I. INTRODUCTION

Kinetic processes are of fundamental interest and importance in many branches of science and engineering, yet theories of nonequilibrium systems have lagged far behind those of equilibrium systems. For example, the theories of equilibrium statistical mechanics provide practical means for calculating the properties of fluids at equilibrium from their structure. And likewise, the structure of fluids at equilibrium, as represented by their pair distribution functions, can be calculated with reasonable accuracy and efficiency using integral equation theories based on the Ornstein-Zernike (OZ) relation with an approximate closure relation, such as the Percus-Yevick (PY) or the hypernetted chain (HNC) equation; see, for example, [1]. The situation is nowhere near so well-developed, however, for systems that are not at equilibrium. Useful theories have been available only for dilute gas systems or for systems only slightly removed from equilibrium, where linear-response theory leads to the linear transport equations with constant transport coefficients, such as Newton’s law of viscosity. Evans and Morriss [2] present a well-organized development of the modern statistical mechanics of nonequilibrium fluids and present practical means of determining the properties of nonequilibrium fluids, such as the transport coefficients for viscosity, thermal conductivity, mass diffusivity, etc., from molecular simulation calculations with computers, e.g., calculation of the viscosity of a liquid far from equilibrium by nonequilibrium molecular dynamics (NEMD).

There have been relatively few attempts at theories of dense, nonequilibrium fluids in the nonlinear regime. Approaches based on fluctuating hydrodynamics have been utilized, in which nonrandom fluctuations have been added in a phenomenological way to the macroscopic continuity equations allowing calculation of the density-density correlation function and from it the nonequilibrium radial distribution function and the structure factor; see, for example, [3]. Similarly, Hess [4,5] proposed and solved a phenomenological evolution equation for the nonequilibrium radial distribution function. Gan and Eu (GE) proposed [6,7] an alternative approach and applied it to dense fluids at both low and high shear rates. They derived a hierarchy of nonlinear integral equations for the nonequilibrium fluctuations from the nonequilibrium 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 nonequilibrium pair distribution function which reduces to the PY integral equation in the equilibrium limit, suggesting that the OZ relation also holds for nonequilibrium fluids, i.e., . The nonequilibrium OZ equation (NEOZ). In essence, the GE theory postulates a nonequilibrium potential which i.e., that of the nonequilibrium fluid.

Unfortunately, the GE theory has not received significant attention or use, and testing to date has been limited. In very recent work [8], Farhat and Eu used the nonequilibrium potential of Gan and Eu [6] in performing Monte Carlo (MC) simulations of a simple fluid under shear; the results showed some deviations from results for the same system by NEMD, reflecting some deficiency or deficiencies in the nonequilibrium potential or the MC algorithm, or in both. Farhat and Gan further showed reasonable agreement between the GE theory and MC, both with the same nonequilibrium potential. Thus, there is considerable promise in the NEOZ approach but no definitive test of its accuracy or reliability. The OZ-based theories of equilibrium fluids have been usefully ex-
tended to complex molecular fluids, even to long-chain polymers [9–11]. If the NEOZ-based theory and the nonequilibrium potential of GE were found to be accurate in definitive testing against simulations, they, too, might be usefully extended for practical applications with complex molecular fluids. If the theory or potential is found to be deficient in such testing, a sound basis is established for seeking improvement.

In this paper, our purpose is to begin exploring the usefulness of the GE theory and to test it against new simulation results generated for this purpose for a simple soft sphere fluid. As an aid to the reader, we summarize the GE theory in Sec. II. In Sec. III we describe our approach to the numerical solution of the NEOZ equation and, in particular, to the versions with the PY closure and with a modified hypenetered chain (MHNC) closure. Special attention is paid to the number of spherical harmonics used in the numerical solution. In Sec. IV we briefly describe our NEMD simulations as well as our equilibrium molecular-dynamics (EMD) calculations with GE’s nonequilibrium potential. We present and discuss our results in Sec. V, and we conclude with a few brief remarks in Sec. VI.

II. SUMMARY OF GAN-EU THEORY

To avoid unnecessary repetition, we will present here only a summary of GE theory, focusing mostly on the details which are needed to formulate the final set of equations to be solved. We refer the interested reader to the original publications [6,7]. The point of departure in the OZ theory for the nonequilibrium structure of dense simple fluids is the non-equilibrium distribution function written in the exponential or canonical form suggested by the solution of the generalized Boltzmann equation. This form, with nonequilibrium effects accounted for via the corresponding terms in the potential energy function, is similar to that used in the equilibrium statistical mechanical theory of fluids. The nonequilibrium part of the potential follows from the solution of the set of equations derived from the generalized Boltzmann equation. This set of equations couples the nonequilibrium potential with the macroscopic observables, which are used to describe the nonequilibrium process of interest. Thus, the initial problem of describing the nonequilibrium structure has been substituted by the problem of describing the equilibrium structure with nonequilibrium potential. The latter task is rather straightforward and once the interparticle potential is specified, one can use the whole machinery of the equilibrium statistical mechanical theory of liquids to generate the corresponding OZ equation and its closure conditions. In [6,7] this goal is achieved by formulating the corresponding Kirkwood hierarchy of equations and adopting the Kirkwood superposition approximation together with the assumption that the non-heat-conducting fluid in question undergoes steady shear flow at uniform density and temperature. It is assumed also that the equilibrium interparticle interaction is pairwise additive. As a result, the nonequilibrium analog of the PY equation has been derived. This PY-like equation can be written in the form of the OZ equation, which couples the nonequilibrium direct $c(r_{12},t)$ and total $h(r_{12},t)$ time-dependent pair correlation functions

\[ c(r_{12},t) = h(r_{12},t) + \rho \int dr_{3} c(r_{13},t) h(r_{32},t) \tag{1} \]

and a PY-like closure relation

\[ c(r,t) = f_{ne}(r,t)[h(r,t) - c(r,t) + 1], \tag{2} \]

where $\rho$ is the number density, $f_{ne}(r,t)$ is the Mayer function for the nonequilibrium pair potential $V_{ne}(r,t)$, i.e., $f_{ne}(r,t) = \exp[-\beta V_{ne}(r,t)] - 1$, and $\beta = 1/(k_{B}T)$.

As one can see, a key quantity of the present theory is the nonequilibrium potential $V_{ne}(r,t)$, which follows from the solution of the corresponding kinetic equation. To proceed further, it is necessary to specify the particular fluid of interest, i.e., its equilibrium potential and shearing flow conditions. Following [6,7], 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 the opposite directions along the x axis. The corresponding set of equations for the nonequilibrium potential $V_{ne}(r)$ has been derived and solved in [6,7]. As a result, the following general expression for the nonequilibrium potential has been proposed:

\[ V_{ne}(r, \theta, \phi) = V(r) + \alpha(r) \frac{\partial V(r)}{\partial r} \left[ \frac{\Pi}{2p} \sin^{2} \theta \sin 2 \phi \right. \]

\[ \left. - \frac{1}{3} \frac{N_{1}}{2p} (2 \sin^{2} \theta \sin^{2} \phi - 1) \right] , \tag{3} \]

where $V(r)$ is the equilibrium potential, $p$ is the hydrostatic pressure, $\Pi$ and $N_{1}$ are the shear and normal stresses, respectively, $m_{x}$ is reduced mass, $\sigma$ is the size parameter of the particles, $\gamma$ is the rate of shearing, i.e., $\gamma = (\partial u_{x}/\partial y)$, $u_{x}$ is the flow velocity along the x axis, and $\alpha(r)$ is a switching factor

\[ \alpha(r) = \begin{cases} g_{0}(r), & r \leq r_{0} \\ 1, & r > r_{0} \end{cases} \tag{4} \]

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

\[ \frac{\gamma}{6} \frac{\tau_{p}}{\eta_{0}} \sqrt{\frac{1}{2} \left( 1 - \frac{4}{9} x^{2} \right)} + \sinh \left\{ \frac{\tau_{p}}{\eta_{0}} \sqrt{\frac{1}{2} \left( \frac{2}{3} x - 1 \right)} \right\} = 0 , \tag{5} \]

where

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

\[ \gamma = \frac{6 \eta_{0} \gamma}{p}, \quad \tau_{p} = \beta \frac{(2 \eta_{0} m_{x}^{1/2})^{1/2}}{\rho \sigma (2\beta)^{1/2}} , \]

\[ \beta = 1/(k_{B}T) . \]
and \( \eta_0 \) is the Newtonian (zero-shear-rate) viscosity. The nonequilibrium potential \( V_{ne}(r) \) (3) is specialized in the coordinate frame with the azimuthal angle around the \( z \) axis denoted as \( \phi \) and the polar angle between vector \( r \) and the \( z \) axis denoted as \( \theta \).

It is assumed that the expression for the nonequilibrium potential (3), which we shall call the full potential, is valid for any degree of departure from equilibrium, i.e., for any values of the shear rate \( \gamma \). At low values of the shear rate, the contribution from the terms involving the normal stress \( N_1 \) can be neglected and for the shear stress \( II \) one can use the Newtonian law of viscosity \( II = -\eta_0 \gamma \). As a result, for \( \gamma < 1 \) we have

\[
V_{ne}(r, \theta, \phi) = V(r) - \eta_0 \gamma \frac{\partial V(r)}{\partial r} \sin 2 \phi \sin^2 \theta. \tag{6}
\]

This expression for the nonequilibrium potential in the low shear limit, proposed in [6,7], will be used for the results presented in this paper; we shall refer to it as the low-shear-rate nonequilibrium potential. Work in progress will examine results with the full potential (3).

As in [6,7], we consider the case of the soft-sphere equilibrium intermolecular potential

\[
V(r) = \frac{a}{r}^{12}, \tag{7}
\]

For this potential, NEMD results for the Newtonian viscosity have been parametrized [12],

\[
\eta_0 = [0.171 + 0.022(e^{6.83y} - 1)]\frac{(m \varepsilon)^{1/2}}{a^2(\beta \varepsilon)^{2/3}}. \tag{8}
\]

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Here, \( \beta \rho \) is a unit second-rank tensor and \( g_{00}(r) \) is the \((00)\) component of the spherical harmonic expansion of \( g(r) \). Alternatively, one could use results from NEMD for both the Newtonian viscosity \( \eta_0 \) and the hydrostatic pressure \( \rho \) in calculating the nonequilibrium potential \( V_{ne} \).

Because of the steady-state shearing conditions, the nonequilibrium pair potential (6) as well as the direct and total correlation functions are time-independent. The NEOZ equation and PY closure relation take the following form:

\[
\hat{h}(k) = \hat{c}(k) + \rho \hat{c}(k) \hat{h}(k) \tag{11}
\]

and

\[
c(r) = f_{ne}(r)[h(r) - c(r) + 1]. \tag{12}
\]

The OZ equation (11) is written in terms of the Fourier transforms of the direct and total correlation functions. This form of the OZ equation is more convenient for numerical calculations than the corresponding version of the OZ equation written in the real \( r \) space. In addition to the PY closure relation (12), we propose the so-called modified HNC (MHNC) closure with a bridge function \( B(r) \) chosen in a form proposed by Verlet [14],

\[
c(r) = \exp[-\beta V_{ne}(r) + h(r) - c(r) + B(r)] - h(r) + c(r) - 1, \tag{13}
\]

where

\[
B(r) = -\frac{[h(r) - c(r)]^2}{2[1 + 0.8h(r) - 0.8c(r)]}. \tag{14}
\]

For \( B(r) = 0 \), the present MHNC closure reduces to the HNC type of the closure, proposed in [6,7].

III. NUMERICAL SOLUTION OF THE THEORY

The OZ equation (11) together with its closure relation (12) [or Eq. (13)], relations (10) and (5) form a closed set of
equations to be solved. Solution of this set of equations can be obtained by expansion in spherical harmonics as has been utilized in the equilibrium theory of molecular fluids. It consists of expanding the correlation functions in spherical harmonics, writing the initial OZ equation as a set of equations for the spherical harmonic expansion coefficients in Fourier \( k \) space, and solving this set using either a direct iteration method or combining the latter with the Newton-Raphson method. This technique is rather standard and details can be found in many places (see, for example, Refs. [15,16]). In the present study, solutions of the corresponding set of equations for the spherical harmonic expansion coefficients have been obtained using the direct iteration method. The forward and inverse Hankel transforms, which are needed to couple the spherical harmonic expansion coefficients in real and Fourier spaces, have been carried out in logarithmic variables, using the method developed by Talman [17]. This method allows us to sample effectively both the rapidly varying part of the correlation functions at small distances and the long-range, slowly decaying portion using a relatively small number of grid points \( n = 512 \), which cover the distance up to \( r/\sigma = 73 \).

**IV. MOLECULAR-DYNAMICS SIMULATIONS**

Like the theoretical calculations, the molecular-dynamics calculations were performed for a soft-sphere fluid with the equilibrium intermolecular potential (7). For the NEMD calculations, the SLLOD (so named because of its close relationship to the Dolls tensor algorithm) equations of motion [2] were integrated using a velocity Verlet integrator with a Nose thermostat [1]. A time step of 0.002 \( t \) was used for the integration, where \( t = \sigma \sqrt{m/\epsilon} \) is the reduced time unit. The soft-sphere potential was truncated at \( r_c = 2.0 \sigma \), and no long-range correction was applied because it is very small. The EMD calculations with the low-shear-rate potential (6) were carried out in the same way but with the shear rate in the SLLOD equations of motion set to zero. NEMD and EMD calculations were performed with 2048 particles, and relatively long simulations were carried out to ensure that the statistical uncertainties are small.

**V. RESULTS AND DISCUSSION**

The soft-sphere fluid was studied at two different values of the packing fraction \( \nu = \pi/6 \rho \sigma^3 = 0.30, 0.45 \) and two dif-
The distortion of the fluid structure due to shear, \( \Delta g_{\text{ne}}(r, \theta, \phi) = g_{\text{ne}}(r, \theta, \phi) - g_{\text{eq}}(r) \) at \( \nu = 0.45, \, \theta = \pi/2, \, \phi = 0, \) \( \gamma^* = 0.75 \) (upper portion of the figure), \( \gamma^* = 0.5 \) (lower portion of the figure). EMD with the low-shear-rate nonequilibrium potential (6) (solid lines), NEMD (symbols). Here \( r^* = ri/\sigma \).

As a first step in testing the theory, we compared PY and MHNC results for the pair distribution function \( g_{\text{eq}}(r) \) of the system with \( \nu = 0.45 \) at equilibrium (\( \gamma^* = 0 \)) against corresponding equilibrium molecular-dynamics (EMD) simulation results. As expected, agreement between theoretical results and results of EMD simulation was good, and the agreement was better in the case of MHNC theory. To estimate the number of harmonics \( l_{\text{max}} \) needed to represent the Mayer function accurately for the nonequilibrium potential (6), in Fig. 1 we compare an exact Mayer function with Mayer functions approximated by a finite number of harmonics. For the shear rate \( \gamma^* = 0.75 \), the Mayer function for the nonequilibrium potential (6) can be accurately represented using eight harmonics. However, with further increase of the shear rate, the number of harmonics needed to describe the Mayer function rapidly increases.

In order to test the accuracy of the PY and MHNC theories in reproducing the structure of the system with the low-shear-rate nonequilibrium potential (6), in Figs. 2–4 we illustrate the distortion of the fluid structure due to shear, here defined as \( \Delta g_{\text{ne}}(r, \theta, \phi) = g_{\text{ne}}(r, \theta, \phi) - g_{\text{eq}}(r) \), where \( g_{\text{ne}} \) and \( g_{\text{eq}} \) are the nonequilibrium and equilibrium pair distribution functions, respectively, for two different values of the shear rate (\( \gamma^* = 0.5, \, 0.75 \)) and at system packing fraction \( \nu = 0.45 \). Here predictions of PY and MHNC theories are compared against the corresponding EMD simulation results for the nonequilibrium potential (6) with hydrostatic pressure obtained from NEMD simulation (Table I). At lower values of the shear rate (\( \gamma^* = 0.5 \)), agreement between both theoretical methods and EMD is very good for the values of the azimuthal angle \( \phi = \pi/4 \) and \( \phi = 3\pi/4 \). For \( \phi = 0 \), PY and MHNC underpredict the depth of the first minimum of the difference \( \Delta g_{\text{ne}}(r, \theta, \phi) \), with MHNC giving slightly better results. For the higher shear rate (\( \gamma^* = 0.75 \)), agreement is also better in the case of MHNC. For \( \phi = \pi/4 \), agreement is very good; for \( \phi = 0 \), MHNC slightly underpredicts the depth of the first minimum of \( \Delta g_{\text{ne}}(r) \); and for \( \phi = 3\pi/4 \), MHNC
underpredicts the value of the first maximum. In all cases use of eight harmonics improves the results in comparison with results obtained with only four harmonics.

Next we investigate the accuracy of the low-shear-rate nonequilibrium potential (6) in predicting the nonequilibrium structure of the system in question. This goal can best be achieved by comparing the results from NEMD against results from EMD with the low-shear-rate potential (6). Figures 5–9 make this comparison at two values of the reduced shear rate used by Gan and Eu, $\gamma = 0.812$ and 0.547 at packing fraction $\nu = 0.45$ and at $\gamma = 0.764$ at packing fraction $\nu = 0.3$; the values of $\gamma$ have been obtained using values of $\gamma^*$, $\rho^*$ from NEMD (see Table I) and $\eta_0$ using the NEMD results parametrization (8). There are notable differences in the magnitude and radial position of peaks in $\Delta g_{ne}(r, \theta, \phi)$ between the NEMD results and the EMD results using the low-shear-rate nonequilibrium potential (6); nevertheless, the low-shear-rate nonequilibrium potential (6) does seem to capture some of the effects of shear on the fluid structure, particularly at the lower shear rate and the lower packing fraction, as would be expected. EMD gives a reasonably accurate prediction for the shift of the first maximum position and for the changes in the phase of oscillation of $g_{ne}(r)$ caused by shearing at $\phi = 0, \pi/4, \pi/2$. However, the corresponding changes in the magnitude of the first maximum of $g_{ne}(r)$ predicted by EMD have an opposite direction in comparison with those predicted by NEMD (see Table II). For the azimuthal angles $\phi = 0$ and $\phi = \pi/2$, shearing causes an increase of the first maximum of $g_{ne}(r)$, 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 an increase of the first maximum of $g_{ne}(r)$ due to shearing. However, at the same time, EMD strongly overestimates this increase. Similar behavior can be seen in the case of the lower packing fraction $\nu = 0.3$. One notable artifact of the low-shear-rate nonequilibrium potential (6) is the displacement of the peaks in $g(r)$ to lower values of $r$ at $\phi = 3\pi/4$, which results from the $\sin 2\phi$ term, which appears in both the low-shear-rate nonequilibrium potential (6) as well as the full potential (3).

In order to have a complete, self-consistent theory of the nonequilibrium structure of fluids under shear, one might expect to calculate the hydrostatic pressure and the Newton-
ian viscosity (needed in the nonequilibrium potential) from the theory itself (and not from external simulations or parametrizations thereof). As a first step to this end, we have calculated the hydrostatic pressure self-consistently from the theory using Eq. (10). Figure 10 shows the change of the pressure due to shear \((p - p_{eq})/Nk_BT\) as a function of shear rate \(\gamma^*\) from the self-consistent MHNC theory with the low-shear-rate nonequilibrium potential (6) and from the NEMD calculations at the two packing fractions \(\nu = 0.45\) and \(\nu = 0.30\), respectively. Clearly, the self-consistent MHNC theory with the low-shear-rate nonequilibrium potential predicts the effects of shear on pressure accurately only at very low shear rates.

Now, we have shown that the MHNC theory is quite accurate in predicting the distortion of the structure due to the low-shear-rate nonequilibrium potential (6). We have shown that the low-shear-rate nonequilibrium potential (6) predicts the distortion of the fluid structure by shear only qualitatively. And we have shown that the self-consistent MHNC theory predicts the hydrostatic pressure poorly. We cannot have great hope for the success of the self-consistent MHNC theory with the low-shear-rate nonequilibrium potential (the combining of all the approximate parts of the theory) to predict the distortion due to shear. Nevertheless, for completeness, in Figs. 11–15 we present the distortion of fluid structure due to shear from the theory and from the NEMD calculations. We must conclude that the theory is not very successful.

VI. CONCLUDING REMARKS

It is an interesting prospect to use the well-developed machinery of equilibrium statistical mechanics with a nonequilibrium potential to predict the structure and properties of fluids in time-invariant, nonequilibrium states such as steady-state shear flow. Gan and Eu’s contribution in this regard [6,7] has not been much noticed. Using the methods of NEMD and EMD with a nonequilibrium potential, we have tested the low-shear-rate version of their theory and some variants on it. We find that the OZ relation with a nonequilibrium potential can be used with the PY closure or (better) with the MHNC closure to predict the distortion of the structure of a simple soft-sphere fluid due to the nonequilibrium potential. We find that the low-shear-rate nonequilibrium potential proposed by Gan and Eu [6,7] yields only a qualitative prediction of the distortion of fluid structure due to shear and, when used self-consistently with the theory,
yields poor predictions of the effect of shear on hydrostatic pressure except at very low shear rates. Not surprisingly, when the low-shear-rate nonequilibrium potential is used self-consistently, the predictions of combined theory are rather poor. Nevertheless, there still lies hope in the use of an improved nonequilibrium potential. In continuing work [18], we are exploring the performance of the Gan-Eu theory with the full nonequilibrium potential (3), and we are seeking even more accurate models of the nonequilibrium potential.

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