Distribution functions of a simple fluid under shear. II. High shear rates

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The distortion of structure of a simple, inverse 12 soft-sphere fluid undergoing plane Couette flow is studied by nonequilibrium molecular dynamics (NEMD) and equilibrium molecular dynamics (EMD) with a high-shear-rate version of the nonequilibrium (NE) potential obtained recently from the NE distribution function theory of Gan and Eu [Phys. Rev. A **45**, 3670; **46**, 6344 (1992)]. The theory suggests a NE potential under which the equilibrium structure of the fluid is that of a NE fluid, and also suggests a corresponding Ornstein-Zernike equation with its closure relations. As in the low-shear-rate case [Yu. V. Kalyuzhnyi, S. T. Cui, P. T. Cummings, and H. D. Cochran, Phys. Rev. E **60**, 1716 (1999)] the agreement between EMD and the modified hypernetted chain version of the theory is good. Although the high-shear-rate version of the NE potential improves the agreement between NEMD and EMD results (in comparison with the low-shear-rate version), its predictions are still unsatisfactory. With the high-shear-rate NE potential, EMD gives qualitatively correct predictions only for the shift of the position of the first maximum of the NE distribution function. The corresponding changes in the magnitude of the first maximum predicted by EMD have an opposite direction in comparison with those predicted by NEMD. It is concluded that the NE potential used is not very successful, and more accurate models for the potential are needed.

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I. INTRODUCTION

In an earlier paper [1], we tested the low-shear-rate version of the integral equation theory for the nonequilibrium (NE) distribution function of a simple fluid under shear, proposed recently by Gan and Eu (GE) [2]. They derived a hierarchy of nonlinear integral equations for the NE fluctuations from the NE canonical distribution function, an approach similar in spirit to the theory of the structure of dense equilibrium fluids. The GE theory leads to an integral equation for the anisotropic NE pair distribution function which reduces to the Percus-Yerick (PY) integral equation in the equilibrium limit, suggesting that the Ornstein-Zernicke (OZ) relation also holds for NE fluids, i.e., the NE OZ equation (NEOZ). In essence, the GE theory postulates a NE potential under which the equilibrium structure of a fluid is that of the NE fluid. With such a potential all of the tools of equilibrium statistical mechanics can be brought to bear on the problem of a simple shearing liquid; furthermore, the possibility of similar progress for molecular liquids is opened up. The best test of the theory is to compare its predictions with NE molecular dynamics (MD) results, which are available only at relatively high shear rates. A successful theory could be usefully applied at lower shear rates. The theory and some variants of it have been tested using the methods of NEMD and equilibrium MD (EMD) with the GE NE potential. From comparison of the results of the theory with results of EMD with the NE potential at lower shear rates, it was concluded that, for a given NE potential, the theory is reasonably accurate, especially with the modified hypernetted chain (MHNC) closure. The EMD results with the NE potential were also compared with the results of NEMD and suggest that the NE potential used is not very accurate. More recently an improved version of the NE potential has been developed [3]. It is expected that this version of the potential, to which we refer as the full NE potential, may provide a more accurate description of the NE structure, extending the range of the theory to the higher-shear-rate regime.

In this paper we continue to explore the performance of the GE theory with the full NE potential. As in our earlier study [1] we compare predictions of the MHNC theory, NEMD predictions, and predictions of the EMD for the full NE potential. The paper is organized as follows. For the sake of completeness, in the next section we give a condensed summary of the GE theory. In Sec. III we present our results and discussion, and in Sec. IV we collect our conclusions.

II. SUMMARY OF GAN-EU THEORY

We refer the reader to the original publications [1–3] for a full discussion of the GE theory. Our terminology and notation follow Ref. [1], and we give only a condensed summary to make the paper self-contained.

Following [1–3], we consider steady-state planar Couette flow of a fluid confined between two infinite parallel plates. The y axis is perpendicular to the plates, which are located at $y=\pm-\frac{1}{2}D$ and move with a uniform velocity $\pm\frac{1}{2}u_0$ in opposite directions along the x axis. The key quantity of the present theory is the NE potential $V_{ne}(\mathbf{r})$, which follows from the solution of the corresponding kinetic equation that has been derived and solved in [2,3]. As a result the following expression for the NE potential has been proposed:

TABLE I. Reduced hydrostatic pressure $p^* = p\epsilon/\sigma^3$, shear stress $\Pi/2p$, and normal stress $N_1/2p$ for the soft-sphere particles at packing fraction $\nu = 0.45$ and reduced temperature $\beta^* = 1$ calculated from NEMD simulation. Here the number in parentheses is the statistical uncertainty in the least significant digit of the corresponding number and t_{run} is the total run length in the reduced time unit τ.

γ^*	p^*	$\Pi/2p$	$N_1/2p$	t_{run}
0.00	8.389(1)	0.0000	0.0000	
0.50	8.468(1)	−0.0400	−0.0014	3200
0.75	8.555(1)	−0.0578	−0.0022	2400
1.00	8.664(1)	−0.0737	−0.0032	980

$$V_{ne}(r,\theta,\phi) = V(r) + \alpha(r) r \frac{\partial V(r)}{\partial r}\left[\frac{\Pi}{2p}\sin^2\theta \sin 2\phi - \frac{1}{3}\frac{N_1}{2p}(2\sin^2\theta \sin^2\phi - 1)\right], \quad (1)$$

where $V(r)$ is the equilibrium potential, p is the hydrostatic pressure, Π and N_1 are the shear and normal stresses, respectively, and $\alpha(r)$ is a switching factor

$$\alpha(r) = \begin{cases} g_{eq}(r), & r \leq r_0 \\ 1, & r > r_0, \end{cases} \quad (2)$$

which is needed to avoid the infinitely large negative value of $V_{ne}(\boldsymbol{r})$ for $r=0$. Here r_0 is defined by the inequality $g_{eq}(r) \leq 1$ for $0 < r \leq r_0$, and $g_{eq}(r)$ is the equilibrium pair distribution function of the present system. The shear stress and normal stress satisfy the algebraic equation

$$\frac{\bar{\gamma}\tau_p p}{6\eta_0}\sqrt{\frac{1}{2}\left(1 - \frac{4}{9}x^2\right)} + \sinh\left\{\frac{\tau_p p}{\eta_0}\sqrt{\frac{1}{2}x\left(\frac{2}{3}x - 1\right)}\right\} = 0, \quad (3)$$

where

$$\frac{N_1}{2p} = x, \quad \frac{\Pi}{2p} = -\frac{1}{2}\sqrt{-x\left(1 + \frac{2}{3}x\right)},$$

$$\bar{\gamma} = \frac{6\eta_0\gamma}{p}, \quad \tau_p = \beta\frac{(2\eta_0 m_r^{1/2})^{1/2}}{\rho\sigma(2\beta)^{1/2}},$$

m_r is the reduced mass, σ is the size parameter of the particles, γ is the rate of shearing, i.e., $\gamma = (\partial u_x/\partial y)$, u_x is the flow velocity along the x axis, and η_0 is the Newtonian (zero-shear-rate) viscosity. The NE potential $V_{ne}(\boldsymbol{r})$ [Eq. (1)] is specialized in the coordinate frame with the azimuthal angle around the z axis denoted as ϕ and the polar angle between vector $\boldsymbol{r}$ and the z axis denoted as θ.

As in [2,3] we consider the case of the soft-sphere equilibrium intermolecular potential

$$V(r) = \epsilon\left(\frac{\sigma}{r}\right)^{12}. \quad (4)$$

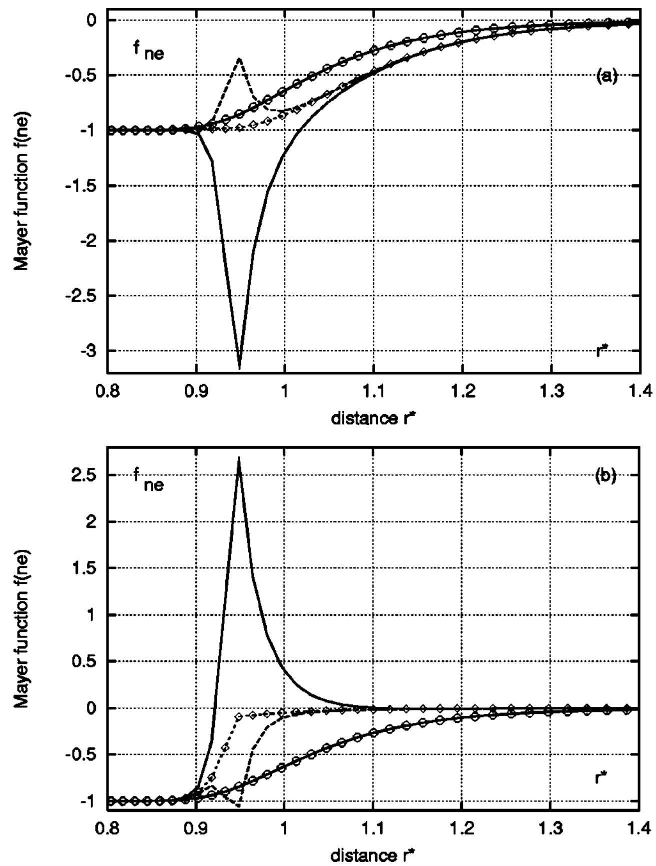

FIG. 1. Mayer function for the high-shear-rate version of the NE potential (1) for the packing fraction $\nu = 0.45$ and azimuthal angle values $\phi = 0$ (a) and $\phi = \pi/2$ (b). Circles represent an exact result for $\gamma^* = 1.0$ ($\bar{\gamma} = 1.07$) and diamonds represent an exact result for $\gamma^* = 9.047$ ($\bar{\gamma} = 10.0, p^* = 8.389, \Pi/2p = -0.223, N_1/2p = -0.237$). Results with $l_{max} = 4$ (solid lines), $l_{max} = 8$ (long dashed line, $\gamma^* = 9.047$), and $l_{max} = 16$ (short dashed line, $\gamma^* = 9.047$) are shown. Here $r^* = r/\sigma$.

For this potential, NEMD results for the Newtonian viscosity have been parametrized [4]:

$$\eta_0 = [0.171 + 0.022(e^{6.83y} - 1)]\frac{(m\epsilon)^{1/2}}{\sigma^2(\beta\epsilon)^{2/3}}, \quad (5)$$

where $y = (1/\sqrt{2})\rho\sigma^3(\beta\epsilon)^{1/4}$ and $m = 2m_r$. This expression for η_0 has been used to calculate the NE potential (1).

The expression for the NE potential (1) involves the value of the hydrostatic pressure p. Following [2,3] one can use the equilibrium value of p obtained from the solution of the Percus-Yevick approximation. However, since the purpose of our study is to examine the accuracy of the NE potential (1), we will follow our earlier study [1] and use the value of the hydrostatic pressure obtained from the corresponding NEMD simulation. For a similar reason, instead of solving Eq. (3), we will use the NEMD values for the shear and normal stresses.

Because of the steady-state shearing conditions, the NE pair potential (1) as well as the direct and total correlation

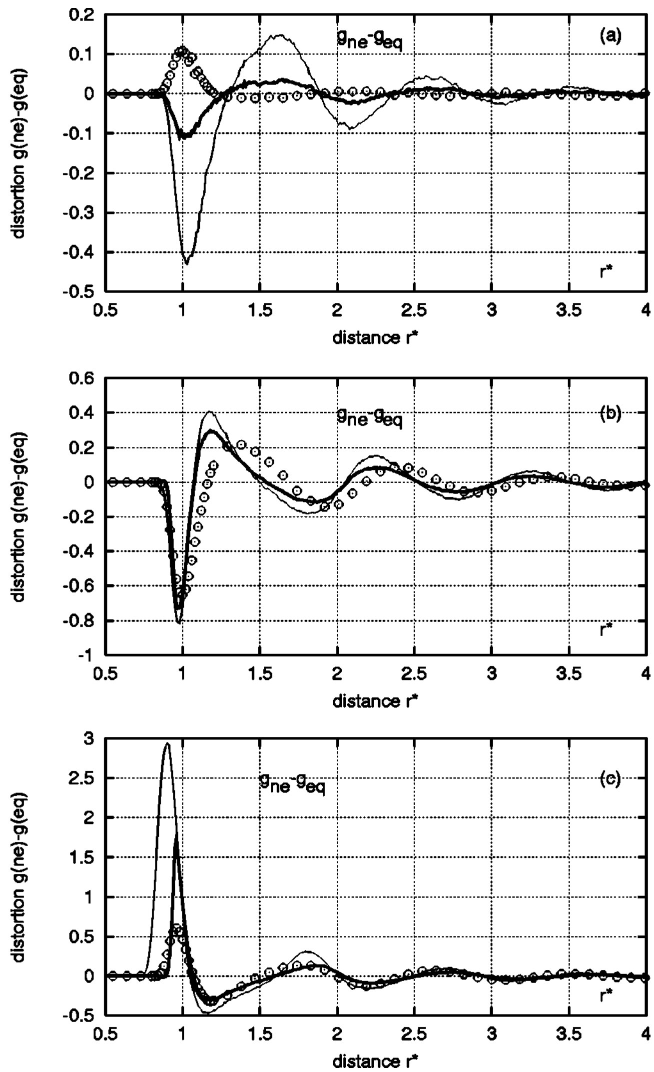

FIG. 2. The distortion of the fluid structure due to shear, $\Delta g_{ne}(r,\theta,\phi)=g_{ne}(r,\theta,\phi)-g_{eq}(r)$ at $\nu=0.45$, $\theta=\pi/2$, $\phi=0$, (a), $\phi=\pi/4$ (b), $\phi=3\pi/4$ (c), and $\gamma^*=0.75$ ($p^*=8.555$, $\Pi/2p=-0.0578, N_1/2p=-0.0022$). NEMD (circles), EMD for the full NE potential (1) (thick solid lines), EMD for the low-shear-rate version of the NE potential [1] (thin solid lines), and $g_{eq}(r)$ (dashed line). Here $r^*=r/\sigma$.

functions $c(\mathbf{r})$ and $h(\mathbf{r})$ are time independent. The NEOZ equation takes the form [1–3]

$$\hat{h}(\boldsymbol{k})=\hat{c}(\boldsymbol{k})+\rho\hat{c}(\boldsymbol{k})\hat{h}(\boldsymbol{k}). \tag{6}$$

As in [1] we will use here the MHNC closure conditions

$$c(\boldsymbol{r})=\exp[-\beta V_{ne}(\boldsymbol{r})+h(\boldsymbol{r})-c(\boldsymbol{r})+B(\boldsymbol{r})]-h(\boldsymbol{r})+c(\boldsymbol{r})-1, \tag{7}$$

which proves to be more accurate than the NE PY approximation proposed in [2,3]. Here

$$B(\boldsymbol{r})=-\frac{[h(\boldsymbol{r})-c(\boldsymbol{r})]^2}{2[1+0.8h(\boldsymbol{r})-0.8c(\boldsymbol{r})]}, \tag{8}$$

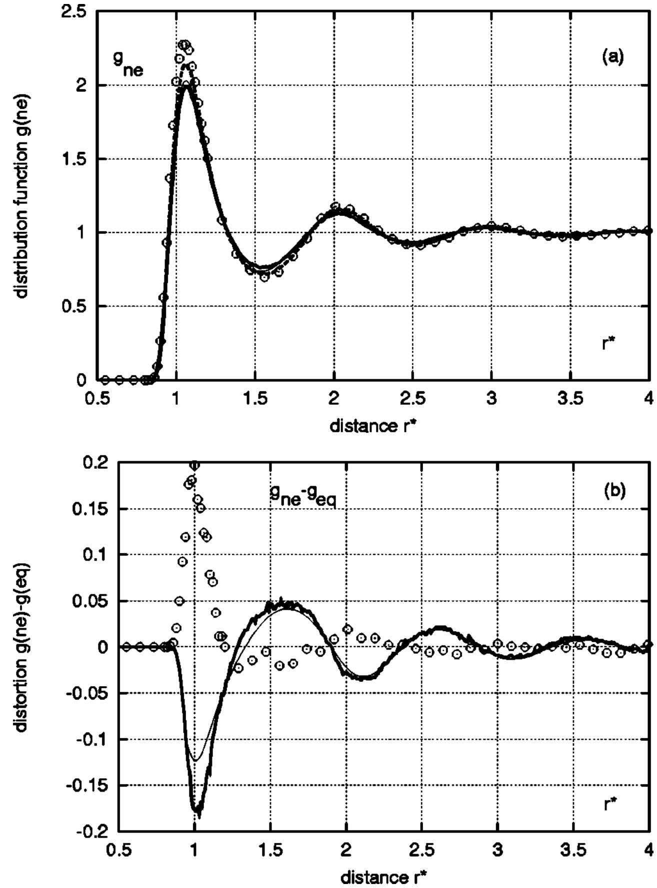

FIG. 3. The pair distribution function of the simple soft-sphere fluid under shear, $g_{ne}(r,\theta,\phi)$ (a) and distortion of the fluid structure due to shear, $\Delta g_{ne}(r,\theta,\phi)=g_{ne}(r,\theta,\phi)-g_{eq}(r)$ (b) at $\nu=0.45$, $\theta=\pi/2$, $\phi=0$, and $\gamma^*=1.0$ ($p^*=8.664, \Pi/2p=-0.0737, N_1/2p=-0.00321$). NEMD (circles), EMD for the full NE potential (1) (thick solid lines), MHNC for the full NE potential (1) (thin solid lines), and $g_{eq}(r)$ (dashed lines). Here $r^*=r/\sigma$.

and $\hat{c}(\boldsymbol{k}),\hat{h}(\boldsymbol{k})$ are the Fourier transforms of the direct $c(\mathbf{r})$ and total $h(\mathbf{r})$ correlation functions, respectively. The NEOZ equation (6) together with the closure relation (7) and NE potential (1) form a closed set of equations to be solved. Solution of this set of equations is obtained by expansion in spherical harmonics as has been utilized in the equilibrium theory of molecular fluids. This consists of expanding the correlation functions in spherical harmonics, writing the initial NEOZ equation as a set of equations for the spherical harmonic expansion coefficients in Fourier k space, and solving this set using a direct iteration method. This technique is rather standard, and details can be found in many places (see, for example, Refs. [5,6]).

III. RESULTS AND DISCUSSION

The present soft-sphere model fluid was studied at values of the packing fraction $\nu=(\pi/6)\rho\sigma^3=0.45$, at reduced temperature $\beta^*=\beta\epsilon=1$, and at three different values of reduced shear rate $\gamma^*=\gamma\tau=\gamma\sigma\sqrt{m/\epsilon}=0.5,0.75,1.0$. Our NEMD and EMD calculations were carried out following the scheme described earlier [1].

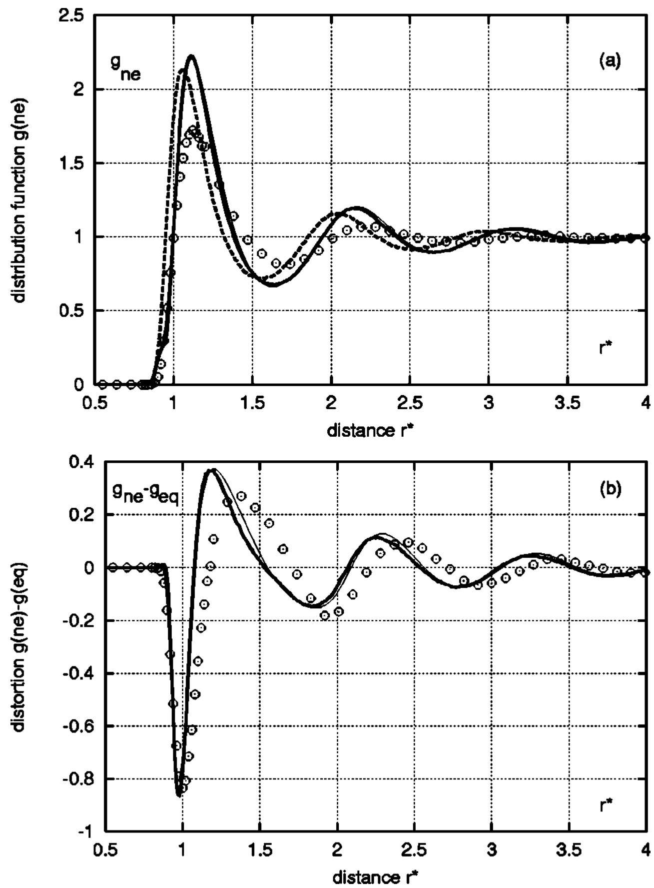

FIG. 4. The same as Fig. 3 but at $\phi = \pi/4$.

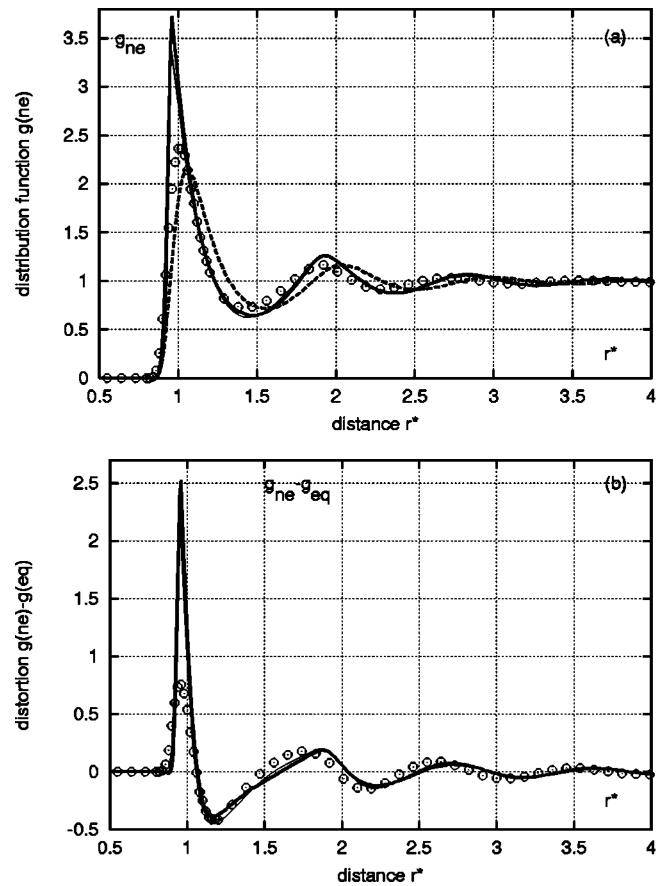

FIG. 5. The same as Fig. 3 but at $\phi = 3\pi/4$.

Table I presents results from the NEMD calculations, including values of the reduced hydrostatic pressure $p^* = p\epsilon/\sigma^3$, shear stress $\Pi/2p$, and normal stress $N_1/2p$, which are used as input to some of the theoretical calculations. To estimate the number of harmonics l_{max} needed to represent the Mayer function accurately for the NE potential (1), in Fig. 1 we compare an exact Mayer function with Mayer functions approximated by a finite number of harmonics. For the shear rate $\gamma^* \leqslant 1.0$, the Mayer function can be accurately represented using four harmonics. However, with further increase of the shear rate, the number of harmonics needed to describe the Mayer function rapidly increases. This can be seen in Fig. 1, where the exact Mayer function for the NE potential at $\gamma^* = 9.047$ ($\overline{\gamma} = 10.0$) is reproduced only by using 16 harmonics. Here in the case of $\gamma^* = 1.0$ the values of the shear Π and normal N_1 stresses are taken from the NEMD simulation (Table I) and in the case of $\gamma^* = 9.047$ are calculated from Eq. (3). We note in passing that in [2,3] numerical analysis of the present version of the theory for values of the shear rate $\overline{\gamma}$ in the range of $10.0 \leqslant \overline{\gamma} \leqslant 200.0$ was carried out taking into account only four harmonics.

To examine the accuracy of the present version of GE theory, in Figs. 2–5 we compare the NEMD, EMD, and MHNC results for the pair distribution functions $g_{ne}(\mathbf{r})$, $g_{eq}(\mathbf{r})$ and for the difference $\Delta g_{ne}(\mathbf{r}) = g_{ne}(\mathbf{r}) - g_{eq}(\mathbf{r})$ at four different values of the azimuthal angle $\phi = 0$, $\pi/4, \pi/2, 3\pi/4$ and two different values of $\gamma^* = 0.75, 1.0$. Here g_{ne} and g_{eq} are the NE and equilibrium pair distribution functions, respectively, NEMD simulation is carried out for the system with the original pair potential (4), and EMD simulation and MHNC theory use the NE potential (1) as an input. Comparison and analysis of the results obtained by the NEMD, EMD, and MHNC methods lead us to conclusions quite similar to those obtained in our earlier study [1]. As in the low-shear-rate case [1], the agreement between EMD and MHNC predictions for both g_{ne} and Δg_{ne} is good and the agreement between NEMD and EMD results is rather poor. Although the full version of the NE potential (1) substantially improves performance of the theory (see Fig. 2), its predictions are still unsatisfactory. EMD with the full NE potential gives qualitatively correct predictions only for the shift of the position of the first maximum and for the changes in the phase of oscillation of $g_{ne}(\boldsymbol{r})$ caused by shearing. However, the corresponding changes in the magnitude of the first maximum of $g_{ne}(\boldsymbol{r})$ predicted by EMD have an opposite direction in comparison with those predicted by NEMD. For the azimuthal angles $\phi = 0$ and $\phi = \pi/2$, shearing causes an increase of the first maximum of $g_{ne}(\boldsymbol{r})$ and for $\phi = \pi/4$ a decrease, while EMD predictions are in the opposite directions. Only in the case of $\phi = 3\pi/4$ do both EMD and NEMD simulations predict increase of the first maximum of $g_{ne}(\boldsymbol{r})$ due to shearing. However, at the same time, EMD strongly overestimates this increase.

IV. CONCLUDING REMARKS

Using the methods of NEMD, MHNC, and EMD with a NE potential, we have tested the high-shear-rate version of the Gan and Eu theory for the structure of fluids under steady-state shear flow conditions [2,3]. We find that none of the NE potentials proposed by Gan and Eu [2,3] yield satisfactory predictions for the distortion of the fluid structure due to shear. We must conclude that this element of the theory is not very successful. In future work we will explore other approaches for obtaining the NE potential.

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[1] Yu. V. Kalyuzhnyi, S. T. Cui, P. T. Cummings, and H. D. Cochran, Phys. Rev. E **60**, 1716 (1999).
[2] H. H. Gan and B. C. Eu, Phys. Rev. A **45**, 3670 (1992).
[3] H. H. Gan and B. C. Eu, Phys. Rev. A **46**, 6344 (1992).
[4] W. T. Ashurst and W. G. Hoover, Phys. Rev. A **11**, 658 (1975).
[5] C. G. Gray and K. E. Gubbins, *Theory of Molecular Fluids* (Clarendon Press, Oxford, 1984).
[6] S. Labik, R. Pospisil, A. Malijevsky, and W. R. Smith, J. Comput. Phys. **115**, 12 (1994).