Distortion of the structure of a simple fluid

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(Received 23 October 1981)

The distortion of the structure of a simple fluid of spherical particles when subjected to a shear is analyzed. The orientational distribution of particles around a central particle is examined via the radial distribution function. General symmetry arguments are advanced. Computer-simulation results using the technique of homogeneous shear nonequilibrium molecular dynamics are reported for the inverse-12 soft-sphere system. It is shown that the fluid displays non-Newtonian behavior.

In this Communication we discuss the distortion of the structure of a fluid under shear by analyzing the radial distribution function. The radial distribution function $g(\vec{r})$ for the fluid becomes anisotropic, and the angular dependence can be taken into account explicity[1] by a Cartesian irreducible tensor expansion with respect to the components of the unit vector $\hat{r}$ where[2] $\hat{r}=\vec{r}/r$ for the particle separation r. For a fluid of spherical particles, one has

$$g(\vec{r})=g^s+\langle \mathrm{g}\rangle^{sy}:\langle\hat{r}\hat{r}\rangle^{sy}+\cdots\ , \tag{1}$$

where the higher terms involve tensors of rank 4, 6, etc.[3] The $\langle\ \rangle^{sy}$ refer to a symmetric traceless tensor and in particular $\langle\hat{r}\hat{r}\rangle^{sy}\equiv\hat{r}\hat{r}-\frac{1}{3}\underline{\delta}$, where $\underline{\delta}$ is the unit tensor. The term g^s is the scalar (isotropic) contribution to $g(\vec{r})$ and $\langle \mathrm{g}\rangle^{sy}$ is a tensor expansion coefficient. These quantities, which are functions of the shear rate γ, are essentially orientational averages

$$g^s=\frac{1}{4\pi}\int d^2\hat{r}\, g(\vec{r}),$$
$$\frac{2}{15}\langle \mathrm{g}\rangle^{sy}=\frac{1}{4\pi}\int d^2\hat{r}\,\langle\hat{r}\hat{r}\rangle^{sy}g(\vec{r})\ . \tag{2}$$

I. COUETTE FLOW

Here we will make use of the special geometry of Couette flow for which the tensorial analysis is simplified. If the flow velocity $\vec{u}$ is in the x direction with the shear rate $\gamma=du_x/dy$, Eq. (1) becomes

$$g(\vec{r})=g^s+g_+(xy)+g_-(\tfrac{1}{2})(x^2-y^2)+g_0(z^2-\tfrac{1}{3})+\cdots\ , \tag{3}$$

where x, y, and z are components of the unit vector parallel to the respective coordinate axes. The tensor $\langle \mathrm{g}\rangle^{sy}$ is thus characterized by three coefficients g_k with $k=+,-,0$, and Eq. (2) reduces to

$$\frac{2}{15}g_k=\frac{1}{4\pi}\int d^2\hat{r}\,Y_k(\hat{r})g(\vec{r})\ , \tag{4}$$

in which Y_k is an angle-dependent function

$$Y_+=2xy\equiv\sin2\phi\sin^2\theta\ ,$$
$$Y_-=x^2-y^2\equiv\cos2\phi\sin^2\theta\ , \tag{5}$$

and

$$Y_0=\tfrac{3}{2}(z^2-\tfrac{1}{3})\equiv\tfrac{3}{2}(\cos^2\theta-\tfrac{1}{3})\ ,$$

where θ and ϕ are the usual polar angles of $\hat{r}$.

II. STRUCTURE DISTORTION

The distortion of the structure of a fluid subjected to shear can be visualized by examining the distribution of particles in a shell between radii R_1 and R_2. The number of particles in this shell per unit solid angle about $\hat{r}$ is related to $g(\vec{r})$ by

$$\mathfrak{N}=\rho\int_{R_1}^{R_2}g(\vec{r})r^2dr\ ,$$

where ρ is the number density, and the total number in the shell is

$$N=\int\mathfrak{N}\,d^2r=4\pi\rho\int g^sr^2dr\ . \tag{6}$$

Thus the anisotropy is given in terms of the g_k contributions to $g(\vec{r})$ or in terms of coefficients n_k where

$$n_k=4\pi\rho\int_{R_1}^{R_2}g_kr^2dr \tag{7}$$

so that one has with Eq. (3)

$$4\pi\mathfrak{N}=N+n_+xy+n_-(\tfrac{1}{2})(x^2-y^2)+n_0(z^2-\tfrac{1}{3})\ , \tag{8}$$

where it is understood that all coefficients depend on the integration limits R_1 and R_2 and are associated with a given γ. An alternative expression to Eq. (8) follows using the polar angles as in Eqs. (4) and (5).

The expression simplifies for particular coordinate planes and the anisotropy distortion can easily be displayed graphically. For example, for the shear plane one has, since $\theta=\pi/2$:

$$4\pi\mathfrak{N}=N-\tfrac{1}{3}n_0+\tfrac{1}{2}(n_+^2+n_-^2)^{1/2}\sin2(\phi+\chi) \quad , \tag{9}$$

where χ is given by $\tan2\chi=n_-/n_+$. Thus the highest probability of nearest neighbors between R_1 and R_2 is in the direction for which $\phi=\pi/4-\chi$ [or $(\frac{5}{4})\pi-\chi$] with respect to the x axis (assuming n_+ is positive).

In similar way, one has for the $x-z(\phi=0)$ or the $y-z(\phi=\pi/2)$ plane:

$$4\pi\mathfrak{N}=N\pm\tfrac{1}{2}n_-\sin^2\theta+n_0(\cos^2\theta-\tfrac{1}{3}) \quad . \tag{10}$$

III. COMPUTER SIMULATION

A 108-particle system whose particles interacted with the soft-sphere potential

$$\Phi=d/r^{12} \tag{11}$$

truncated at $r=2.5$ was studied by the homogeneous shear nonequilibrium molecular dynamics[4] at the state point $\rho(4T)^{-1/4}=0.8$, which is close to the melting transition. Histograms for g_k based on Eq. (3) were constructed and Fig. 1 gives the results for the variation of g_k with interparticle separation r for three values of the shear rate: $\gamma=0.5$, 1.0, and 2.0. Table I shows the corresponding values of N and the anisotropy coefficients n_k of Eq. (7). To evaluate the integral, Eq. (7) was split into three regions I, II, and III to represent the inner, middle, and outer parts of the first coordination shell as follows: I, $R_1=0$ and $R_2=1.1$, which is the maximum in $g^s(r)$; II, $R_1=1.1$ and $R_2=1.35$, where $g^s(1.35)\approx1.0$; and III, $R_1=1.35$ and $R_2=1.6$ where this upper limit corresponds to the first nonzero minimum in $g^s(r)$. The label Σ in the table corresponds to the integration between $R_1=0$ and $R_2=1.6$.

There are several remarks:

1. Note that one can further define pressure coefficients p_k analogous to the coefficients n_k by

$$p_k=-\tfrac{2}{15}\pi\rho^2\int g_k\Phi' r^3dr \quad , \tag{12}$$

where Φ' is the derivative of the pair potential. Since these quantities are related to the components of the pressure tensor by

$$\begin{aligned} p_+&\equiv p_{xy} \quad ,\\ p_-&=\tfrac{1}{2}(p_{xx}-p_{yy}) \quad ,\\ p_0&=\tfrac{1}{2}[p_{zz}-\tfrac{1}{2}(p_{xx}+p_{yy})] \quad , \end{aligned} \tag{13}$$

they link g_k or n_k with a viscosity coefficient.[5] We have included numerical values of p_k in the table.

2. While one would expect g_+ or n_+ to be nonzero, we note that the corresponding coefficients n_- and n_0 are also nonzero according to the computer simulation. And they have significance: They show that even the simple system of inverse-12 spherical particles is associated with non-Newtonian behavior and differences in the normal pressure components. In particular, a nonzero n_- implies a rotation of the symmetry axis away from the Newtonian preferential angle of 45° in the xy plane and, furthermore, with the nonzero n_0, it also implies an anisotropic accumulation of particles in the xz and yz planes.

These points, and others, can be displayed graphically via Eq. (10), and we constructed Fig. 2 which is a polar diagram of $4\pi\mathfrak{N}$ for the intermediate shear rate $\gamma=1$ in the xy plane as an illustration. Curves

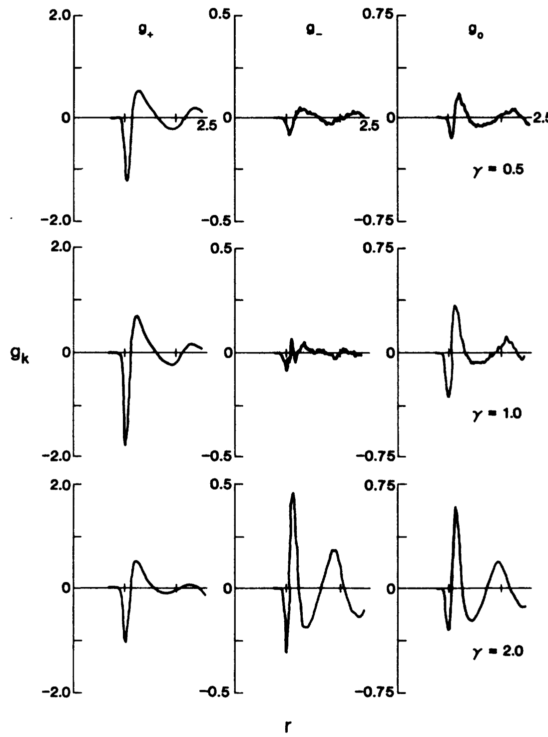

FIG. 1. Calculation of the expansion coefficients g_+, g_-, and g_0 defined by Eqs. (3)–(5) for a soft-sphere fluid at state point $\rho(4T)^{-1/4}=0.8$. Results are given for three shear rates, $\gamma=0.5$, 1.0, and 2.0.

TABLE I. Values of the coefficients N and n_k for the soft-sphere fluid at $\rho(4T)^{-1/4}=0.8$ for three shear rates; Eqs. (6) and (7). The integration was carried out in three regions I, II, and III of the first coordination shell. The symbol Σ represents the total. The pressure coefficient p_k of Eq. (12) has been included for the total integration.

	N	n_+	n_-	n_0
		$\gamma=0.5$		
I	3.01	−0.76	−0.05	−0.05
II	6.49	0.76	0.07	0.17
III	4.51	0.52	0.05	−0.15
Σ	14.01	0.52	0.07	−0.03
p_k		−1.52	−0.07	−0.12
		$\gamma=1.0$		
I	3.27	−1.05	−0.02	−0.06
II	5.94	1.09	0.02	0.24
III	3.85	0.50	0.03	−0.17
Σ	13.06	0.54	0.03	0.01
p_k		−2.36	−0.11	−0.30
		$\gamma=2.0$		
I	3.09	−0.66	0.04	0.08
II	6.21	0.78	0.00	0.16
III	4.44	0.16	−0.34	−0.57
Σ	13.74	0.28	−0.30	−0.33
p_k		−1.74	−0.20	−0.12

for the integration of region I and for total Σ are superimposed.

3. Although n_+ and n_0 are nonzero, the contribution of the coefficients is at most $\frac{1}{8}$ of N according to Table I. Hence, we can consider them as realistic measures of a distortion and also argue that higher-order contributions, disregarded in Eq. (1) would be equally as small, if not negligible.

4. In model liquids of spherical colloidal particles, experimental results on the shear-flow-induced distortion of the structure have recently been obtained via light scattering techniques.[6]

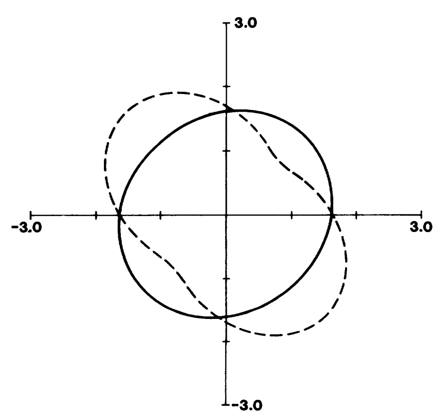

FIG. 2. Polar diagram of $4\pi\mathfrak{N}$ for region I (dashed curve), and the full first coordination shell Σ (solid curve) for the soft-sphere fluid under a shear of $\gamma=1$ in the plane of the shear. (See Table I.)

IV. SUMMARY

We can conclude by remarking that the distribution functions, manifested by the coefficients g^s, g_k or N and n_k, give information over and above that one would obtain by examining only the behavior of the thermophysical properties of a system. One can see from Eq. (12) that these latter properties only effectively probe the distribution at short r (i.e., region I). Here we have looked, for the first time, at the full anisotropy via the powerful technique of nonequilibrium molecular dynamics. This present study should be extended to cover a larger range of state points and values of the shear rate for a model fluid, and should be extended to other model fluids, but already the simple spherical inverse-12 system reveals a complexity of fluid behavior which one usually associated only with molecular liquids.

Work carried out at the National Bureau of Standards. Supported by the Department of Energy, Office of Basic Energy Sciences.

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[2]All parameters are in reduced units as defined, for example, in, D. J. Evans and H. J. M. Hanley, Phys. Rev. A 20, 1648 (1979).

[3]An equivalent expansion in spherical harmonics has been given by D. J. Evans, Phys. Rev. A 23, 1988 (1981).

[4]D. J. Evans, Mol. Phys. 37, 1745 (1979).

[5]For example the shear viscosity (η) follows from the constitutive relation $p_{xy} = -\eta\gamma$. Hence the coefficient g_+ is associated with η.

[6]N. A. Clark and B. J. Ackerson, Phys. Rev. Lett. 44, 1005 (1980).