Shear viscosity and normal pressure differences in the scope of the extended Kirkwood-Smoluchowski equation

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The potential contribution to the viscosity in liquids is calculated from the pair-correlation function, which may be obtained by solving the extended Kirkwood-Smoluchowski (KS) equation. A secondary boundary condition near the hard core ($r=1^+$) for the excess pair probability current density in the relative pair space is derived rigorously and applied to the extended KS equation. The intermolecular potential consists of hard core plus arbitrary soft tail. The viscosity coefficients calculated in this work prove to be essentially functions of the square root of the shear rate rather than functions of the shear rate itself. We give the explicit representation for the viscosity coefficients in the case of hard spheres. The shear thinning of the shear viscosity is recovered. The viscosity of the normal pressure difference $\frac{1}{2}(p_{xx}-p_{yy})$ is found to be positive. The normal pressure difference of the second kind $\frac{1}{2}[p_{zz}-\frac{1}{2}(p_{xx}+p_{yy})]$ vanishes in the first-order perturbation calculation with respect to the deformation.

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I. INTRODUCTION

The Kirkwood-Smoluchowski (KS) equation for the pair-correlation function (PCF) may be extended to quite a wide range of shear rate for the case of special geometry of the plane Couette flow [1,2]. Some interesting results of the analytic treatment of the extended KS equation were displayed in Ref. [2], where the boundary condition (BC) near the hard core should be corrected. In this article we first calculate the PCF by treating the BC near the hard core correctly, and obtain the potential contribution to the viscosity coefficients by using the PCF calculated. For hard spheres especially, we show the viscosity coefficients explicitly both in analytic and in graphic representation. We recover the shear thinning of shear viscosity and the positivity of the viscosity of normal pressure difference $\frac{1}{2}(p_{xx}-p_{yy})$, which are observed in the molecular-dynamics simulations [3–6]. The viscosity coefficients calculated in this article are found to be functions of the square root of the shear rate, more exactly, the square root of the rotation rate, rather than functions of the shear rate itself. The replacement of the repulsive part of intermolecular potential by a hard core is very effective in dense fluids [7,8] and provides us with a convenient BC at the hard core. The effective diameter of the hard core may depend upon density and temperature but in this work we have the hard-sphere diameter fixed at a reference length σ.

The extended KS equation for the PCF g in the Couette flow reads

$$\begin{aligned}&\frac{\partial}{\partial t}g+\mathbf{u}\cdot\nabla g+\nabla\cdot\mathbf{j}=0\ ,\\&\mathbf{j}=-\frac{1}{\tau}\nabla g+\frac{1}{\tau k_B T}[-\nabla w-(m\sigma^2/2)\dot{\mathbf{u}}]g\ ,\end{aligned}\tag{1}$$

where $\dot{\mathbf{u}}=d\mathbf{u}/dt$, and $w=-k_BT\ln g_{\rm eq}$ is the potential of mean force in equilibrium in the configurational relative pair space. The flow velocity $\mathbf{u}$ is given by $\mathbf{u}=\mathbf{r}\cdot\gamma$, where we assume the following shear-rate tensor in the plane Couette flow:

$$\gamma\equiv\nabla\mathbf{u}=\begin{bmatrix}0&0&0\\\gamma&0&0\\0&0&0\end{bmatrix}\ ,\tag{2}$$

with the uniform shear rate $\gamma\equiv\partial u_x/\partial y$. The relative coordinate vector $\mathbf{r}$ is in the unit of the reference length σ, $\nabla\equiv\partial/\partial\mathbf{r}$, $\tau=\sigma^2/D$, $D=2k_BT/\zeta$, and k_B and ζ are the Boltzmann's constant and the isotropic friction coefficient, respectively.

In Eq. (1) $\mathbf{j}$ is the excess pair probability current density, where it is to be noted that the mean force $-\nabla w$ is subtracted by the inertial force in the relative pair space $(m\sigma^2/2)\dot{\mathbf{u}}$, and a molecule at $\mathbf{r}$ feels the effective force $-\nabla w-(m\sigma^2/2)\dot{\mathbf{u}}$. For homogeneous simple fluids Eq. (1) may be derived from the Fokker-Planck (FP) equation for pair-particle distribution function $f^{(2)}(\mathbf{r}_1,\mathbf{v}_1,\mathbf{r}_2,\mathbf{v}_2)$, which depends upon both position and velocity [9,10]. One of the important approximations in deriving Eq. (1) is in the following: When the FP equation is multiplied by the peculiar velocity $\mathbf{V}_i=\mathbf{v}_i-\mathbf{u}$ $(i=1,2)$ and integrated in the six-dimensional velocity space $(\mathbf{v}_1,\mathbf{v}_2)$, we neglect $\langle\mathbf{V}_1\mathbf{V}_2f^{(2)}\rangle$ and the off-diagonal elements of $\langle\mathbf{V}_i\mathbf{V}_if^{(2)}\rangle$ for $i=1$ or 2, where the angular bracket denotes the integration over the six-dimensional velocity space. Since $\mathbf{u}\cdot\nabla\mathbf{u}=0$ in the Couette flow, we can put $\dot{\mathbf{u}}=\partial\mathbf{u}/\partial t+\mathbf{u}\cdot\nabla\mathbf{u}=\partial\mathbf{u}/\partial t$. That the nonlinear term $\mathbf{u}\cdot\nabla\mathbf{u}$ vanishes not by the linearization but by the geometrical property of the Couette flow implies the applicability of Eq. (1) to a wide range of shear rate, even when we drop the term $\dot{\mathbf{u}}$ in the stationary case. If we put $g=g_{\rm eq}+g_{\rm eq}^{1/2}\psi$, where $g_{\rm eq}$ is the equilibrium PCF, and substitute it into Eq. (1), we obtain in the Couette flow the following equation for ψ:

$$\left[-\tau\frac{\partial}{\partial t}+\Delta+V\right]\psi+\tau\left[\gamma_r-\frac{m}{\zeta}\frac{\partial}{\partial t}\gamma_r\right]\frac{\partial}{\partial\phi}\psi=\tau\left[\gamma_d-\frac{m}{\zeta}\frac{\partial}{\partial t}\gamma_d\right]\left[\left[x\frac{\partial}{\partial y}+y\frac{\partial}{\partial x}-\frac{xy}{k_B\mathrm{Tr}}w'\right]\psi+4\frac{xy}{r}q'\right], \quad (3)$$

where q is defined by $q=g_{\mathrm{eq}}^{1/2}$, Δ is the Laplace operator, the prime denotes the differentiation with respect to r, and ϕ is the azimuthal angle. The function $V(r)$ is defined by

$$V(r)=-\left[q''+\frac{2}{r}q'\right]\Big/q\ . \quad (4)$$

The shear-rate tensor $\boldsymbol{\gamma}$ given by Eq. (2) is decomposed into its deformation and its rotation part in Eq. (3):

$$\boldsymbol{\gamma}=\boldsymbol{\gamma}_d+\boldsymbol{\gamma}_r\ . \quad (5)$$

We may represent the deformation and the rotation rate tensor more generally by introducing their own scalar parameters γ_d and γ_r, respectively:

$$\boldsymbol{\gamma}_d=\gamma_d\begin{bmatrix}0&1&0\\1&0&0\\0&0&0\end{bmatrix},\quad \boldsymbol{\gamma}_r=-\gamma_r\begin{bmatrix}0&1&0\\-1&0&0\\0&0&0\end{bmatrix}. \quad (6)$$

We have $\gamma_d=\gamma_r=\gamma/2$ in the plane Couette flow.

We assume the intermolecular potential to be given by

$$v(r)=v_h(r)+v_a(r)\ , \quad (7)$$

where v_h is the hard-sphere potential: v_h becomes infinite for $r\le 1$ and zero otherwise. The second term v_a is any additional soft tail. For the fluid system of hard spheres we have to put $v_a=0$.

In the next section we develop the perturbation theory with respect to the deformation rate and obtain an equation for the first-order deviation from equilibrium. In Sec. III we introduce the BC's at the hard core ($r=1$) and at infinity in the relative pair space, and derive the BC near the hard core ($r=1^+$). In Sec. IV, by using these BC's, we calculate the deviation of PCF from equilibrium, which is again applied to obtaining the explicit expressions of viscosity coefficients in Sec. V.

II. PERTURBATION EXPANSION IN THE DEFORMATION RATE

In the previous works [10,11] the deviation of PCF from equilibrium was calculated in the first order of the shear rate itself. But the rotation and the deformation tensor are physically independent quantities and we may expand the function ψ in terms of the deformation rate γ_d (multiplied by the relaxation-time coefficient τ) only, as

$$\psi=\sum_{n=1}^{\infty}\psi_n(\tau\gamma_d)^n\ . \quad (8)$$

Since the reference state is rotating in this perturbation expansion with respect to the deformation rate, the unperturbed term ψ_0 should contain the effect of centripetal acceleration. But in the first-order perturbation calculation in γ_d this zeroth-order coefficient ψ_0 has been put *a posteriori* to zero. The reason is stated in the following. The effect of centripetal acceleration on the PCF is caused by the inertial term $(m\sigma^2/2)\dot{\mathbf{u}}$ in Eq. (1). When the shear-rate tensor is given by Eqs. (5,6), the acceleration $\dot{\mathbf{u}}$ may be written as follows: $\dot{\mathbf{u}}=(\gamma_d^2-\gamma_r^2)(x,y,0)$, where the relations $d\mathbf{r}/dt=(\partial/\partial t+\mathbf{u}\cdot\partial/\partial\mathbf{r})\mathbf{r}=\mathbf{u}$ and $\boldsymbol{\gamma}_d\cdot\boldsymbol{\gamma}_r+\boldsymbol{\gamma}_r\cdot\boldsymbol{\gamma}_d=0$ are used. So the inertial term is in second order of the deformation rate and has no effect on the first-order solution in the deformation rate. The part of PCF independent of the deformation rate looks like $\exp[-w/(k_BT)+m\sigma^2\gamma_r^2(x^2+y^2)/(4k_BT)]$, where the potential due to the centripetal acceleration has been added. But this effect from the centripetal acceleration is cancelled by the second-order effect of deformation in the inertial term, for $\dot{\mathbf{u}}=(\gamma_d^2-\gamma_r^2)(x,y,0)=0$ in the stationary plane Couette flow ($\gamma_d=\gamma_r$). In this sense, the first-order solution for the distortion of PCF in this article is not exactly in first order of the deformation rate but still includes the second-order effect of the inertial term.

We again expand ψ_n in spherical harmonics:

$$\psi_n(r,\theta,\phi)=\sum_{m=-\infty}^{\infty}\sum_{l\ge|2m|}R_n^{(l,2m)}(r)Y_l^{(2m)}(\theta,\phi)\ , \quad (9)$$

where the symmetry of the Couette flow $\psi_n(r,\theta,\phi+\pi)=\psi_n(r,\theta,\phi)$ has been used, i.e., $R_n^{(l,2m-1)}=0$ for all integer m. Substitution of (8) and (9) into (3) leads to a system of the coupled differential equations for the radial coefficients $R_n^{(l,2m)}$. For the stationary situation, i.e., $\partial\psi/\partial t=\partial\gamma_d/\partial t=\partial\gamma_r/\partial t=0$, we obtain the following equation for the first-order coefficient $R_1^{(l,2m)}$:

$$[L_r^{(l)}+V(r)+k_m^2]R_1^{(l,2m)}=(-i\sqrt{32\pi/15})\delta_{l,2}(\delta_{m,1}-\delta_{m,-1})rq'\ , \quad (10)$$

where

$$L_r^{(l)}=\frac{\partial^2}{\partial r^2}+\frac{2}{r}\frac{\partial}{\partial r}-\frac{l(l+1)}{r^2}\ , \quad (11)$$

$k_m=\exp[is_m\pi/4]|2m\tau\gamma_r|^{1/2}$ for $\tau\gamma_r>0$, and $s_m=\mathrm{sgn}(m)$. The relation $4xy/r^2=-i\sqrt{32\pi/15}[Y_2^2(\theta,\phi)-Y_2^{-2}(\theta,\phi)]$ has been used in transforming the second term in the angular brackets in the right-hand side (rhs) of Eq. (3). If $q(r)=g_{\mathrm{eq}}^{1/2}(r)=0$ for $r\le 1$, the quantities, such as $q(1)/q(1)=0/0$ and $1/q(1)=1/0$, cannot be well defined. So we assume $q(r)$ to be infinitesimally small but nonzero for $r\le 1$ so that $q(1)/q(1)=1$, $1/q(1)-1/q(1)=0$, and so on. To this end we may consider that $q(r)$ can be parametrized in the region $r\le 1$, as $q(r)=q(r,\epsilon)\to 0$ for $r\le 1$, as $\epsilon\to 0$.

The function $V(r)$ is singular at $r=1$ and may be decomposed as

$$V(r)=V_1(r)+\tilde{V}(r)\ , \quad (12)$$

where $V_1(r)=V(r)-\tilde{V}(r)$, $\tilde{V}(r)=-(\tilde{q}''+2\tilde{q}'/r)/\tilde{q}$, and

$\tilde{q}(1)=q(1^+)$ and $\tilde{q}(r)=q(r)$ for $r>1$. We neglect $\tilde{V}$ in our approximation, but we take the singular term V_1 exactly in Eq. (10) to obtain

$$[L_r^{(l)}+V_1(r)+k_m^2]R_1^{(l,2m)} =(-i\sqrt{32\pi/15})\delta_{1,2}(\delta_{m,1}-\delta_{m,-1})rq' . \quad (13)$$

The function V_1 vanishes for $r>1$, but the singular effect at $r=1$ plays an important role via the BC near the hard core in solving the differential equation (13), which we discuss in the following section.

III. BOUNDARY CONDITIONS AND REDUCTION OF THE SYSTEM OF EQUATIONS

We may consider the following BC's for the excess pair probability current density j:

$$j_r(r)=0 \quad \text{at } r=1 , \quad (14)$$

$$\lim_{r\to\infty} j_r(r)=0 , \quad (15)$$

where the subscript r stands for the radial component. The BC (14) comes from the impossibility of a pair of hard cores overlapping and the BC (15) implies the stochastic independence of a pair of molecules infinitely distant from each other. From the above BC's (14) and (15) we can write the following BC's in terms of $R_1^{(l,2m)}$ as

$$[R_1^{(l,2m)}/q]'_{r=1}=0 , \quad (16)$$

$$[R_1^{(l,2m)}/q]'_{r=\infty}=0 , \quad (17)$$

where we have used the fact that $g_{\text{eq}}=q^2=1$ at $r=\infty$. We also assume the continuity of g/g_{eq} at $r=1$, which implies

$$[R_1^{(l,2m)}/q]_{r=1}=[R_1^{(l,2m)}/q]_{r=1^+} . \quad (18)$$

But the first derivative of g/g_{eq}, $(g/g_{\text{eq}})'$ need not be continuous at $r=1$, and we may write generally

$$\left[\frac{R_1^{(l,2m)}}{q}\right]' = \left[\frac{R_1^{(l,2m)}}{q}\right]'_{r=1} + \lim_{n\to\infty}\left[\frac{q}{\tilde{q}}\right]^n \left[\left[\frac{\tilde{R}_1^{(l,2m)}}{\tilde{q}}\right]' - \left[\frac{R_1^{(l,2m)}}{q}\right]'_{r=1}\right] , \quad (19)$$

where $\tilde{R}_1^{(l,2m)}(1)=R_1^{(l,2m)}(1^+)$ and $\tilde{R}_1^{(l,2m)}(r)=R_1^{(l,2m)}(r)$ for $r>1$. It is to be noted that $\lim_{n\to\infty}[q(r)/\tilde{q}(r)]^n$ guarantees the "absolute" zero at $r=1$ (while, as mentioned before, $q/\tilde{q}$ itself is infinitesimally small but nonzero at $r=1$) and is equal to unity for $r>1$.

In order to derive a BC near the hard core it is more convenient to rearrange Eq. (13) with respect to the function $R_1^{(l,2m)}/q$ as

$$q[L_r^{(l)}+k_m^2-\tilde{V}(r)]\frac{R_1^{(l,2m)}}{q}+2q'\left[\frac{R_1^{(l,2m)}}{q}\right]' =-i\left[\frac{32\pi}{15}\right]^{1/2}\delta_{l,2}(\delta_{m,1}-\delta_{m,-1})rq' . \quad (20)$$

Under the continuity condition of $R_1^{(l,2m)}/q$ at $r=1$ (18) and the representation of its first derivative (19), we can integrate Eq. (20) from $r=1$ to $r=1^+$, which results in

$$\left[\frac{R_1^{(l,2m)}}{q}\right]'_{r=1^+}+\left[\frac{R_1^{(l,2m)}}{q}\right]'_{r=1} =-i\left[\frac{32\pi}{15}\right]^{1/2}\delta_{l,2}(\delta_{m,1}-\delta_{m,-1}) , \quad (21)$$

where we have taken the limit $n\to\infty$ after integration. If we require the BC (16), which is sufficient for the radial component of the excess pair probability current density to vanish at $r=1$, as stated in (14), we can obtain a BC at $r=1^+$ from the result above, as

$$[R_1^{(l,2m)}/q]'_{r=1^+}=-i\left[\frac{32\pi}{15}\right]^{1/2}\delta_{l,2}(\delta_{m,1}-\delta_{m,-1}) . \quad (22)$$

With the BC's (22) and (17) we may integrate the differential equation (13) in the range $1<r<\infty$ excluding the singular point $r=1$, where the effect of the singularity at $r=1$ is included in the BC (22). It should be noticed that the BC (22) is inhomogeneous if $l=2$ and $m=\pm1$, and homogeneous otherwise.

For $l\neq2$ or $m\neq\pm1$, Eq. (13) becomes homogeneous and the differential operator $L_r^{(l)}$ becomes Hermitian under the pertaining homogeneous mixed boundary conditions (22) and (17) at $r=1^+$ and ∞, respectively. Since the constant $k_m^2=i2m\tau\gamma_r$ in the left-hand side (lhs) of Eq. (13) is purely imaginary while the eigenvalues of the Hermitian operator $L_r^{(l)}$ are real, the solutions of the homogeneous equations for $l\neq2$ or $m\neq\pm1$ become trivial, i.e.,

$$R_1^{(l,2m)}=0 \quad \text{for } l\neq2 \text{ or } m\neq\pm1 . \quad (23)$$

Thus it is enough to examine Eq. (13) for $l=2$ and $m=\pm1$ only, which can be rewritten for $r>1$ explicitly as

$$[L_r^{(2)}+k_m^2]R_1^{(2,2m)}=-im\left[\frac{32\pi}{15}\right]^{1/2}rq' \quad (24)$$

for $l=2$ and $m=\pm1$, where the singular term V_1 does not appear since $V_1=0$ for $r>1$, but its singular effect at $r=1$ is included in the BC (22). Equation (24) is to be solved under the following BC's at $r=1^+$ and infinity:

$$[R_1^{(2,2m)}/q]'_{r=1^+}=-im\left[\frac{32\pi}{15}\right]^{1/2} , \quad (25)$$

$$[R_1^{(2,2m)}/q]'_{r=\infty}=0 , \quad (26)$$

which can be deduced from (22) and (17) for $l=2$ and $m=\pm1$, respectively.

The BC (25) is inhomogeneous and we have in this case

not only an inhomogeneous solution but also a nontrivial homogeneous one:

$$R_1^{(2,2m)}=R_1^{I(2,2m)}+R_1^{H(2,2m)} , \tag{27}$$

where the superscripts I and H denote the inhomogeneous and the homogeneous solutions, respectively. For the sake of convenience we require that the inhomogeneous solution $R_1^{I(2,2m)}$ satisfies the following homogeneous BC's at $r=1^+$ and infinity:

$$[R_1^{I(2,2m)}/q]'_{r=1^+}=0 , \tag{28}$$

$$[R_1^{I(2,2m)}/q]'_{r=\infty}=0 , \tag{29}$$

where $m=\pm 1$. The homogeneous solution $R_1^{H(2,2m)}$ consequently has to satisfy the following BC's at $r=1^+$ and infinity:

$$[R_1^{H(2,2m)}/q]'_{r=1^+}=-im\left[\frac{32\pi}{15}\right]^{1/2} , \tag{30}$$

$$[R_1^{H(2,2m)}/q]'_{r=\infty}=0 , \tag{31}$$

where $m=\pm 1$, so that $R_1^{(2,2m)}=R_1^{I(2,2m)}+R_1^{H(2,2m)}$, which is stated in Eq. (27), may satisfy the BC's (25) and (26) at $r=1^+$ and ∞, respectively.

IV. FIRST-ORDER DISTORTION OF PCF IN THE DEFORMATION

The only homogeneous solution of Eq. (24) that satisfies the BC's (30) and (31) is

$$R_1^{H(2,2m)}(r)=D_m h_2^{[(3-m)/2]}(k_m r) , \tag{32}$$

where

$$D_m=-im\left[\frac{32\pi}{15}\right]^{1/2}\Big/\left[\frac{\partial}{\partial r}\left\{h_2^{[(3-m)/2]}(k_m r)/q(r)\right\}\right]_{r=1^+} ,$$

and $h_l^{(j)}$ is the spherical Hankel function of the first ($j=1$) or second ($j=2$) kind.

Under the homogeneous BC's (28) and (29), the differential operator $L_r^{(2)}$ in Eq. (24) is Hermitian and it is convenient to represent the inhomogeneous solution by making use of the Green's function, which satisfies the following equation:

$$[L_r^{(2)}+k_m^2]G_m(r|\rho)=r^{-2}\delta(r-\rho) , \tag{33}$$

where $\delta(r-\rho)$ is the Dirac delta function. The Green's function G_m consists of a pair of independent homogeneous solutions of (33) A_m and B_m, which satisfy the following BC's corresponding to the BC's (29) and (28), respectively:

$$[A_m/q]'_{r=\infty}=0 , \tag{34}$$

$$[B_m/q]'_{r=1^+}=0 . \tag{35}$$

The solutions for A_m and B_m pertaining to the BC's (34) and (35) are given by, irrespective of the proportional coefficients,

$$A_m(r)=h_2^{[(3-m)/2]}(k_m r) , \tag{36}$$

$$B_m(r)=h_2^{(1)}(k_m r)+C_m h_2^{(2)}(k_m r) , \tag{37}$$

where $C_m=-C_m^{(1)}/C_m^{(2)}$ and

$$C_m^{(j)}=\left[q(r)\frac{\partial}{\partial r}\{h_2^{(j)}(k_m r)/q(r)\}\right]_{r=1^+} \tag{38}$$

for $j=1,2$. We may represent the Green's function G_m in terms of A_m and B_m as

$$G_m(r|\rho)=\frac{1}{W_m}\begin{cases}B_m(r)A_m(\rho) & \text{for } 1<r\le\rho\\ A_m(r)B_m(\rho) & \text{for } 1<\rho\le r\end{cases} , \tag{39}$$

where $W_m/\rho^2=\Delta\{B_m(r),A_m(r)\}_{r=\rho}=-\rho^{-2}(2i/k_m)C_m^{[(3-m)/2]}/C_m^{(2)}$ is the Wronskian of B_m and A_m.

Given the Green's function explicitly, we can obtain the inhomogeneous solution of Eq. (24) as

$$\begin{aligned}R_1^{I(2,2m)}&=\int_{\rho>1}G_m(r|\rho)\left\{-im\left[\frac{32\pi}{15}\right]^{1/2}\rho q'(\rho)\right\}\rho^2 d\rho\\ &=-\frac{im}{W_m}\left[\frac{32\pi}{15}\right]^{1/2}\left[A_m(r)\int_{1<\rho<r}B_m(\rho)\rho^3 q'(\rho)d\rho+B_m(r)\int_{r<\rho<\infty}A_m(\rho)\rho^3 q'(\rho)d\rho\right] ,\end{aligned} \tag{40}$$

where A_m and B_m are given by (36) and (37), respectively. If we use the relation

$$\int_1^r h_2^{[(3-t/2)]}(k_m\rho)\rho^3\tilde{q}'(\rho)d\rho=r^3 h_2^{[(3-t)/2]}(k_m r)\tilde{q}(r)-h_2^{[(3-t)/2]}(k_m)q(1^+)+S^{[(3-t)/2]}(r;k_m) , \tag{41}$$

where $t=\pm 1$ and

$$S^{[(3-t)/2]}(r;k_m)=\frac{1}{k_m}\int_1^r e^{itk_m\rho}(k_m\rho^2+it\rho)\tilde{q}(\rho)d\rho , \tag{42}$$

we can rewrite Eq. (40) as

$$R_1^{I(2,2m)} = -\frac{1}{2}\left[\frac{32\pi}{15}\right]^{1/2}[-2imq(1^+)h_2^{[(3-m)/2]}(k_m r)/C_m^{[(3-m)/2]} + mk_m\{C_m^{(1)}h_2^{(2)}(k_m r) - C_m^{(2)}h_2^{(1)}(k_m r)\}S^{[(3-m)/2]}(\infty;k_m)/C_m^{[(3-m)/2]} + mk_m h_2^{(1)}(k_m r)S^{(2)}(r;k_m) - mk_m h_2^{(2)}(k_m r)S^{(1)}(r;k_m)] , \tag{43}$$

where we have used the following relation:

$$C_m^{(1)}h_2^{(2)}(k_m) - C_m^{(2)}h_2^{(1)}(k_m) = \frac{2i}{k_m} . \tag{44}$$

The first-order radial solution $R_1^{(2,2m)}(r)$ consists of the homogeneous and the inhomogeneous one given explicitly by Eq. (32) and (43), respectively. Thus we finally obtain

$$R_1^{(2,2m)} = R_1^{I(2,m)} + R_1^{H(2,2m)} = -\frac{1}{2}\left[\frac{32\pi}{15}\right]^{1/2}[mk_m\{C_m^{(1)}h_2^{(2)}(k_m r) - C_m^{(2)}h_2^{(1)}(k_m r)\}S^{[(3-m)/2]}(\infty;k_m)/C_m^{[(3-m)/2]} + mk_m h_2^{(1)}(k_m r)S^{(2)}(r;k_m) - mk_m h_2^{(2)}(k_m r)S^{(1)}(r;k_m)] , \tag{45}$$

in the range of $r > 1$.

Substitution of the trivial homogeneous radial solutions for $l \neq 2$ or $m \neq \pm 1$, given by (23), into the rhs of Eq. (9) for $n = 1$, leads to the first-order solution simplified as

$$\psi_1(r,\theta,\phi) = \sum_{m=\pm 1} R_1^{(2,2m)}(r)Y_2^{(2m)}(\theta,\phi) . \tag{46}$$

As assumed in (18), $R_1^{(2,2m)}/q(r)$ is continuous at $r=1$, and the function $R_1^{(2,2m)}/q(r)$, where $R_1^{(2,2m)}$ is given by (45) for $r > 1$, may be extended continuously to the point $r=1$. Since $R_1^{(2,2)}(r)$ is the complex conjugate of $R_1^{(2,-2)}(r)$, we can represent ψ_1/q for $r \geq 1$ by substituting (45) into the above equation and by making use of the continuation to $r=1$, as

$$\psi_1(r,\theta,\phi)/q(r) = -\left[\frac{32\pi}{15}\right]^{1/2}\frac{1}{\bar{q}(r)} \times \mathrm{Re}[\{F_1(k,r)+F_2(k,r)\}Y_2^{(2)}(\theta,\phi)] \tag{47}$$

for $r \geq 1$, where

$$F_1(k,r) = k[C^{(1)}h_2^{(2)}(kr) - C^{(2)}h_2^{(1)}(kr)]S^{(1)}(\infty;k)/C^{(1)} , \tag{48}$$

$$F_2(k,r) = kh_2^{(1)}(kr)S^{(2)}(r;k) - kh_2^{(2)}(kr)S^{(1)}(r;k) , \tag{49}$$

$k \equiv k_{+1}$, $C^{(j)} \equiv C_{+1}^{(j)}$ for $j=1,2$ and $\mathrm{Re}(\cdots)$ denotes the real part of $(\cdots)$. It is to be noted that in obtaining the solution (47) we neglected the soft term $\tilde{V}$ in Eq. (10), where $V = V_1 + \tilde{V}$, but took into account the singular term V_1 exactly, which provided us with the boundary condition at $r = 1^+$ (22). By using the solution given by (47) we calculate the viscosity coefficients in the following section.

V. VISCOSITY COEFFICIENTS

We now calculate the viscosity coefficient of shear pressure and those of normal pressure differences. We consider only the potential contribution to these coefficients, for in dense fluids they are predominant over the kinetic contributions. First, we derive the general representations for viscosity coefficients from the first-order solution (47), and second, we apply them to the hard-sphere fluid.

In homogeneous fluids the symmetric traceless pressure tensor is represented in terms of the nonequilibrium PCF [10,11] as

$$p_{\mu\nu} = -\frac{n^2}{2\sigma^3}\int r_\mu * r_\nu r^{-1}v'(r)g(\mathbf{r})d^3r , \tag{50}$$

where n is the number of molecules per volume σ^3, the Greek subscripts μ,ν denote the Cartesian components, and $a_\mu * b_\nu$ represents the symmetric traceless tensor of second rank defined by

$$a_\mu * b_\nu = \tfrac{1}{2}(a_\mu b_\nu + a_\nu b_\mu) - \tfrac{1}{3}\delta_{\mu\nu}\mathbf{a}\cdot\mathbf{b} \tag{51}$$

with the Kronecker delta symbol $\delta_{\mu\nu}$. When we substitute the first-order approximation for the PCF, $g = g_{\mathrm{eq}} + g_{\mathrm{eq}}^{1/2}\psi_1\tau\gamma_d$, into the rhs of Eq. (50), the isotropic contribution vanishes for symmetry reasons and we obtain the following representation for the pressure tensor in the first-order approximation with respect to the deformation rate:

$$p_{\mu\nu} = -\frac{n^2}{2\sigma^3}\tau\gamma_d\int r_\mu * r_\nu r^{-1}v'(r)g_{\mathrm{eq}}(r) \times\{\psi(\mathbf{r})/g_{\mathrm{eq}}^{1/2}(r)\}d^3r . \tag{52}$$

We introduce the following three quantities of pressure tensor:

$$p_+ \equiv p_{xy} \ , \quad p_- \equiv \tfrac{1}{2}(p_{xx}-p_{yy}) \ ,$$
$$p_0 \equiv \tfrac{1}{2}\{p_{zz}-\tfrac{1}{2}(p_{xx}+p_{yy})\} \ , \tag{53}$$

and thereby we define the corresponding viscosity coefficients:

$$\eta_0^{\pm} \equiv -p_0^{\pm}/\gamma \ . \tag{54}$$

By making use of the expression for the pressure (52) and the definitions (53) and (54) we can represent the viscosity coefficients as

$$\eta_0^{\pm} = \frac{\tau n^2}{4\sigma^3}\int\int\int \begin{Bmatrix} \frac{1}{2}\sin^2\theta\sin^2\phi \\ \frac{1}{2}\sin^2\theta\cos 2\phi \\ \frac{1}{4}(3\cos^2\theta-1) \end{Bmatrix} \times r v'(r) g_{\rm eq}(r)\{\psi_1(r,\theta,\phi)/q(r)\} r^2 \times \sin\theta\, dr\, d\theta\, d\phi \ , \tag{55}$$

where the relations $\gamma_d = \gamma/2$ and $q = g_{\rm eq}^{1/2}$ have been used, and the integral is to be performed in polar coordinates.

A. For the intermolecular potential of hard core plus additional soft tail

Since the first-order solution $\psi_1(r,\theta,\phi)$ obtained in (47) is proportional to $\exp(i2\phi)$, the third integral in the r.h.s. of the equation above vanishes, which means

$$\eta_0 = 0 \tag{56}$$

in the first-order approximation with respect to the deformation rate. But $\eta_0 \neq 0$ in the second-order approximation, which implies η_0 is the second-order effect of the deformation. Substitution of the previous result for ψ/q, which is given by (47), into Eq. (55) leads to

$$\eta_{\pm} = \frac{2\pi\tau n^2}{15\sigma^3}\mathrm{Re}\left[\begin{Bmatrix} -i \\ -1 \end{Bmatrix}\int_{1\le r<\infty} r^3 v'(r) g_{\rm eq}(r)\{F_1(k,r)+F_2(k,r)\}/\tilde{q}(r)dr\right] . \tag{57}$$

The function $g_{\rm eq}$ is discontinuous at $r=1$ because of the hard-sphere potential v_h. But we assume the function y defined by

$$y(r) \equiv e^{v_h(r)/(k_B T)} g_{\rm eq}(r) \ , \tag{58}$$

to be continuous, provided that the additional tail $v_a(r)$ of the intermolecular potential is finite for $r>0$, which is true in the case of the Percus-Yevick equation for hard spheres [12]. Since $\exp\{-(1/k_B T)v_h(r)\}=0$ or 1 for $r \le 1$ or $r>1$, respectively, we can transform $v_h'(r)g_{\rm eq}(r)$, as

$$v_h'(r) g_{\rm eq}(r) = -k_B T\{e^{-v_h(r)/(k_B T)}\}' y(r) = -k_B T y(r)\delta(r-1) \ . \tag{59}$$

On making use of the equation above, the expression (57) becomes

$$\eta_{\pm} = \frac{2\pi k_B T\tau n^2}{15\sigma^3}\mathrm{Re}\left[\begin{Bmatrix} i \\ 1 \end{Bmatrix} g_{\rm eq}^{1/2}(1^+)F_1(k,1)\right] - \frac{2\pi\tau n^2}{15\sigma^3}\mathrm{Re}\left[\begin{Bmatrix} i \\ 1 \end{Bmatrix}\int_1^{\infty} r^3 v_a'(r) g_{\rm eq}^{1/2}(r)\{F_1(k,r)+F_2(k,r)\}dr\right] , \tag{60}$$

where the relations $v = v_h + v_a$, $y(r) = \tilde{q}^2(r)$, $y(1) = g_{\rm eq}(1^+)$, and $F_2(k,1)=0$ have been used. It is to be noticed that the singular effect at $r=1$ is extracted in the first term in the rhs of Eq. (60). The function $F_1(k,1)$ is given by

$$F_1(k,1) = 2iS^{(1)}(\infty;k)/C^{(1)} = \frac{E_1(k)+E_2(k)}{3[6+(1/k_B T)f(1^+)](1-ik)-[8+(1/k_B T)f(1^+)]k^2+2ik^3} \ , \tag{61}$$

$$E_1(k) = 4k^2\int_1^{\infty} e^{ik(r-1)}(kr^2+ir)dr = -12i-12k+4ik^2 \ , \tag{62}$$

$$E_2(k) = 4k^2\int_1^{\infty} e^{ik(r-1)}(kr^2+ir)\{g_{\rm eq}^{1/2}(r)-1\}dr \ , \tag{63}$$

where $k = |\tau\gamma|^{1/2}\exp(i\pi/4)$ and $f(r) = k_B T(\partial/\partial r)[\ln g_{\rm eq}]$ is the mean force at r in the relative pair space. The relation $C^{(1)}h_2^{(2)}(k) - C^{(2)}h_2^{(1)}(k) = 2i/k$ has been substituted into the definition of F_1 stated in Eq. (48) and the expression has been simplified. In the numerator in the rhs of (61) the integral has been decomposed into two parts. Since $\mathrm{Re}(ik) = -|\tau\gamma|^{1/2}/\sqrt{2} < 0$ for nonvanishing shear rate and $g_{\rm eq}(r) \to 1$ for $r \to \infty$, the integrals E_1 and E_2 exist for $\gamma \neq 0$. In order to obtain the Newtonian viscosity, we can take the limit of zero shear rate after integration.

If we assume the density correlation $(g_{\rm eq}-1)$ to decay exponentially, which seems to be true for most approximations, the integrand of the integral E_2 may be expanded for small shear rates in power series of k as

$$E_2(k) = 4k^2\int_1^{\infty} ir\{1-ik+\tfrac{1}{2}(r^2-1)k^2+\cdots\} \times \{g_{\rm eq}^{1/2}(r)-1\}dr \ , \tag{64}$$

for $|\tau\gamma| \ll 1$. Thus $E_2 \approx k^2$ for $|\tau\gamma| \ll 1$, and from (61), (62), and (64) we obtain the following Newtonian shear viscosity coefficient:

$$\eta_+(0^+) = \frac{8\pi k_B T \tau n^2}{15\sigma^3} \frac{g_{\rm eq}^{1/2}(1^+)}{6 + \frac{1}{k_B T} f(1^+)} + \eta'_+ , \qquad (65)$$

where 0^+ means the zero-shear-rate limit and η'_+ is the contribution from the second term of (60), which is small in dense fluids compared to the first one.

B. Viscosity coefficients for hard spheres

Since there is no additional tail ($v_a = 0$) for hard-sphere potential, the second term in the rhs of Eq. (60) vanishes in this case and we obtain the following useful representation for the viscosity coefficients of hard spheres:

$$\eta_\pm^{\rm HS}(\gamma) = \frac{2\pi k_B T \tau n^2}{15\sigma^3} {\rm Re} \left[\begin{Bmatrix} i \\ 1 \end{Bmatrix} g_{\rm eq}^{1/2}(1^+) F_1(k,1) \right] , \qquad (66)$$

where the superscript HS in $\eta_\pm^{\rm HS}$ denotes the hard sphere. For hard spheres the second term of (65) vanishes and the Newtonian viscosity becomes

$$\eta_+^{\rm HS}(0^+) = \frac{8\pi k_B T \tau n^2}{15\sigma^3} \frac{g_{\rm eq}^{1/2}(1^+)}{6 + \frac{1}{k_B T} f(1^+)} . \qquad (67)$$

We need the functional form of the equilibrium PCF $g_{\rm eq}$ in order to calculate the integral E_2. To this end we use the following approximation for the density correlation function $s(r) = g_{\rm eq}(r) - 1$, which was previously calculated in Refs. [1,2]:

$$s_{\rm PYH}(r) = 2\,{\rm Re} \left[\frac{a}{r} e^{(r-1)/\xi} \right] \qquad (68)$$

for $r > 1$, where a and ξ are complex functions of n_*, the number of molecules per molecular volume. The subscript PYH means the Percus-Yevick equation for hard spheres. It is noted that the approximation $s_{\rm PYH}$ differs in the global shape from the exact solution of the Percus-Yevick equation for hard spheres [12] but it gives the correct values of compressibility and pressure as the exact solution. The advantage of the approximate representation (68) is that it is analytic in the whole range of $r > 1$ while the exact solution of the Percus-Yevick equation is piecewise analytic. Its graphical representation is given in Refs. [1,2]. By making use of the approximation (68) we can calculate the viscosity coefficients given by (66) numerically. The relaxation-time coefficient τ introduced phenomenologically in this work may be determined by comparing our Newtonian viscosity for hard spheres with that from the molecular-dynamics simulations for hard spheres. We made use of the Erpenbeck's results for hard spheres [6,13,14]. For the number of molecules per molecular volume $n_* \equiv \frac{4}{3}\pi(\sigma/2)^3 n = 0.4628$, we have $\tau \simeq 11.3 t_C$, where t_C is the Boltzmann mean free time: $t_C = (4n\sigma^2\sqrt{\pi k_B T/m})^{-1}$. The dependence of the scaled viscosity coefficients $\eta_\pm^{\rm HS}/\eta_E$ on the scaled shear rate $t_C\gamma$ are shown in Figs. 1 and 2, where η_E is the Enskog value for the Newtonian viscosity: $\eta_E = \frac{5}{6} n m D_B \{1.016[1 + \frac{8}{5} g_{\rm eq}(1^+)]^2 + (768/25\pi) n_*^2 g_{\rm eq}^2(1^+)\}$ and $D_B = k_B T t_C/(2m)$ is the Boltzmann self-diffusion constant. The value of the mean force at $r = 1^+$, $f(1^+)$, in the representation (66) has been replaced by that from the exact solution of the Percus-Yevick equation for hard spheres. Here we find again the shear thinning of the shear viscosity which was observed in computer experiments [3–6] and other theories [15]. The viscosity coefficient for the normal pressure difference $\eta_- \equiv \frac{1}{2}(p_{xx} - p_{yy})/\gamma$ is positive, which is also true for the molecular-dynamics simulation [16]. As mentioned before, η_0 is zero in the first-order perturbation calculation with respect to the deformation.

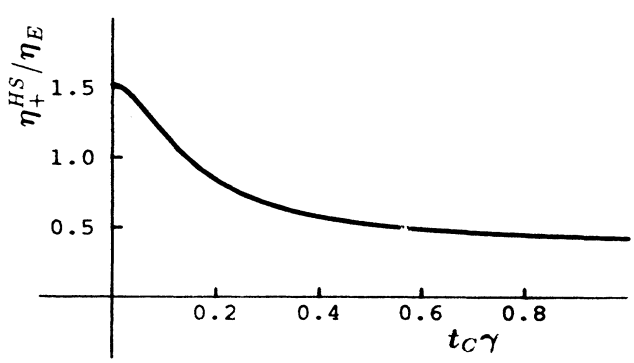

FIG. 1. Shear viscosity coefficient for hard spheres in the unit of the Enskog's viscosity η_E. t_C is the Boltzmann mean free time. $n_* = 0.4628$.

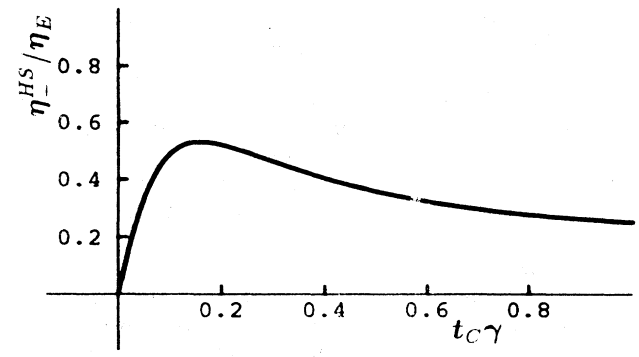

FIG. 2. Viscosity coefficient of the normal pressure difference $(p_{xx} - p_{yy})/2$ for hard spheres. Its value is represented in the unit of the Enskog's viscosity η_E, and t_C is the Boltzmann mean free time. $n_* = 0.4628$.

VI. DISCUSSION

In the previous work [2] the PCF was already calculated by solving the extended KS equation. But the complete derivation of the boundary condition near the hard core ($r = 1^+$) has been achieved only in this work. Thus the secondary boundary condition near the hard core in

Refs. [1,2] should be replaced by that derived in this work. The most important point of departure in this work is to decompose the shear-rate tensor into the rotation and the deformation part and take only the deformation tensor as perturbation. This is different from the conventional calculations of nonequilibrium PCF [10,11], where the shear-rate tensor itself is taken as perturbation parameter. The next important point is to take into account the singular effect at the hard core ($r=1$) exactly in the approximate calculation, i.e., to take V_1 exactly in (10) and (12), and derive the correct boundary condition near the hard core ($r=1^+$), which is stated in (22). It is strongly desired to develop the second-order perturbation theory in the deformation rate so that we may obtain a nontrivial value for η_0 and hopefully better results for η_+ and η_-. The behaviors of the viscosity coefficients derived agree qualitatively well with the molecular-dynamics simulation results, i.e., the shear thinning [3–6] and the positivity of the viscosity coefficient for normal pressure difference [16]. The viscosity coefficients derived here are essentially functions of $\sqrt{2\tau\gamma_r}=\sqrt{\tau\gamma}$ (rather than $\tau\gamma$ itself), where γ_r is the rotation rate, i.e., functions of the square root of the rotation rate. This may be related to the nonanalytic behavior of the viscosity coefficients at least in a limited range of shear rate. The dependence of shear viscosity on the square root of shear rate seems conditional: It has something to do with the competition between the dimensionless shear rate $\tau\gamma$ and the quantity $\Lambda=6+f(1^+)/(k_BT)$. We may obtain the term of square root of shear rate, when $\Lambda \ll \tau\gamma < |\xi|^{-2}$, where ξ is the complex correlation length in the unit of reference length σ. This point is to be investigated in later works. A more correct knowledge about the equilibrium PCF is desired to investigate the behavior of the viscosity coefficients in the relationship with the thermodynamic properties of more realistic model fluids.

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