\eta(t)&=\Delta G_\eta^{(C)}(t)+\Delta G_\eta^{(B)}(t)\ ,\\\Delta G_\eta^{(B)}(t)&=\frac{L}{2}\sum_{i,j}\sum_{\vec{\nu}}{}'\nu_x\int_0^t ds F_y[\vec{Q}_{ij}(s)+\vec{\nu}L]\ ,\end{aligned} \quad (41)$$

in which the correction, $\Delta G_\eta^{(B)}(t)$, to the infinite-checkerboard expression, $\Delta G_\eta^{(C)}(t)$, remains in integral form and apparently cannot be expressed as an elementary function of the $\vec{Q}_i$ and $\vec{u}_i$.

The appearance of this second term in Eq. (41) is perhaps not surprising. Erpenbeck and Wood [19] demonstrated that the diagonal version of that term arises in one form of the dynamical pressure under periodic boundary conditions,

$$\begin{aligned}p&=-\frac{1}{3V}\overline{W}_2\ ,\\\overline{W}_2&=-\frac{L}{2}\lim_{t\to\infty}\sum_{\vec{\nu}}\sum_{i\neq j}\frac{1}{t}\int_0^t ds\,\vec{\nu}\cdot\vec{F}[\vec{R}_{ij}(s)+\vec{\nu}L]\ .\end{aligned} \quad (42)$$

[The $i=j$ terms are eliminated from Eq. (41) in comparing with this result to account for the exclusion of self-interactions in the derivation of the latter.] In this case, we see that the pressure can be expressed as the diagonal form of $\Delta G_\eta^{(B)}$ divided by the time, thereby converting it into a time average. In view of the $1/V$ factor in Eq. (42), the average of this diagonal form becomes at long times a bulk term growing linearly with the time. The off-diagonal form, however, by symmetry, has a zero expectation value, so that the average of its square might well be expected to yield quite different behavior both with time and system size.

While the displacement function, Eq. (41), yields the GK shear viscosity through Eq. (11), we can also show, through a simple modification of the proof leading to Eq. (39), that

$$\begin{aligned}\eta(t;N)&=\eta_f(t;N)\ ,\\\eta_f(t;N)&=a_\eta\langle J_\eta(t)\Delta G_\eta(t)\rangle\ ,\end{aligned} \quad (43)$$

so that the GK viscosity can also be written in an Einstein-like form, i.e., in terms of a mean-squared displacement,

$$\begin{aligned}\eta_f(t;N)&=\tfrac{1}{2}a_\eta\frac{d}{dt}S_\eta(t;N)\ ,\\S_\eta(t;N)&=\langle[\Delta G_\eta(t)]^2\rangle\ .\end{aligned} \quad (44)$$

Within the present context, we refer to η_f as simply another form of the GK shear viscosity. Of course, the actual EKH transport coefficients of the formal theory of Sec. II, whether given by $\eta_E^{(C)}$ or $\eta_E^{(T)}$ for PBC, should in the thermodynamic limit become equal to η at least at long times if that theory is correct. Nonetheless, simple considerations of the three contributions to the viscosity coefficient,

$$\begin{aligned}\eta_f(t;N)&=\eta_E^{(C)}(t;N)+2\eta_E^{(CB)}(t;N)+\eta_E^{(B)}(t;N)\ ,\\\eta_E^{(CB)}(t;N)&=\frac{\beta}{2V}\frac{d}{dt}\langle\Delta G_\eta^{(C)}(t)\Delta_\eta^{(B)}(t)\rangle\ ,\\\eta_E^{(B)}(t;N)&=\frac{\beta}{2V}\frac{d}{dt}\langle[\Delta G_\eta^{(B)}(t)]^2\rangle\ ,\end{aligned} \quad (45)$$

arising from the substitution of Eq. (41) into Eq. (44), do not suggest a ready explanation of how $\eta(t;N)$ or $\eta_f(t;N)$ might reduce to $\eta_E^{(C)}$ with increasing system size. In fact, the behavior of $\eta_E^{(C)}$ can be partially understood through consideration of the microscopic current to which it corresponds,

$$\begin{aligned}J_\eta^{(C)}(t)&=\frac{d}{dt}\Delta G_\eta^{(C)}(t)\ ,\\&=\sum_i\left[mu_{xi}u_{yi}+\tfrac{1}{2}\sum_j\sum_{\vec{\nu}}^{xij}{}'Q_{xij}F_y(\vec{Q}_{ij}+\vec{\nu}L)\right]\ ,\end{aligned}$$

differing from the full expression in the appearance of the infinite-checkerboard Q_{xij} multiplying the force rather than the separation of the images causing the force. The effect of this circumstance is most easily seen for short-range potentials, say of range $\sigma \ll L$. Then at the earliest times, the ij term of the potential part of $J_\eta^{(C)}$ for interacting pairs (i.e., having $|\vec{Q}_{ij}+\vec{\nu}L| < \sigma$ for some $\vec{\nu}$) lying near opposite x boundaries of the primary cell, is greatly increased in magnitude over the corresponding term of J_η in that $|\vec{Q}_{ij}+\vec{\nu}L|$ is small, of order σ. While the number of such terms is $O(L^2)$, each contributes a correlation of $O(L^2)$ to $\eta_E^{(C)}$ so as to dominate the $O(L^3)$ terms of J_η, each yielding an $O(1)$ contribution to η_f. Thus at early times the difference, $\eta_E^{(C)}-\eta_f$, is positive and of $O(L)$.

To further investigate whether $\eta_E^{(C)}(t;N)$ can indeed yield the shear viscosity coefficient, we turn to numerical calculations. Because we have recently calculated the Green-Kubo shear viscosity η_f [using the relation Eq. (44)] with moderate precision for equimolar mixtures of hard spheres having a diameter ratio of 0.4 and a mass ratio of 0.03 over a range of densities [20,21], we consider that same system here but for a single value of the specific volume $V/V_0=5$, where

$$V_0=\frac{\sqrt{2}}{2}\sum_{s=1}^{n_s} N_s\sigma_s^3 , \tag{46}$$

where N_s and σ_s are the number and diameter of spheres of species s, respectively, $n_s=2$ is the number of species, and V_0 is a reference volume which reduces to the close-packed volume in the single-component case. We have evaluated $\eta_E^{(C)}(t;N)$, as well as the corrections $\eta_E^{(CB)}(t;N)$ and $\eta_E^{(B)}(t;N)$, through numerical differentiation of $S_\eta^{(C)}(t;N)$, Eq. (30), and the related quantities on the right-hand side of Eq. (45) using the Monte Carlo molecular dynamics (MCMD) method described previously [22]. This consists of the evaluation of estimates of ensemble averages through Monte Carlo averaging over the initial toroidal phase, $\mathbf{x}^N(0)$, and time averaging over each trajectory by summing over "time origins" at intervals of δt.

To adequately explain the present calculation, we expand our notation and define $\vec{Q}_i(t;\mathbf{x}^N)$ and $\vec{u}_i(t;\mathbf{x}^N)$ to be the infinite-checkerboard positions and velocities in the c.m. frame of reference, given the initial toroidal phase $\mathbf{x}^N$, as in Eq. (28). Similarly, we define the infinite-checkerboard EKH function,

$$G_\eta^{(C)}(t;\mathbf{x}^N)=\sum_i Q_{xi}(t;\mathbf{x}^N)u_{yi}(t;\mathbf{x}^N) , \tag{47}$$

from which we evaluate the time average along an $M+1$ time-origin trajectory (overhanging bar),

$$\overline{S_\eta^{(C)}}(t;N)=\frac{1}{M+1}\sum_{m=0}^{M}\{G_\eta^{(C)}[t;\mathbf{x}^N(m\delta t)] - G_\eta^{(C)}[0;\mathbf{x}^N(m\delta t)]\}^2 , \tag{48}$$

where we emphasize particularly that $\mathbf{x}^N(t)$ refers to the toroidal coordinates. We can rewrite this wholly in terms of the phase along the trajectory starting at $\mathbf{x}^N(0)$, viz., $\vec{Q}_i(t)$ and $\vec{u}_i(t)$, by recognizing

$$\begin{aligned}\vec{Q}_i[t;\mathbf{x}^N(s)]&=\vec{Q}_i(t+s)-\vec{\nu}_i(s)L ,\\ \vec{u}_i[t;\mathbf{x}^N(s)]&=\vec{u}_i(t+s) ,\\ \vec{\nu}_i(s)L&=\vec{Q}_i(s)-\vec{q}_i(s) ,\end{aligned} \tag{49}$$

so that

$$\begin{aligned}G_\eta^{(C)}[t;\mathbf{x}^N(s)]&=\sum_i[Q_{xi}(t+s)-\nu_{xi}(s)L]u_{yi}(t+s)\\ &=G_\eta^{(C)}(t+s)-\sum_i \nu_{xi}(s)Lu_{yi}(t+s) .\end{aligned} \tag{50}$$

Thus we see that not only the $G_\eta^{(C)}$ but also the $\vec{\nu}_i$ must be known at each time origin in order to compute the $S_\eta^{(C)}$ function relative to it.

The MCMD calculations of $\eta_E^{(C)}$, $\eta_E^{(CB)}$, and $\eta_E^{(B)}$, along with η_f have been performed for systems of 108, 500, 864, 1372, and 4000 particles. Statistical uncertainties for each are obtained from the variance over the various trajectories of which there are 50 or more for each N. In each instance, the trajectories extended to 6000 Boltzmann mean free times, t_{00}, with time origins spaced between $t_{00}/4$ and t_{00}, depending on N. In Fig. 2 we show the estimates for the time-dependent "viscosities"

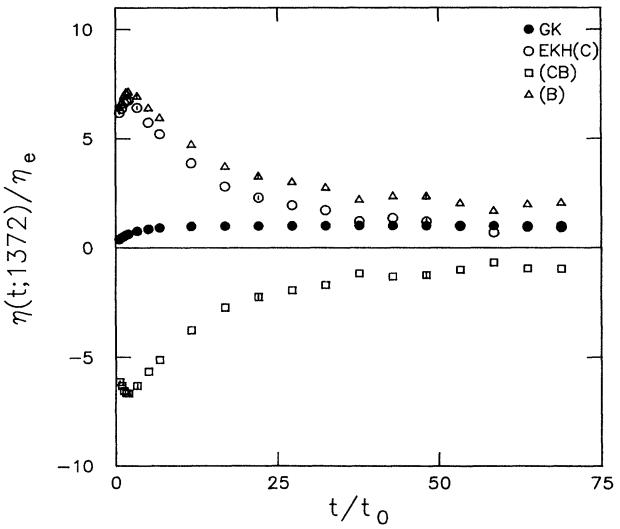

FIG. 2. Various time-dependent shear viscosity contributions, $\eta(t;N)$, reduced by the Enskog-theory value η_e, as functions of time t relative to the mean free time t_0 for an equimolar mixture of $N=1372$ hard spheres having diameter ratio 0.4 and mass ratio 0.03 for a volume $V=5V_0$, where V_0 is the reference volume, Eq. (46). The Green-Kubo viscosity $\eta_f(t;N)$, Eq. (44), is shown by the filled circles, the infinite-checkerboard Einstein-Kubo-Helfand viscosity $\eta_E^{(C)}$, Eq. (31), is shown by the open circles, and the corrections defined in Eq. (45), $\eta_E^{(CB)}$ and $\eta_E^{(B)}$, are given by the open squares and triangles, respectively. The error bars indicate one standard deviation but are mostly smaller than the plotting symbols.

of Eq. (45), reduced by the Enskog-theory result η_e, the latter evaluated [22] using the Mansoori-Carnahan-Starling-Leland [23] equation of state to be

$$\eta_e = 0.283\,0779 \frac{m_1}{(m_1\beta)^{1/2}\sigma_1^2} \tag{51}$$

(where m_1 is the mass and σ_1 the diameter of the larger particle), as functions of time, reduced by the observed mean free time t_0, for the 1372-particle system. Although not evident from the figure, we note that the error bars for the GK estimate η_f are roughly an order of magnitude smaller than for the other quantities and, moreover, η_f attains (at least approximately) its long-time asymptote somewhat earlier. Furthermore, we note the similarity between $\eta_E^{(C)}$ and $-\eta_E^{(CB)}$ but remark that the sum $\eta_E^{(C)}+\eta_E^{(CB)}$ is found to exhibit an early-time dependence on t similar in shape to $\eta_E^{(C)}$ although of smaller magnitude. Of course, η_f is, within computer rounding errors, the sum, Eq. (45), of the other functions in the figure. The results for the other values of N are qualitatively similar to Fig. 2. The large positive excursions in $\eta_E^{(C)}$ and $\eta_E^{(B)}$ having maxima at about two collisions are found to increase linearly with $N^{1/3}$ in agreement with the argument given above, but clearly have no physical significance. While one might, as we argued above in the case of the toroidal EKH functions, suppose that, for large enough systems, the early time behavior of $\eta_E^{(C)}$ (before most particles have passed within a distance σ of the boundary) should correspond to the GK theory, that is clearly not the case. Instead, only the long-time values appear to approximate the GK result, as seen for $N=1372$ in Fig. 2.

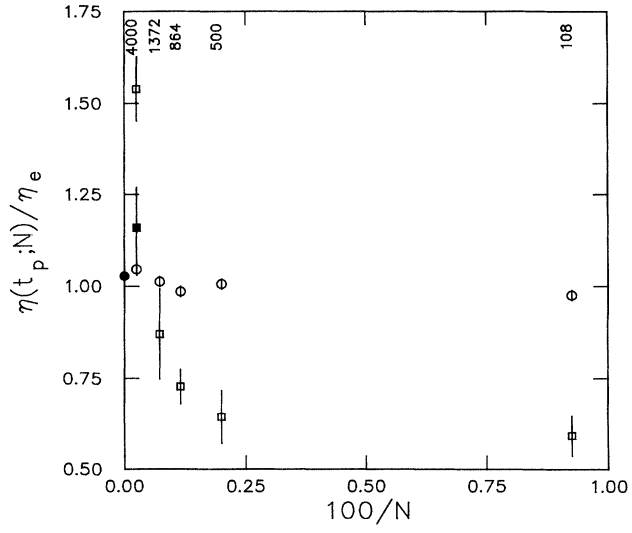

FIG. 3. The long-time values of the shear viscosity, $\eta(t_p;N)$, with $t_p \sim 70t_0$ and t_0 the mean free time, reduced by the Enskog-theory value η_e, as functions of $1/N$ for the hard-sphere mixture of Fig. 2. The infinite-checkerboard Einstein-Kubo-Helfand viscosities, $\eta_E^{(C)}$, are the open squares, the Green-Kubo viscosities, η_f, are the open circles, and the large-system limit of the GK result from Ref. [18], which includes a long-time tail correction, is the filled circle. The filled square is the 4000-particle value of $\eta_E^{(C)}$ at a time of $90t_0$. The number N of particles for each pair of results is marked across the top of the figure. The error bars indicate one standard deviation.

We test the conjecture that $\eta_f(t_p;N)$ and $\eta_E^{(C)}(t_p;N)$, with $t_p \sim 70t_0$, agree in the large system limit in Fig. 3 in which we plot the estimates of both these quantities (the average of the final 10 observations of which every fifth point is plotted in Fig. 2) as a function of $1/N$ as well as the large-system limit from our earlier work. Even though the results for $N \leq 1372$ are consistent with the conclusion that the values of $\eta_E^{(C)}(70t_0;N)$ extrapolate to the correct thermodynamic limit, the 4000-particle result lies significantly too high. Clearly the results to $70t_0$ do not support the conjectured large-system agreement.

An alternative approach is suggested by the fact that the time required for $\eta_E^{(C)}$ to "attain" its asymptote appears to increase with increasing system size. To test the possibility that the 4000-particle system has not been extended to large enough t, we have rerun that calculation to a time of $90t_0$, finding further decay of $\eta_E^{(C)}$ to a value, shown by the filled square in Fig. 3, much closer to the GK value. It appears that the large $O(N^{1/3})$ structure found at early times requires an increasing long time to decay as the system size increases. This suggest that extrapolation of the long-time values to the thermodynamic limit (i.e., reversing the canonical order of the limits) could possibly yield agreement with the GK value. Because the statistical uncertainties in $\eta_E^{(C)}$ increase as a function of time, the determination of the viscosity in this way appears problematic. Nonetheless, the suggestion that one must invert the order of the long-time and thermodynamic limits given in Eq. (2) seems, to say the least, surprising.

We conclude therefore that for systems under PBC the EKH relations are of practical value only for self-diffusion. For shear viscosity, the infinite-checkerboard form introduces a large unphysical short-time contribution which decays only slowly with time, so as to make the recovery of the true shear viscosity coefficient difficult. While the toroidal EKH function may yield the self-diffusion coefficient in the manner suggest by Fig. 1, it seems obvious that the unphysical aspects which dominate the infinite-checkerboard viscosity have counterparts in the toroidal approach and that the behavior suggested by the figure will not apply. On the other hand, the calculation through S_η [whether using $\Delta G_\eta(t)$ evaluated through numerical integration from Eq. (40) or explicitly through Eq. (41)] proceeds straightforwardly [6,8–10], in complete analogy to the self-diffusion case.

IV. McQUARRIE EXPRESSION

In his statistical mechanics textbook [5] McQuarrie discussed the calculation of transport coefficients at the formal level, including not only the usual EKH expression, Eqs. (9) and (10), but also a formula which can be written as

$$\eta_M = \lim_{t\to\infty} \text{tlim} \eta_M(t;N) ,$$
$$\eta_M(t;N) = \tfrac{1}{2} a_\eta \frac{d}{dt} M_\eta(t;N) ,$$
$$M_\eta(t;N) = N\langle \Delta g_i^2(t)\rangle , \tag{52}$$
$$g_i(t) = m r_{xi}(t) v_{yi}(t) ,$$

which we call the McQuarrie formula; McQuarrie left its proof as an exercise for the reader. It is given, also without proof, by Hoheisel and Vogelsang [10]. Comparing it with the EKH formula, Eqs. (9) and (10), we see that the two-particle correlations $\langle \Delta g_i(t)\Delta g_j(t)\rangle$ $(i\neq j)$ in $\Delta G_\eta^2(t)$ have been eliminated. Moreover Chialvo, Cummings, and Evans [13] (CCE) purport to prove formally that these neglected terms vanish thus: Simplify the EKH expression from Eqs. (9) and (10) to read

$$\eta_E(t;N) = \eta_M(t;N) + N(N-1) a_\eta \frac{d}{dt} f_{12}(t;N) ,$$
$$f_{ij}(t;N) = -\langle g_i(t) g_j(0)\rangle , \tag{53}$$

by virtue of the time independence of the terms $\langle r_{xi}(t) v_{yi}(t) r_{xj}(t) v_{yj}(t)\rangle$ which follows from the Liouville theorem. For systems which are "mixing," the argument goes, the phase at long times t is uncorrelated with that at time 0. Because $g_i(t)$ is not a constant of the motion (for which f_{ij} would then be the average of the square of a phase function), f_{12} approaches a product of averages,

$$\lim_{t\to\infty} f_{12}(t) = -\langle g_1(t)\rangle\langle g_2(0)\rangle , \tag{54}$$

in which $f_{12}(t)$ is the large-system limit of $f_{12}(t;N)$. The factors on the right obviously vanish and the "proof" is completed.

In fact, the proof is incorrect because the breaking of the average into two factors in Eq. (54) is valid only to leading order in N. Because the factor multiplying df_{12}/dt in Eq. (53) is itself of $O(N)$, it follows that one needs to show that $\lim_{t\to\infty} df_{12}/dt$ vanishes both to leading order and to $O(1/N)$. Presumably the leading term vanishes (as it must simply on dimensional grounds), but the $1/N$ dependence is almost certainly nonzero, as we shall see.

The existence of long-time correlations between velocities $\vec{v}_i$ and positions $\vec{r}_j$ which become linear in the time for large t are well known. Typically these are of $O(1)$ when i and j refer to a single particle and of $O(1/N)$ when they refer to a distinct pair. For example, the correlation function,

$$w_{ij}(t) = \langle v_{xj}(0) r_{xi}(t)\rangle \tag{55}$$

would, based on the CCE argument, vanish at long times. It can, however, be readily evaluated in the zero-momentum, canonical ensemble used by CCE by substituting $v_{x1} = -\sum_{i>1} v_{xi}$ into Eq. (55) for $w_{12}(t)$ to yield

$$w_{12}(t) = -\frac{1}{N-1} w_{11}(t) . \tag{56}$$

In the long-time limit, one sees from Eqs. (9) and (10) that w_{11} approaches the self-diffusion coefficient, so that $w_{12}(t)$ approaches $D/(N-1)$, not zero.

While correlations of position and velocity can vanish in certain instances, for f_{12} it appears not to be the case. Indeed, $c_{12}(t;N) = df_{12}(t;N)/dt$ can be separated into kinetic, cross, and potential contributions if one simply reverses the steps which took us from the Green-Kubo to the EKH formulas in Sec. II. Explicitly taking the derivative of $f_{12}(t;N)$, we obtain

$$c_{12}(t;N) = c_{12}^{(K)}(t;N) + c_{12}^{(\phi)}(t;N) ,$$
$$c_{12}^{(K)}(t;N) = -m^2\langle v_{x1}(t) v_{y1}(t) r_{x2}(0) v_{y2}(0)\rangle , \tag{57}$$
$$c_{12}^{(\phi)}(t;N) = -m\langle r_{x1}(t) F_{y1}(t) r_{x2}(0) v_{y2}(0)\rangle ,$$

in which $\vec{F}_1$ is the total force on particle 1 due to the other particles. Using the Liouville theorem to express $c_{12}^{(K)}(t;N)$ as an average over the phase at time t and using time-reversal invariance of the trajectory, we find

$$c_{12}^{(K)}(t;N) = m^2\langle v_{x1}(0) v_{y1}(0) r_{x2}(t) v_{y2}(t)\rangle . \tag{58}$$

Expressing the right-hand side as the time integral of its derivative, we obtain

$$c_{12}^{(KK)}(t;N) = c_{12}^{(KK)}(t;N) + c_{12}^{(K\phi)}(t;N) ,$$
$$c_{12}^{(KK)}(t;N) = m^2\int_0^t ds\,\langle v_{x1}(0) v_{y1}(0) v_{x2}(s) v_{y2}(s)\rangle , \tag{59}$$
$$c_{12}^{(K\phi)}(t;N) = m\int_0^t ds\,\langle v_{x1}(0) v_{y1}(0) r_{x2}(s) F_{y2}(s)\rangle ,$$

in which we have used the obvious result that $c_{12}^{(K)}(0;N) = 0$. Observe that $c_{12}^{(KK)}(t;N)$ is just the contribution from distinct pairs to the usual kinetic part of the shear viscosity from the Green-Kubo relation, as seen from Eqs. (2), (5), and (7). Its integrand certainly does not vanish identically nor can one expect the integral to vanish. Moreover, one cannot expect its long-time limit to cancel with the cross and potential terms; the latter, for example, are expected to be of higher order in the density than the kinetic contribution in that only the kinetic contribution to the shear viscosity survives in the low-density limit. The assumption of mixing enables one to evaluate the long-time behavior of the integrand of $c_{12}^{(KK)}$, Eq. (59), in the manner demonstrated for the self-diffusion coefficient in Sec. III. Indeed, for the zero-momentum ensemble considered by CCE, this correlation vanishes at long times, but this hardly implies that its integral $c_{12}^{(KK)}$ also vanishes at long times.

On the other hand, neither the failure of the CCE proof nor the nonzero long-time limit for $w_{12}(t)$ above proves that c_{12} is nonzero in the long-time limit. CCE [13] have attempted to calculate the long-time behavior of c_{12} through molecular dynamics calculations for a truncated Lennard-Jones potential subject to periodic boundary conditions for systems of 108 to 864 particles. They evaluated the quantity $g_i(t)g_j(0)$ from neither the toroidal, $\vec{r}_i(t)$, nor the infinite-checkerboard, $\vec{R}_i(t)$, coordinate specification, but from a hybrid so-called BPBC calculation, fully described in the paper, and recently criticized by ABM [12]. Although the results appear to be consistent with the conclusion that $f_{12}(t;N)$ becomes

linear in t at long times, it seems that the statistical fluctuations are much too large to permit one to draw any conclusion with respect to the value of the slope in the large-system limit.

We have seen in Sec. III that the application of the EKH formula for shear viscosity to finite periodic systems is fraught with difficulties while calculations based on the GK formula proceed smoothly. The essential element of the McQuarrie formula is that it expresses the shear viscosity as a function of a one-particle (or self-) correlation function, analogous to the self-diffusion coefficient, not that it is of the EKH form. Therefore, if one wishes to investigate numerically the validity of the McQuarrie formula, it would seem best to evaluate the shear viscosity through the Green-Kubo time-correlation function, evaluating separately the one- and two-particle contributions. However, when we so decompose the shear viscosity using Eqs. (2) and (7), two distinct decompositions arise rather naturally, depending on how we write the one-particle term of the microscopic current, Eq. (7),

$$\begin{aligned}
&\eta(t;N)=\eta^{(\alpha 1)}(t;N)+\eta^{(\alpha 2)}(t;N)\ ,\\
&\eta^{(\alpha n)}(t;N)=\frac{\beta N}{V}\int_0^t ds\rho_\eta^{(\alpha n)}(s;N)\ ,\\
&\rho_\eta^{(\alpha 1)}(t;N)=\langle j_\eta^{(\alpha 1)}(0)j_\eta^{(\alpha 1)}(t)\rangle\ ,\\
&\rho_\eta^{(\alpha 2)}(t;N)=(N-1)\langle j_\eta^{(\alpha 1)}(0)j_\eta^{(\alpha 2)}(t)\rangle\ ,
\end{aligned} \tag{60}$$

where $\eta^{(\alpha n)}$ is the n-particle contribution for decomposition α. We label the decomposition a that which follows immediately from Eq. (7),

$$j_\eta^{(ai)}(t)=mv_{xi}(t)v_{yi}(t)+\tfrac{1}{2}\sum_{j\neq i} r_{xij}(t)F_y[\vec{r}_{ij}(t)]\ . \tag{61}$$

and decomposition b that which arises when the force terms for the (ij) pair are rewritten as $\vec{r}_i\vec{F}(\vec{r}_{ij})+\vec{r}_j\vec{F}(\vec{r}_{ji})$,

$$j_\eta^{(bi)}(t)=mv_{xi}(t)v_{yi}(t)+r_{xi}(t)\sum_{j\neq i}F_y[\vec{r}_{ij}(t)]\ . \tag{62}$$

The equivalence of the two forms for $\eta(t;N)$ from Eq. (60) follows from the relation

$$\sum_i j_\eta^{(ai)}=\sum_i j_\eta^{(bi)}\ . \tag{63}$$

From the present point of view, the principal differences between these two forms are that (1) $j_\eta^{(bi)}$ is integrable in closed form,

$$\begin{aligned}
&\Delta g_\eta^{(\alpha i)}(t)=\int_0^t ds j_\eta^{(\alpha i)}(s)\ ,\\
&g_\eta^{(bi)}(t)=mr_{xi}(t)v_{yi}(t)\ ,
\end{aligned} \tag{64}$$

while $j_\eta^{(ai)}(t)$ is not, and (2) $j_\eta^{(ai)}$ is translationally invariant while $j_\eta^{(bi)}$ is not. [Note that $g_\eta^{(bi)}(t)$ is identical to $g_i(t)$ of Eq. (52).] If, then, we take the time integral in Eq. (60) inside the ensemble averages to yield

$$\begin{aligned}
&\eta^{(a1)}(t;N)=\frac{\beta N}{V}\langle j_\eta^{(a1)}(0)\Delta g_\eta^{(a1)}(t)\rangle\ ,\\
&\eta^{(a2)}(t;N)=\frac{\beta N(N-1)}{V}\langle j_\eta^{(a1)}(0)\Delta g_\eta^{(a2)}(t)\rangle\ ,
\end{aligned} \tag{65}$$

we *know* that $\eta^{(an)}$ are translationally invariant but might well expect $\eta^{(bn)}$ not to be.

Now the McQuarrie form for $\eta(t;N)$ follows from Eq. (52) and the relationship,

$$\langle j_\eta^{(bi)}(0)\Delta g_i(t)\rangle=\langle j_\eta^{(bi)}(t)\Delta g_i(t)\rangle\ ,$$

which is proven as in Sec. II in establishing Eq. (15); one obtains

$$\eta_M(t;N)=\eta^{(b1)}(t;N)\ . \tag{66}$$

By studying the time dependence of $\eta^{(bn)}(t;N)$ and $\rho_\eta^{(bn)}(t;N)$ one would expect to demonstrate rather straightforwardly whether the two-particle term has a significant long-time contribution to the viscosity, without appeal to the exotic CCE definition of the displacement function under periodic boundary conditions.

Nonetheless, when we consider a molecular dynamics calculation using periodic boundary conditions, the GK current is given by Eq. (27) rather than Eq. (7) and the equations for the one-particle currents become

$$\begin{aligned}
&j_\eta^{(ai)}=mu_{xi}u_{yi}+\tfrac{1}{2}\sum_j\sum_{\vec{\nu}}{}'(Q_{xij}+\nu_x L)F_y(\vec{Q}_{ij}+\vec{\nu}L)\ ,\\
&j_\eta^{(bi)}=mu_{xi}u_{yi}+\sum_j\sum_{\vec{\nu}}{}'(Q_{xi}+\tfrac{1}{2}\nu_x L)F_y(\vec{Q}_{ij}+\vec{\nu}L)\ ,
\end{aligned} \tag{67}$$

so that $j_\eta^{(bi)}$ is no longer integrable and the correspondence Eq. (66) breaks down. Thus for the numerical calculation of the "McQuarrie" shear viscosity, one might consider a number of different quantities:

(1) $\eta_M(t;N)$ directly from Eq. (52) as attempted by CD. If the infinite-checkerboard coordinates were used in this calculation, the result would be the one-particle portion of $\eta_E^{(C)}(t;N)$ of Sec. III. A necessary but not sufficient condition for the validity of the McQuarrie formula via $\eta_M(t;N)$ is the recovery of the correct viscosity from $\eta_E^{(C)}(t;N)$ (which includes both the one- and two-particle contributions). As we have already seen, $\eta_E^{(C)}$ does not appear to yield the correct shear viscosity coefficient.

(2) The one-particle contribution $\eta^{(b1)}$ based on $j_\eta^{(bi)}$ of Eq. (67) which would be expected to depend on the coordinate frame.

(3) The one-particle $\eta^{(a1)}$ which clearly is translationally invariant and, therefore, could conceivably have physical significance.

We choose, then, this third calculation as the only meaningful form for the McQuarrie viscosity for finite periodic systems.

We have estimated $\eta^{(a1)}(t;N)$ and $\eta^{(a2)}(t;N)$ for the same system treated in Sec. III in order to make contact with the rather extensive calculations of the viscosity which have previously been reported, *viz.*, the GK Monte Carlo molecular dynamics calculations [20,21] of the transport properties of an equimolar binary mixture of hard spheres having a diameter ratio of 0.4 and a mass

ratio of 0.03. For hard spheres, however, the $j_\eta^{(ai)}$, Eq. (67), contain impulsive contributions from collisions and therefore cannot be evaluated directly. Instead, we compute the quantities

$$S_\eta^{(a1)}(t;N)=N\langle[\Delta g_\eta^{(a1)}(t)]^2\rangle ,$$
$$S_\eta^{(a2)}(t;N)=N(N-1)\langle\Delta g_\eta^{(a1)}(t)\Delta g_\eta^{(a2)}(t)\rangle , \quad (68)$$

which we differentiate numerically to obtain

$$\eta_E^{(an)}(t;N)=\tfrac{1}{2}a_\mu\frac{d}{dt}S_\eta^{(an)}(t;N) . \quad (69)$$

These functions are equivalent to the desired $\eta^{(an)}$ through the relations

$$\eta^{(an)}(t;N)=\eta_E^{(an)}(t;N) , \quad (70)$$

which are proven using the method leading to Eq. (39) in Sec. III.

The previous calculations [20,21] for this hard-sphere mixture include the shear viscosity coefficient for a range of system sizes for densities throughout the fluid regime. Here we have considered a single value of the reduced volume, $5V_0$, with the reference volume given by Eq. (46), for systems of 108, 500, 864, and 1372 particles. The current calculations are very similar to those reported earlier for this density [20], except that we include the calculation of these two additional time-correlation functions. For the $N=108$ case, we form the $S_\eta^{(a2)}(t;N)$ estimates by averaging over the $N(N-1)$ possible pairs of particle indices in the second part of Eq. (68). For larger N, we estimate it through the difference between $S_\eta(t;N)$ and $S_\eta^{(a1)}(t;N)$; except for round-off errors, the two calculations are identical, but the latter method avoids the time-consuming summation of the $N(N-1)$ terms.

In Fig. 4 we plot $\eta_E^{(a1)}(t;N)$ and $\eta_E^{(a2)}(t;N)$, scaled by the value η_e from the Enskog theory, Eq. (51), as functions of time in units of the observed mean free time t_0 for the four system sizes. As a check on these calculations, for $N=108$ we have compared the sum $\eta_E^{(a1)}+\eta_E^{(a2)}$ with the usual Green-Kubo result, finding agreement within the expected round-off errors. The calculations represent Monte Carlo molecular dynamics averages over 20 or more trajectories for each of four system sizes, $N=108$, 500, 864, and 1372 (with extensive time averaging of the time correlation functions over the $6000t_{00}$ length trajectories), each trajectory being initiated from a phase which appears uncorrelated with its predecessor with respect to the observed time-correlation functions. Based on the apparent long-time values in the figure, we see that the one- and two-particle contributions to the time-dependent shear viscosity are very similar in magnitude, each contributing roughly $\frac{1}{2}$ to the total reduced shear viscosity. The latter was found to have a simple $1/N$ dependence on system size,

$$\frac{\eta(t_c;N)}{\eta_e}=1.0142\pm0.0059-\frac{4.35\pm1.20}{N} \quad (71)$$

at the "crossover" time $t_c\sim28t_0$ (see [20] for details) at this density, based on calculations for the same four values of N. While the current calculations are not so extensive as those leading to Eq. (71), we can obtain an estimate for $\eta^{(a2)}(t_c;N)$ which is more precise than that shown in the figure by fitting the current, relatively precise results for $\eta^{(a1)}(t_c;N)$ by the linear least-squares relation

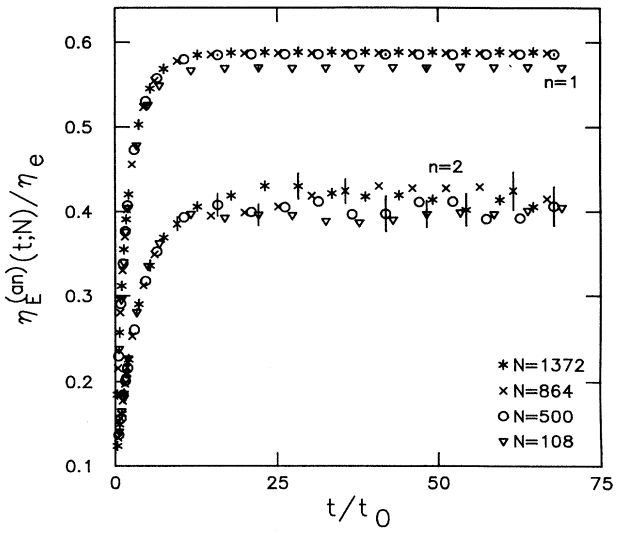

FIG. 4. The one- and two-particle components of the time-dependent shear viscosity, $\eta_E^{(an)}(t;N)$, for decomposition a, Eqs. (60) and (67), reduced by the Enskog-theory value η_e, as functions of time t relative to the main free time t_0 for mixtures of $N=108$ (triangles), 500 (circles), 864 (crosses), and 1372 (asterisks) hard spheres as in Fig. 2. The error bars indicate one standard deviation, but are smaller than the plotting symbols for $n=1$.

$$\frac{\eta^{(a1)}(t_c;N)}{\eta_e}=0.5900\pm0.0003-\frac{2.16\pm0.12}{N} \quad (72)$$

and subtracting from Eq. (71) to obtain

$$\frac{\eta^{(a2)}(t_c;N)}{\eta_e}=0.4242\pm0.0059-\frac{2.19\pm1.21}{N} . \quad (73)$$

While the $1/N$ dependence of $\eta^{(a2)}$ is only poorly determined, the large-system limit is clearly nonzero, so that the two-particle contribution to the shear viscosity is significantly different from zero.

V. SUMMARY

Let us now summarize our findings with respect to the calculation of the shear viscosity for systems subject to periodic boundary condition; the situation with respect to self-diffusion is relatively straightforward and will not be discussed further. We have approached this calculation from the point of view of both the Green-Kubo and the Einstein-Kubo-Helfand expressions. In the GK approach, we express the viscosity coefficient $\eta(t;N)$ as a time integral of the stress-stress autocorrelation function. By integrating the stress tensor itself over the time, one

can write equally well the GK viscosity in the form either of two time-correlation functions between the stress tensor and its integral, Eqs. (11) and (43), or, through one additional time integration, as the time derivative of a mean-squared displacement, Eq. (44). From the numerical point of view, there would appear to be little to choose among these four expressions, except for the case of hard spheres for which only the last of these relations has a singularity-free quantity to be averaged.

The EKH approach expresses the viscosity as the time derivative of a mean-squared displacement, with the displacement function given explicitly by Eq. (29), for which we have detailed both a toroidal and an infinite-checkerboard treatment of particle positions. The toroidal form seems obviously impractical in that the mean-squared displacement is bounded in time. The infinite-checkerboard treatment yields a viscosity $\eta_E^{(C)}(t;N)$ which exhibits an unphysical linear growth with $N^{1/3}$ at short times. Monte Carlo molecular dynamics results show this unphysical feature to begin to decay after a few mean free times, apparently approaching a long-time asymptote for times which increase with increasing N. Although $\eta_E^{(C)}(t;N)$ at large but fixed time does not converge with increasing N to the Green-Kubo value, the long-time values may do so.

The formal McQuarrie expression for the shear viscosity, which has been touted by CD [11] and by CCE [13] as an effective, single-particle approach to the shear viscosity, has been criticized by ABM [12] who showed the CD proof of translational invariance of the McQuarrie viscosity, $\eta_M(t;N)$, to be invalid and the one-particle microscopic current to lack translational invariance. Moreover, ABM repeated the calculations of CD (using the same peculiar, unjustified method for evaluating the EHK and McQuarrie displacement functions) for the same high-density, supercritical state of the Lennard-Jones fluid both by molecular dynamics and Brownian dynamics, obtaining results for the so-called viscosity in agreement with CD but differing significantly from ABM's Green-Kubo result. ABM concluded therefore that, at the very least, the CD calculation does not yield the true viscosity.

Here we have attempted to apply the McQuarrie relation to finite periodic systems, without recourse to the Chialvo-Debenedetti methods. We find that the literal application of the McQuarrie formula corresponds to the calculation of the one-particle portion of $\eta_E^{(C)}(t;N)$ by virtue of the McQuarrie requirement that the two-particle contribution vanishes. Thus our failure to obtain the viscosity from $\eta_E^{(C)}(t;N)$ would seem to imply that the one-particle part would not be helpful in establishing in the McQuarrie formula, unless the one-particle portion were to somehow converge to the true viscosity on a more rapid time scale than the two-particle portion approached zero. Instead, we have evaluated the one- and two-particle contributions to the Green-Kubo viscosity and find both contributions to be of similar magnitude for a low-density mixture of hard spheres. In lieu of an analytical proof of its validity, we conclude that the available evidence indicates that the McQuarrie formula is not valid and that additional numerical calculations to establish it seem impractical. As a practical matter, then, only the Green-Kubo approach, in any of its four variations, provides a feasible method for computing the shear viscosity.

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