

# Self-assembly of dumbbell-shaped supramolecules with simulated annealing and Monte Carlo simulation

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**Abstract.** The self-assembly structures of dumbbell-shaped supramolecules are investigated using a simple sphere-rod-sphere (SRS) model. Through the simulated annealing Monte Carlo simulation under NVT condition, two variations of this model, i.e. the rigid/semi-rigid model, are compared by their order parameters. We found that, by varying the interactions of this SRS model, various nanostructures such as cross-linked networks, clusters phases, bundle-like nanowires and other order phases are discovered. The formation mechanism of these novel nanostructures is discussed.

## 1. Introduction

The self-assembly of supramolecules have received particular attentions in past decades, especially in recent advance in molecular nanostructure determination and nanotechnology. [1, 2] Early in the year 1923, Vorländer<sup>[3]</sup> had recognized that the anisotropic shape of the molecule is an important or even the dominant factor in determining the self-assembly behavior of liquid crystalline. Rigid supramolecule has the similar character of liquid crystal molecule which has non-spherical rigid shape and possesses anisotropic properties in thermal conductivity, optics and electromagnetics. These properties enable these liquid-crystal-like molecules applied in many important fields, such as the computer and electronic industry.

In the current study, we focus on a kind of dumbbell-shaped rigid supramolecule, which has similar molecular shape as linear liquid crystal but with two tunable terminal groups. This class of linear liquid crystal may have more complex phase structures and transitions which are still not well understood right now. In this study, we construct a simplified model to simulate the self-assembly structure of this kind of supramolecule, and the general properties of them may provide more potential applications and understandings.

## 2. Models

In this work, the self-assembly of dumbbell-shaped supramolecule is constructed by a simplified sphere-rod-sphere (SRS) model, see details in Fig. 1. Here, the interaction between spheres employs the Lennard Jones type potential, the interaction between ellipsoids uses Gay-Berne (GB) potential, and the interaction between ellipsoid and sphere employs a variant of GB potential. [4] There are two variations of this model, a semi-rigid model constrained with a harmonic potential and a completely rigid model.



**Figure 1.** Schematic illustration of the sphere-rod-sphere model.

### 2.1 The Lennard-Jones potential

The Lennard-Jones potential (also referred to as the LJ-6-12 potential) is a mathematically simple model that approximates the interaction between a pair of neutral atoms or molecules.

$$U^{LJ}(r_{ij}) = 4\varepsilon \left[ \left( \frac{\sigma}{r_{ij}} \right)^{12} - \left( \frac{\sigma}{r_{ij}} \right)^6 \right] \quad (1)$$

where  $\varepsilon$  is the depth of the potential well,  $\sigma$  is the finite distance at which the inter particle potential is zero. In our simulation,  $\sigma = 0.2$  and  $\varepsilon = 1$ , the energy is in units of  $\varepsilon$ .

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## 2.2 The Gay-Berne potential

The Gay-Berne (GB) potential can be regarded as an anisotropic and shifted version of the Lennard-Jones (LJ) interaction suitable for uniaxial molecules, where the strength  $\varepsilon$  and the range parameter  $\sigma$  depend on the orientations of the two particles and their intermolecular vector. The interaction between ellipsoids uses Gay-Berne [5] (GB) potential. The Gay-Berne potential was first introduced to model the site-site potential for a pair of anisotropic but cylindrically symmetric molecules. The functional form is based on the Gaussian overlap model proposed by Berne, et al.[6] The model is thus defined by the following expressions:

$$U(\vec{u}_i, \vec{u}_j, \hat{r}_{ij}) = 4\varepsilon(\vec{u}_i, \vec{u}_j, \hat{r}_{ij}) \left\{ \left[ \frac{\sigma_0}{r_{ij} - \sigma(\vec{u}_i, \vec{u}_j, \hat{r}_{ij}) + \sigma_0} \right]^{12} - \left[ \frac{\sigma_0}{r_{ij} - \sigma(\vec{u}_i, \vec{u}_j, \hat{r}_{ij}) + \sigma_0} \right]^6 \right\} \quad (2)$$

where  $\vec{u}_i$  and  $\vec{u}_j$  are unit vectors describing the orientations of the two molecules and  $\hat{r}_{ij}$  is the intermolecular vector. The strength parameter has the form:

$$\varepsilon(\vec{u}_i, \vec{u}_j, \hat{r}_{ij}) = \varepsilon_0 \varepsilon^{\mu}(\vec{u}_i, \vec{u}_j, \hat{r}_{ij}) \varepsilon^{\nu}(\vec{u}_i, \vec{u}_j) \quad (3)$$

$$\varepsilon(\vec{u}_i, \vec{u}_j) = [1 - \chi^2(\vec{u}_i \cdot \vec{u}_j)^2]^{-1/2} \quad (4)$$

$$\varepsilon^{\nu}(\vec{u}_i, \vec{u}_j, \hat{r}_{ij}) = 1 - \frac{\chi^{\nu}}{2} \left\{ \frac{[\hat{r}_{ij} \cdot (\vec{u}_i + \vec{u}_j)]^2}{1 + \chi^{\nu}(\vec{u}_i \cdot \vec{u}_j)} + \frac{[\hat{r}_{ij} \cdot (\vec{u}_i - \vec{u}_j)]^2}{1 - \chi^{\nu}(\vec{u}_i \cdot \vec{u}_j)} \right\} \quad (5)$$

The range parameter is defined by the following equation:

$$\sigma(\vec{u}_i, \vec{u}_j, \hat{r}_{ij}) = \sigma_0 \left\{ 1 - \frac{\chi}{2} \left[ \frac{(\vec{u}_i \cdot \hat{r}_{ij} + \vec{u}_j \cdot \hat{r}_{ij})^2}{1 + \chi(\vec{u}_i \cdot \vec{u}_j)} + \frac{(\vec{u}_i \cdot \hat{r}_{ij} - \vec{u}_j \cdot \hat{r}_{ij})^2}{1 - \chi(\vec{u}_i \cdot \vec{u}_j)} \right] \right\}^{-1/2} \quad (6)$$

The first parameters we considered for the GB potential are chosen to fit the interaction curves of two molecules arranged in a linear fashion for side-by-side and end-to-end orientations. The fitted parameters were:  $\mu = 2$ ,  $\nu = 1$ ,  $\sigma_e/\sigma_s = 5$ ,  $\varepsilon_e/\varepsilon_s = 5$ ,  $\sigma_0 = 0.2$ .

## 2.3 The variant Gay-Berne potential

The interaction between ellipsoid and sphere employs a variant of GB potential.

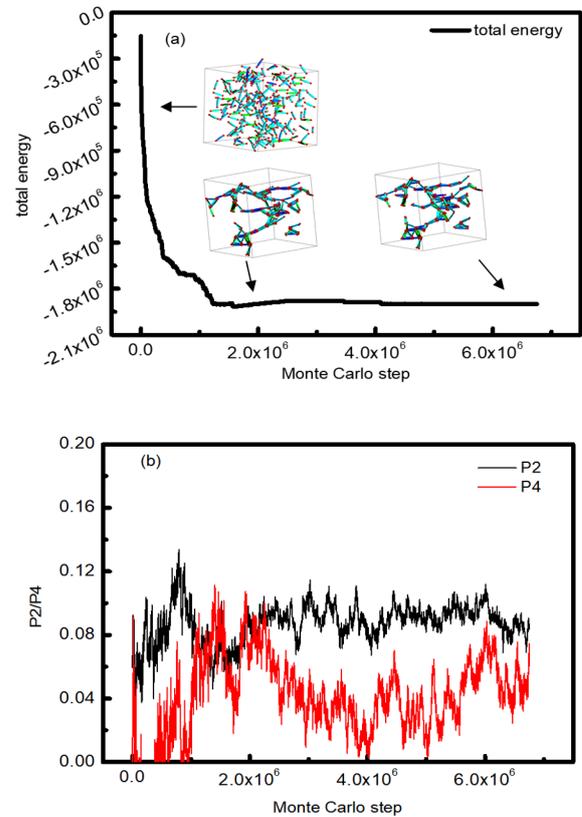
$$\sigma(\hat{r}_{ij}, \vec{u}_j) = \sigma_0 [1 - \chi(\hat{r}_{ij} \cdot \vec{u}_j)^2]^{-1/2} \quad (7)$$

$$\varepsilon(\hat{r}_{ij}, \vec{u}_j) = \varepsilon_{RS} \left[ 1 - \left( 1 - \left( \frac{\varepsilon_E}{\varepsilon_S} \right)^{\chi} (\hat{r}_{ij} \cdot \vec{u}_j) \right) \right]^{\mu} \quad (8)$$

In our simulation,  $\varepsilon_E/\varepsilon_S = 5$  and  $\varepsilon_{RS} = 1.5$ .

## 3. Results and discussion

We have performed off-lattice Monte Carlo (MC) simulations of a system of dumbbell shaped mesogens described above in the canonical ( $NVT$ ) ensemble simulating samples of  $N = 648$ , and 1024 particles modeled with the coarse grained pair potential described before. The phase diagram has been explored by performing the simulated annealing MC runs. With different parameters, they exhibit isotropic ( $I$ ) phases, various cross-linked ( $CL$ ) networks, clusters ( $C$ ) phases, bundle-like nanowires ( $C/CL$ ) and other order phases. After the simulated annealing calculation, every final configuration is stabilized with a long time equilibrium run. The total energy  $E$  of the system, as a function of the Monte Carlo step, decreases rapidly and reaches equilibrium, as can be seen in Fig.2. (a).



**Figure 2.** Equilibrium for the simulated system  $\varepsilon_0 = 1$ , (a) The total energy of the system as a function of the Monte Carlo step; (b) The P2 and P4 of the system as a function of Monte Carlo step.

In order to characterize the phase behavior of the system the second-rank orientational order parameter [7, 8] and the fourth-rank orientational order parameter [7, 9] are computed via:

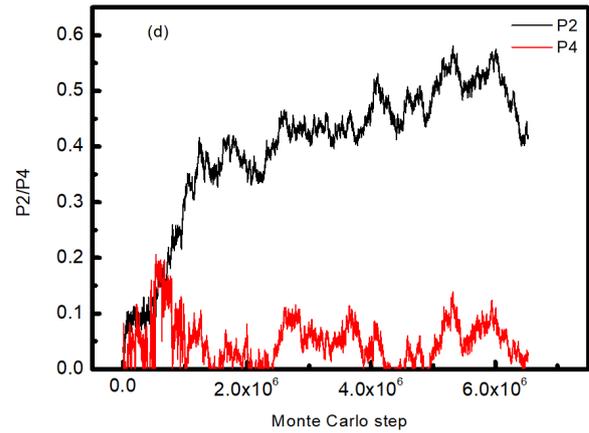
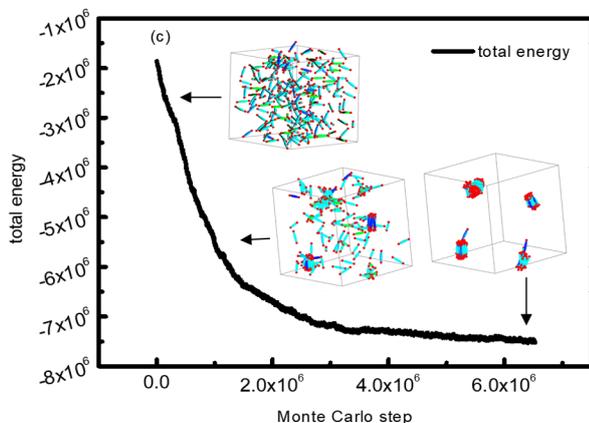
$$S_{\alpha\beta} = \frac{1}{N} \sum_{i=1}^N \frac{1}{2} (3e_{i\alpha}e_{i\beta} - \delta_{\alpha\beta}) \quad (9)$$

where  $\alpha, \beta = x, y, z$  are the indices referring to the laboratory frame,  $\delta_{\alpha\beta}$  the Kronecker symbol, and  $\langle \dots \rangle$  the ensemble average.  $P_2$  the largest eigenvalue of the order parameter  $S_{\alpha\beta}$ .

$$\langle P_4 \rangle = \frac{35}{8} \langle \cos^4 \beta \rangle - \frac{30}{8} \langle \cos^2 \beta \rangle + \frac{3}{8} \quad (10)$$

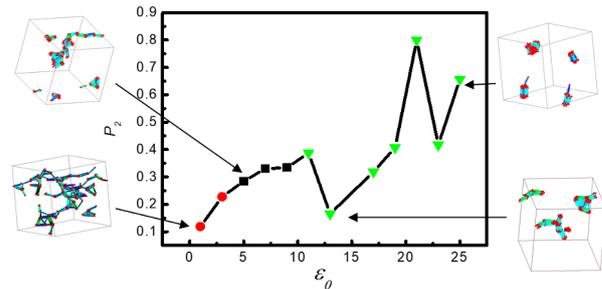
where  $\cos \beta = \vec{u} \cdot \vec{d}$ , the director  $\vec{d}$  is the eigenvector corresponding to the  $P_2$ .

The order parameter is a crucial factor in relating to experiment, since it determines the observed anisotropy in second/fourth rank tensor properties. Fig. 2(b) shows the evolution of  $P_2$  and  $P_4$  with the Monte Carlo step. As one can see from the plot, both  $P_2$  and  $P_4$  are small at high temperatures indicating the isotropic (*I*) phase. Ideally,  $P_2$  and  $P_4$  equal zero in the isotropic (*I*) phase but in practice attain small positive values of about 0.1. However, a non-vanishing value of  $S$  in the isotropic (*I*) phase is also due to a small but significant finite-size effect [8]. Focusing on the lower  $T^*$  first,  $P_2$  increases with temperature down to 26 (Monte Carlo step =  $9 \times 10^5$ ) indicating the new phase, that is *CL* phase, exists. When the depth of the potential well between rods  $\epsilon_0 = 25$ , the resulting difference becomes obvious in Fig. 3(b). The clusters (*C*) phases is found at  $T^* = 10$  (Monte Carlo step =  $1.5 \times 10^6$ ). In contrast, the comparison of Fig. 2(b) and Fig. 3(b) at low temperature shows that the latter one has a lower  $P_2$  value. This tendency for translational order along the molecular axis grows stronger as the system is cooled below the *I-C* phase boundary. This can also be seen in the evolution of the total energy, as plotted in Fig. 3(a).



**Figure 3.** Equilibrium for the simulated system  $\epsilon_0 = 25$ , (a) The total energy of the system as a function of the Monte Carlo step; (b) The  $P_2$  and  $P_4$  of the system as a function of Monte Carlo step.

To further reduce the computational load, we further apply the rigid model to check the value of  $P_2$  with  $\epsilon_0$  changing from 1 to 25 in Fig. 4. The results indicate that many phase structures can be obtained by tuning the value of  $\epsilon_0$  and the regular changing with  $\epsilon_0$  may be utilized to design novel nano materials.



**Figure 4.** Plots of  $P_2$  as function of  $\epsilon_0$ . Different phases are denoted with different symbols: Cross Linked networks (CL  $\bullet$ ), Clusters (C  $\blacktriangledown$ ), C/CL ( $\blacksquare$ ).

## 4. Conclusion

The phase structures of a simplified dumbbell-shaped supramolecule model are systematically studied with simulated annealing MC simulation. The design of the model with detailed interaction formulism is described. By varying the interaction parameters, various self-assembly structures such as isotropic, cross-linked networks, clusters phases, bundle-like nanowires and other order phases are obtained. This flexible model may serve as a generic model to study the phase structures and transitions of a large class of symmetric or asymmetric dumbbell-shaped supramolecules. Related studies are on the way.

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