PHYSICAL REVIEW A VOLUME 46, NUMBER 2 15 JULY 1992

Mutual and self-diffusion in fluids undergoing strong shear

Sten Sarman, Denis J. Evans, and Andras Baranyai*
Research School of Chemistry, Australian National University Canberra 2601, Australian Capital Territory, Australia
(Received 28 February 1992)

We derive a Green-Kubo relation for the mutual diffusion tensor (MDT) of a binary fluid mixture subject to a strong Couette shear field. We calculate the MDT of a Lennard-Jones (LJ) mixture and the self-diffusion tensor (SDT) of a pure LJ fluid as functions of state point and strain rate. The qualitative dependence of the diffusion tensors upon these variables is explained in greater detail by analyzing the velocity and mass current autocorrelation functions. Finally, we compare the zero-color field color conductivity with the SDT. For nonzero shear rates we find that the color conductivity and the SDT are different, confirming the prediction by Evans, Baranyai, and Sarman [Mol. Phys. (to be published)], according to which these two transport coefficients should only be related at zero shear rate.

PACS number(s): 03.40.Gc, 02.50.+s, 51.10.+y

I. INTRODUCTION

When a fluid is subject to a simultaneous Couette shear field and a concentration or temperature gradient, Curie's principle [2] states that the shear field, being a tensorial quantity, cannot affect vectorial quantities such as mass or heat currents. However, when the shear rate is large, nonlinear effects become important and Curie's principle breaks down. Then the shear field *modifies* (but does not generate) the mass and heat fluxes. Furthermore both diffusion and thermal conductivity coefficients need to be replaced by second-rank tensors, with elements that vary with the imposed strain rate, reflecting the symmetry of planar Couette flow.

The earliest attempt to calculate the self-diffusion tensor (SDT) of strongly shearing fluids by nonequilibrium molecular dynamics (NEMD) was made by Heyes *et al.* [3]. These authors conjectured, but did not derive, Einstein relations between the mean-square displacements (MSD's) and the diagonal elements of the SDT. In a series of papers [4–6,1] we have derived both Einstein and Green-Kubo (GK) relations for diagonal and off-diagonal elements of both the self-diffusion tensor and the thermal conductivity tensor for single-component fluids undergoing strong shear.

In the case of self-diffusion, one can inspect the expressions for the microscopic MSD's and compare them with the macroscopic ones obtained from the convective diffusion equation [4,6]. The MSD's can then be transformed to integrals of the velocity autocorrelation functions. A limitation of this method is that it is only possible to obtain GK relations for the diagonal elements of the SDT. A more general and rigorous method [5] is to derive microscopic analogs of the mass or energy continuity equations expressed in Lagrangian convected coordinates. These equations can be combined with constitutive relations (such as Fick's law or Fourier's law) in a manner that is surprisingly similar to the nonshearing case [7], leading to both GK and Einstein relations for the complete diffusion or thermal conductivity tensors for fluids under shear.

It is well known that the most efficient methods for calculating the linear transport coefficients employ nonequilibrium-molecular-dynamics algorithms. These algorithms use fictitious mechanical fields that interact with the system in question, generating irreversible thermodynamic currents (or forces). The form for the interaction between these fictitious fields and the system is chosen so that the currents generated by the fictitious fields are trivially but exactly related to the same currents generated by real Navier-Stokes forces (e.g., temperature or chemical potential gradients, strain rates, etc.). The proof of the correctness of these algorithms [7] is based on the known GK relations for the Navier-Stokes transport coefficients and on a formal analysis of the linear mechanical response of the system to the fictitious external fields. In general, the NEMD algorithms permit much more efficient calculation of the Navier-Stokes transport coefficients than does a direct calculation of the transport coefficients from the GK relations themselves.

It may be thought that since GK relations are now known for a number of weak vector processes taking place in strongly shearing fluids, NEMD algorithms could likewise be derived for these nonlinear far-from-equilibrium systems. Unfortunately, it has recently been proved [1] that this is not the case. When a system is simultaneously subject to a strong shear field and a weak mechanical vector field (the fictitious field), the linear response of the system to this weak field is a sum of two terms: one takes the form of the desired GK expression for the relevant transport coefficient but the other term involves a complicated derivative of a time correlation. This means that for all practical purposes, NEMD methods do not exist for weak vector processes taking place under strong tensorial fields.

In this work we give a derivation of the GK relations for the various components of the mutual diffusion tensor (MDT) of a shearing fluid. We present the results of computer simulations of the SDT and the MDT for fluids under shear. We also compare the SDT and the color conductivity tensor (CCT) of pure Lennard-Jones (LJ) fluids and of LJ mixtures in order to explore the effects of

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the shear field upon the self diffusion and color conductivity. We evaluate the difference between the zero field CCT and the SDT at different state points in order to verify the conclusion in Ref. [1]. The paper is organized as follows, in Sec. II we review the necessary theory, in Sec. III the results are presented and discussed, and finally we present our conclusion in Sec. IV.

II. THEORY

A. Equations of motion

The system that we study consists of N_1 particles of component 1 with mass m_1 and number density n_1 and N_2 particles of component 2 with mass m_2 and number density n_2. The total number of particles in the system is $N=N_1+N_2$. The volume of the system is V, the number density is $n=N/V$. The mass densities are $\rho_1=n_1m_1$, $\rho_2=n_2m_2$, and $\rho=\rho_1+\rho_2=n_1m_1+n_2m_2$. The position coordinates and the momenta of particle i of species ν are denoted by $\mathbf{r}_i^\nu$ and $\mathbf{p}_i^\nu$, respectively. The system is subject to a Couette strain field $\gamma=\partial u_x/\partial y$, where u_x is the streaming velocity in the x direction. The equations of motion for such a system are given by the Sllod equations, so named because of their relationship to the Dolls tensor algorithm [7]

$$\dot{\mathbf{r}}_i^\nu=\frac{\mathbf{p}_i^\nu}{m_\nu}+\mathbf{i}\gamma y_i^\nu, \quad \dot{\mathbf{p}}_i^\nu=\mathbf{F}_i^\nu-\mathbf{i}\gamma p_{yi}^\nu-\alpha\mathbf{p}_i^\nu \ . \tag{1}$$

In these equations $\mathbf{r}_i^\nu$ is the laboratory position of particle i of species ν, $\mathbf{F}_i^\nu$ is the interatomic force on particle i of species ν due to the other particles, and $\mathbf{i}$ is the unit vector in the x direction. At a low Reynolds number, the streaming velocity at the position of the particle i of species ν is $\mathbf{i}\gamma y_i^\nu$, so the peculiar velocity of the particle is $\mathbf{p}_i^\nu/m_\nu$. The Gaussian thermostatting multiplier α is given by

$$\alpha=\frac{\displaystyle\sum_{\nu=1}^{2}\frac{1}{m_\nu}\sum_{i=1}^{N_\nu}\mathbf{F}_i^\nu\cdot\mathbf{p}_i^\nu-\gamma p_{xi}^\nu p_{yi}^\nu}{\displaystyle\sum_{\nu=1}^{2}\frac{1}{m_\nu}\sum_{i=1}^{N_\nu}\mathbf{p}_i^{\nu 2}} \ . \tag{2}$$

The equations of motion for a one-component system can be recovered by setting $N_1=N$ and $N_2=0$.

We also studied the color conductivity [7] of a one-component system subject to simultaneous Couette strain fields and color fields. In this case the equations of motion become

$$\begin{aligned}\dot{\mathbf{r}}_i&=\frac{\mathbf{p}_i}{m}+\mathbf{i}\gamma y_i \ ,\\ \dot{\mathbf{p}}_i&=\mathbf{F}_i+c_i\mathcal{F}_c-\mathbf{i}\gamma p_{yi}-\alpha(\mathbf{p}_i-c_im\mathbf{J}_c/n) \ ,\end{aligned} \tag{3}$$

where

$$\mathbf{J}_c=\frac{1}{mV}\sum_{i=1}^{N}c_i\mathbf{p}_i \tag{4}$$

is the color current, $c_i=(-1)^i$ is the color charge and $\mathcal{F}_c$ is the color field. The system is color neutral, i.e.,

$$\sum_{i=1}^{N}c_i=0 \ . \tag{5}$$

In this case the Gaussian thermostatting multiplier required to keep the peculiar kinetic energy

$$E_k=\frac{1}{2m}\sum_{i=1}^{N}(\mathbf{p}_i-c_im\mathbf{J}_c/n)^2 \tag{6}$$

constant is given by

$$\alpha=\frac{\gamma J_{cx}J_{cy}Vm^2/n+\displaystyle\sum_{i=1}^{N}(\mathbf{F}_i\cdot\mathbf{p}_i-\gamma p_{xi}p_{yi}-c_i\mathbf{F}_i\cdot\mathbf{J}_cm/n)}{\displaystyle\sum_{i=1}^{N}(\mathbf{p}_i-c_im\mathbf{J}_c/n)^2} \ . \tag{7}$$

It is important to note that heating effects can be neglected only in the linear regime, i.e., for low shear rates and color fields. Far from equilibrium, e.g., when a high shear rate is applied, the thermostatting mechanism has to be fully specified because it also influences the properties of the system.

B. Self-diffusion tensors for fluids subjected to Couette strain fields

When a single-component fluid is subject to steady planar Couette flow the self-diffusion coefficient becomes a self-diffusion tensor with shear-rate-dependent components. In Cartesian coordinates the steady-state diffusion tensor can be written as

$$\mathbf{D}=\begin{bmatrix}D_{xx} & D_{xy} & 0\\ D_{yx} & D_{yy} & 0\\ 0 & 0 & D_{zz}\end{bmatrix} \ . \tag{8}$$

The xz, yz, zx, and zy are identically zero because of symmetry. In a previous work [5] the following Green-Kubo relations for the various components of this tensor were derived

$$D_{\alpha\beta}=\frac{1}{m^2}\int_0^\infty\langle p_\alpha(t)p_\beta(0)\rangle_\gamma dt \ , \tag{9}$$

where $\alpha,\beta=x,y,z$. The ensemble average is taken over shearing steady states, hence the subscript γ. We can operationally define this ensemble by considering some equilibrium ensemble at $t=-\infty$, being subject for all subsequent time, to thermostatted planar Couette flow [Eqs. (1) and (2)]. At $t=0$ the system is assumed to have completely relaxed to a steady state. Thus the time correlation function referred to in (9) correlates the Cartesian components of momentum at times $0,t$ long after the transients leading to the establishment of the steady state have decayed.

Note that the p_α in this equation are the peculiar momenta of (1). These relations can be integrated to give the Einstein relations for the mean-square displacement. The diagonal components become

$$\langle q_\alpha(t)^2\rangle_\gamma = 2D_{\alpha\alpha}t \ , \tag{10}$$

where

$$\mathbf{q}_i^\nu(t) \equiv \mathbf{r}_i^\nu(0) + \int_0^t ds \frac{\mathbf{p}_i^\nu(s)}{m_\nu} \tag{11}$$

is the convected Lagrangian position of particle i. (In a one-component system the species index ν can be omitted.) It is not possible to obtain separate Einstein relations for the two nonzero off-diagonal elements of the diffusion tensor [6]. It is only possible to obtain an Einstein relation for the sum of these two elements,

$$\langle q_x(t) q_y(t)\rangle_\gamma = (D_{xy}+D_{yx})t \ . \tag{12}$$

In general the self-diffusion tensor for a fluid under Couette flow is nonsymmetric. The x mass current generated by a y concentration gradient is not necessarily equal to the y current generated by an x gradient. However, it is easy to prove that by measuring the time dependence of concentrations alone, it is only possible to determine the symmetric part of the diffusion tensor [6].

An alternative route to the GK relations for the diagonal components of the SDT is to derive the above MSD's from the macroscopic convective diffusion equation [8,4,6]. One then assumes that the macroscopic and microscopic MSD's are the same and GK relations are thus recovered from the MSD's instead of the other way around. Unfortunately, it is not possible to derive any GK relations for the off-diagonal elements by this method.

One can consider subjecting a shearing steady state to a color field [Eqs. (3)–(7)]. For this purpose we again consider an equilibrium ensemble at $t=-\infty$ being subject to thermostatted shear flow for all time. At $t=0$ we assume that the system has fully relaxed to a shearing steady state. At $t=0$ we now turn on a color field and study the system as it relaxes to a steady state under the combined influences of planar Couette flow, the color field, and the thermostat. In this work we will be concerned with the situation where the shear rate is large but the color field is weak. In this case we expect a linear response to the color field. We can define a steady-state color conductivity tensor $\mathbf{C}$ with the Cartesian components α,β as

$$C_{\alpha\beta} = \lim_{t\to\infty} \frac{\langle J_{c\alpha}(t)\rangle_\gamma}{\mathcal{F}_{c\beta}} \ . \tag{13}$$

At zero strain rate $\gamma=0$ the color conductivity tensor is isotropic and in the limit of the zero-color field the conductivity is related to the self-diffusion coefficient

$$\begin{aligned} D_{\gamma=0} &= \frac{1}{\beta n} \lim_{\mathcal{F}_{c\alpha}\to 0} C_{\alpha\alpha(\gamma=0)} \\ &= \frac{1}{\beta n} \lim_{\mathcal{F}_{c\alpha}\to 0} \lim_{t\to\infty} \frac{\langle J_{c\alpha}(t)\rangle_{\gamma=0}}{\mathcal{F}_{c\alpha}} \\ &= \frac{1}{N}\int_0^\infty ds \langle J_{c\alpha}(s) J_{c\alpha}(0)\rangle_{\gamma=0} \ . \end{aligned} \tag{14}$$

$\beta=1/k_B T, k_B$ is Boltzmann's constant and T is the absolute temperature. Away from equilibrium we define T as the kinetic temperature, i.e., $T=E_k/3Nk_B$. Unfortunately, it has been proved [1] that Eq. (14) or any simple generalization is not valid when a system is subject to large strain rates. From the results in [1], one can derive the following relation:

$$\begin{aligned} \frac{1}{\beta n} \lim_{\mathcal{F}_{c\alpha}\to 0} C_{\alpha\beta(\gamma)} = \frac{1}{\beta n} \lim_{\mathcal{F}_{c\alpha}\to 0} \lim_{t\to\infty} \frac{\langle J_{c\beta}(t)\rangle_\gamma}{\mathcal{F}_{c\alpha}} &= -\lim_{t\to\infty} \frac{1}{N}\int_0^t ds \langle J_{c\alpha}(0) J_{c\beta}(-s)\rangle_\gamma \\ &\quad - \lim_{t\to\infty} \frac{1}{N}\int_0^t ds \frac{\partial}{\partial \mathcal{F}_{c\beta}} \langle J_{c\alpha}(0) P_{xy}(-s)\rangle_{\gamma_c} \Big|_{\mathcal{F}_c=0} \gamma \ . \end{aligned} \tag{15}$$

The GK integral on the first line of this equation is the equal to the self-diffusion tensor (9). The second line is the color field derivative of the steady-state time correlation function (SSTCF). The subscript γc means that the color field is turned on at time zero in a system while the shear has been acting since time minus infinity.

It is very time consuming to calculate the derivative of the SSTCF numerically, so the evaluation of the self-diffusion tensor from the color conductivity cannot compete favorably with the direct evaluation of the GK relation (9). We know of no way of reducing this term to a form suitable for easy computation. Note that the form of (15) is not only valid for color and shear fields; the color field can be any kind of vectorial field and the shear field can be replaced by any second-rank tensorial field.

C. Mutual diffusion tensor

The mutual diffusion tensor (MDT) is more complicated than the self-diffusion tensor because the MDT consists of a product of a thermodynamic factor and an integral over a time correlation function. The derivation of the GK expressions for the MDT of a shearing fluid is essentially the same as the derivation of the corresponding relation for an equilibrium fluid. It is convenient to consider an equilibrium grand canonical ensemble at $t=-\infty$, which is subject to thermostatted planar Couette flow for all subsequent time. We again assume that at $t=0$ the system has relaxed to a shearing steady state.

To begin with, it is useful to define the instantaneous number density of species ν, evaluated using Lagrangian coordinates

$$n_\nu(\mathbf{q},t)=\sum_{i=1}^{N_\nu}\delta(\mathbf{q}_i^\nu(t)-\mathbf{q}) \ . \tag{16}$$

Using the thermostatted Sllod equations of motion, the derivative with respect to time is

$$\begin{aligned}\frac{\partial n_\nu(\mathbf{q},t)}{\partial t}&=\frac{\partial}{\partial t}\sum_{i=1}^{N_\nu}\delta(\mathbf{q}_i^\nu(t)-\mathbf{q})\\&=-\nabla\cdot\sum_{i=1}^{N_\nu}\delta(\mathbf{q}_i^\nu(t)-\mathbf{q})\dot{\mathbf{q}}_i^\nu(t)\\&=-\frac{1}{m_\nu}\nabla\cdot\sum_{i=1}^{N_\nu}\delta(\mathbf{q}_i^\nu(t)-\mathbf{q})\mathbf{p}_i^\nu(t)\equiv-\frac{1}{m_\nu}\nabla\cdot\mathbf{J}_\nu \ .\end{aligned} \tag{17}$$

This is the continuity equation expressed in Lagrangian coordinates. The influence of the thermostat in this (and the following) equation(s) is subtle. The time dependence of the phase functions in this equation is generated from the *thermostatted* Sllod equations of motion. This is in spite of the fact that the thermostatting multiplier α does not appear explicitly in the equation(s). Note also that the time derivative of a function of the Lagrangian coordinates is equal to the hydrodynamic streaming derivative, i.e.,

$$\left.\frac{\partial n_\nu(\mathbf{q},t)}{\partial t}\right|_{\mathbf{q}}=\left.\frac{\partial n_\nu(\mathbf{r},t)}{\partial t}\right|_{\mathbf{r}}+\mathbf{u}\cdot\nabla n_\nu(\mathbf{r},t) \ . \tag{18}$$

In order to derive a Green-Kubo expression for the MDT of a binary mixture we have chosen work in the center-of-mass frame with the mass fraction as the concentration unit. The mass fraction of species 1 is related to the number densities

$$w_1=\frac{n_1m_1}{n_1m_1+n_2m_2}=\frac{\rho_1}{\rho_1+\rho_2} \ . \tag{19}$$

If we consider a small change of the mass fraction δw_1 we have

$$\delta w_1=w_1w_2\left[\frac{\delta n_1}{n_1}-\frac{\delta n_2}{n_2}\right] \tag{20}$$

and

$$\delta\dot w_1=w_1w_2\left[\frac{\delta\dot n_1}{n_1}-\frac{\delta\dot n_2}{n_2}\right] \ . \tag{21}$$

When the local forms of these expressions are Fourier transformed with respect to the space coordinates one obtains

$$\begin{aligned}\delta\dot w_1(\mathbf{k},t)&=w_1w_2\left[\frac{\delta\dot n_1(\mathbf{k},t)}{n_1}-\frac{\delta\dot n_2(\mathbf{k},t)}{n_2}\right]\\&=iw_1w_2\mathbf{k}\cdot\left[\frac{\mathbf{J}_1(\mathbf{k},t)}{\rho_1}-\frac{\mathbf{J}_2(\mathbf{k},t)}{\rho_2}\right]\\&=\frac{i\mathbf{k}}{\rho}\cdot\mathbf{J}_1(\mathbf{k},t) \ .\end{aligned} \tag{22}$$

Note that this relation is valid for any value of $\mathbf{k}$; it is not an approximation for small $\mathbf{k}$.

We assume a frequency- and wave-vector-dependent macroscopic constitutive relation

$$\tilde{\mathbf{J}}_1(\mathbf{k},\omega)=\rho\tilde{\mathbf{D}}_{12}(\mathbf{k},\omega)_\gamma\cdot i\mathbf{k}\delta\tilde w_1(\mathbf{k},\omega) \ , \tag{23}$$

where

$$\tilde f(\omega)=\int_0^\infty f(t)e^{i\omega t}dt \tag{24}$$

denotes the Fourier-Laplace transform with respect to time. Combining (22)–(24) leads to

$$i\omega\delta\tilde w_1(\mathbf{k},\omega)-\delta w_1(\mathbf{k},0)=-\mathbf{k}\cdot\tilde{\mathbf{D}}_{12}(\mathbf{k},\omega)_\gamma\cdot\mathbf{k}\delta\tilde w_1(\mathbf{k},\omega) \ . \tag{25}$$

We will now relate the frequency and wave-vector-dependent MDT to shearing, steady-state time correlation functions. By construction, the $t=0$ appearing in (25) refers to a time after which the initial transients that generate the shearing steady state have decayed. As mentioned above for $t\geq 0$, all averages are assumed to be stationary. Because the thermostatted Sllod equations of motion conserve particle number N_ν the *zero-wave-vector* number and composition fluctuations are a constant of the motion and retain their initial ($t=-\infty$) equilibrium grand canonical values.

Multiplication of both sides of Eq. (25) with $\delta w_1(-\mathbf{k},0)$ and averaging over our initial grand canonical ensemble gives

$$i\omega\tilde c(\mathbf{k},\omega)_\gamma-c(\mathbf{k},0)_\gamma=-\mathbf{k}\cdot\tilde{\mathbf{D}}_{12}(\mathbf{k},\omega)_\gamma\cdot\mathbf{k}\tilde c(\mathbf{k},\omega)_\gamma \ , \tag{26}$$

which can be rewritten as

$$\tilde c(\mathbf{k},\omega)_\gamma=\frac{c(\mathbf{k},0)_\gamma}{i\omega+\mathbf{k}\cdot\tilde{\mathbf{D}}_{12}(\mathbf{k},\omega)_\gamma\cdot\mathbf{k}} \ , \tag{27}$$

where $c(\mathbf{k},t)_\gamma$ is defined as

$$c(\mathbf{k},t)_\gamma=\langle\delta w_1(\mathbf{k},t)\delta w_1(-\mathbf{k},0)\rangle_\gamma \ . \tag{28}$$

As discussed above, the distribution of phases $\mathbf{\Gamma}(0)$, $N_1(0)$, and $N_2(0)$ used to perform this average is generated from an initial equilibrium grand canonical distribution of phases at $t=-\infty$, namely $\mathbf{\Gamma}(-\infty)$, $N_1(-\infty)$, and $N_2(-\infty)$. The system evolves forward in time via Eqs. (1) and (2) until $t=0$ when the averaging is performed. At $t=0$ the system is assumed to have relaxed to a time-independent thermostatted shearing steady state characterized by the fixed values of the state variables N_1,N_2,V,γ,E_K. We note that our equations of motion (1) and (2) preserve particle numbers so that $N_\nu(-\infty)=N_\nu(t)$ for all t,ν.

Defining

$$\Phi(\mathbf{k},t)_\gamma=-\ddot{c}(\mathbf{k},t)_\gamma=\langle\delta\dot{w}_1(\mathbf{k},t)\delta\dot{w}_1(-\mathbf{k},0)\rangle_\gamma$$

$$=-\frac{1}{\rho^2}\mathbf{kk}:\langle\mathbf{J}_1(\mathbf{k},t)\mathbf{J}_1(-\mathbf{k},0)\rangle_\gamma \tag{29}$$

we find

$$\tilde{\Phi}(\mathbf{k},\omega)_\gamma=i\omega[c(\mathbf{k},0)_\gamma-i\omega\tilde{c}(\mathbf{k},\omega)_\gamma] . \tag{30}$$

Eliminating $\tilde{c}(\mathbf{k},\omega)$ from (27) gives

$$\mathbf{k}\cdot\tilde{\mathbf{D}}_{12}(\mathbf{k},\omega)_\gamma\cdot\mathbf{k}=\frac{\tilde{\Phi}(\mathbf{k},\omega)_\gamma}{c(\mathbf{k},0)_\gamma-[\tilde{\Phi}(\mathbf{k},\omega)_\gamma/i\omega]} . \tag{31}$$

Using (28) and (29) the components of the zero frequency and wave-vector mutual diffusion tensor are given by

$$\begin{aligned}
D_{12\alpha\beta(\gamma)}&=\lim_{\omega\to 0}\frac{1}{\rho^2}\frac{\langle\tilde{J}_{1\alpha}(\mathbf{k}=0,\omega)J_{1\beta}(-\mathbf{k}=0,0)\rangle_\gamma}{\langle\delta w_1(\mathbf{k}=0,0)\delta w_1(-\mathbf{k}=0,0)\rangle_\gamma}\\
&=\frac{1}{\rho^2}\frac{\int_0^\infty\langle J_{1\alpha}(0,t)J_{1\beta}(0,0)\rangle_\gamma dt}{\langle\delta w_1(0,0)^2\rangle_\gamma}=\frac{V^2}{\rho^2}\frac{\int_0^\infty\langle J_{1\alpha}(t)J_{1\beta}(0)\rangle_\gamma dt}{\langle\delta w_1(0,0)^2\rangle_\gamma}\\
&=\frac{V^2}{\rho^2}\frac{\int_0^\infty\langle J_{1\alpha}(t)J_{1\beta}(0)\rangle_\gamma dt}{\langle\delta w_1(0,0)^2\rangle_{\mathrm{eq}}}=\frac{\int_0^\infty\langle J_{1\alpha}(t)J_{1\beta}(0)\rangle_\gamma dt}{\rho^2\langle\delta w_1^2\rangle_{\mathrm{eq}}}\\
&=\frac{1}{\rho^2 w_1^2 w_2^2\left\langle\left[\frac{N_1}{\langle N_1\rangle}-\frac{N_2}{\langle N_2\rangle}\right]^2\right\rangle_{\mathrm{eq}}}\int_0^\infty\langle J_\alpha(t)J_\beta(0)\rangle_\gamma dt .
\end{aligned} \tag{32}$$

We have carried out the derivation of the final form of (32) rather slowly in order to make the various steps more obvious. In the first line we simply set $\mathbf{k}$ to zero. This is possible because both the numerator and denominator are finite and nonzero at $\mathbf{k}=\mathbf{0}$. In the second line we take the $\omega=0$ value of the temporal Fourier transform and write the product zero-wave-vector mass fluxes in terms of the global currents defined in (21). In the third line we note that because the equations of motion conserve the composition, the second moment of the zero-wave-vector composition fluctuation is independent of the shear rate and can be evaluated from the generating grand canonical equilibrium ensemble. We also replace the zero-wave-vector expression for the fluctuation. Then finally the last form of the equation shows the composition fluctuations explicitly.

Alternatively the mutual diffusion coefficient can be written in terms of integrals $G_{\mu\nu}$, of *nonequilibrium* pair-correlation functions (PCF) $g_{\mu\nu}^{(2)}(\mathbf{r}_1,\mathbf{r}_2)_\gamma$ between one particle at $\mathbf{r}_1$ of species μ and another particle at $\mathbf{r}_2$ of species ν under steady thermostatted shear N,V,γ,E_K

$$G_{\mu\nu}=\int d\mathbf{r}_2[g_{\mu\nu}^{(2)}(\mathbf{r}_1,\mathbf{r}_2)_\gamma-1] . \tag{33}$$

We know that under shear $g_{\mu\nu}^{(2)}(\mathbf{r}_1,\mathbf{r}_2)_\gamma\neq g_{\mu\nu}^{(2)}(\mathbf{r}_1,\mathbf{r}_2)_{\gamma=0}$, however, from the above arguments it is clear that the integrals $G_{\mu\nu}$ are independent of γ. The mutual diffusion tensor can be written as

$$D_{12\alpha\beta(\gamma)}=\frac{V^2}{Nw_1w_2m_1m_2}\frac{\int_0^\infty\langle J_\alpha(t)J_\beta(0)\rangle_\gamma dt}{[1+n_1x_2(G_{11}+G_{22}-2G_{12})]} . \tag{34}$$

Since the $G_{\mu\nu}$ take on their equilibrium grand canonical values, the MDT can be written in terms of the composition derivative of the equilibrium chemical potentials as

$$D_{12\alpha\beta(\gamma)}=\frac{V^2}{Nm_1m_2}\left[\frac{\partial\mu_1}{\partial w_1}-\frac{\partial\mu_2}{\partial w_1}\right]_{\mathrm{eq}}\times\int_0^\infty\langle J_\alpha(t)J_\beta(0)\rangle_\gamma dt , \tag{35}$$

where μ_1 and μ_2 are the chemical potentials of the two species at equilibrium (i.e., $t=-\infty$). This expression is remarkably similar in appearance to the corresponding equilibrium expression to which it reduces when $\gamma=0$.

In our present numerical work we have not attempted to evaluate the "thermodynamic factor." Further, we assume that the grand canonical ensemble averages employed in the time correlation functions in (35) can be replaced by canonical ensemble averages carried out at the most probable composition predicted by the grand canonical ensemble.

D. Technical details

In this work we deal with a pure LJ fluid and a binary equimolar LJ mixture. In the mixture a particle of species μ interacts with another particle of species ν via the following pair potential:

$$u_{\mathrm{LJ}}=4\varepsilon_{\mu\nu}\left[\frac{\sigma_{\mu\nu}^{12}}{r^{12}}-\frac{\sigma_{\mu\nu}^{6}}{r^{6}}\right] , \tag{36}$$

where $\sigma_{\mu\nu}$ is the zero of the potential, $\varepsilon_{\mu\nu}$ is the depth of the attractive minimum, and $r=|\mathbf{q}^\mu-\mathbf{q}^\nu|$, the scalar distance between the particles. In order to decrease the computational effort, the potential has been truncated,

$$u(r)=\begin{cases} u_{\rm LJ}(r)-u_{\rm LJ}(r_c)\,, & r<r_c \\ 0, & r\geq r_c\,, \end{cases} \tag{37}$$

the parameter r_c being the cutoff radius beyond which the interaction potential is set equal to zero. The different parameters in the potential have been chosen to model an argon-krypton (denoted 1-2) mixture with $\sigma_{11}=3.405$ Å, $\sigma_{22}=3.633$ Å, $\varepsilon_{11}/k_B=119.6$ K, $\varepsilon_{22}/k_B=167.0$ K, $\sigma_{12}=(\sigma_{11}+\sigma_{22})/2$, and $\varepsilon_{12}=(\varepsilon_{11}\varepsilon_{22})^{1/2}$. The potential was truncated at $r_c=2.5\sigma_{\mu\nu}$, i.e., the cutoff radii are slightly different for the different kinds of interactions. The masses of the two different species are $m_1=39.95$ u, $m_2=83.80$ u. The LJ diameter and the mass of the argon atom, σ_{11} and m_1, have been used as length units and mass units, respectively. The time unit τ has been taken to be $\sigma_{11}(m_1/\varepsilon_{11})^{1/2}$, which is equal to about 2 ps. In the pure LJ system we used all the 1 or 1-1 parameters, i.e., those parameters that are adjusted to model pure argon. The number of particles was 256. The equations of motion of the pure triple-point LJ fluid, except at a shear rate of $1.0\tau^{-1}$, were integrated by using a fifth-order Gear corrector-predictor method with a time step of 0.004τ In all the other systems, including the pure triple-point LJ fluid at a shear rate of $1.0\tau^{-1}$, we used a fourth-order Gear predictor-corrector method with a time step of 0.002τ. The error bars have been calculated by dividing the simulation runs into four equal parts and taking the standard deviation of the subaverages.

III. RESULTS AND DISCUSSION

We have simulated two different systems, a pure LJ fluid, and an equimolar LJ mixture. The pure LJ fluid and the mixture were studied at their triple points and one low-density high (supercritical) temperature state point. The temperatures and densities are given in Table I.

One of the major aims of this work has been to estimate the difference between the SDT and the zero-color-field limit of the CCT. Therefore we have calculated these quantities for the pure triple-point LJ fluid at various shear rates. The results are summarized in Table II. All the data in these tables, except the self-diffusion coefficient of the pure triple-point LJ fluid at a shear rate of $1.0\tau^{-1}$, have been obtained by using run lengths of 800τ and the upper limits in the GK integrals for the self-diffusion coefficients, (9) has been taken to be 4.0τ. The corresponding values for the exceptional case are 4000τ and 2.0τ.

TABLE I. Systems and state points.

System	k_BT/ε_{11}	$n_1\sigma_{11}^3$
Pure LJ fluid	0.722	0.8442
	2.000	0.3000
Equimolar LJ mixture	0.965	0.7137
	2.500	0.3000

One can immediately make the following observations. The difference between the SDT and the CCT in the zero-color-field limit varies from state point to state point. For the triple-point LJ fluid the components of the CCT are ~20–25 % smaller than the corresponding SDT values. Since the calculation of the difference term is very difficult these results underline the rather pessimistic conclusion drawn in our previous paper [1] about the feasibility of an efficient NEMD algorithm for the evaluation of transport coefficients for weak vectorial fluxes in the presence of strong shear fields or other dissipative tensorial fields. At small shear rates the match of the SDT and CCT values not unexpectedly becomes better.

One can draw a number of conclusions about the dependence of the SDT and CCT upon color field and shear rates. For the triple-point LJ fluid the diagonal elements of the SDT and the CCT increase with γ until $\gamma\tau\sim1.0-1.5$. For higher shear rates they fall off again. When the color field is very high, ~3.0, the CCT decreases with the shear rate.

In Fig. 1 the various components of the SDT as a function of γ for the high-temperature low-density state point of the pure LJ fluid are displayed. The run lengths have been 4000τ and the upper limit in the GK integral has been 4.0τ. In this case the xx component of the SDT increases with the shear rate up to $\gamma\tau=0.8$, then it falls off again. The maximum of D_{xx} is only about 10% higher than the equilibrium value. The D_{yy} and the D_{zz} elements

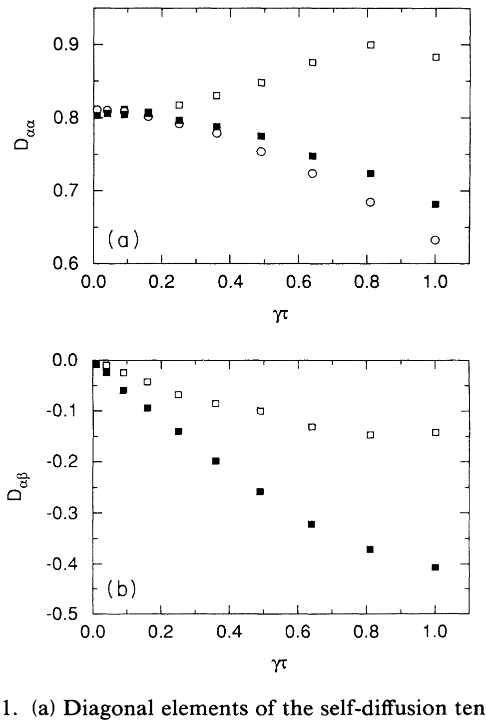

FIG. 1. (a) Diagonal elements of the self-diffusion tensor as a function of the shear rate for a pure Lennard-Jones fluid at the low-density high-temperature state point. The element D_{xx} is depicted by open squares, D_{yy} with open circles, and D_{zz} with filled squares. (b) Off-diagonal elements of the self-diffusion tensor for the same system as above. The element D_{xy} is depicted by open squares and D_{yx} by filled squares.

TABLE II. $D_{\alpha\alpha}$ and $C_{\alpha\alpha}$ values as a function of strain rate and color field for the pure Lennard-Jones liquid at its triple point. The error is ±0.002. At this state point the off-diagonal elements are less than 0.01.

Color field \ Shear rate (γ)		0.0	0.5	1.0	1.5	2.0
		Color conductivity tensor elements (computed by NEMD method)				
0.5	xx	0.032	0.042	0.047	0.048	0.046
	yy	0.032	0.041	0.045	0.046	0.038
	zz	0.032	0.038	0.039	0.039	0.035
1.0	xx	0.033	0.043	0.048	0.048	0.045
	yy	0.033	0.042	0.045	0.045	0.038
	zz	0.033	0.039	0.041	0.039	0.038
2.0	xx	0.042	0.048	0.052	0.049	0.046
	yy	0.042	0.044	0.045	0.047	0.042
	zz	0.042	0.041	0.042	0.040	0.038
3.0	xx	0.066	0.054	0.053	0.050	0.047
	yy	0.066	0.050	0.046	0.046	0.044
	zz	0.066	0.049	0.043	0.041	0.038
		Diffusion tensor elements (computed by GK method)				
0.0	xx	0.031	0.052	0.0626[a]	0.063	0.062
	yy	0.031	0.051	0.0578[a]	0.056	0.050
	zz	0.031	0.043	0.0502[a]	0.051	0.048

[a] Calculated from 1 million time steps with errors of ±0.0006.

decrease monotonically with γ, and D_{yy} is smaller than D_{zz}.

In the triple-point LJ fluid (but not in the hot dilute fluid) $D_{xx} > D_{yy} > D_{zz}$ and $C_{zz} > C_{yy} > C_{zz}$. This behavior seems to be correlated with the anisotropic kinetic-energy distribution, which is $T_x > T_y > T_z$, where

$$T_\alpha = \frac{1}{Nk_B} \sum_{i=1}^{N} \frac{p_{i\alpha}^2}{2m} . \tag{38}$$

One can see that this is the case by looking at the diagonal components of the velocity autocorrelation function (VCF) depicted in Fig. 2(a). At equilibrium the equipartition principle states that the kinetic energy of each translational degree of freedom is equal to $\frac{1}{2}k_B T$, thus $\langle v_\alpha(0) v_\alpha(0) \rangle = k_B T/m$ independently of α. However, one can see in Fig. 2(a) that $\langle v_\alpha(0) v_\alpha(0) \rangle$ is different for different α's. It is reasonable to believe that if the kinetic energy is higher in one direction, then the diffusion in that direction should be enhanced. One has to be cautious when one tries to attribute some meaning to the relative magnitudes of the diagonal elements of the SDT and the CCT because the kinetic-energy distribution is induced by the thermostat; in this case we have used a Gaussian thermostat that removes heat isotropically from the system. It is likely that other kinds of thermostats produce other kinetic-energy distributions and other relative magnitudes of the elements of the diffusion tensor.

The only off-diagonal elements that are different from zero are C_{xy} and C_{yx}. The element C_{yx} is greater than C_{xy}. This means that the current in the y direction, generated by a field in the x direction, is larger than the current in the x direction generated by a field of the same magnitude in the y direction. The off-diagonal elements are smaller roughly by an order of magnitude than the diagonal elements for the pure triple-point LJ fluid. The cross-coupling coefficients D_{xy} and D_{yx} were so close to zero that we could not calculate them for this system. However, since the correlation functions $\langle v_x(t) v_y(0) \rangle$ and $\langle v_y(t) v_x(0) \rangle$ shown in Fig. 2(b) are different, the two cross-coupling elements are not identical. Figure 1(b) shows D_{xy} and D_{yx} as a function of γ for the pure LJ fluid at the low-density and high-temperature state point. Here $|D_{xy}| < |D_{yx}|$ as previously, although they are negative. In this hot dilute system the off-diagonal contribution is substantial.

The diagonal elements of the SDT can be calculated by either GK relations (9) or by Einstein relations (10). We have calculated the mean-square displacements (11) as a function of time for the hot dilute system. The result is displayed in Fig. 3. In Table III we compare the values of the elements of the SDT obtained from the mean-square displacements with the corresponding GK values. The run length used to calculate these data was 4000τ. As one can see, the agreement is very good. Note that it is only possible to obtain the sum of the off-diagonal elements by evaluating the mean-square displacements. However, this sum agrees very well with the sum of the

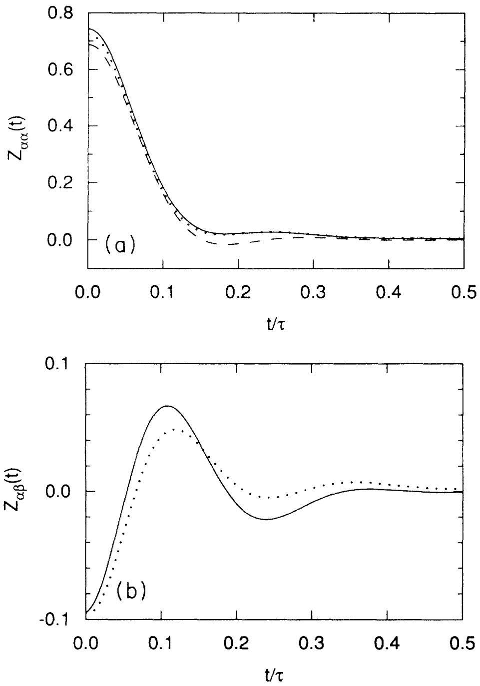

FIG. 2. (a) Diagonal velocity autocorrelation functions $Z_{\alpha\alpha}(t)=\langle v_\alpha(t)v_\alpha(0)\rangle$, $\alpha=x$ (full curve), y (dotted curve), and z (dashed curve), for the triple-point Lennard-Jones fluid at a reduced shear rate $\gamma\tau=1.0$. (b) Off-diagonal velocity autocorrelations $Z_{xy}(t)=\langle v_x(t)v_y(0)\rangle$ (full curve) and $Z_{yx}(t)=\langle v_y(t)v_x(0)\rangle$ (dotted curve) for the same system as above.

individual off-diagonal elements from the GK evaluations. These results provide a good cross check of the programming accuracy.

The variation of the SDT with the shear rate can be understood in greater detail by considering how the shear field changes the VCF's and the structure of the fluid. Firstly, we note that at equilibrium the fluid is isotropic and the atoms are surrounded by spherically symmetric coordination shells. Secondly, at high densities the VCF consists of a large positive part for short times immediately followed by a negative tail at longer times. The negative region is due to backscattering when an atom collides with its neighbors in the first coordination shell. The self-diffusion coefficient, which is equal to the time integral of the VCF, is greatly reduced by this backscattering.

TABLE III. Green-Kubo vs mean-square displacements.

	Green-Kubo	Mean-square displacement
D_{xx}	0.883±0.009	0.894±0.008
D_{yy}	0.632±0.003	0.628±0.007
D_{zz}	0.681±0.0005	0.681±0.006
D_{xy}	− 0.142±0.005	
D_{yx}	− 0.407±0.004	
$D_{xy}+D_{yx}$		−0.56±0.01

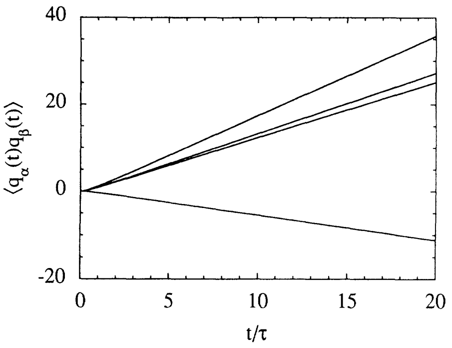

FIG. 3. Various components of the mean-square-displacement tensor as a function of the shear rate for a pure Lennard-Jones fluid at the low-density high-temperature state point and a reduced shear rate $\gamma\tau=1.0$. From top to bottom, $\langle[q_x(t)]^2\rangle$, $\langle[q_z(t)]^2\rangle$ $\langle[q_y(t)]^2\rangle$, and $\langle q_x(t)q_y(t)\rangle$ as functions of time.

All this changes when the fluid is subjected to a shear field. The nearest-neighbor coordination shell becomes ellipsoidal rather than spherical. This decreases the backscattering, so the negative part of the VCF's is greatly reduced. This can be seen in Fig. 2(a), where the diagonal elements of the VCF are displayed. The net effect is that the magnitude of the diagonal elements of the SDT increases. This effect is important at high densities. At lower densities there is no negative part of the equilibrium VCF, so the change of the SDT with shear is more moderate.

Another effect that becomes important as the shear rate increases is due to the high pressure. This causes the VCF to decay faster and thus the GK integral and the SDT decrease. Eventually this effect will dominate over the reduced backscattering, so there will be a maximum of the SDT as a function of the shear rate. The mechanism is likely to cause the decrease of the yy and zz components of the SDT of the hot dilute LJ fluid. In Fig. 4, where the VCFs of this system are displayed, one can see that the yy and zz VCF's decay faster than the xx VCF. The equilibrium VCF, which has not been displayed, is located between the xx and the yy VCF.

Although in this paper we do not calculate the thermodynamic factor, we note that because it is the same for every element in the mutual diffusion tensor, the calcula-

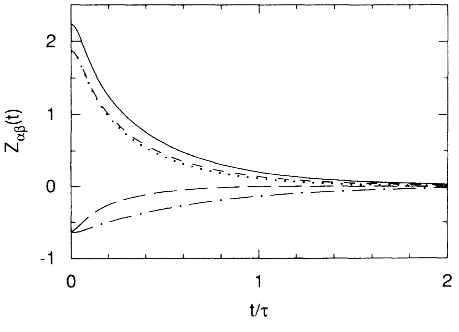

FIG. 4. Velocity autocorrelation functions $Z_{\alpha\beta}(t)=\langle v_\alpha(t)v_\beta(0)\rangle$, $\alpha,\beta=x,x$ (full curve), y,y (dotted curve), z,z (short-dashed curve), x,y (long-dashed curve) and y,x (dot-dashed curve), for the low-density high-temperature pure Lennard-Jones fluid at a reduced shear rate $\gamma\tau=1.0$.

TABLE IV. Mutual diffusion tensors.

$\gamma\tau$	0.0	1.0	0.0	1.0
k_BT/ε_{11}	2.5	2.5	0.965	0.965
$n_1\sigma_{11}^3$	0.3	0.3	0.7137	0.7137
L_{xx}	0.10	0.11	0.016	0.024
L_{yy}	0.10	0.09	0.016	0.023
L_{zz}	0.10	0.08	0.016	0.019
L_{xy}	0.00	−0.01	0.000	
L_{yx}	0.00	−0.05	0.000	

tion of the GK integral yields information about the relative magnitudes of the various components and the symmetry of the diffusion tensor. Also, because the LJ mixture is a very nearly ideal mixture, the thermodynamic factor can be expected to be fairly close to unity.

The values of the integrals of the mass current autocorrelation functions

$$L_{\alpha\beta}=\int_0^\infty \langle J_{1\alpha}(t)J_{1\beta}(0)\rangle dt \tag{39}$$

of the triple-point mixture and the hot dilute mixture are displayed in Table IV. The run lengths have been 16 000τ and the upper limit in the GK integral above has been 6.0τ at the triple point and 4.0τ in the low-density high-temperature system. The error is about ±1 in the last digit given in the table. The increase of the diffusion coefficients for this triple-point mixture at $\gamma\tau=1.0$ compared to equilibrium value is quite modest, only about 50% for the xx and yy components and even less for the zz component. The shear-induced shift of the various diffusion coefficients of the hot dilute mixture follow the same pattern as the self-diffusion coefficients of the pure LJ fluid. The xx component increases slightly and the yy and zz components decrease with the shear rate. The xy and yx elements are negative and different so the MDT is nonsymmetric at this state point. We also have $|L_{xy}|<|L_{yx}|$, which is similar to the behavior of the self-diffusion coefficients.

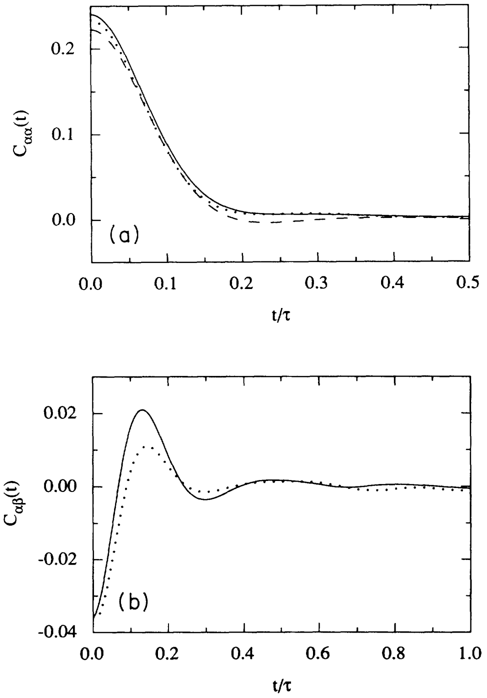

FIG. 5. (a) Diagonal mass current autocorrelation functions $C_{\alpha\alpha}(t)=V\langle J_{1\alpha}(t)J_{1\alpha}(0)\rangle/k_B$, $\alpha=x$ (full curve), y (dotted curve), and z (dashed curve), for the triple-point Lennard-Jones mixture at a reduced shear rate $\gamma\tau=1.0$. (b) Off-diagonal mass current autocorrelation functions $C_{xy}(t)=V\langle J_{1x}(t)J_{1y}(0)\rangle/k_B$ (full curve) and $C_{yx}(t)=V\langle J_{1y}(t)J_{1x}(0)\rangle/k_B$ (dotted curve) for the same system as above.

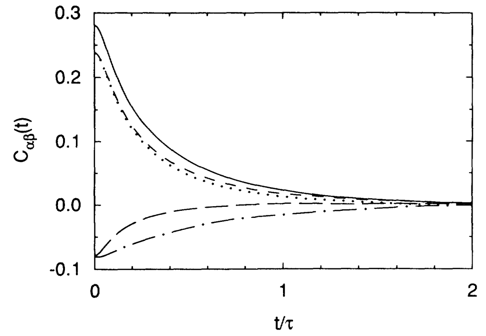

FIG. 6. Mass current autocorrelation functions $C_{\alpha\beta}(t)=V\langle J_{1\alpha}(t)J_{1\beta}(0)\rangle/k_B$, $\alpha,\beta=x,x$ (full curve), y,y (dotted curve), z,z (short-dashed curve), x,y (long-dashed curve) and y,x (dot-dashed curve), for the low-density high-temperature pure Lennard-Jones fluid mixture at a reduced shear rate $\gamma\tau=1.0$.

The diagonal mass current correlation functions $\langle J_{1\alpha}(t)J_{1\alpha}(0)\rangle$ of the triple-point LJ mixture at $\gamma\tau=1.0$ are displayed in Fig. 5(a). They are very similar to the velocity autocorrelation function of the pure LJ fluid at the same shear rate. This is not unexpected because when the two species become equal the mutual diffusion coefficient is the same as the self-diffusion coefficient. The off-diagonal correlation functions $\langle J_{1\alpha}(t)J_{1\beta}(0)\rangle$ are depicted in Fig. 5(b). It is impossible to determine the sign of the time integral of these functions, so one can conclude that the MDT is almost diagonal at the triple point.

Finally, in Fig. 6 we show the mass current correlation functions of the hot dilute mixture at $\gamma\tau=1.0$. These correlation functions are also very similar to those of the pure LJ fluid. The explanation for the behavior of the different momentum current correlation functions is basically the same as the discussion above on the VCF's.

IV. CONCLUSION

We have derived a Green-Kubo relation for the mutual diffusion tensor of fluid mixtures subject to strong Couette shear fields when Curie's principle and local thermodynamic equilibrium have broken down. At first sight this derivation might seem to be rather difficult. In the absence of shear the familiar GK relation for mutual diffusion consists of a product of a thermodynamic factor and a nonequilibrium time correlation integral. Under strong shear, however, when the local thermodynamic equilibrium approximation has broken down, the thermodynamic factor has in fact no known thermodynamic meaning. Instead this term is expressed as a sum of integrals of steady-state equal-time pair-correlation functions. In our theory there is in fact no *need* to attach thermodynamic meaning to this term. Furthermore if the nonequilibrium shearing steady state was generated from an initial grand canonical distribution by advancing time using equations of motion that conserve the molar composition of the mixture, the thermodynamic factor must also be a constant of the motion. Our GK relation reduces to the familiar expression for the mutual diffusion coefficient when the applied shear rate goes to zero.

In the vicinity of phase boundaries we expect that the wave-vector dependence of both the MDT and the thermodynamic factor may become quite complex. In such circumstances our use of zero-wave-vector information may not be relevant to the discussion of experimental results for coexistence regions exhibiting complex long-wavelength structures.

We verified that the zero-field color conductivity does not equal the SDT. The immediate consequence of this is that a useful synthetic NEMD algorithm for efficiently computing the diffusion tensor of shearing fluids does not exist.

We have also examined the behavior of the SDT, the MDT, and different velocity and mass current autocorrelation functions as functions of the shear field. We found that at the triple point, the diagonal elements of the SDT of the pure fluid and the MDT of the mixture increased with the shear rate. The off-diagonal elements were negligible. The increase of the diagonal elements can be attributed to the diminished possibility of backscattering at high shear rates.

At lower densities the behavior is somewhat different. The *xx* element of the SDT increases to a maximum that is about 20% higher than the equilibrium value, then it decreases again. The *yy* and the *zz* components decrease with the shear rate. The off-diagonal elements of the SDT are negative and their magnitude increases with shear rate. Even in this case the qualitative behavior of the SDT of the pure fluid and the MDT is very similar. The reason for this is that when the two species of the mixture become identical the MDT and the SDT are the same. In our LJ mixture the potential parameters have been adjusted to model an argon-krypton mixture, which means that the two components of the mixture are fairly similar.

Finally, we note that to observe large effects of the diffusion tensor (i.e., a factor of 2 change from equilibrium close to the triple point), the applied shear rate must be of the order of unity in reduced units. This means that for the inert gas fluids, the effect of shear on the diffusion coefficient for even the highest shear rates achievable in the laboratory is minute. In order to see in the laboratory the effects revealed in our computer simulations, one should look at fluids that are observed to be non-Newtonian, since by definition, reduced shear rates of unity are easily observable for these fluids.

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*Permanent address: Laboratory of Theoretical Chemistry, Eötvös University, Budapest, Múzeum krt 6-8., Hungary.

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