Shear viscosity from a dynamic density-functional theory

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Based on a dynamic version of the density-functional theory, we obtain a stationary density profile around a particle in a shear flow and calculate the shear viscosity of monatomic liquids. Our results are compared with those obtained from both equilibrium and nonequilibrium computer experiments. An approach similar to the one developed for the shear viscosity is suggested, which in principle enables us to calculate a friction constant and consequently a self-diffusion constant, and some results from the zeroth order approximation are presented.

The density-functional theory (DFT) for nonuniform liquids plays an important role in quantitative studies on freezing and glass transitions of liquids and on the related problems including the liquid-crystal interface and nucleation [1,2]. It is also useful in studies of liquid properties such as the radial distribution function and equation of state [3]. In view of the wide applicability of the DFT, we recently gave a dynamic extension of the DFT by deriving a Langevin-diffusion (LD) equation for time evolution of the density field $n(\mathbf{r};t)$ [4,5]. General properties of the LD equation, such as two H theorems describing relaxation to equilibrium and the origin of a multiplicative noise current, are discussed in detail in Ref. [5].

In this paper we apply the LD equation to investigate shear viscosity of monatomic liquids. For this purpose we consider a stationary shear flow and a stationary density profile $n_{st}(\mathbf{r})$ around an arbitrary particle, which is considered to be put on the origin in our coordinate system. If there were no shear flow, the stationary density profile $n_{st}(\mathbf{r})$ would be given, with use of the radial distribution function $g(r)$ and the equilibrium uniform density n_L, as $n_L g(r)$. The density profile $n_{st}(\mathbf{r})$ deviates from $n_L g(r)$ because of the shear flow, and this deviation can be used to calculate a shear part of the stress tensor, thus yielding the shear viscosity [6]. Later we will generalize this idea to a friction constant.

Let us start from the general LD equation [5]

$$\frac{\partial n(\mathbf{r};t)}{\partial t} = D_b \nabla \cdot \{n(\mathbf{r};t)\nabla \delta F/\delta n(\mathbf{r};t) - \mathbf{f}(\mathbf{r};t)\} ,\qquad (1)$$

where the (nondimensional) free energy functional F is given by

$$F = \int d\mathbf{r}\, n(\mathbf{r})\{\ln[n(\mathbf{r})\Lambda^3]-1\}$$
$$- \sum_{k=1}^{\infty} \int d\mathbf{r}_1 \cdots \int d\mathbf{r}_k \{C_k(\mathbf{r}_1,\ldots,\mathbf{r}_k)/k!\}$$
$$\times \{n(\mathbf{r}_1)-n_L\} \cdots \{n(\mathbf{r}_k)-n_L\} ,\qquad (2)$$

with C_k and Λ denoting the direct correlation function of kth order and the thermal wavelength, respectively. The random flow $\mathbf{f}(\mathbf{r};t)$ satisfies the fluctuation-dissipation theorem (FDT)

$$\langle f_i(\mathbf{r};t)f_j(\mathbf{r}';t')\rangle = 2n(\mathbf{r};t)\delta(\mathbf{r}-\mathbf{r}')\delta(t-t')\delta_{ij}/D_b .\qquad (3)$$

The bare diffusion constant D_b [7] is defined to be

$$D_b = k_B T/(m\Gamma) ,\qquad (4)$$

where $k_B T\,(=1/\beta)$ and m denote temperature in energy unit and mass of a liquid atom, respectively. The $1/\Gamma$ is a measure of a relaxation time for a particle to attain a Maxwellian distribution in momentum space. Thus $1/\Gamma$ is not related to any slowing down observed in dense liquids. We will confirm this assertion later in connection with the density dependence of $1/\Gamma$. We consider the simplest version of the DFT in which we retain terms up to $k=2$ in the expansion in Eq. (2) and neglect the random flow $\mathbf{f}(\mathbf{r};t)$ on the right-hand side of Eq. (2) [2]. Thus our theory takes into account pair correlations only, with all the higher order correlations, represented by C_n ($n \geq 3$) neglected. As will be shown later, this approximation reproduces experimental viscosity rather well for stable (nonsupercooled) liquids. For denser supercooled liquids, higher order correlations are expected to play more and more important roles in producing the effective (cage) field $\delta F/\delta n(\mathbf{r},t)$ [see Eq. (1)], which confines a particle in a small region, thus reducing freedom for particle motion [8]. Taking into account effects of both stationary flow $\mathbf{u}(\mathbf{r})$, producing particle flow $n(\mathbf{r};t)\mathbf{u}(\mathbf{r})$, and the force field $-\nabla\phi(r)$ due to the particle at the origin, producing particle flow $-\beta D_b n(\mathbf{r};t)\nabla\phi(r)$, we obtain from Eq. (1)

$$\frac{\partial n(\mathbf{r};t)}{\partial t} = -\nabla\cdot\mathbf{J}(\mathbf{r};t) ,\qquad (5)$$

$$\mathbf{J}(\mathbf{r};t) = -D_b\nabla n -\beta D_b n\nabla\left\{\int d\mathbf{r}'V_{\text{eff}}(|\mathbf{r}-\mathbf{r}'|)n(\mathbf{r}';t)\right.$$
$$\left.+\phi(r)\right\}+n\mathbf{u}(\mathbf{r}) ,\qquad (6)$$

where $\phi(r)$ denotes the interatomic potential, $V_{\text{eff}}(r)$ $\equiv -k_B T C_2(r)\equiv -k_B T C(r)$, and the direct correlation function $C(r)$ is related to $h(r)\equiv g(r)-1$ by the Ornstein-Zernike equation [3]

$$h(r) = C(r) + n_L \int d\mathbf{r}' C(|\mathbf{r} - \mathbf{r}'|) h(r') . \qquad (7)$$

Since we are interested in a stationary density profile, we put $\partial n(\mathbf{r}; t)/\partial t = 0$ in Eq. (5) and replace $n(\mathbf{r}; t)$ by $n_{st}(\mathbf{r})$. First let us consider the equilibrium solution $n_{eq}(\mathbf{r})$ when $\mathbf{u}(\mathbf{r}) = 0$. In this equilibrium case, $\mathbf{J}(\mathbf{r}) = 0$ and it is readily seen from Eq. (6) that

$$\ln[g(r)] \equiv \ln[n_{eq}(r)/n_L]$$
$$= -\beta n_L \int d\mathbf{r}' V_{\text{eff}}(|\mathbf{r} - \mathbf{r}'|)[g(r') - 1] - \beta\phi(r) , \quad (8)$$

where the boundary condition $n_{eq}(\mathbf{r}) \to n_L$ as $r \to \infty$ is taken into account. From the relation $-\beta V_{\text{eff}}(r) = C(r)$, we immediately notice that Eq. (8) is equivalent to the hypernetted chain (HNC) equation for $g(r)$ [3]. Thus our approach, when applied to an equilibrium situation, gives the HNC theory for $g(r)$.

Coming back to effects of velocity field $\mathbf{u}(\mathbf{r})$, we consider a shear flow

$$\mathbf{u}(\mathbf{r}) = \Upsilon y \mathbf{e}_x , \qquad (9)$$

where $\mathbf{e}_x$ denotes a unit vector in the x direction and Υ is a rate of strain. Assuming that Υ is small, we seek a solution of the form

$$n_{st}(\mathbf{r}) = n_L g(r)[1 + w(\mathbf{r})\Upsilon/D_b + o(\Upsilon)] , \qquad (10)$$

where $o(\Upsilon)/\Upsilon \to 0$ as $\Upsilon \to 0$ and $g(r)$ is given from the HNC equation, as we have just seen above. Inserting Eq. (10) into Eq. (5), we obtain from $\partial n/\partial t = 0$,

$$g\nabla^2 w - n_L g \nabla^2 H(\mathbf{r}) + \nabla g \cdot \nabla w - n_L \nabla g \cdot \nabla H(\mathbf{r})$$
$$= xy g'(r)/r , \qquad (11)$$

$$H(\mathbf{r}) \equiv \int d\mathbf{r}' C(|\mathbf{r} - \mathbf{r}'|) g(r') w(\mathbf{r}') . \qquad (12)$$

As will be discussed below, Eq. (11) turns out to have a solution of the form [6]

$$w(\mathbf{r}) = xy A(r) , \qquad (13)$$

with $A(r)$, a function of magnitude of $\mathbf{r}$, satisfying the complicated integro-differential Eq. (20) below. Once the solution $A(r)$ to Eq. (20) is found, we can calculate the x-y component of the stress tensor [3,6],

$$\sigma_{xy} = (n_L/2) \int d\mathbf{r} \, xy\phi'(r) n_{st}(\mathbf{r})/r$$
$$= (n_L^2 \Upsilon/2D_b) \int d\mathbf{r}(xy)^2 g(r)\phi'(r) A(r)/r , \qquad (14)$$

where $\phi'(r) = d\phi/dr$, and we have neglected a kinetic contribution to σ_{xy}, since it is very small at a liquid density. From the definition of the shear viscosity η, $\sigma_{xy} = \eta\Upsilon$, we finally have

$$\eta = (n_L^2/2D_b) \int d\mathbf{r}(xy)^2 g(r)\phi'(r) A(r)/r$$
$$= (2\pi n_L^2/15 D_b) \int dr \, r^5 g\phi' A . \qquad (15)$$

Now we turn to the derivation and the method of solution of Eq. (20). First we note that a Fourier transform (FT) of a function $xyf(r)$, with $f(r)$ an arbitrary function of $r = |\mathbf{r}|$, is given by

$$\int d\mathbf{r} \, xyf(r)\exp(i\mathbf{k}\cdot\mathbf{r})$$
$$= (k_x k_y/k^2)[-\mathcal{T}_f''(k) + \mathcal{T}_f'(k)/k] , \quad (16)$$

where $\mathcal{T}_f$ denotes a FT of $f(r)$. Similarly an inverse FT of a function $k_x k_{by} \mathcal{T}_f(k)$ is given by

$$(2\pi)^{-3} \int d\mathbf{k} \, k_x k_y \mathcal{T}_f(k)\exp(-i\mathbf{k}\cdot\mathbf{r})$$
$$= (xy/r^2)[-f''(r) + f'(r)/r] . \quad (17)$$

Using Eqs. (12), (13), and (16), we have

$$\mathcal{T}_H(\mathbf{k}) = k_x k_y \mathcal{T}_M(k) , \qquad (18)$$

$$\mathcal{T}_M(k) \equiv [\bar{C}(k)/k^2][-\mathcal{T}_{Ag}''(k) + \mathcal{T}_{Ag}'(k)/k] . \quad (19)$$

From Eqs. (17) and (18), we see that $H(\mathbf{r})$ has the same form as $w(\mathbf{r})$, Eq. (13), and we obtain from Eq. (11), after simple algebra,

$$[r^2 A]'' + (2/r + g'/g)[r^2 A]' - 6A + n_L\{N'' - N'/r\}$$
$$+ n_L(g'/g)[M'' - M'/r]' = rg'/g , \qquad (20)$$

where $N(r)$ is the inverse FT of $\mathcal{T}_N(k) = -k^2 \mathcal{T}_M(k)$.

In order to solve the inhomogeneous linear equation (20) for $A(r)$, we regard the function $A(r)$ as an N-dimensional vector $\mathbf{a} \equiv \{a_i\}$ $(i = 1, \ldots, N)$, with $a_i = A(r = \Delta i)$, and transform Eq. (20) to a linear algebraic equation

$$\sum_j L_{i,j} a_j = b_i \quad \text{or} \quad L\mathbf{a} = \mathbf{b} , \qquad (21)$$

where $b_i = (\Delta i)g'(r = \Delta i)/g(r = \Delta i)$ and L is an $N \times N$ matrix. We note that both differentiation with respect to r and the (inverse) FT of $A(r)$ are linear operations, which can be described with the use of appropriate (non-diagonal) $N \times N$ matrices L_{nd} as $L_{\text{nd}}\mathbf{a}$. As to a simple multiplication like $r^2 A(r)$, this is expressed as $L_d \mathbf{a}$ with the use of a diagonal matrix $L_{d,i,j} = (i\Delta)^2 \delta_{ij}$. This explains how we get Eq. (21). Usually we find that elements of the matrix L_{ij} vanish for $\Delta i \leq r_c \equiv \Delta i_c$ because of the structure of the radial distribution function $g(r)$, and the L has no inverse matrix. To remove this difficulty, we reduce the size of the vector $\mathbf{a}$ (the matrix L) from N $(N \times N)$ to $N - i_0$ $[(N - i_0) \times (N - i_0)]$ and obtain a solution to Eq. (21) or (11) for $r \geq r_0$. Since a small r region does not contribute to the integral in Eq. (14), because of the presence of $g(r)$, our method of solution to Eq. (21) presents no problem. We tried several values for Δ and N and obtained a reliable solution to Eq. (11).

We now apply the theory developed above to a soft-core system [9,10], with the interaction $\phi(r)$ given by

$$\phi(r) = \epsilon(\sigma/r)^n \quad (n = 12) , \qquad (22)$$

for which a thermodynamic state is specified by one parameter

$$\rho^* \equiv \sigma^3(N/V)/(k_B T/\epsilon)^{1/4} . \qquad (23)$$

The freezing and the melting points of the $n = 12$ soft-core system are $\rho_f^* = 1.150$ and $\rho_m^* = 1194$, respectively

[9]. About 20 years ago Ashurst and Hoover (AH) performed a nonequilibrium molecular dynamics (MD) to study dense-fluid shear viscosity [11]. By simulating a Couette flow, they successfully obtained (stationary) nonequilibrium pair distribution function $n_{st}(\mathbf{r})$, Eq. (10). In Fig. 1 we compare η's from our theory, η_{DFT}, and from computer experiments, η_{AH}. It is appropriate here to explain how we determine the bare diffusion constant D_b, Eq. (4). As noted before, $1/\Gamma$ represents a relaxation time for a local momentum distribution to attain a Maxwellian distribution. This is roughly estimated, with thermal velocity $v_{th} \equiv (k_B T/m)^{1/2}$ and the average interparticle distance $l \equiv (V/N)^{1/3}$, to be

$$\Gamma^{-1} = \alpha(l/v_{th}) \ . \tag{24}$$

That is, we assume that Γ^{-1} is of the order of the mean collision time, with α a parameter not determined within our theory. In plotting Fig. 1 we adjusted α so that η_{DFT} coincides with η_{AH} at $\rho^* = 1.1(\alpha = \frac{1}{16})$. From Fig. 1 we see that our theory can reproduce the overall experimental results rather satisfactorily below the freezing point. Ashurst and Hoover expressed the nonequilibrium stationary pair distribution as [11]

$$n_{st}(\mathbf{r}) = n_L g(r)[1 + (xy/r^2)\nu(r)\Upsilon] \ . \tag{25}$$

The $\nu(r)$ in Eq. (25) is related to $A(r)$, defined by Eq. (13), via $\nu(r) = A(r)r^2/D_b$. For convenience of comparison we express the shear viscosity as

$$\eta = (2\pi n_L^2/15)\int_0^\infty dr \phi'(r)r^5 B(r) \ , \tag{26}$$

where $B(r) = g(r)\nu(r)/r^2$, and also from our theory it is $g(r)A(r)/D_b$.

If one employs a Maxwell model $\eta = G\tau_M$, with G and τ_M the rigidity and the Maxwell viscoelastic relaxation time, respectively, the $\nu(r)$ in Eq. (25) becomes $\nu_M(r) = -\tau_M r g'(r)/g(r)$ [11]. In Fig. 2 we plot three
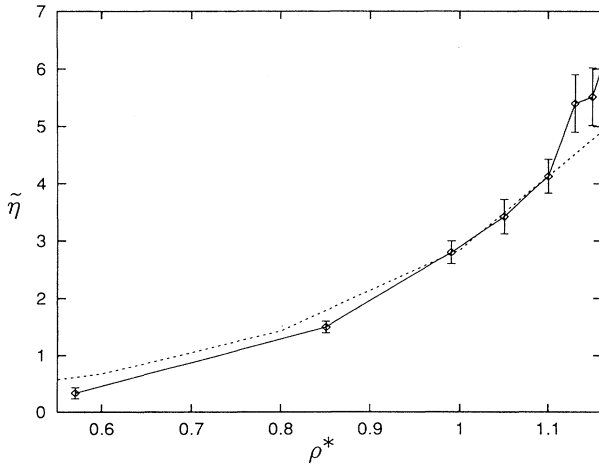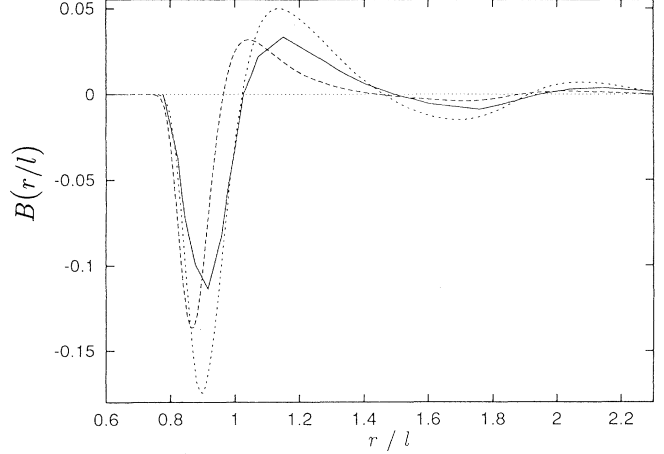

FIG. 2. $B(r)$ from our theory $B_{DFT}(r)$ (dotted curve), the nonequilibrium MD $B_{AH}(r)$ (full curve), and the viscoelastic approximation $B_{VE}(r)$ (dashed curve) for $\rho^* = 0.81$.

$B(r)$: $B_{AH}(r)$ from Ref. [9], $B_{DFT}(r)$ from our theory, and $B_M(r)$ from the Maxwell model, with τ_M chosen to give good fit to $B_{AH}(r)(\rho^* = 0.81)$. Although there is some discrepancy in magnitude of $B(r)$ between $B_{AH}(r)$ and $B_{DFT}(r)$, the agreement with experiment is not bad, especially in view of the fact that we are comparing the integrand for the viscosity. In passing we note that if α is changed from $\frac{1}{16}$ to $\frac{1}{11}$, $B_{AH}(r)$ and $B_{DFT}(r)$ nearly coincide. Our theory is compared to the Maxwell model for various ρ^* values by plotting in Fig. 3 $g(r)A(r)$ and $-g'(r)/r$, which are mutually related via $g(r)A(r) = -[g'(r)/r](D_b\tau_M)$. It is seen from Fig. 3 that our theory is well correlated with the Maxwell model, although we cannot directly compare the magnitude of these functions because of the different scales. To study shear viscosity of a soft-core $(n = 12)$ system in the higher density (supercooled) region $(\rho^* \geq \rho_f^*)$, Amar and Mountain [12] performed equilibrium MD experiments and obtained η with the use of the Green-Kubo formula. In Fig. 4 we compare η_{DFT} with η_{AM} in a supercooled region of ρ^* and notice that the agreement between theory (dynamic DFT) and experiment deteriorates as the density becomes high. This is expected because our theory is based on the crudest approximation for $F[n]$ and consequently uses, as the input data, $g(r)$ from the HNC theory.

Up to now we have been concerned with shear flow and shear viscosity. In view of the importance of the Stokes law [13] for high density liquids, it is of some interest to extend our approach so that it can be used to study a friction constant ζ. For this purpose, we consider a particle fixed in a uniform flow

FIG. 1 Shear viscosity $\tilde{\eta} \equiv \eta\{\sigma^2/(m\epsilon)^{1/2}\}(k_B T/\epsilon)^{-2/3}$ from our theory $\tilde{\eta}_{DFT}$ (dotted curve) and the nonequilibrium MD by Ashurst and Hoover $\tilde{\eta}_{AH}$ (full curve) as functions of ρ^* in the region below a freezing point $\rho_f^* = 1.15$.

$$\mathbf{u}(\mathbf{r}) = u_0 \mathbf{e}_x \ . \tag{27}$$

Of course we know from hydrodynamics [14,15] that the flow pattern is considerably distorted from the one expressed by Eq. (27) near the origin because of the presence of the fixed particle. In spite of this fact let us em-
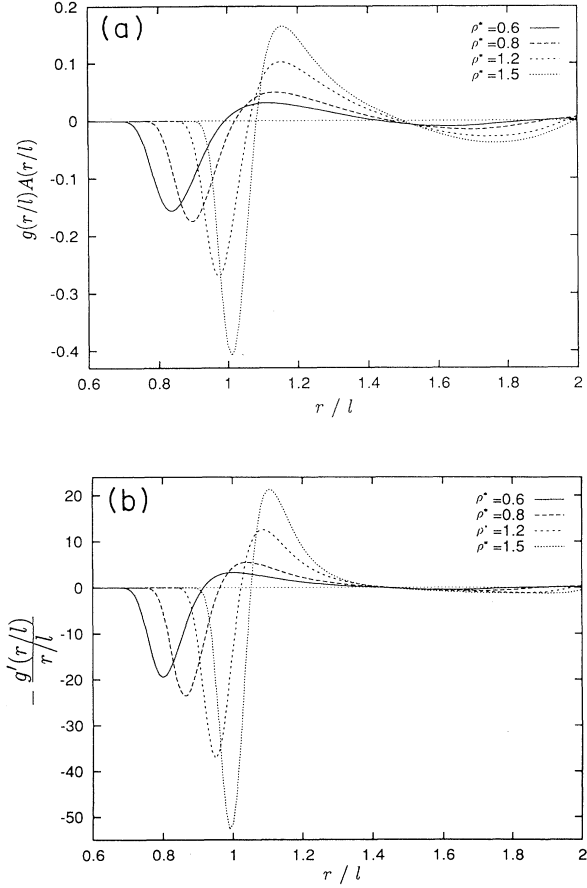
FIG. 3. Comparison of $g(r)A(r)$ from our theory (a) and $-g'(r)/r$ from the viscoelastic approximation (b) for various ρ^*, the values of which are indicated.
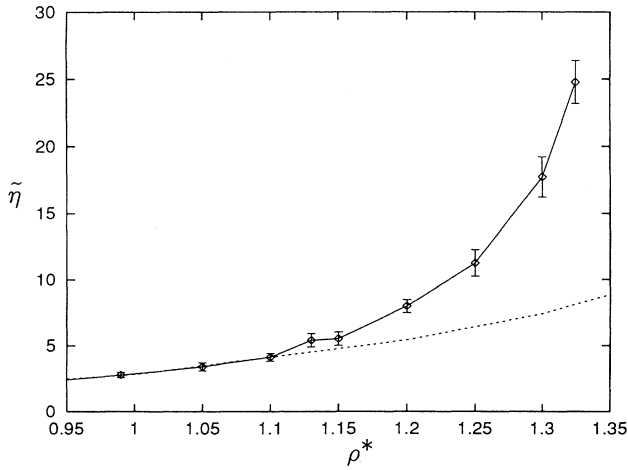
ploy the flow (27) in our diffusion equations (5) and (6) and express a stationary density profile $n_{st}(\mathbf{r})$ around a fixed particle as

$$n_{st}(\mathbf{r})=n_L g(r)[1+w(\mathbf{r})u_0/D_b+o(\Upsilon)] , \qquad (28)$$

for small u_0. Inserting Eq. (28) into Eq. (5) with $\partial n/\partial t=0$, we have

$$g\nabla^2 w-n_L g\nabla^2 H(\mathbf{r})+\nabla g\cdot\nabla w-n_L\nabla g\cdot\nabla H(\mathbf{r})=xg'(r)/r . \qquad (29)$$

Instead of Eq. (13) we have a solution to Eq. (29) of the form $w(\mathbf{r})=xA(r)$, with

$$[rA]''+(2/r+g'/g)[rA]'$$
$$-(2/r)A+n_L K'+n_L(g'/g)G''=g'/g , \qquad (30)$$

where $K(r)$ and $G(r)$ are the inverse FT of $T_K(k)=kT_C(k)T'_{gA}(k)$ and $T_G(k)\equiv T_K(k)/k^2$, respectively. The friction constant is obtained by calculating the force $\mathbf{F}$ on a fixed particle due to the flow (27). Thus from

$$\mathbf{F}=\int d\mathbf{r}\, n_{st}(\mathbf{r})\nabla\phi(r)=\zeta u_0\mathbf{e}_x , \qquad (31)$$

we have

$$\zeta=(n_L/3D_b)\int d\mathbf{r}\, g(r)r\phi'(r)A(r) . \qquad (32)$$

Figure 5 shows the self-diffusion constant $D_{DFT}\equiv k_B T/(m\zeta)$ together with the simulation results D_{expt} [10], with α in Eq. (24) set to be the same as before. As expected from our neglect of effects of flow modification near a fixed particle, the discrepancy between theory and experiment in the self-diffusion constant is larger than that in the shear viscosity. If we take into account a more realistic flow field around a fixed particle, we obtain better results, and this point is left for future investigation.

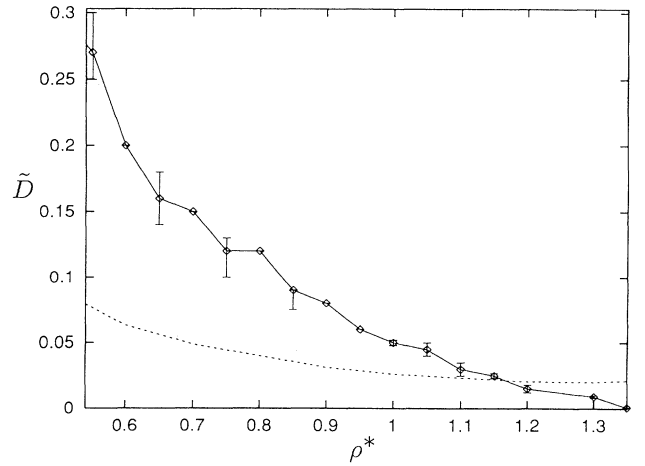Finally, in Fig. 6, we show the density profile $n_{st}(\mathbf{r})$;

FIG. 4. Shear viscosity $\tilde{\eta}$ from our theory $\tilde{\eta}_{DFT}$ (dotted curve) and the equilibrium MD by Amar and Mountain $\tilde{\eta}_{AM}$ (full curve) as functions of ρ^* in the region of supercooling.

FIG. 5. Self-diffusion constant $\tilde{D}\equiv D\sigma^{-1}(m/k_B T)^{1/2}(k_B T/\epsilon)^{1/12}$ from our theory $\tilde{D}_{DFT}$ (dotted curve) and computer experiments D_{exp} (full curve) [10].
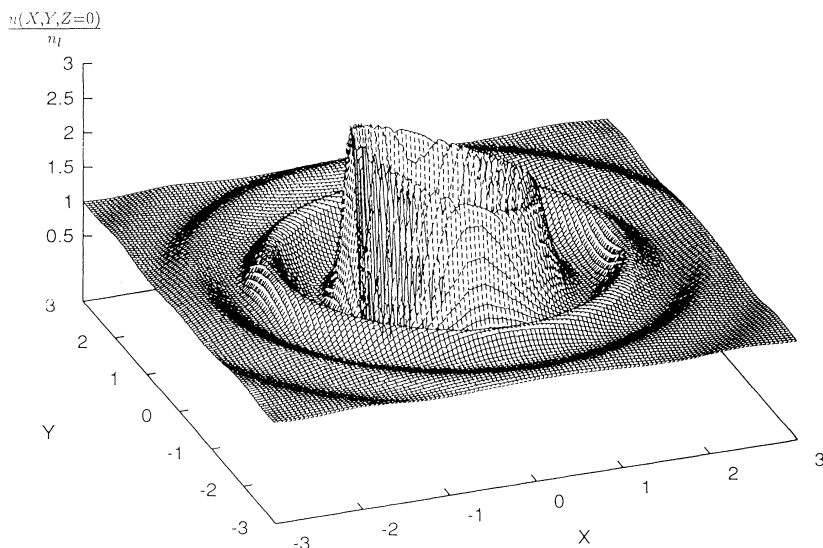
$\frac{n(X,Y,Z=0)}{n_l}$

FIG. 6. The stationary density profile $n_{st}(x,y,z=0)$ around a particle.

more precisely, $n_{st}(x,y,z=0)$, in a uniform flow ($\rho^*=1.0$), where we choose a rather large value for u_0 [$=0.361/\tau$, $\tau\equiv l(m/\epsilon)^{1/2}(1/\sigma)^6$] in order to make the deviation of $n_{st}(\mathbf{r})$ from $n_L g(r)$ visible. The front side is seen to be denser than the rear side, which as a whole produces the drag on the particle fixed at the origin, $x=y=z=0$, Eq. (31).

In this paper we developed a simple theory for the shear viscosity and the friction constant based on a dynamic DFT, which is somewhat modified to take effects of a flow field into account. Application to the soft-core system ($n=12$) shows that it works rather well for stable liquids. We note that $g(r)$ is determined from the HNC theory, Eq. (8), within the framework of our theory, in sharp contrast to other previous theories, which, similar

to our approach, aim at calculating the distortion of $g(r)$ due to a flow field [6]. Although in this paper application of a dynamic DFT is limited to a simple liquid, we note that it is applicable to more complex liquids, such as binary mixtures and molecular liquids, on which we hope to report in the near future.

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[7] We call D_b, Eq. (4), a bare diffusion constant, borrowing the terminology from the mode-coupling theory [K. Kawasaki, Ann. Phys. (Leipzig) **61**, 1 (1970)]. Since the LD Eq. (1) is highly nonlinear, it is supposed that any slowing down, which could occur in dense liquids, is properly taken care of by the LD equation, not by the constant D_b.

[8] The DFT for static structures of liquids seems now to be proceeding to a nonperturbative approximation such as a weighted DFT [W. A. Curtin and N. W. Ashcroft, Phys. Rev. A **32**, 2909 (1985)]. As to a dynamic DFT, we mention a recent work by A. Yoshimori (private communication). In a polarization relaxation problem Yoshimori used a dynamic DFT with the mean spherical approximation (MSA) for the input two-body correlation $C(r)$. He also took effects of C_3 into consideration by using the $C_3(\mathbf{r}_1,\mathbf{r}_2)$ obtained from the superposition approximation. However, this turned out to give rise to too enhanced cage effects.

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[14] At this point it is important to stress the difference between the shear flow and uniform flow cases. For the shear flow case we do not fix a particle at an origin but only take a coordinate system in which one tagged particle always is located at the origin. For the case of uniform flow we actually fix one particle at the origin [if we take a moving coordinate system, all the particles stand still and $u(r)=0$], and this particle disturbs flow field considerably.

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