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SHEAR-INDUCED ANISOTROPY OF THE STRUCTURE OF DENSE FLUIDS

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The static structure factor $S(k)$ of a dense fluid under shear is determined directly in a nonequilibrium molecular dynamics simulation rather than via the pair-correlation function. Three scattering geometries are considered. The results can be compared with kinetic theory and with SANS (D 11) data for colloidal dispersions.

1. Introduction

The shear-induced anisotropy of colloidal dispersions has been observed in light [1] and neutron scattering [2–4] experiments. It can be compared with results based on the kinetic theory [5, 6] and the nonequilibrium molecular dynamics (NEMD) calculations [7–10]. The latter method, originally invented for simple fluids, is applicable provided that the interaction between the colloidal particles (rather than the particle–solute interaction) dominates the structure and the dynamics of the system. So far, this comparison of NEMD with scattering results involved a numerical Fourier transformation (FT) of the pair-correlation function extracted from the computer simulation [9, 10] or an optical FT from snapshot pictures of the particle positions of a two-dimensional model fluid [11]. To circumvent certain shortcomings involved in both methods (the use of a finite number of terms in an expansion with respect to spherical harmonics or equivalent Cartesian basis functions in the first case, poor statistics in the second case) it is desirable to supplement the molecular dynamics with a "measuring device" analogous to a small angle scattering detector such as D 11 at ILL. This was done. First results are available for a Lennard-Jones liquid under pressure and for a dense model fluid of r^{-12} soft spheres with an additional screened Coulomb interaction. Computer "scattering data" are presented for three geometries at shear rates below and above the transition into shear-induced ordered state.

2. Molecular dynamics

In the molecular dynamics simulation, the equations of motion of N spherical particles (with mass m) are integrated numerically (e.g. by a predictor–corrector method). The quantities of interest such as energy, pressure, pair-correlation function and the static structure factor are evaluated from the known positions and momenta of the particles according to the rules of statistical physics and then averaged over many time steps [2, 13]. Periodic boundary conditions are used in order to avoid boundary layer effects. The volume V of the basic periodicity box is determined by N and the number density $n = N/V$. In the present case, test runs were made for $N = 128$ and results are presented for $N = 512$ at the density $n = 0.84$ in standard reduced Lennard-Jones and soft spheres units. The interaction potential is $\phi^{LJ} = 4\,(r^{-12} - r^{-6})$ and $\phi^{SS} = r^{-12}$ in these cases. The temperature T is kept constant by rescaling the magnitude of the particle velocities. The temperatures $T = 1.0$ and $T = 0.25$ (in reduced units) were chosen. Additional constraints are imposed in order to simulate a plane Couette flow with the flow velocity v in x-direction and its gradient in y-direction;

$$\gamma = \frac{\partial v_x}{\partial y}$$

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is the shear rate. Both, the homogeneous shear algorithm [12] which imposes a constant value of γ and a modified method which only adjusts an average shear rate $\bar{\gamma}$ but allows a nonlinear, pluglike flow profile [13], were used. The results to be shown are for the latter case.

3. Static structure factor

In the simulation, the direct evaluation of the static structure factor $S(\boldsymbol{k})$ can either be performed as a time average of the one-particle average

$$S(\boldsymbol{k}) = \frac{1}{N}\left[\left(\sum_i \cos \boldsymbol{k}\cdot\boldsymbol{r}^i\right)^2 + \left(\sum_i \sin \boldsymbol{k}\cdot\boldsymbol{r}^i\right)^2\right], \tag{1}$$

or of the two-particle average

$$S(\boldsymbol{k}) = 1 + \frac{1}{N}\sum_{i\neq j}\sum \cos \boldsymbol{k}\cdot(\boldsymbol{r}^i - \boldsymbol{r}^j), \tag{2}$$

where $\boldsymbol{r}^i$ and $\boldsymbol{r}^j$ are the position vectors of particles i and j. Both methods were tested. The first one, being faster, was used for production runs. The "allowed" wavevectors $\boldsymbol{k}$ have to be chosen appropriately for the cubic scattering volume (with length L) which is smaller than or equal to the periodicity box. To mimic a small angle detector normal to the z-plane the $\boldsymbol{k}$ values $k_x = K_x k_0$, $k_y = K_y k_0$, $k_z = 0$ with $k_0 = 2\pi/L$ and $K_x, K_y = 0, \pm 1, \pm 2, \ldots$ are chosen. "Detectors" normal to other directions are obtained in a similar way.

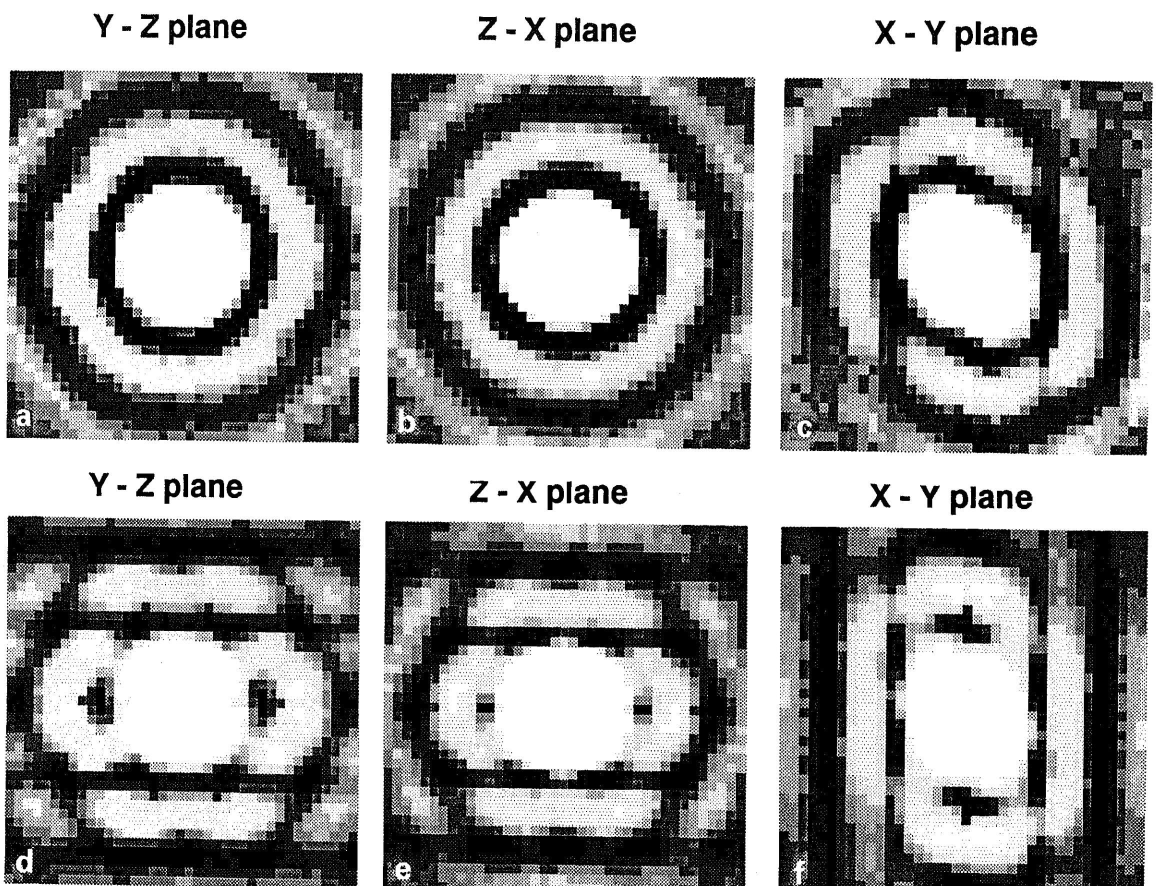

Fig. 1. The static structure factor for a model dispersion under planar shear (flow in x-, gradient in y-direction). A flow instability leads to an ordering transition (lower row) which is reflected by characteristic distortions of the structure factor in all three planes (see text).

To demonstrate the essential features of the method, $S(\boldsymbol{k})$ in the shear plane (x–y), as well as in the y–z- and z–x-planes (perpendicular to the flow velocity and to its gradient, respectively) are shown in fig. 1 for the shear rates $\gamma = 1.3$ (upper row) and $\gamma = 1.5$ (lower row) in reduced soft sphere units. At the lower shear rate the expected distortion [5–10] of the local order is found in particular in the x–y-plane. Qualitatively, the behavior is explained by a simple kinetic theory [5] for a hard sphere fluid [14]. At the higher shear rate a transition into a partially (long range) ordered state has set in. The particles move in tubes (strings) parallel to the streamlines. The tubes, in turn, have the tendency to attain maximal distances from each other and form a hexagonal pattern in a cross section normal to the velocity [13]. The flow is pluglike; regions of different spatial order coexist [13]. The long range order is reflected by high peaks in $S(\boldsymbol{k})$. Scattering patterns similar to those shown for z–x-plane (normal to the velocity gradient) have recently been observed for dense disperisons of spherical particles [3, 4].

4. Concluding remarks

In this note it has been demonstrated that $S(\boldsymbol{k})$ of sheared fluids can be computed from NEMD, in analogy to SANS experiments. For a future quantitative comparison between experiments, computer simulations and kinetic theory, the coefficients of an angular Fourier analysis of $S(\boldsymbol{k})$ should be used. The program ANISK developed for this purpose [15] has also been applied to our computer data.

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References

[1] N.A. Clark and B.J. Ackerson, Phys. Rev. Lett. 44 (1980) 1005; B.J. Ackerson and N.A. Clark, Physica A 118 (1983) 221.
[2] B.J. Ackerson, J.B. Hayter, N.A. Clark and L. Cotter, J. Chem. Phys. 84 (1986) 2344.
[3] S. Hess. H.M. Laun, K. Hahn, R. Bung and R. Oberthür, ILL Exp. Report 1986, p. 395.
[4] R.H. Ottewill and P. Lindner, private communication.
[5] S. Hess, Phys. Rev. A 22 (1980) 2844; J.C. Rainwater and S. Hess, Physica A 118 (1983) 371; J. Schwarzl and S. Hess, Phys. Rev. A 33 (1986) 4277; H.-M. Koo and S. Hess, Physica A 145 (1987) 361.
[6] D. Ronis, Phys. Rev. Lett. (1984) 473.
[7] D.J. Evans, H.J.M. Hanley and S. Hess, Phys. Today 37 (1984) (No. 1) 26.
[8] S. Hess and H.J.M. Hanley, Phys. Rev. A 25 (1982) 1801; Int. J. Thermophys. 4 (1983) 97; S. Hess, J. Phys. (Paris) 46 (1985) C3-191; H.J.M. Hanley, J.C. Rainwater and S. Hess, Phys. Rev. A 36 (1987) 1795.
[9] H.J.M. Hanley, J.C. Rainwater, N.A. Clark and B.J. Ackerson, J. Chem. Phys. 79 (1983) 4448.
[10] J.C. Rainwater, H.J.M. Hanley and S. Hess, Phys. Lett. A 126 (1988) 450.
[11] H.J.M. Hanley, G.P. Morris, T.R. Welberry and D.J. Evans, Physica A 149 (1988) 406.
[12] See, for example, D.J. Evans and G.P. Morriss, Comput. Phys. Rep. 1 (1984) 299; D.J. Evans and W.G. Hoover, Ann. Rev. Fluid Mech. 18 (1986) 243.
[13] S. Hess and W. Loose, in: Constitutive Laws and Microstructure, D.R. Axelrad and W. Muschik, eds. (Springer, Berlin, 1988), p. 93.
[14] T. Weider, Diplomarbeit, TU Berlin 1988, unpublished.
[15] P. Lindner and S. Hess, these Proceedings, Physica B 156 & 157 (1989) 512.