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A hybrid model for molecular-dynamics simulations of semiflexible main-chain liquid-crystalline polymer melts

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There are rigid units in the main chains of main-chain liquid-crystalline polymers (LCPs) that restrict bending movements and create the liquid-crystal properties. Between the rigid units, there are often flexible alkyl chains that give a certain amount of flexibility and determine the molecule's mesophase stabilities. The Gay-Berne/Lennard-Jones (GB/LJ) model was proposed in 1997¹ for simulating LCPs. It had been proved to be successful in many studies.²⁻⁴ In the GB/LJ model, rigid units are taken as ellipsoidal particles whose interactions are described by GB potential,⁵ which is particularly effective in modeling mesogenic system.^{6,7} The flexible chains are represented by a series of united LJ atoms each representing an alkyl group. Despite the accuracy of the GB/LJ model, the simulation time is very long due to the large number of LJ atoms. On the other hand, another model called bead-spring mode,⁸ where rigid units are described by spherical beads and flexible spacers are described by springs, is more efficient than the GB/LJ model but fails to describe detailed molecular features of LCPs. For instance, it cannot describe the odd-even effects. To improve the efficiency of the GB/LJ model and the accuracy of the bead-spring model, this note proposes a hybrid model called GB-spring-bead model.

In the hybrid model, all mesogenic elements are represented by GB units, while the flexible spacers between rigid units are modeled by two springs and a bead in the middle, with each spring connecting to its adjacent GB unit. The comparisons between the hybrid model, the GB/LJ model, and the bead-spring model are shown in Fig. 1.

In the hybrid model, a strength compensation coefficient W_s and a mass compensation coefficient W_m of the flexible unit, which are related to the number of flexible spacers (n_s) in the GB/LJ model by Eq. (1), are used in the calculations of potentials and equations of motion.

$$W_m = (n_s^3 - n_s - 0.5)/n_s^2, \quad W_s = 4(n_s - 3)/n_s. \quad (1)$$

The nonlinear spring potential of the flexible unit assumes the following form:

$$V_{sp} = -0.5K_s(r_i - R_0)^2 + 0.5K_a C_e(\theta_i - \theta_0)^2 + 0.5K_t(\theta_{ijk} - \theta_0)^2, \quad (2)$$

where r_i is the distance from the center of the bead site to the adjacent ending point of the GB site, θ_i is the angle between the GB long axis and the connection line from the GB site to the bead site, and θ_{ijk} is the angle between two displacements from the bead site to two adjacent GB sites. The energy parameters K_s , K_a , and K_t assume values of 3.6128×10^{-20} , 8.654×10^{-19} , and 8.654×10^{-19} J, respectively. $\theta_0 = 180^\circ$ is defined as the equilibrium angle. The equilibrium distance is given by

$$R_0 = 0.5(3n_s - 5.0)/2.0. \quad (3)$$

The energy coefficient C_e , which is related to the number of flexible spacers, is expressed as

$$C_e = 2.0(C_l + 1.0)/n_s, \quad (4)$$

where C_l is equal to the integral part of the value $n_s/2.0$, with the fraction being ignored.

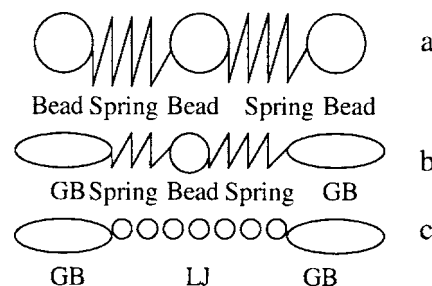


FIG. 1. (Color online) Schematic diagrams of a unit: (a) the bead-spring model, (b) the hybrid model, and (c) the GB/LJ model.

TABLE I. The comparison of computational cost between the GB/LJ model and current model (benchmark figures on an IBM T42 PM 1.6 GHz). N_c is the number of chains, $N1$ the total number of particles in the GB/LJ model, $N2$ the total number of particles in the hybrid model, $T1$ the CPU running time of simulating 50 steps for the GB/LJ model, and $T2$ the CPU running time of simulating 50 steps for the hybrid model.

N_c	$N1^a$	$N2^a$	$T1$ (s)	$T2$ (s)
36	2304	684	28	5
64	4096	1216	82	12
100	6400	1900	177	24
144	9216	2736	340	41
169	10816	3211	453	45

^aPolymerization $M=10$, flexible spacers $m=6$ and $n_s=6$.

In the hybrid model, the interaction energy between GB units is presented by the original GB potential.⁵ The interaction energy between a GB site and a bead is described by the generalized potential from the work of Cleaver *et al.*⁹ multiplied by the strength compensation coefficient W_s . The interaction-energy between two flexible sites is given by the standard shifted 12:6 LJ potential multiplied by the strength compensation coefficient W_s . The total potential is calculated by:

$$V_{\text{tot}} = V_{\text{GB}} + V_{\text{LJ}} + V_{\text{LJ/GB}} + V_{\text{sp}}. \quad (5)$$

To compare simulation results of our model with those of the GB/LJ model, simulation programs of both the hybrid model and the GB/LJ model are developed. The conditions of simulation are the same as those in Ref. 2. The simulation system contains 64 polymer chains with the number of rigid units $M=10$. The initial configuration is started from a low molecular density in an all-*trans* configuration aligned parallel to the z axis of the simulation box. Molecules are arranged with a random center of mass vector, and particle velocities are taken from a Maxwell-Boltzmann distribution. The time step is 3 fs. The initial NPT ensemble is calculated using extended system method¹⁰ for producing the system equilibration. The constant pressure is set to zero and the constant temperature varies from 500 to 350 K. In all cases equilibration takes 6–9 ns. After achieving equilibration, the NVE ensemble is carried out to collect data at selected equilibrated state points. During the simulation, the orientations of GB sites are monitored by calculating the order parameters.¹¹

The comparison of computing time for the GB/LJ model and the hybrid model are shown in Table I. The CPU running time required for the hybrid model is about 18% of that used by the GB/LJ model when the number of molecular chains is 40. The running time required is reduced to less than 10% of the GB/LJ model as the number of molecular chains exceeds 150. It implies that the hybrid model greatly improves the simulation efficiency of the GB/LJ model for studying the properties of semiflexible main-chain LCPs on a large scale.

To verify the accuracy of the hybrid model, the results of simulations are compared with those using the GB/LJ model and the actual experimental results. The phase-transition phenomena of semiflexible main-chain LCPs with $n_s=6$ as the system temperature decreases from 500 to 350 K are shown in Fig. 2(I). The orientational order parameters (S_2) are cal-

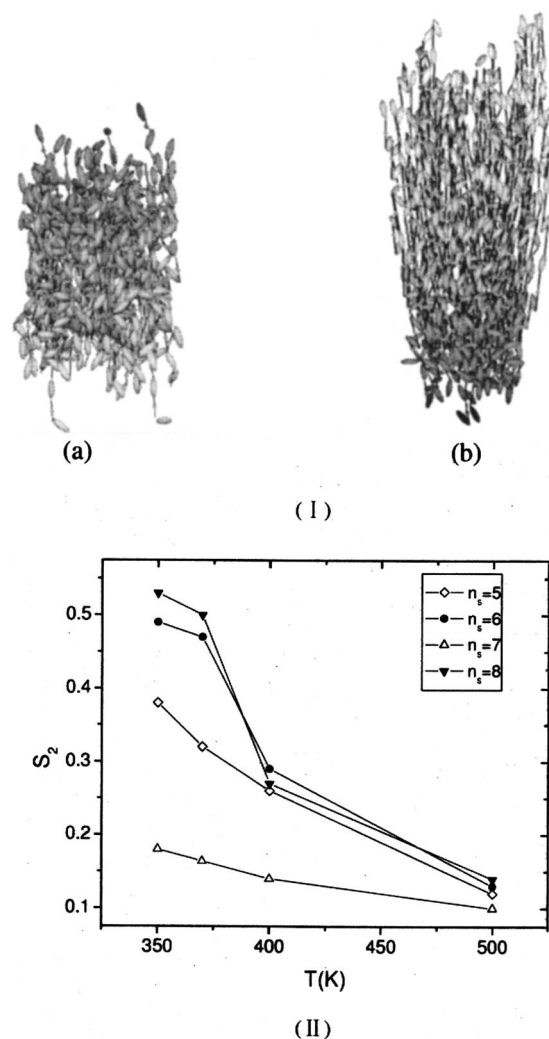


FIG. 2. (Color online) (I) Snapshots of a LCP system with $n_s=6$ (a) in isotropic state $T=500$ K and (b) in liquid-crystalline state $T=350$ K. (II) Orientational order parameter as a function of temperature.

culated and are shown in Fig. 2(II). When the system temperature $T=500$ K, the liquid-crystalline polymer chains entangle each other and have no alignment order ($S_2=0.18$) exhibiting an isotropic phase [as shown in Fig. 2(I)(a)]. When the temperature decreases from 500 to 350 K, spontaneous orientation ordering happens ($S_2=0.49$ at $T=350$ K). The visualization of the molecular chain arrangement suggests that the liquid-crystalline phase at $T=350$ K is nematic but not smectic because there is no interlayer conformation [as shown in Fig. 2(I)(b)]. The phenomena of phase transition observed using the hybrid model agrees with those using GB/LJ model² and the actual experimental results.¹²

The odd-even effect of the thermodynamics of LCPs, which has been verified by experimental results,¹² is tested with simulations using the hybrid model [as shown in Fig. 2(II)]. Results show that S_2 is apparently higher when the number of flexible spacers n_s is even in comparison to those when n_s is odd at the same temperature. The same effect was not observed in simulations using the bead-spring model.

In conclusion, since the simulation time using the hybrid model is much less than that using the GB/LJ model, while it can still describe detailed behaviors of LCPs much more

accurate than the bead-spring model, the hybrid model has proven to be useful in making it viable to run large-scale molecular simulations such as microfluid flow.

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