NONEQUILIBRIUM STRUCTURAL CHANGES OF A VISCOELASTIC LIQUID UNDER OSCILLATORY SHEAR

Hiroshi Komatsugawa and Shuichi Nosé
Department of Physics, Faculty of Science and Technology, Keio University,
3-14-1 Hiyoshi,Kohoku-ku,Yokohama 223, Japan

The nonequilibrium phase diagram of a concentrated liquid under an oscillatory shear is obtained by means of constant pressure nonequilibrium molecular dynamics (NEMD) simulations and compared with that in constant volume condition.

Ackerson and Pusey investigated the structural changes of concentrated colloidal suspension under an oscillatory shear by the light scattering experiment[1]. They observed two types of layered structures with increase of the shear amplitude. The difference between two structures is the orientation of the triangular lattice in each layer, which is rotated by 30° at the transition point. They refer to these structures as the "fcc " and "layer" structures, respectively.

We reproduced the phase change from the "fcc" to "layer" structures by means of the constant volume NEMD simulation[2]. We also studied the phase change from a liquid to layered structures, and obtained the nonequilibrium phase diagram in the space of the number density ρ, the amplitude of shear rate γ_0, and the frequency ω_0[3]. In the present study, we have carried out constant pressure NEMD simulations, and compared with results at the constant volume.

We use the NEMD simulations with the SLLOD algorithm and the Lees-Edwards periodic boundary condition to impose a homogeneous shear deformation[4]. The constraint method is employed to fix the kinetic temperature and the pressure. The WCA potential is employed to simulate the colloidal system. The choice of reduced units is the same as the previous studies[2-3]. The system size N in our simulation is 504 ($6 \times 4 \times 3 \times 7$) in the calculation of the phase diagrams and 2520 ($6 \times 7 \times 5 \times 12$) in the calculation of the particle configurations. A sinusoidally changing shear rate $\dot{\gamma}(t) = \gamma_0 \cos(\omega_0 t)$ is applied to a liquid at the number density $\rho = 0.86$ and the reduced temperature $T = 0.75$ just below the triple point of the WCA potential. The direction of the shear velocity and the velocity gradient is chosen along the x and the y axes, respectively.

In Figs. 1, we show particle projections onto the $y - z$ plane at $\omega_0 = 20.0$ and $\gamma_0 = 6.0$. In the constant volume case (Fig. 1(a)), a coexistence of liquids and layered structures is observed and this coexistence region exists up to $\gamma_0 \simeq 10.0$. The transition point can not be determined directly in this case. The points indicated in the phase diagram (Fig. 2(a)) are the positions where a new structure is partially observed. In the constant pressure case (Fig. 1(b)), the liquid changes to the layered structure without coexistence.

The nonequilibrium phase diagrams in the space of γ_0 and ω_0 are shown in Figs. 2. The phase diagram obtained by constant pressure method agrees fairly well with those in constant volume case. At higher ω_0, the structural changes similar to that in the experiment is obtained, while at lower ω_0, the "fcc" structure does not appear.

The frequency dependence of the structure indicates that the dynamical behavior is dominated by the viscous properties related to the Brownian motion at low ω_0 and by the elastic properties related to the shear at high ω_0. The Peclet number $P_e = \tau\dot{\gamma}$ is introduced as a ratio of these two competitive factors, where τ is the Brownian relaxation time and $1/\dot{\gamma}$ is the inverse of the shear rate. In our case, the phase boundary between a liquid and layered structures is situated near $\gamma_0 = 4.0$. This value corresponds to $P_e \simeq 1$ in our WCA system[3]. Then, the phase change occurs where the influence of the two competitive factors are comparable.

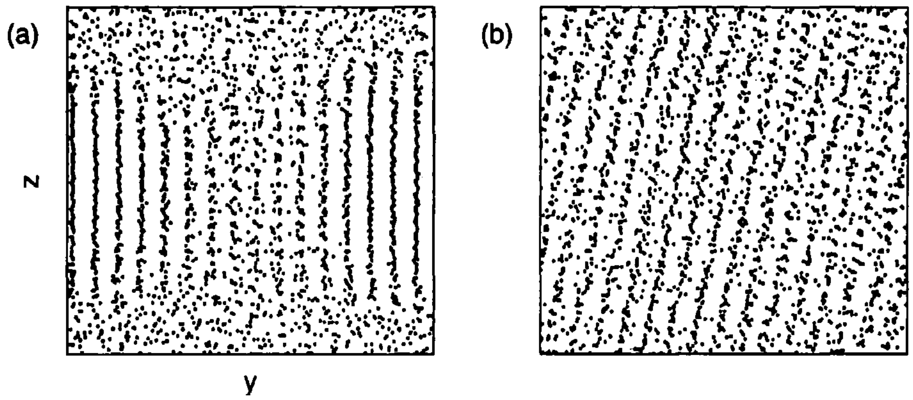

Fig.1. The snapshots projected onto $y - z$ plane; (a) constant volume, (b) constant pressure.

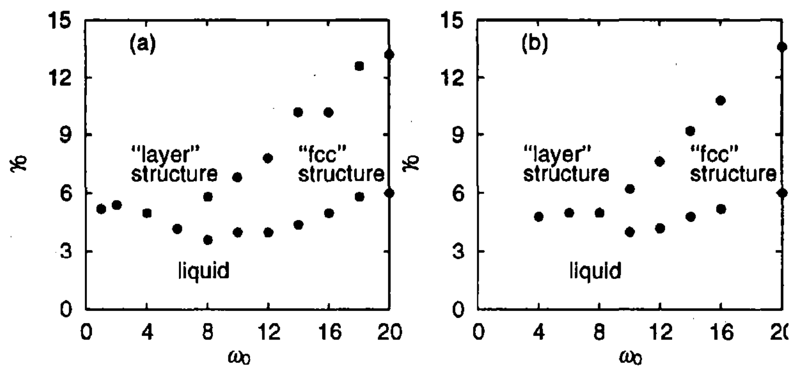

Fig. 2. The nonequilibrium phase diagrams in the space of ω_0 and γ_0;
(a) constant volume, (b) constant pressure.

REFERENCE

[1] B.J.Ackerson and P.N.Pusey, Phys. Rev. Lett. **61**, 1033(1988).
[2] H.Komatsugawa and S.Nosé, Phys. Rev. E**51**, 5944(1995).
[3] H.Komatsugawa and S.Nosé, Phys. Rev. E. In press.
[4] D.J.Evans and G.P.Morriss, *Statistical Mechanics of Nonequilibrium Liquid (Academic Press, New York, 1900)*, Chap.4-6.