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Shear-induced distortion of intramolecular and intermolecular correlations in liquids: Time-dependent density-functional theory

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Shear viscosity of molecular liquids is formulated and calculated with use of a time-dependent density-functional theory. Allowing for nonrigidity of each molecule, we obtain shear-induced distortion of both intramolecular and intermolecular correlations self-consistently, which makes it possible to calculate the shear viscosity. As a by-product we derive and solve a hypernetted-chain closure for equilibrium correlations in deformable molecular liquids. [S1063-651X(96)09007-1]

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I. INTRODUCTION

The density-functional theory (DFT) of nonuniform fluids plays an important role in classical many-body theory [1]. The theory has been employed in quantitative studies on liquid-solid transformations [2], interfacial and nucleation phenomena, and nonperiodic crystals, among others [2–4]. The versatile and successful use of the DFT may be ascribed to its significant computational simplicity and physical clarity.

Motivated by the general applicability and usefulness of the DFT, one of us developed a time-dependent DFT, which could shed some light on dynamic aspects of the various processes mentioned above [5]. As an application of the dynamic version of the DFT, we recently studied the shear viscosity of simple liquids by calculating the shear-induced distortion of two-body correlations [6], which may be represented by the radial distribution function $g(r)$ in the case of an equilibrium situation. By comparing our results with the nonequilibrium molecular dynamics by Ashurst and Hoover [7], we concluded that at least in the equilibrium (e.g., nonsupercooled) liquid state, our theory reproduces both distortion and shear viscosity fairly well [6].

In this paper we consider the viscosity of molecular liquids based on the time-dependent DFT [5] and the general density-functional formulation of molecular liquids by Chandler, McCoy, and Singer [8] with the molecular liquid itself described within the framework of the interaction site model (ISM) [9]. Since we are interested not only in the distortion of the intermolecular correlations but also in the shear-induced deformation of a molecule itself, we consider liquids composed of nonrigid molecules. This in turn compels us to treat inter- and intramolecular correlations in a self-consistent way. Although our main concern is centered around a nonequilibrium (under shear) situation, we must first consider the equilibrium (without shear) situation, since we need the equilibrium correlations as input data in our theory [6], and for the purpose we propose and solve an alternative hypernetted-chain (HNC) closure.

The remainder of this paper is outlined as follows. In Sec. II we present some definitions of various correlation functions within the framework of the ISM [9]. We study equilibrium correlations based on the DFT with the aid of an idea due to Percus [10] (which is called the Percus trick) and derive a set of integral equations. Section III deals with a shear flow based on the time-dependent DFT and the shear viscosity is expressed in terms of the distortion of the intermolecular correlations. In Sec. IV we give our numerical results and Sec. V contains some remarks and a summary.

II. EQUILIBRIUM STRUCTURES OF MOLECULAR LIQUIDS

In this section we consider equilibrium structures of molecular liquids based on the ISM [9] and the DFT [1,8].

A. Correlation functions

To be concrete we consider a one-component molecular liquid and employ the standard notation of the ISM [8,9]. The density of the site α at position $\mathbf{r}$ is defined to be

$$n_\alpha(\mathbf{r}) \equiv \sum_{i=1}^{N} \delta(\mathbf{r}-\mathbf{r}_{i,\alpha}), \qquad (1)$$

where N is the total number of the molecules and $\mathbf{r}_{i,\alpha}$ denotes the position of the site α of the ith molecule. We introduce the equilibrium intra- and intermolecular correlations $\omega_{\alpha\beta}(\mathbf{r},\mathbf{r}')$ and $h_{\alpha\beta}(\mathbf{r},\mathbf{r}')$, respectively, by

$$\begin{aligned}\chi_{\alpha\beta}(\mathbf{r},\mathbf{r}') &\equiv \langle [n_\alpha(\mathbf{r})-\langle n_\alpha(\mathbf{r})\rangle][n_\beta(\mathbf{r})-\langle n_\beta(\mathbf{r})\rangle]\rangle \\ &= n\,\omega_{\alpha\beta}(\mathbf{r},\mathbf{r}')+n^2 h_{\alpha\beta}(\mathbf{r},\mathbf{r}'),\end{aligned} \qquad (2)$$

where $n=N/V$, with V the volume of the system. The intramolecular correlation $\omega_{\alpha\beta}(\mathbf{r},\mathbf{r}')$ gives the probability density of finding a site β of a molecule at $\mathbf{r}'$ when a site α of the same molecule is at $\mathbf{r}$, thus satisfying the condition

$$\omega_{\alpha\alpha}(\mathbf{r},\mathbf{r}')=\delta(\mathbf{r}-\mathbf{r}'), \qquad \int d\mathbf{r}'\,\omega_{\alpha\beta}(\mathbf{r},\mathbf{r}')=1. \qquad (3)$$

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The Ornstein-Zernike (OZ) relation for monatomic liquids is generalized within the ISM as

$$\omega^{-1}=I-nc^{(0)}, \quad \chi^{-1}=(n\omega)^{-1}-c \tag{4}$$

or, more explicitly,

$$\sum_{\gamma}\int d\mathbf{r}'[\delta_{\alpha\gamma}\delta(\mathbf{r}-\mathbf{r}')-nc^{(0)}_{\alpha\gamma}(\mathbf{r},\mathbf{r}')]\omega_{\gamma\beta}(\mathbf{r}',\mathbf{r}'')=\delta_{\alpha\beta}\delta(\mathbf{r}-\mathbf{r}''), \tag{5}$$

$$h_{\alpha\beta}(\mathbf{r},\mathbf{r}''')=\sum_{\gamma\delta}\int d\mathbf{r}'\int d\mathbf{r}''\omega_{\alpha\gamma}(\mathbf{r},\mathbf{r}')c_{\gamma\delta}(\mathbf{r}',\mathbf{r}'')\times[\omega_{\delta\beta}(\mathbf{r}'',\mathbf{r}''')+nh_{\delta\beta}(\mathbf{r}'',\mathbf{r}''')]. \tag{6}$$

We will call Eqs. (4)–(6) the ISM OZ relations. It is noted that for liquids every two-body correlation, say, $h_{\alpha\beta}(\mathbf{r},\mathbf{r}')$, depends on only $|\mathbf{r}-\mathbf{r}'|$. Thus, hereafter we will use a convolution notation $*$, with which Eq. (6) is expressed as

$$h_{\alpha\beta}=\sum_{\gamma,\delta}\omega_{\alpha\gamma}*c_{\gamma\delta}*[\omega_{\delta\beta}+nh_{\delta\beta}]. \tag{6$'$}$$

B. Free-energy density-functional for molecular liquids

We assume that each molecule consists of S sites and to our system, as described in the preceding subsection, we add one molecule $(i=0)$, which is the same as other molecules and will be called the blue molecule. To apply the Percus trick [10], which is expressed by Eqs. (13) and (14) below, we suppose that the site α_0 of the blue molecule is held fixed at the origin of our coordinate system.

We now consider the free-energy functional $F[n(\mathbf{r}),n^{(0)}(\mathbf{r})]$, with $n^{(0)}(\mathbf{r})$ denoting the microscopic density of the blue molecule, of our system, which is expressed as the sum of three contributions

$$F=F_N+F_0+F_{\text{int}} \tag{7}$$

where $F_N(F_0)$ is the free energy of the system composed of N molecules (the blue molecule) and F_{int} denotes the interaction between the blue molecule and the surrounding molecules. With the aid of the DFT for polyatomic liquids by Chandler McCoy, and Singer [8], and corresponding to our previous choice of the free-energy density-functional theory for simple liquids [6], we take, as F_N,

$$F_N/(k_BT)=\sum_{\alpha}\int d\mathbf{r}\; n_\alpha(\mathbf{r})[\ln n_\alpha(\mathbf{r})\Lambda_\alpha^3-1]-\tfrac{1}{2}\sum_{\alpha,\gamma}\int d\mathbf{r}\int d\mathbf{r}'\,\delta n_\alpha(\mathbf{r})\overline{c_{\alpha\gamma}}(\mathbf{r},\mathbf{r}')\,\delta n_\gamma(\mathbf{r}'), \tag{8}$$

where $\overline{c_{\alpha\gamma}}(\mathbf{r},\mathbf{r}')=c_{\alpha\gamma}(\mathbf{r},\mathbf{r}')+c^{(0)}_{\alpha\gamma}(\mathbf{r},\mathbf{r}')$, $\delta n_\alpha(\mathbf{r})=n_\alpha(\mathbf{r})-n$, and Λ_α is the thermal wavelength for the site species α. As noted in [8(a)], F_N [Eq. (8)] produces the extended reference interaction site model (RISM) theory [11] for equilibrium two-body correlations. $-k_BTc_{\alpha\gamma}(\mathbf{r},\mathbf{r}')$ and $-k_BTc^{(0)}_{\alpha\gamma}(\mathbf{r},\mathbf{r}')$ represent the effective inter- and intramolecular interaction between the site α and the site γ, respectively. In writing down F_0 and F_{int} we note that the site α_0 of the blue molecule interacts with another site α of the blue (or the surrounding) molecule through the true site-site potential $\phi^a_{\alpha\alpha_0}(r)$ [or $\phi^e_{\alpha\alpha_0}(r)$]. From this it follows that

$$\begin{aligned}F_0/(k_BT)={}&\sum_{\alpha\ (\neq\alpha_0)}\int d\mathbf{r}\; n^{(0)}_\alpha(\mathbf{r})[\ln n^{(0)}_\alpha(\mathbf{r})\Lambda_\alpha^3-1]\\&-\tfrac{1}{2}\sum_{\alpha\ (\neq\alpha_0),\gamma\ (\neq\alpha_0)}\int d\mathbf{r}\int d\mathbf{r}'n^{(0)}_\alpha(\mathbf{r})c^{(0)}_{\alpha\gamma}\\&\times(\mathbf{r},\mathbf{r}')n^{(0)}_\gamma(\mathbf{r}')\\&+\sum_{\alpha\ (\neq\alpha_0)}\int d\mathbf{r}[\phi^a_{\alpha_0\alpha}(r)/(k_BT)]n^{(0)}_\alpha(\mathbf{r}),\end{aligned} \tag{9}$$

$$\begin{aligned}F_{\text{int}}/k_BT={}&-\sum_{\alpha\ (\neq\alpha_0),\gamma}\int d\mathbf{r}\int d\mathbf{r}'n^{(0)}_\alpha(\mathbf{r})c_{\alpha\gamma}(\mathbf{r},\mathbf{r}')n_\gamma(\mathbf{r}')\\&+\sum_{\gamma}\int d\mathbf{r}[\phi^e_{\alpha_0\gamma}(r)/(k_BT)]n_\gamma(\mathbf{r}),\end{aligned} \tag{10}$$

where $n^{(0)}_\alpha(\mathbf{r})$ $(\alpha\neq\alpha_0)$ denotes the density of the site α of the blue molecule.

C. Closure equation for equilibrium correlations

Equilibrium density fields $n_{\alpha,\text{eq}}(\mathbf{r})$ for all α and $n^{(0)}_{\alpha,\text{eq}}(\mathbf{r})$ $(\alpha\neq\alpha_0)$ are determined as the solution to the variational equations

$$\delta F/\delta n_\alpha(\mathbf{r})=\mu_\alpha, \tag{11}$$

$$\delta F/\delta n^{(0)}_\alpha(\mathbf{r})=\mu^{(0)}_\alpha \quad (\alpha\neq\alpha_0). \tag{12}$$

The Percus trick [10] links the two-body equilibrium correlations, say $g_{\alpha\alpha_0}(r)$, to the one-body distribution $n_{\alpha,\text{eq}}(\mathbf{r})$ in the presence of a particle (of species α_0) fixed at the origin. From this we have

$$ng_{\alpha\alpha_0}(r)\equiv nh_{\alpha\alpha_0}+1=n_{\alpha,\text{eq}}(\mathbf{r}), \tag{13}$$

$$\omega_{\alpha\alpha_0}(r)=n^{(0)}_{\alpha,\text{eq}}(\mathbf{r}), \tag{14}$$

where we note that the equilibrium densities $n_{\alpha,\text{eq}}(\mathbf{r})$ and $n^{(0)}_{\alpha,\text{eq}}(\mathbf{r})$ $(\alpha\neq\alpha_0)$ depend on only r from the isotropy of the system around a fixed site α_0. The chemical potentials μ_α and $\mu^{(0)}_\alpha$ are determined from the boundary conditions $g_{\alpha,\text{eq}}(r)\to 1$ as $r\to\infty$ and the normalization, the second equation of (3). From Eqs. (11)–(14) we have

$$\ln g_{\alpha\alpha_0}(r)=\sum_{\gamma}\overline{c_{\alpha\gamma}}*nh_{\gamma\alpha_0}+c_{\alpha\gamma}*\omega_{\gamma\alpha_0}[1-\delta_{\gamma\alpha_0}]-\beta\phi^e_{\alpha\alpha_0}(r), \tag{15}$$

$$\ln\omega_{\alpha\alpha_0}(r)=\sum_{\gamma}c_{\alpha\gamma}*nh_{\gamma\alpha_0}+c^{(0)}_{\alpha\gamma}*\omega_{\gamma\alpha_0}[1-\delta_{\gamma\alpha_0}]-\beta\phi^a_{\alpha\alpha_0}(r)+C, \tag{16}$$

where the constant C is determined from the normalization Eq. (3).

If $c_{\alpha\beta}$ and $c^{(0)}_{\alpha\beta}$ are regarded as known functions, Eqs. (15) and (16) are solved for $g_{\alpha\beta}=h_{\alpha\beta}+1$ and $\omega_{\alpha\beta}$. Inserting these results into the ISM OZ relation, we obtain a closed equation for the direct correlation matrices c and $c^{(0)}$. We give here some comments on our closure (15) and (16). With use of the ISM OZ relation, it is not difficult to derive from Eq. (15) the HNC equation [12]

$$g_{\alpha\beta}\equiv 1+h_{\alpha\beta}=\exp[-\beta\phi^{e}_{\alpha\beta}+h_{\alpha\beta}-c_{\alpha\beta}]. \tag{17}$$

Equation (16), which represents a different closure, can be interpreted as follows. The right-hand side of Eq. (16) divided by $-\beta$, which denotes the effective potential on the site α of the blue molecule, consists of the intramolecular contribution $-\beta\Sigma_{\gamma}c^{(0)}_{\alpha\gamma}*\omega_{\gamma\alpha_0}[1-\delta_{\gamma\alpha_0}]+\phi^{a}_{\alpha\alpha_0}(r)$ and the intermolecular one $-\beta\Sigma_{\gamma}c_{\alpha\gamma}*nh_{\gamma\alpha_0}$. The former is concerned with binding and the thermal expansion of each molecule and the latter with packing or solvent effects. The interesting interplay of these two contributions in high-density liquids is planned to be discussed elsewhere [13], where we will investigate isomerization phenomena.

III. TIME-DEPENDENT DFT AND SHEAR VISCOSITY

In this section we consider a stationary shear flow and calculate the stationary density profiles $n_{\alpha,\mathrm{st}}(\mathbf{r})$ and $n^{(0)}_{\alpha,\mathrm{st}}(\mathbf{r})$ around an arbitrary site α_0, which is considered to be at an origin in our (moving) coordinate system, of the arbitrarily chosen blue molecule. If there were no shear flow, $n_{\alpha,\mathrm{st}}(\mathbf{r})$ and $n^{(0)}_{\alpha,\mathrm{st}}(\mathbf{r})$ would be just the equilibrium density profiles $n_{\alpha,\mathrm{eq}}(\mathbf{r})$ and $n^{(0)}_{\alpha,\mathrm{eq}}(\mathbf{r})$ studied in the preceding section. As stated in [6], the stationary shear flow distorts the equilibrium density profiles and produces a shear stress in which we are interested [14,7].

The velocity field $\mathbf{u}(\mathbf{r})=\gamma y\mathbf{e}_x$ is characterized by the rate of strain γ and $\mathbf{e}_x$ denotes the unit vector in the x direction. Following the general prescription [5], we write down the nonlinear diffusion equation for $n_{\alpha}(\mathbf{r},t)$ and $n^{(0)}_{\alpha}(\mathbf{r},t)$ $(\alpha\neq\alpha^{(0)})$ as

$$\begin{aligned}\partial n_{\alpha}(\mathbf{r},t)/\partial t&=\boldsymbol{\nabla}\cdot[\{D_{\alpha,b}n_{\alpha}(\mathbf{r},t)\boldsymbol{\nabla}\delta F/\delta n_{\alpha}(\mathbf{r},t)\}\\&\quad-n_{\alpha}(\mathbf{r},t)\mathbf{u}(\mathbf{r})]\\&=-\boldsymbol{\nabla}\cdot\mathbf{J}_{\alpha}(\mathbf{r},t),\end{aligned} \tag{18}$$

$$\begin{aligned}\partial n^{(0)}_{\alpha}(\mathbf{r},t)/\partial t&=\boldsymbol{\nabla}\cdot[\{D_{\alpha,b}n^{(0)}_{\alpha}(\mathbf{r},t)\boldsymbol{\nabla}\delta F/\delta n^{(0)}_{\alpha}(\mathbf{r},t)\}\\&\quad-n^{(0)}_{\alpha}(\mathbf{r},t)\mathbf{u}(\mathbf{r})]\\&=-\boldsymbol{\nabla}\cdot\mathbf{J}^{(0)}_{\alpha}(\mathbf{r},t),\end{aligned} \tag{19}$$

where the free energy F is given by Eq. (7) and $D_{\alpha,b}$ is the bare diffusion constant of the site α. Here we have assumed that the bare diffusion constants for inter- and intramolecular diffusion are the same and will omit the subscript b hereafter for the sake of notational simplicity. The fluxes $\mathbf{J}_{\alpha}(\mathbf{r},t)$ and $\mathbf{J}^{(0)}_{\alpha}(\mathbf{r},t)$ are given explicitly after some algebra as

$$\begin{aligned}\mathbf{J}_{\alpha}(\mathbf{r},t)&=-D_{\alpha}\boldsymbol{\nabla}n_{\alpha}+D_{\alpha}n_{\alpha}\boldsymbol{\nabla}\Bigg(\sum_{\gamma}\overline{c_{\alpha\gamma}}*n_{\gamma}\\&\quad+\sum_{\gamma\ (\neq\alpha_0)}c_{\alpha\gamma}*n^{(0)}_{\gamma}-\beta\phi^{e}_{\alpha\alpha_0}\Bigg)+n_{\alpha}\mathbf{u},\end{aligned} \tag{20}$$

$$\begin{aligned}\mathbf{J}^{(0)}_{\alpha}(\mathbf{r},t)&=-D_{\alpha}\boldsymbol{\nabla}n^{(0)}_{\alpha}+D_{\alpha}n^{(0)}_{\alpha}\boldsymbol{\nabla}\Bigg(\sum_{\gamma\ (\neq\alpha_0)}c^{(0)}_{\alpha\gamma}*n^{(0)}_{\gamma}\\&\quad+\sum_{\gamma}c_{\alpha\gamma}*n_{\gamma}-\beta\phi^{a}_{\alpha\alpha_0}\Bigg)+n^{(0)}_{\alpha}\mathbf{u},\end{aligned} \tag{21}$$

where the last terms on the right-hand sides of Eqs. (20) and (21) represent the fluxes due to the shear flow.

We consider first the case of no shear flow $\gamma=0$. The stationary state is nothing but an equilibrium one and the condition of no fluxes $\mathbf{J}_{\alpha}=\mathbf{J}^{(0)}_{\alpha}=\mathbf{0}$ is equivalent to the variational equations (11) and (12), whose solutions are given by $n_{\alpha,\mathrm{eq}}(\mathbf{r})$ and $n^{(0)}_{\alpha,\mathrm{eq}}(\mathbf{r})$ [see Eqs. (13) and (14)].

We turn now to the distortions produced by the shear flow. Assuming that the rate of strain γ is small, let us express the stationary density profiles as

$$n_{\alpha,\mathrm{st}}(\mathbf{r})=ng_{\alpha\alpha_0}(r)[1+\gamma p_{\alpha}(\mathbf{r})/D_{\alpha}+o(\gamma)], \tag{22}$$

$$n^{(0)}_{\alpha,\mathrm{st}}(\mathbf{r})=\omega_{\alpha\alpha_0}(r)[1+\gamma q_{\alpha}(\mathbf{r})/D_{\alpha}+o(\gamma)], \tag{23}$$

where $p_{\alpha}(\mathbf{r})$ and $q_{\alpha}(\mathbf{r})$ denote the distortions of inter- and intramolecular correlations, respectively, and $o(\gamma)/\gamma\to 0$ as $\gamma\to 0$. From $\boldsymbol{\nabla}\cdot\mathbf{J}=\boldsymbol{\nabla}\cdot\mathbf{J}^{(0)}=0$ we obtain, after straightforward but tedious calculations, the following integro-differential equations for p_{α} and q_{α}:

$$\begin{aligned}&\boldsymbol{\nabla}\cdot[g_{\alpha\alpha_0}\boldsymbol{\nabla}p_{\alpha}]-\boldsymbol{\nabla}\cdot\Bigg[g_{\alpha\alpha_0}\boldsymbol{\nabla}\Bigg(\sum_{\gamma}\overline{c_{\alpha\gamma}}*ng_{\gamma\alpha_0}p_{\gamma}\\&\quad+\sum_{\gamma\ (\neq\alpha_0)}c_{\alpha\gamma}*\omega_{\gamma\alpha_0}q_{\gamma}\Bigg)\Bigg]=y\mathbf{e}_x\cdot\boldsymbol{\nabla}g_{\alpha\alpha_0},\end{aligned} \tag{24}$$

$$\begin{aligned}&\boldsymbol{\nabla}\cdot[\omega_{\alpha\alpha_0}\boldsymbol{\nabla}q_{\alpha}]-\boldsymbol{\nabla}\cdot\Bigg[\omega_{\alpha\alpha_0}\boldsymbol{\nabla}\Bigg(\sum_{\gamma}c_{\alpha\gamma}*ng_{\gamma\alpha_0}p_{\gamma}\\&\quad+\sum_{\gamma\ (\neq\alpha_0)}c^{(0)}_{\alpha\gamma}*\omega_{\gamma\alpha_0}q_{\gamma}\Bigg)\Bigg]=y\mathbf{e}_x\cdot\boldsymbol{\nabla}\omega_{\alpha\alpha_0}\quad(\alpha\neq\alpha_0).\end{aligned} \tag{25}$$

Here we comment on our notation. In order to avoid excessive subscripts we have written $n_{\alpha,\mathrm{st}}(\mathbf{r})$ or $p_{\alpha}(\mathbf{r})$ in Eq. (22) instead of more precise expressions $n_{\alpha,\mathrm{st}}(\mathbf{r}|\alpha_0)$ or $p_{\alpha}(\mathbf{r}|\alpha_0)$. The latter makes us aware of the situation that the site of species α_0 of the blue molecule is held fixed at the origin of the (moving) coordinate. We will keep the notation in Eqs. (22) and (23) for a while, but in our expression for the shear viscosity [Eq. (34)] we employ the latter notation to avoid confusion.

From the special form of the inhomogeneous terms on the right-hand side of Eqs. (24) and (25), we readily see that the distortions $p_{\alpha}(\mathbf{r})$ and $q_{\alpha}(\mathbf{r})$ can be expressed as

$$p_{\alpha}(\mathbf{r})=xya_{\alpha}(r),\quad q_{\alpha}(\mathbf{r})=xyb_{\alpha}(r), \tag{26}$$

with a_α and b_α depending on only the magnitude of $\mathbf{r}$,r. Following procedures similar to those described in [6], we can transform Eqs. (24) and (25) to

$$\begin{aligned}(r^2a_\alpha)''&+(2/r+g'_{\alpha\alpha_0}/g_{\alpha\alpha_0})[r^2a_\alpha]'-6a_\alpha\\&-\left(\sum_{\gamma}(D_\alpha/D_\gamma)n\mathcal{P}[A_{\alpha\gamma}]+(g'_{\alpha\alpha_0}/g_{\alpha\alpha_0})(\mathcal{P}[\overline{A_{\alpha\gamma}}])'\right.\\&\left.+\sum_{\gamma\ (\neq\alpha_0)}(D_\alpha/D_\gamma)\mathcal{P}[B_{\alpha\gamma}]+(g'_{\alpha\alpha_0}/g_{\alpha\alpha_0})(\mathcal{P}[\overline{B_{\alpha\gamma}}])'\right)\\&=\gamma g'_{\alpha\alpha_0}/g_{\alpha\alpha_0},\end{aligned}\qquad(27)$$

$$\begin{aligned}(r^2b_\alpha)''&+(2/r+\omega'_{\alpha\alpha_0}/\omega_{\alpha\alpha_0})[r^2b_\alpha]'\\&-6b_\alpha\left(\sum_{\gamma}(D_\alpha/D_\gamma)n\mathcal{P}[F_{\alpha\gamma}]+(\omega'_{\alpha\alpha_0}/\omega_{\alpha\alpha_0})\right.\\&\times(\mathcal{P}[\overline{F_{\alpha\gamma}}])'+\sum_{\gamma\ (\neq\alpha_0)}(D_\alpha/D_\gamma)\mathcal{P}[E_{\alpha\gamma}]\\&\left.+(\omega'_{\alpha\alpha_0}/\omega_{\alpha\alpha_0})(\mathcal{P}[\overline{E_{\alpha\gamma}}])'\right)=\gamma\omega'_{\alpha\alpha_0}/\omega_{\alpha\alpha_0},\end{aligned}\qquad(28)$$

where f' denotes differentiation with respect to the argument of f (here r) and $\mathcal{P}[f]\equiv-f''+f'/r$. We define the functions A, B, C, and D in Eqs. (27) and (28), each with two greek suffices, by specifying their Fourier transformations. The Fourier transformation of $A_{\alpha\gamma}$, $\mathcal{F}[A_{\alpha\gamma}]\equiv\int d\mathbf{r}\,A_{\alpha\gamma}\exp(i\mathbf{k}\cdot\mathbf{r})$, is given by

$$\mathcal{F}[A_{\alpha\gamma}]=\mathcal{F}[\overline{c_{\alpha\gamma}}]\{(\mathcal{F}[a_\gamma g_{\gamma\alpha_0}])'-k^{(-1)}(\mathcal{F}[a_\gamma g_{\gamma\alpha_0}])'\}.\qquad(29)$$

$\mathcal{F}[B_{\alpha\gamma}]$ is given by replacing $a_\alpha g_{\gamma\alpha_0}$ and $\overline{c_{\alpha\gamma}}$ in Eq. (29) by $b_\gamma\omega_{\gamma\alpha_0}$ and $c_{\alpha\gamma}$, respectively. $\mathcal{F}[E_{\alpha\gamma}]\equiv\mathcal{F}[c^{(0)}_{\alpha\gamma}]\mathcal{F}[B_{\alpha\gamma}]/\mathcal{F}[c_{\alpha\gamma}]$, $\mathcal{F}[F_{\alpha\gamma}]\equiv\mathcal{F}[c_{\alpha\gamma}]\mathcal{F}[A_{\alpha\gamma}]/\mathcal{F}[\overline{c_{\alpha\gamma}}]$, and $\mathcal{F}[\underline{A}_{\alpha\gamma}]\equiv-\mathcal{F}[A_{\alpha\gamma}]/k^2$ and the same relation holds between B and B, E and E, and F and F.

Finally in this section we express the shear viscosity η in terms of the distortion $a_\alpha(r)$ or, more precisely, $a_\alpha(r|\alpha_0)$. For the purpose we consider the momentum conservation equation

$$d\mathbf{p}(\mathbf{k})/dt=i\mathbf{k}\cdot\sigma(\mathbf{k}),\qquad(30)$$

where $\mathbf{p}(\mathbf{k})=\Sigma_\alpha\Sigma_j\mathbf{p}_{j,\alpha}\exp(i\mathbf{k}\cdot\mathbf{r}_{j,\alpha})$, with $\mathbf{p}_{j,\alpha}$ denoting momentum of a site α of the jth molecule. The xy component of the stress tensor $\sigma_{xy}(\mathbf{k})$ becomes $-\eta\gamma V$ in the limit of $k\rightarrow0$. With use of the equation of motion

$$\begin{aligned}d\mathbf{p}_{i,\alpha}/dt=&-\sum_{j\ (\neq i)}\sum_{\beta}[\mathbf{r}_{i\alpha,j\beta}\phi^{e'}_{\alpha\beta}(r_{i\alpha,j\beta})/r_{i\alpha,j\beta}]\\&-\sum_{\beta\neq\alpha}[\mathbf{r}_{i\alpha,j\beta}\phi^{a'}_{\alpha\beta}(r_{i\alpha,j\beta})/r_{i\alpha,j\beta}],\end{aligned}\qquad(31)$$

it is readily derived that

$$\begin{aligned}\sigma_{xy}(k\rightarrow0)=-\tfrac{1}{2}\Bigg(&\sum_{i,\alpha}\sum_{j\ (\neq i),\beta}x_{i\alpha,j\beta}y_{i\alpha,j\beta}\phi^{(e)'}_{\alpha\beta}\\&\times(r_{i\alpha,j\beta})/r_{i\alpha,j\beta}\\&+\sum_{\beta\neq\alpha}x_{i\alpha,j\beta}y_{i\alpha,j\beta}\phi^{(a)'}_{\alpha\beta}(r_{i\alpha,j\beta})/r_{i\alpha,j\beta}\Bigg)\\&+\sum_{i,\alpha}(p_{i,\alpha,x}p_{i,\alpha}/m_\alpha).\end{aligned}\qquad(32)$$

Here we neglect the kinetic contribution, the last term, because its contribution is very small at the liquid density [15,7] and note that in the limit $V\rightarrow\infty$ the intramolecular contribution vanishes. Thus, if we take the average $\langle\sigma_{xy}(k\rightarrow0)\rangle$ in the stationary shear flow, we can express it in terms of distortion as

$$\langle\sigma_{xy}(k\rightarrow0)\rangle=-(N/2)\sum_{\beta,\alpha_0}\int d\mathbf{r}(xy/r)\phi^{e'}_{\beta\alpha_0}(r)n_\beta(\mathbf{r}|\alpha_0).\qquad(33)$$

Since this is equal to $-\eta\gamma V$, it follows from Eqs. (22) and (26) that

$$\eta=(n^2/2)\sum_{\alpha,\alpha_0}\int d\mathbf{r}(xy)^2g_{\alpha\alpha_0}(r)\phi^{e'}_{\alpha\alpha_0}(r)a_\alpha(r|\alpha_0)/(D_\alpha r).\qquad(34)$$

We note that this expression for η is similar to Eq. (15) in [6].

Before proceeding to numerical calculations, we remark that the nonlinear diffusion equations (18) and (19) govern the time evolution of the density fields on an atomic scale. If we introduced slowly varying order parameters such as the amplitudes of the density waves in liquid-solid interfaces, we could derive Cahn-Hilliard-like equations for the order parameters with square gradient terms in the effective free energy [2,16].

IV. NUMERICAL RESULTS

Model for a diatomic homonuclear liquid

In Sec. III we formulated the shear viscosity for a general one-component molecular liquid. Now we specify our system further to be composed of two-site ($S=2$) homonuclear molecules. To be concrete, let us take liquid nitrogen, for which the interatomic potential $\phi^e_{\alpha\beta}(r)=\phi^e(r)$ (α,β=1,2) was chosen within the rigid-molecule model to be a Lennard-Jones potential

$$\phi^e(r)=4\varepsilon[(\sigma/r)^{12}-(\sigma/r)^6],\qquad(35)$$

with $\sigma=3.341A$ and $\varepsilon=0.6075\times10^{-14}$ erg [17,11(b)]. We introduce here nonrigidity by choosing a Morse potential for the intramolecular interaction

$$\phi^a(r)=U_e[1-\exp\{-a(r-r_e)\}]^2,\qquad(36)$$

with $U_e=1.5865\times10^{-11}$ erg, $a=2.443\ \mathrm{A}^{-1}$, and $r_e=1.1$ A [18].

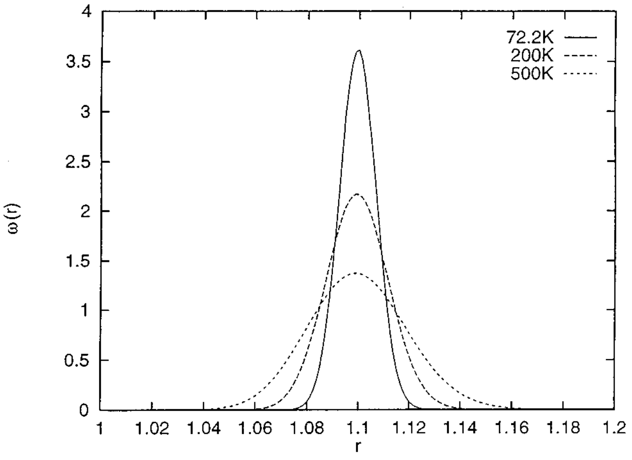

FIG. 1. Equilibrium correlation $\omega(r)$ in units of A^{-3} for some temperatures with r in units of A for $n=0.0186\ \mathrm{A}^{-3}$.

From the symmetry inherent in our model system, there are five unknown quantities for the static correlations introduced in Sec. II, that is, $g_{11}=g_{22}=g_{12}\equiv g$, $c_{11}=c_{22}=c_{12}\equiv c$, $\omega_{12}\equiv\omega$, $c_{11}^{(0)}=c_{22}^{(0)}$, and $c_{12}^{(0)}$. The generalized HNC equations (17) and (16) take the form

$$g=1+h=\exp[-\beta\phi^e+h-c], \tag{37}$$

$$\ln\omega=2nc*h+c_{11}^{(0)}*\omega-\beta\phi^a+C. \tag{38}$$

The ISM OZ relations (5) and (6) are reduced, respectively, to

$$c_{11}^{(0)}=-c_{12}^{(0)}*\omega, \quad \omega=n[c_{12}^{(0)}+c_{11}^{(0)}*\omega], \tag{39}$$

$$h=c+2\omega*c+\omega*c*\omega+2n[c*h+\omega*c*h]. \tag{40}$$

Thus the set of equations (37)–(40) forms the closed equations for the five unknowns.

The thermodynamic state of liquid N_2 we are mainly interested in is represented by $T=72.2$ K and $n=0.0186\ \mathrm{A}^{-3}$ [11(b)]. Since our main concern in this paper is nonequilibrium effects associated with the shear flow, here we only summarize equilibrium properties obtained from our coupled HNC equations, discussing them in detail separately in the future [13]. In Fig. 1 the equilibrium correlation $\omega(r)$ is shown for several temperatures. We immediately observe that $\omega(r)$ becomes broad due to thermal motion as T increases. Also it turns out that the average bond length $\langle d\rangle\equiv\int d\mathbf{r}\, r\omega(r)$ becomes large as T increases due to the asymmetry of the Morse potential around its minimum at $r=r_e$. As for the density dependence of $\omega(r)$ we only note that $\langle d\rangle$ decreases as n increases with T kept constant, which may be called a packing effect. The intermolecular correlation $g(r)$ is modified only slightly compared to the rigid molecular model, maximally around $r\approx4$ A by 10^{-4}, which gives rise to a slight change in the internal energy and the equation of state.

Asserting these qualitative arguments, we now proceed to distortions produced by the shear flow. We plot in Fig. 2(a) the intramolecular distortion $b(r)\omega(r)$ [see Eqs. (26) and (23)] and in Fig. 2(b) the stationary distribution $n_{\mathrm{st}}^{(0)}(\mathbf{r})$ on the $z=0$ plane with γ chosen to be rather large in order to make the distortion discernible. Figure 2(a) shows that the distortion extends a little asymmetrically around the equilibrium intramolecular point $r_e=1.1$ A only by 0.2 A. From Fig. 2(b) the favorable orientation of molecules is seen to be on the line $y=-x$. This tendency is similar to the one observed in the intermolecular situation [see Fig. 3(b)]. Figures 3(a) and 3(b) show the intermolecular distortion $a(r)g(r)$ [see Eqs. (22) and (26)] and the stationary distribution $n_{\mathrm{st}}(\mathbf{r})/n$ on the $z=0$ plane, respectively. By comparing Fig. 3(a) with Fig. 2 in [6], which depict the same quantity for different systems (with different scales), we notice that the distortions in both systems look rather similar as a whole. However, for liquid N_2, in contrast with simple liquids [6], we have no positive bump around the position corresponding to the second peak of $g(r)$. As a result, the second peak of the two-body intermolecular correlation is not distorted much by the shear flow [Fig. 3(b)] compared to the case of atomic or simple liquids [6]. We remark that shear stress in the Couette flow is produced by the distortion $g(r)a(r)$ together with the (mainly repulsive) intermolecular interaction Eq. (34). From our results that the density is high (low) on $y=-x$ ($y=x$) line under the condition that a (blue) particle is fixed at the origin, we notice that the blue particle experiences shear force in the positive-x direction as it should in the flow field $\mathbf{u}(\mathbf{r})=\gamma y\mathbf{e}_x$.

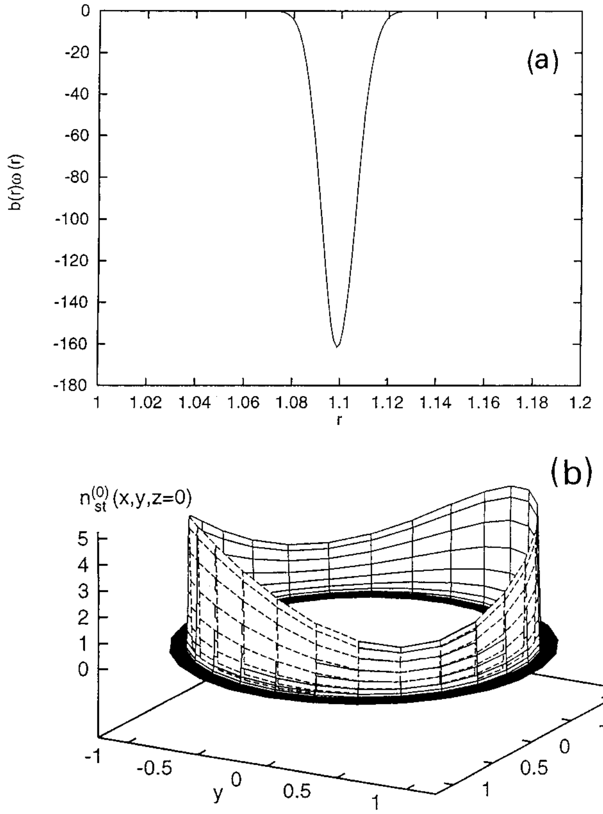

FIG. 2. (a) Intramolecular distortion $b(r)\omega(r)$ in units of A^{-3} with r in units of A. For $r\geqslant1.2$ A and $r\leqslant1$ A, we note that $b(r)\omega(r)\simeq0$. (b) Stationary distribution $n_{\mathrm{st}}^{(0)}(\mathbf{r})$ on the $z=0$ plane in units of A^{-3} with x and y in units of A. The black rim shows the plane $n_{\mathrm{st}}^{(0)}=0$. We note that $n_{\mathrm{st}}^{(0)}\simeq0$ for $r\geqslant1.2$ A and $r\leqslant1$ A with $r^2=x^2+y^2$.

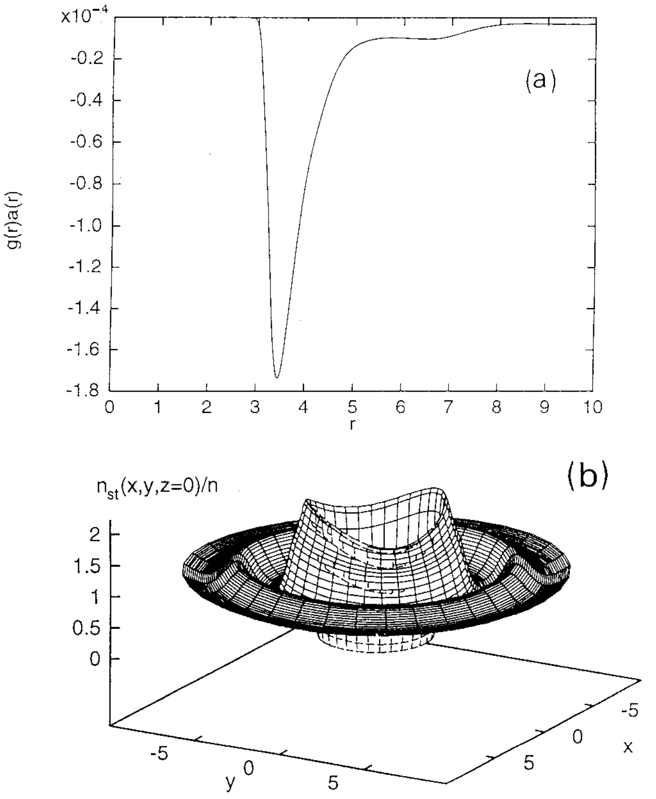

FIG. 3. (a) Intermolecular distortion $a(r)g(r)$ with r in units of A. (b) Stationary distribution $n_{\mathrm{st}}(\mathbf{r})$ on the $z=0$ plane with x and y in units of A.

The shear viscosity is calculated from Eq. (34), which takes the following form for the homonuclear $S=2$ system with all the irrelevant subscripts omitted:

$$\eta=(2n^2)\int d\mathbf{r}(xy)^2 g(r)\phi^{e\prime}(r)a(r)/Dr, \tag{41}$$

To calculate the shear viscosity based on Eq. (41) we must estimate the bare diffusion constant $D\equiv k_B T/m\Gamma$, where $1/\Gamma$ denotes the relaxation time of each atom (site) in momentum space. For monatomic liquids, $1/\Gamma$ was estimated to be $1/\Gamma=\alpha l/v_{\mathrm{th}}$, where l is the interparticle distance and v_{th} the thermal velocity. We chose α to be $\frac{1}{16}$ for a soft-core system in order to get good overall agreement with molecular-dynamics results at typical liquid densities [6]. For liquid N_2 let us set the momentum relaxation time tentatively equal to $1/\Gamma=\alpha\tau$, with τ the intramolecular vibration period $\tau=2\pi/\Omega$. The frequency Ω is estimated based on the model intramolecular potential (36) to be $(4a^2U_e/m)^{1/2}\simeq 5\times 10^{14}$. For the thermodynamic state mentioned above, we calculate pressure to be $p=44\times 10^6$ Pa from our radial distribution function. The viscosity for the thermodynamic state is about 340×10^{-6} Pa s, which is obtained from our theory by setting α equal to $\frac{1}{100}$ [19]. If packing or other intermolecular effects tend to make τ smaller, the factor α becomes larger. For the rigid model of N_2, η is obtained to be only slightly larger (less than 1%) than for the nonrigid model, with the same α being used for the calculation. Finally, we comment that from our calculation η decreases as we decrease density, with temperature kept constant. In this process pressure decreases. From experiments [19] we know that η decreases as pressure decreases in accord with our results. From the above it seems that η of diatomic liquids can be calculated semiquantitatively based on the time-dependent DFT of simple liquids [6].

V. REMARKS

In this paper we formulated the shear viscosity of molecular liquids by extending a time-dependent DFT so that it could be applied to polyatomic liquids. The calculated viscosity, together with equilibrium and nonequilibrium correlations, seems to reproduce experimental results rather well. By allowing for an intramolecular distortion we show quantitatively that a molecule itself is distorted just like intermolecular correlations. It would be interesting if one could observe such distortion experimentally. Our final remark is concerned with the free-energy functional Eq. (7), which is proposed based on the assumption that an atom (site) fixed at some position interacts with other sites via a bare intersite potential, while the other sites interact each other via an effective interaction c or $c^{(0)}$. Although this is consistent with the so-called extended RISM functional idea, we need some theoretical justification for this proposal. We plan to discuss this point together with an application of Eq. (7) to some isomerization problems in the future.

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