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Simple Shear Flows of Suspensions of Brownian Ellipsoids Interacting Via the Gay-Berne Potential

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Brownian dynamics simulations of shear flows were carried out for the suspensions of ellipsoids interacting via the Gay-Berne potential. When the number density of ellipsoid was increased through a compression process of the primitive cell, the phase transition from an isotropic phase to a nematic one occurred. In the simple shear flow for the suspension which exhibits the LC phase at equilibrium, the orientation behavior was examined. The kayaking motion and the intermittent rotation of director were observed at low shear rates. In their director motions, the director is out of the vorticity plane. At high shear rates, however, the flow-aligning was found.

Keywords: Brownian dynamics; liquid crystals; shear flow; Gay-Berne potential; tumbling

INTRODUCTION

Solutions of rodlike polymers exhibit a phase transition from an isotropic phase to a liquid crystalline one as the polymer concentration increases. Doi[1] developed the theory for concentrated solutions of rodlike polymers by incorporating the Maier-Saupe potential into the Smoluchowski equation for rotary motion of rods. In a simple shear flow the Doi theory well describes the periodic behaviors of director

such as the tumbling and wagging motions if the use of decoupling approximation is avoided[2]. Recentry, Faraoni et al.[3] have analyzed the rigid-rod model by expanding the orientational distribution function in spherical harmonics. In their simulation of simple shear flows it is pointed out that in-plane tumbling is always unstable and out-of plane periodic solutions like kayaking are present.

On the other hand, the microscopic structures of complex fluids have been studied using Brownian dynamics (BD). For the concentrated solutions of rodlike polymers the translational and rotational diffusivities were calculated by BD and compared with the predictions of Doi-Edwards theory[4]. Ding and Yang[5] performed the BD simulations of rodlike polymer solution under simple shear flows. The Lebwohl-Lasher nematogen model is used in their simulation and the mean-field approximation is avoided, so that the spatial inhomogeneity can be incorporated. Their simulation results indicate that the director wagging and damped oscillation share the same molecular origin as the director tumbling. However, their simulation is restricted to the two-dimensional orientation.

This paper investigates the orientational behavior of the suspension of ellipsoidal particles, which is in the nematic phase at rest, under the shear flow through the Brownian dynamics simulation.

MODEL AND SIMULATION METHOD

We used the Gay-Berne (GB) potential[6] as an inter-particle potential of ellipsoidal particles given by

$$\phi_{GB} = 4\varepsilon\left(\hat{u}_i, \hat{u}_j, \hat{r}\right)\left\{\left(\frac{\sigma_0}{r - \sigma\left(\hat{u}_i, \hat{u}_j, \hat{r}\right) + \sigma_0}\right)^{12} - \left(\frac{\sigma_0}{r - \sigma\left(\hat{u}_i, \hat{u}_j, \hat{r}\right) + \sigma_0}\right)^{6}\right\},$$

where the well depth of the potential $\varepsilon\left(\hat{u}_i, \hat{u}_j, \hat{r}\right)$ and the inter-particle separation $\sigma\left(\hat{u}_i, \hat{u}_j, \hat{r}\right)$ are orientational-dependent Lennard-Jones parameter. For a detailed discussion of this model, see Gay and Berne[6]. In this work, we used the following values for the

GB parameters: $\nu = 2$, $\mu = 1$, $\sigma_e / \sigma_s = 3$ and $\varepsilon_e / \varepsilon_s = 0.2$. Therefore, the particle is the ellipsoid with the aspect ratio $\sigma_r = 3$.

The Non-Equilibrium Brownian Dynamics (NEMD) simulation for the suspension of ellipsoids is carried out by solving the translational and rotational equations of motion with respect to the center of gravity of the particle. The translational and rotational equations of motion are given by

$$\boldsymbol{F}_{GBi} - \boldsymbol{F}_{Vi} + \boldsymbol{F}_{Bi} = \boldsymbol{0},$$
$$\boldsymbol{T}_{GBi} - \boldsymbol{T}_{Vi} + \boldsymbol{T}_{Bi} = \boldsymbol{0},$$

where $\boldsymbol{F}_{GB}$ and $\boldsymbol{T}_{GB}$ are the force and torque resulting from particle interaction via the GB potential, respectively. The shear force $\boldsymbol{F}_V$ and torque $\boldsymbol{T}_V$ for the ellipsoid are

$$\boldsymbol{F}_{V,i} = 3\pi\eta_s\sigma_r\sigma_0\left\{X^A\,\hat{\boldsymbol{u}}_i\hat{\boldsymbol{u}}_i + Y^A\left(I - \hat{\boldsymbol{u}}_i\hat{\boldsymbol{u}}_i\right)\right\}\left(\boldsymbol{v}_i - \boldsymbol{U}\right),$$
$$\boldsymbol{T}_{V,i} = \pi\eta_s\left(\sigma_r\sigma_0\right)^3\left[\left\{X^C\,\hat{\boldsymbol{u}}_i\hat{\boldsymbol{u}}_i + Y^C\left(I - \hat{\boldsymbol{u}}_i\hat{\boldsymbol{u}}_i\right)\right\}\left(\boldsymbol{\omega}_i - \boldsymbol{\Omega}\right)\right] + Y^H\left(\boldsymbol{\varepsilon}\,.\,\hat{\boldsymbol{u}}_i\hat{\boldsymbol{u}}_i\right) : \boldsymbol{D}$$

where η_S denotes the solvent viscosity, $\boldsymbol{v}_i$ the translational velocity of the particle, $\boldsymbol{U}$ the velocity of background fluid, $\boldsymbol{\omega}_i$ the angular velocity of the particle, $\boldsymbol{\Omega}$ the angular velocity of the background fluid, and $\boldsymbol{D}$ the rate of deformation tensor. X^A, Y^A, X^C, Y^C and Y^H are the resistance functions of the prolate ellipsoid. Furthermore, the Brownian force and torque with respect to the directions of primary axes are assumed to be Gaussian.

We have performed the Brownian dynamics simulations with $N = 216$ particles in a cubic box, using periodic boundary conditions. The dimensionless time step used ranges from 10^{-4} to 10^{-3}, depending on the shear rate. During the simulation we fixed the dimensionless temperature: $T^* \left(= Tk_B / \varepsilon_0\right) = 1$.

To examine the structure of the system, we estimate the state of orientation using the order parameter defined by

$$S = \frac{1}{N}\sum_{i=1}^{N}\left(3\cos^2\beta_i - 1\right)/2$$

where β_i is the angle between the director and the unit vector $\boldsymbol{u}_i$ specifying the orientation of the single particle.

RESULTS

Equilibrium State

We compressed the system to obtain the liquid crystalline state. This process corresponds to the concentrating process of the suspension. The system is sufficiently relaxed during 1×10^5 time-steps after the compression. Figure 1 shows the dependence of order parameter on number density of ellipsoid $\rho^*\left(=\rho\sigma_0^3\right)$. At $\rho^*\le 0.1$ the system seems to be isotropic. However, the order parameter rapidly increases with increasing concentration of the ellipsoid at $\rho^*\ge 0.1$. This change corresponds to the phase transition from the isotropic phase to the liquid crystalline one for a lyotropic system like the solution of rod-like polymers.

The instantaneous configurations at $\rho^*=0.10, 0.18, 0.25$ are shown in Fig.2(a), (b) and (c), respectively. Although the order parameter of the system at $\rho^*=0.10$ is relatively low, the existence of short range ordering, that means that the ellipsoids locally orient,

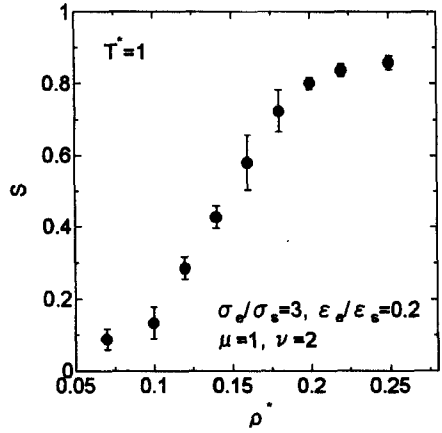
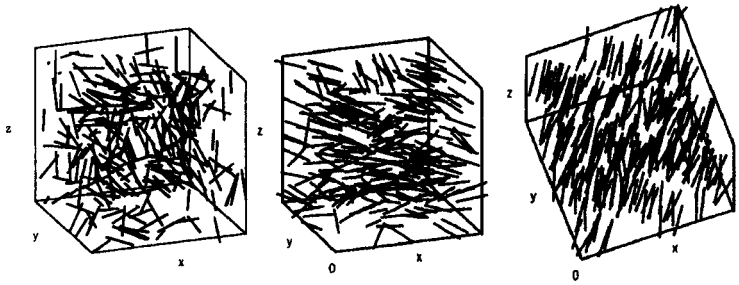


FIGURE 1 Dependence of order parameter on number density of ellipsoid.



(a) $\rho^* = 0.10$ (b) $\rho^* = 0.18$ (c) $\rho^* = 0.25$

FIGURE 2 Instantaneous configurations at equilibrium for various number densities.

is observed in Fig.2(a). At $\rho^* = 0.18$, the whole system exhibits the nematic phase. Furthermore, a dim layer structure indicating a smectic phase seems to be formed at $\rho^* = 0.25$.

Shear Flows

Next, we examined the orientational behavior of the system under shear flows. The target of the simulation is the system which exhbits the nematic phase at equiribrium. Here, we chose the system of $\rho^* = 0.18$.

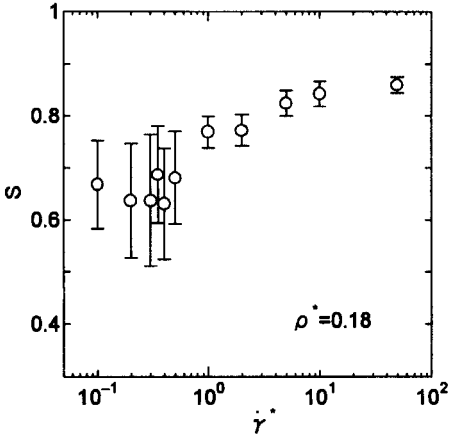


FIGURE 3 Shear rate dependence of order parameter.

Figure 3 shows the shear rate dependence of order parameter. At low shear rates the averaged value of order parameter is nearly independent of shear rate though the fluctuation of the order parameter is large. However, the order parameter increases with increasing shear rate for $\dot{\gamma}^*(=\tau_r\dot{\gamma})>0.5$, where $\tau_r\left(=3\pi\eta_s\sigma_0^{\ 3}/4k_BT\right)$ is the characteristic time.

For more detailed understanding of orientation of the system, the changes of orientation angle of director and order parameter with time at $\dot{\gamma}^*=0.2$ are presented in Fig.4. θ is the angle between the projection of the director onto the vorticity plane (x-y plane) and the x axis, and ϕ the angle between the projection and the director. The director is out of the vorticity plane, and continuously tumbles although it sometimes hesitates to rotate. This periodic motion of director is called a kayaking motion. The kayaking is also predicted in the stability analysis for the Doi theory in terms of the distribution function[3]. The analysis shows that the kayaking is stable at low shear rates for small values of the potential intensity proportional to the polymer concentration.

The corresponding change of order parameter with time is shown in Fig.5. The order parameter significantly fluctuates; it seems that the order parameter decreases largely when the director rotates quickly with small angles of ϕ.

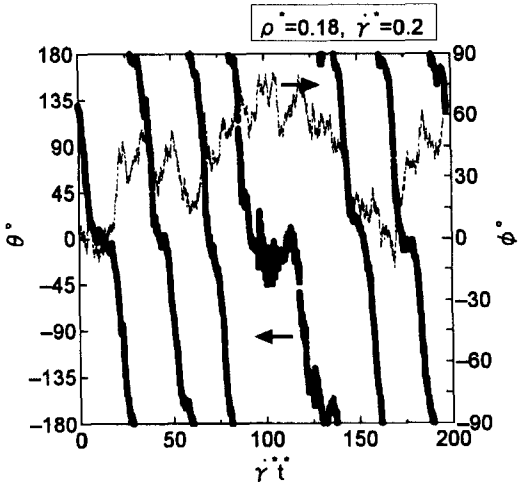


FIGURE 4 Change of orientation angles with time at $\dot{\gamma}^*=0.2$.

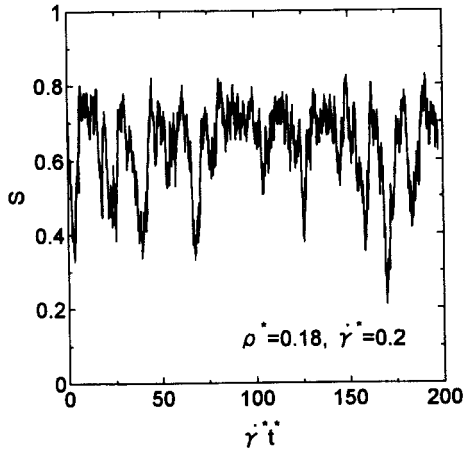


FIGURE 5 Change of order parameter with time at $\dot{\gamma}^* = 0.2$.

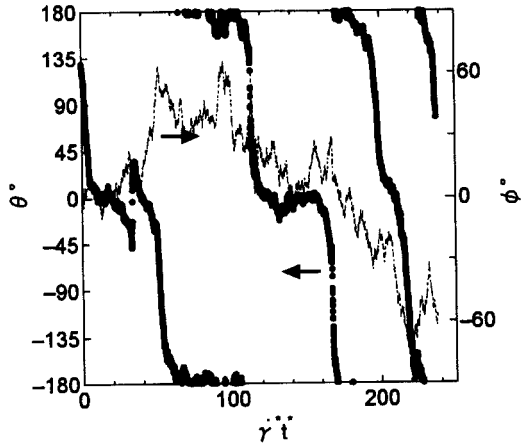


FIGURE 6 Change of orientation angle with time at $\dot{\gamma}^* = 0.3$

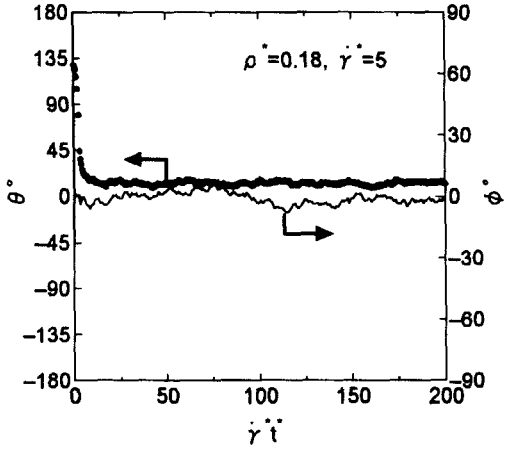


FIGURE 7 Change of orientation angle with time at $\dot{\gamma}^* = 5$.

Figure 6 shows the change of director angle with time at $\dot{\gamma}^* = 0.3$. The director oscillates once after the initial rotation, and then rotates out of the vorticity plane through 180 degrees. After the director rotation, however, the director stays without kayaking in the x-z plane for about three cycles of rotation. In the director motion at $\dot{\gamma}^* = 0.3$ this intermittent director rotation is predominant rather than the continuous rotation like the tumbling.

At high shear rates the system exhibits flow-aligning because of the large shear force, as shown in Fig.7. The director has an flow-induced orientational angle of $\theta \cong 15$ degrees at $\dot{\gamma}^* = 5$. This angle was nearly constant regardless of shear rate for $\dot{\gamma}^* \geq 2$. We have previously carried out the MD simulation of shear flows of liquid crystals with the Gay-Berne potential whose parameters are as same as those in the present work[7]. The result obtained in the MD simulation for the system of $\rho^* = 0.3$ showed a constant orientational angle of $\theta \cong 20$ degrees. Therefore, the orientational angle in the present simulation is valid for the ellipsoid with the Gay-Berne potential.

CONCLUDING REMARKS

The suspensions of ellipsoids interacting via the Gay-Berne potential were analyzed through the BD simulation in the equilibrium state and under the shear flow. We have confirmed that the system exhibits the liquid crystalline phase in high concentration of ellipsoid. In the shear flows for the system exhibiting the nematic phase in the equilibrium state, we have observed a variety of orientation behaviors according to the shear rates; kayaking, intermittent rotation of director and flow-aligning. Especially, it must be noted that the rotation of director is out-of-plane whenever it occurs.

In the present simulation the aspect ratio of the ellipsoid is only three. However, this aspect ratio is too small to be applied to liquid crystalline polymers. Therefore, further investigation is necessary for a suspension containing more elongated ellipsoids.

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