

A Deformable Gay-Berne Model for the simulation of Liquid Crystals and Soft Materials

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Abstract

We present a Deformable Gay-Berne (DGB) pair potential for ellipsoidal particles that allows for dynamic fluctuations in their shape and interaction anisotropy. We investigate the effect that various intrinsic distributions of shape and interaction parameters have on the liquid crystal phases formed in a system of deformable Gay-Berne particles. We show that deformability can stabilise smectic formation and that mesomorphic phase transitions are accompanied by a change of molecular shape.

Key words: Molecular Models, Liquid Crystals, Monte Carlo simulations.

1 Introduction

Molecular flexibility and more generally molecular deformability, can be considered as the possibility that a molecule has of deviating from a single rigid geometry to adopt more than one form and possibly a continuous distribution of shapes. In a condensed phase the average shape of the constituent units: molecules, or more generally soft particles, can change from one phase to the other as a result of the different weighting of the intrinsic distribution of internal degrees of freedom $\{\phi\}$ determining the shape of the particles. This ability to adjust to the surrounding environment plays an important role in a variety of important and very diverse scientific problems in soft materials [1, 2] ranging from the phase organization and packing of dendrimeric [3, 4] and micellar [5, 6] systems, to bioactivity [7]. A closely related problem is that of polydispersity [1, 8], which deals with materials formed by a given (fixed) mixture or a distribution of rigid particles of different size and/or aspect ratios, the standard case for colloidal dispersions or for polymers [2], and can have important effects on the structure and the phase transitions [9, 10]. For instance a dispersion in particle size

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can suppress the ability to form a regular lattice and thus crystallization in hard-sphere colloids [11]. In the case of liquid crystals, polydispersity influences both the isotropic-nematic [12, 13] and the nematic-smectic transition [14, 15]. Simulations also showed that in systems of hard spherocylinders, the most extensively studied, the formation of regular layered phases depends on the length/width ratio (L/D) [14, 16] and it is not surprising that polydispersity hinders the formation of smectic phases above a certain threshold (18% [15]), while columnar arrangements dominate at higher polydispersity. Similarly, introducing flexibility in hard rods in suspension was found to destabilise the smectic, increasing the critical smectic concentration to higher values and to shorten the lattice spacing of the resulting layers [17, 18]. This is quite understandable since introducing flexibility in a rod of length L , diameter D inevitably lowers the average aspect ratio L/D .

The effects of the more general type of deformability we wish to consider here are more complicated and difficult to predict, since we are also interested in deformations that increase the aspect ratio, making the particle more anisotropic. In this case the effect contrary to the one just mentioned could take place, and the overall tendency of the molecules to become more or less spherical as temperature and local ordering conditions change is important. The most apparent case is perhaps that of liquid crystal dendrimers, that deform from a nominally spherical shape to an elongated one [3, 4, 19]. In simpler molecules like 5CB, it has been found that the percentage of elongated conformations with the alkyl chain in all-trans increases on going from the isotropic to the nematic phase [20]. In another case, a fully atomistic study of the odd-even effect in a nematogenic cinnamate series [21], we found, examining the equilibrium molecular length and breadth histograms at a given temperature, that much of the physics could be explained in terms of a change in effective shape. Unfortunately, atomistic treatment of deformability and even coarse grained beads and spring type hybrid models (see e.g. [22, 23]) are too demanding to be used as a general tool for this class of problems. Indeed essentially all current molecular resolution models for the simulation of liquid crystal phases [24], be them purely repulsive [25] or attractive-repulsive (Gay–Berne [26]) are based on an assumption of molecular rigidity.

In this Letter we wish to introduce a simple generalization of the Gay–Berne (GB) model [27] where the ellipsoidal shape of the particle is maintained while letting the axes, and thus the particle aspect ratio, free to fluctuate and adjust to their equilibrium values, depending on the thermodynamic conditions and environment. As a first application, we shall then investigate the effects of allowing for molecular deformability on a selected region of the GB phase diagram, using Monte Carlo simulations. We also investigate the effect of changing the a priori or intrinsic shape distribution (ID) by choosing a few different ones with very similar moments. We shall then discuss the results and comment on the possibilities offered by this new variant of the model.

2 Model

We consider a system of deformable particles interacting through a generalised biaxial Gay–Berne potential [28] that, like the original uniaxial GB one [26], is a sum of pair-

wise repulsive and attractive contributions with a 12-6 inverse distance dependence:

$$U_{ab}^{GB} = 4\epsilon_{\{\epsilon_i\}}^{(\mu,\nu)}(\omega_a, \omega_b, \hat{\mathbf{r}}_{ab}) \left[\left\{ \frac{\sigma_c}{r - \sigma_{\{\sigma_i\}}(\omega_a, \omega_b, \hat{\mathbf{r}}_{ab}) + \sigma_c} \right\}^{12} - \left\{ \frac{\sigma_c}{r - \sigma_{\{\sigma_i\}}(\omega_a, \omega_b, \hat{\mathbf{r}}_{ab}) + \sigma_c} \right\}^6 \right] \quad (1)$$

where σ_c is a shift parameter. The energy and shape contact functions $\epsilon_{\{\epsilon_i\}}^{(\mu,\nu)}(\omega_a, \omega_b, \hat{\mathbf{r}}_{ab})$ and $\sigma_{\{\sigma_i\}}(\omega_a, \omega_b, \hat{\mathbf{r}}_{ab})$ depend on the orientations of the two particles, ω_a, ω_b , and on their separation vector \mathbf{r}_{ab} , and are defined in terms of the set of axis lengths $\{\sigma_i\}$ ($(i = x, y, z)$) and of well depths $\{\epsilon_i\}$ in the corresponding directions as well as the tuning parameters μ and ν . In eq.1 we use the biaxial version of the GB pair potential both for the sake of generality and because it provides efficient combination rules, useful to compute the energy between dissimilar particles [29]. Notice that, although the potential in eq.1 is formally the same as the standard biaxial one, there is a fundamental difference in that the σ_i are now considered variables and can change during the course of the simulation. The canonical ensemble average of a property A depending on the positional-orientational variables $\{X\}$ and on a set of internal degrees of freedom $\{\phi\}$ with an intrinsic distribution (ID) $P_0(\{\phi\})$, can be written as

$$\langle A \rangle = \frac{\int A(\{X, \phi\}) \exp[-U(\{X, \phi\})/kT] \{dX\} \{P_0(\{\phi\})d\phi\}}{\int \exp[-U(\{X, \phi\})/kT] \{dX\} \{P_0(\{\phi\})d\phi\}} \quad (2)$$

thus justifying the use of the classical Metropolis algorithm [30] for the sampling of the $\{\phi\}$ variables in calculating observables. The simple deformable variant of the GB model we propose here is based on the assumption that the axes σ_i , instead of being fixed, can be considered as internal degrees of freedom with ID $P_0(\sigma_i)$, that is then used to sample σ_i when implementing the Monte Carlo procedure. Since here we only simulate uniaxial particles, for simplicity we adopt in the rest of the paper only the standard notation for uniaxial ellipsoids, i.e. molecular length σ_e , molecular width σ_s , and interaction strengths ϵ_e and ϵ_s . In practice we just sample the molecular length σ_e , while the molecular width σ_s is determined by the constraint of keeping the molecular volume V constant. Since for an ellipsoidal uniaxial particle $V = \frac{1}{6}\pi(\sigma_s^0)^2\sigma_e^0$, we derive the actual molecular width as $\sigma_s = \sigma_s^0(\sigma_e^0\sigma_e)^{\frac{1}{2}}$, where, from here on, we indicate with the superscript zero the fixed shape parameters $\sigma_s^0 = 1$, $\sigma_e^0 = 3$ and the relative strengths $\epsilon_s^0 = 1$, $\epsilon_e^0 = 0.2$. Distances and interaction energies are scaled with respect to the chosen reference molecular units: σ_s^0 for distances, and ϵ_s^0 for energies, while temperatures are in dimensionless units ϵ_s^0/k . We also assume the GB parameters, $\mu = 1$ and $\nu = 3$, as in [31]. The change in molecular shape can also be coupled to a change of the intermolecular anisotropic interaction parameters, e.g. by assuming some functional relationship between size and interaction. Here the assumption is that, as the constant volume implies that if the i-dimension increases the other decreases, the energy well depth in a direction has a power-law inverse dependence on the molecule dimension in that direction: $\epsilon_i = \epsilon_i^0(\sigma_i^0/\sigma_i)^\alpha$, with $\alpha > 0$. In practice, here we have arbitrarily set the exponent α to $k = \log 5 / \log 3$ in order to obtain the inversion of the well depths ϵ_e and ϵ_s when the long and short dimensions values exchange. To distinguish the effect of the shape variation from the effect of the energy variation we have also studied a model with fixed interaction parameters ($\alpha = 0$). We have chosen three types of $P_0(\sigma_e)$ with identical average and very similar moments (see table 1): a triangular ("T") and a

gaussian ("G") distribution, and a third, asymmetric one ("A") derived by fitting, shifting and scaling the molecular length distribution of the 4-cyano-4'-n-pentyl-biphenyl (5CB) mesogen in a vacuum (see, e.g. [32]). The latter ID was obtained from an atomistic Molecular Dynamics simulation at 300 K of an isolated molecule, modelled with the AMBER force field [33], and represents an example of the length distribution that could be expected for a molecule formed by a rigid core and a flexible alkyl chain. Finally, the behaviour of these models has been compared with a fourth, rigid shape one, with a delta (" δ ") intrinsic distribution.

We would like to point out that this particular choice of the energy and shape distributions, the constraint on the molecular volume and the energy-shape dependence have been made to facilitate the comparison with the rigid model and do not intend to denote realism. On the other hand, the method is quite general and a realistic knowledge of the actual relationship between shape change and interaction energy of a given molecule, if available, could be effectively implemented to define a realistic ID for a molecular level simulation.

3 Simulations and results

We have performed about one hundred Monte Carlo (MC) simulations [30] in the isobaric-isothermic (NPT) ensemble at dimensionless pressure $P^*=10$, on samples of $N=1000$ particles in a cooling-down sequence of runs with a dimensionless temperature step 0.1, starting in each case from isotropic configurations, and we have studied a temperature range sufficiently large to enclose the smectic-nematic and nematic-isotropic phase transitions. We have adopted an orthogonal simulation box with periodic boundary conditions, allowing its sides to fluctuate independently during the MC evolution of the system. This was achieved by attempting, for each particle, either a rototranslational move (with a 90% probability) or else a deformation move that changes the value of σ_e , σ_s (using the constant volume rule) and where necessary ϵ_e and ϵ_s (if $\alpha > 0$). The σ_e values are extracted with the probability given by the selected ID. We have computed average thermodynamic observables by sampling configurational values every 100 cycles, one cycle being a random sequence of N attempted MC moves. The simulation equilibration runs have not been shorter than 400 kcycles, followed by 500 kcycles production runs. Among the calculated properties, to monitor the phase change of the system with temperature we have chosen the average GB energy $\langle U^* \rangle$, the number density $\langle N/V \rangle$, the second rank order parameter $\langle P_2 \rangle = \langle 3 \cos^2 \beta - 1 \rangle / 2$ with the angle β defining the orientation of the long molecular axis with respect to the director, the average molecular length $\langle \sigma_e \rangle$, and its effective distribution $P(\sigma_e)$.

Figures 1 and 2 report the main results of the simulations for the various systems. We see that all of them exhibit the same phase sequence: a wide smectic phase at low temperature, followed by a nematic and by an isotropic phase, as it can be easily observed following the temperature-behaviour of energy, order parameter and density. The ID is influential and its effect is evident on the phase transition temperatures (summarised in table 1), which appear to be particularly sensitive to molecular deformability. The

simulations with variable shape but fixed interaction ($\alpha = 0$) reveal that, for GB molecules, systems having different IDs with the same average length present the same nematic-isotropic transition temperature. On the contrary a certain dispersion in the particle length (second central moment $\mu_2 \neq 0$) is to increase T_{SN} with respect to the rigid case. Moreover the smectic-nematic transition temperature appears to be sensitive to the type of distribution (indeed the "T", "G" and "A" models all show different T_{SN}) demonstrating that this transition is strongly shape-driven. This effect is not completely unexpected as it is known, both experimentally and from simulations, that for many mesogens containing flexible chains the increase of terminal chain length stabilises, at least initially, the smectic phase depressing the nematic one [34, 35]. By further adding the variability in the interaction energies ($\alpha = k$), an overall increase of the average energy is registered, and the nematic-isotropic transition temperature is lowered with respect to the rigid model (i.e. the transition is energy driven, and the deformability favours the isotropic phase), but again the similarities between the energy distributions are sufficient to obtain the same transition temperature for all the flexible models. Quite surprisingly, the smectic-nematic transition temperatures do not vary with respect to the $\alpha = 0$ case.

The deformability of the model allows to follow the temperature dependence of length dependent observables and in particular of the average length $\langle \sigma_e \rangle = \int P(\sigma_e) \sigma_e d\sigma_e$ (figure 3). This can be compared with the first moment of the intrinsic distribution, which is $\sigma_e^0 = 3$ in all cases. Interestingly, we find $\langle \sigma_e \rangle$ to be phase dependent and to present small discontinuities at the phase transitions: for each model it decreases with temperature, and at the nematic-isotropic transition the molecular average length becomes lower than the first moment of its ID. On the other hand in the smectic phase the molecular length is larger than the first moment of the ID, with attendant stabilization of the smectic phase and an effect contrary to what registered for flexibility as commonly intended. Thus each transition is accompanied by a change in the molecular shape, which is possibly responsible for the slight increase of first order character with respect to the " δ " model which is registered in energy, density and order plots (figures 1,2).

Table 1

Nematic-Isotropic T_{NI} and Smectic-Nematic T_{SN} transition temperatures of the systems studied as function of energy and shape IDs. The central moments of the distributions, $\mu_n = \langle (\sigma_e - \langle \sigma_e \rangle)^n \rangle$, $n = 2 - 4$, calculated numerically, are also shown. Dimensionless units are used.

ID	α	$\mu_2 \times 10^3$	$\mu_3 \times 10^4$	$\mu_4 \times 10^4$	$\mu_5 \times 10^6$	T_{SN}	T_{NI}
δ	0	0.00	0.00	0.00	0.00	2.55	3.45
T	0	6.67	0.00	1.07	-0.02	2.85	3.45
G	0	6.67	0.00	1.32	0.06	2.95	3.45
A	0	6.67	-2.08	1.02	-7.09	2.65	3.45
T	k	6.67	0.00	1.07	-0.02	2.85	3.15
G	k	6.67	0.00	1.32	0.06	2.95	3.15
A	k	6.67	-2.08	1.02	-7.09	2.65	3.15

Finally, we analyse qualitatively the variation of the actual shape distributions $P(\sigma_e)$ with temperature and with respect to the corresponding IDs (figure 4). Some general trends can be identified: first, we notice that the effect of the exponent α is negligible and the shape distributions in the first row of figure 4 ($\alpha = 0$) look very similar to the ones in the second row ($\alpha = k$). More interestingly, in the smectic phase we can observe a pronounced shift and skewness of the distribution towards higher lengths: consequently, the smectic phase becomes stabilised and the phase transition from smectic to nematic results in a sudden change of shape distribution. On the contrary, in the nematic and isotropic phase all distributions remain very close to the respective IDs, the different phase being revealed only by small skew toward higher (nematic phase) or smaller molecular lengths (isotropic phase).

4 Conclusions

We have proposed a modification of the uniaxial Gay–Berne model suitable to describe particles with adjustable shape and interaction. We have considered the effects of different intrinsic distributions of the molecular shape, including one derived from a realistic conformational distribution, on a system of ellipsoids with aspect ratio $L/D = 3$, typical for thermotropic liquid crystals. We have found that small differences in the shape of the parent distribution chosen are sufficient to determine differences in the smectic-nematic transition, while the nematic-isotropic transition temperature is sensitive only to differences between the first moments of the molecular length distributions. Conversely, the addition of a variability of interaction parameters, linked to the change of aspect ratio, does not modify the smectic-nematic transition but decreases the nematic-isotropic transition temperature. Summarising, the simulations have shown that the nematic phase is destabilised both by the deformability of shape, which favours the smectic phase, and by the deformability of interactions, which favours the isotropic phase. In all the cases considered, we have seen that the phase transitions are assisted by a change in the molecular shape, which becomes more spherical with increasing temperature. We believe that this new variant of GB potential will be useful in the study of the phase behaviour of lyotropic micellar systems and thermotropic liquid crystals, particularly dendrimers, and in general for a more realistic molecular-level descriptions of a variety of mesogens.

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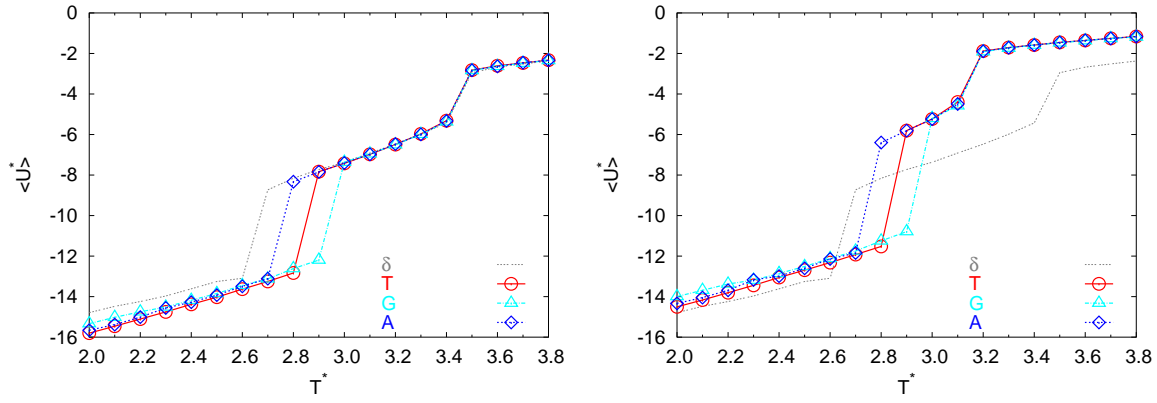


Figure 1. Average Gay-Berne energy as function of temperature for the various shape distributions (left: $\alpha = 0$; right: $\alpha = k$).

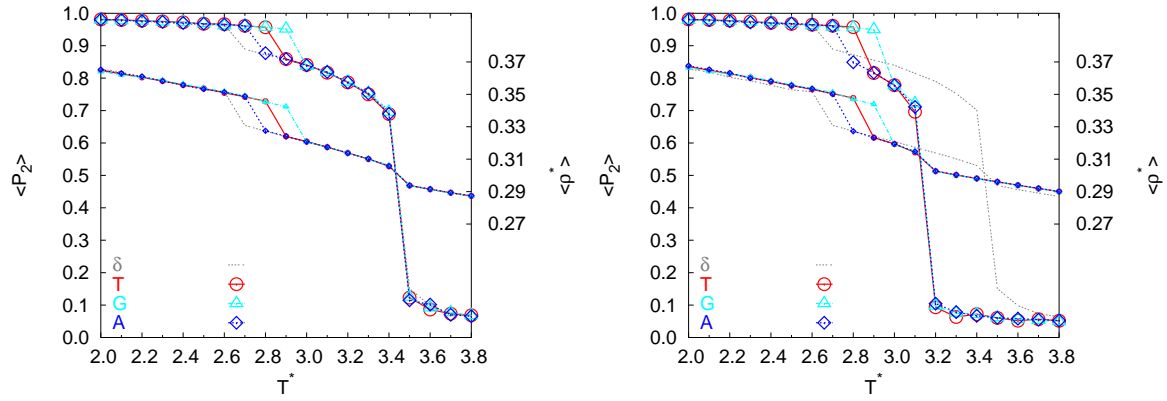


Figure 2. Average orientational order parameter (big symbols) and density (small symbols) as function of temperature for the various shape distributions (left: $\alpha = 0$; right: $\alpha = k$).

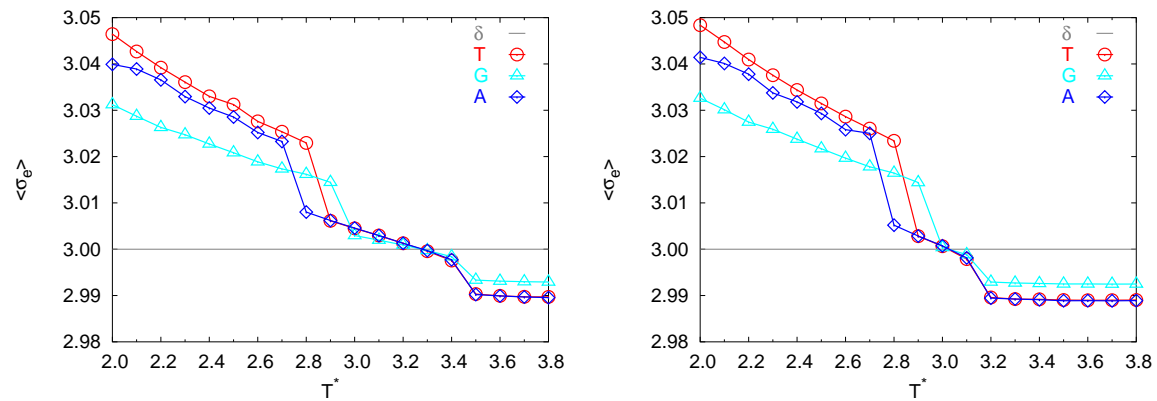


Figure 3. The observed average length $\langle \sigma_e \rangle$ as a function of temperature (left: $\alpha = 0$; right: $\alpha = k$).

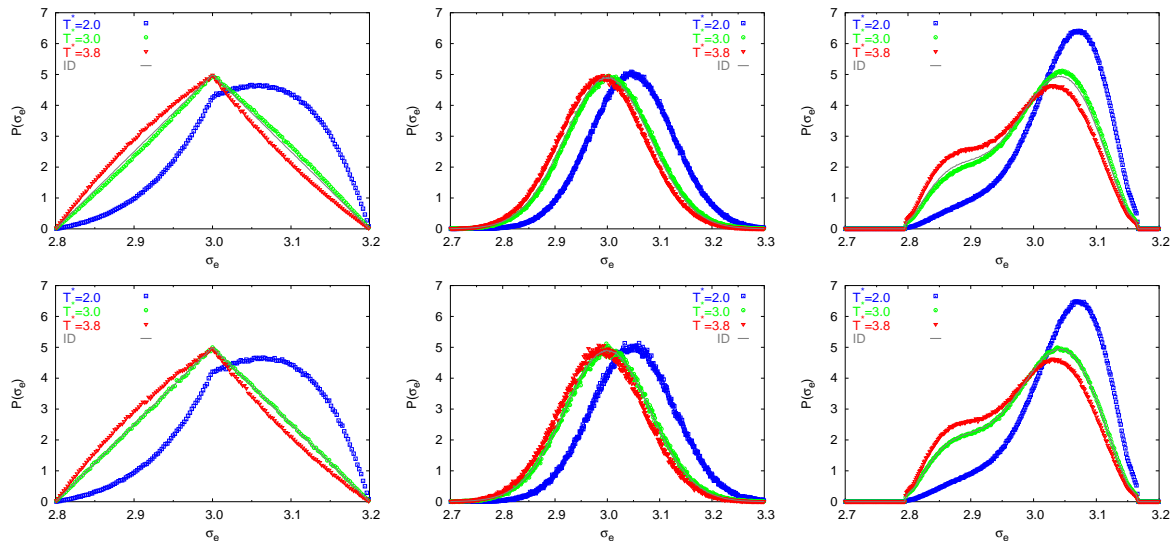


Figure 4. Temperature dependent profiles of the distribution of the long molecular axis length $P(\sigma_e)$, ($\alpha = 0$, top; $\alpha = k$, bottom), for the “T” (left), “G” (centre) and “A” (right) compared with their respective intrinsic distributions (grey continuous lines), in the smectic ($T^* = 2.0$, blue), nematic ($T^* = 3.0$, green) and isotropic phase ($T^* = 3.8$, red).