Computer simulation of binary mixtures of anisotropic hard particles

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Abstract
We performed isobaric Monte Carlo simulations of binary mixtures of hard disc-like particles called spherical discs. The shape of the spherical discs is determined by a sweep of the centre of a sphere of radius L on a disc of radius D. Simulations of binary mixtures of 370 spherical discs with $D/L = 2.5$ and 110 spherical discs with $D/L = 5$ indicated microphase separation of column clusters of larger discs in a fluid of smaller discs.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Theories and computer simulations have shown that, without attractive interaction, hard anisotropic molecules form liquid crystal structures. Monodisperse systems of hard anisotropic molecules: hard ellipsoids of revolution [1, 2], hard spherocylinders [3–6], and cut spheres [7], have been studied already by using computer simulation techniques.

For monodisperse systems of hard anisotropic particles, the history of theoretical and computer simulation studies was started by Onsager [8]. For binary mixtures, it was started by Odijk and Lekkerkerker [9] in the study of binary mixtures of hard rods of different lengths. They extended Onsager's theory [8] to the binary mixture; further results were reported by Vroege and Lekkerkerker [10].

Extension to binary mixtures from monodisperse systems causes various effects on phase behaviours. Columnar structure, which is unstable for monodisperse systems of aligned hard spherocylinders, is observed for binary mixtures of aligned hard spherocylinders of different lengths [11]. The stability of the layered structure of parallel hard spherocylinders is enhanced when we add hard spheres [12, 13]. Phase separations are indicated in rod–rod mixtures [9, 10, 14], rod–sphere mixtures [12, 13, 15], rod–disc mixtures [16–18], and so forth. Experimental support for these theories and simulations is provided by virus systems of rod–sphere mixtures [19, 20] and by rod–disc mixtures of polymer-stabilized colloids [21].

In this paper, we show results of isobaric Monte Carlo (MC) simulations of binary mixtures of hard spherical discs of different diameters with the same thickness.

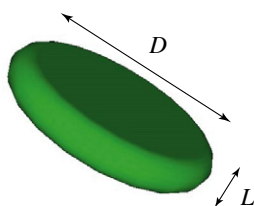[1] Author to whom any correspondence should be addressed.
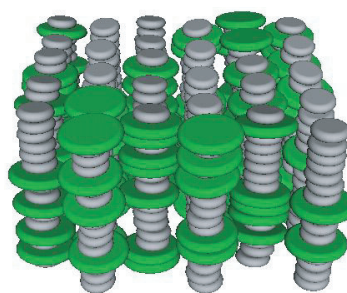
Figure 1. The spherical disc.

Figure 2. The initial structure of the present binary mixture.

2. Molecular model

The shape of the model molecule for the present study is a spherical disc. It is an extension of a spherocylinder [22]. The spherocylinder is a cylinder each end of which is capped with a hemisphere. Its shape is determined by a sweep of the centre of a sphere on a line segment. In the extension of this to a disc, the shape is determined by a sweep of the centre of a sphere of diameter L on a core disc of diameter D. An overview of the spherical disc is given by figure 1. D is the diameter of the disc and L the thickness.

3. Simulation

We performed isobaric MC simulations of binary mixtures of hard spherical discs of different diameters with the same thickness. We refer to molecules of smaller diameter as type 1 and molecules of larger diameter as type 2.

For molecular type j, we denote the diameter as D_j, the thickness as L_j, the volume of a molecule as v_j, the number of molecules in the system as N_j. In the present study, we set $L_1 = L_2 = L$, $D_1/L_1 = 2.5$, $D_2/L_2 = 5$, $N_1 = 370$, and $N_2 = 110$. We use normalization of pressure: $p^* = pL^3/(k_B T)$, where p is the actual pressure, k_B the Boltzmann constant, and T the temperature.

For preparation of an initial structure, a close packed structure of larger discs was relaxed at pressure $p^* = 1.0$. After that, 370 randomly chosen discs were changed to smaller discs. The initial structure made by this procedure for the binary mixture is shown by figure 2.

The initial structure of the binary mixture consists of hexagonal columns made of small and large discs. After we performed constant volume MC simulation to relax the particle positions, we relaxed the binary system at $p^* = 1.0$. Except for $p^* = 1.0$ and 0.7, we use a transient or equilibrated configuration of higher pressure as an initial structure for simulation at lower pressure. For $p^* = 0.7$, we tried equilibrium configurations at $p^* = 0.8$ and 0.6 as initial structures. The history of the present MC simulation is indicated by figure 3.

In figure 3, the unit of MC time consists of $N_1 + N_2$ MC trials for configurations of randomly selected discs and three trials (on average) with box dimensions with randomly chosen x-, y-, and z-directions. The volume fraction η is defined as

$$\eta = \frac{N_1 v_1 + N_2 v_2}{V}, \tag{1}$$

where V is the volume of the system. In the simulation process, the acceptance ratio of trial movements on particle configurations and system dimensions was controlled between 0.4 and 0.6 on average.
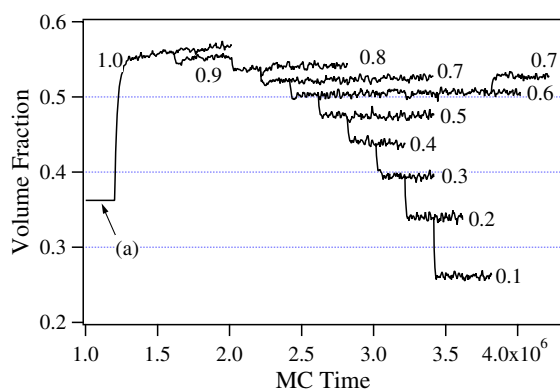
Figure 3. The profile of the simulation. The volume is fixed at stage (a). The number indicates the normalized pressure p^* for each stage.
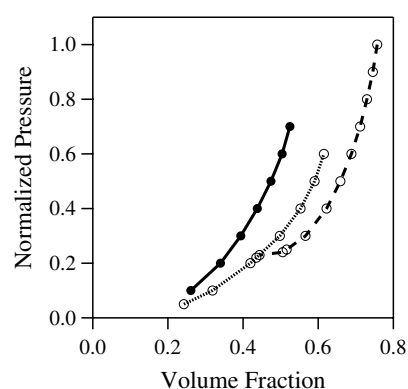

Figure 4. Equation-of-state data. Solid curve with solid circles: simulation data for the present mixture. Dashed curve with open circles: branch of the hexagonal column phase of monodisperse larger discs. Dotted curve with open circles: isotropic branch of monodisperse larger discs.
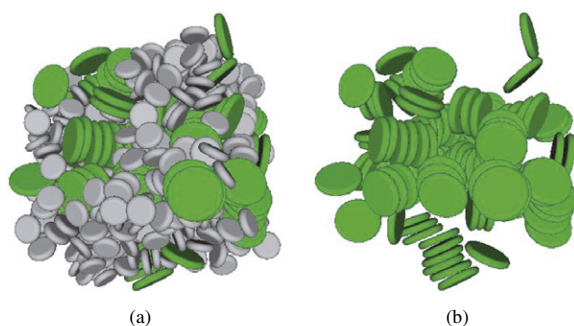

Figure 5. (a) A snapshot of the mixture at $p^* = 0.7$. (b) Small discs are removed from (a) to see the structure of the larger discs.
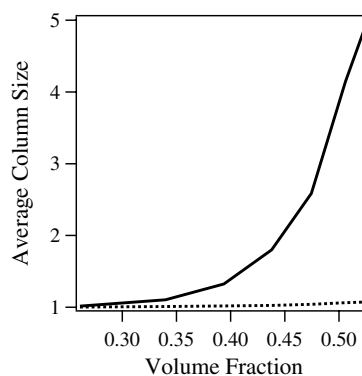

Figure 6. The average column size depending on the volume fraction. The solid curve is the average column size for columns of large discs. The dotted line is that for small discs.

4. Results

In figure 4, we show equation-of-state data for the present binary mixture and a monodisperse system of larger discs [22]. The data for the present mixture are calculated from data displayed in figure 3.

Because particles are confined in a smaller space compared to monodisperse large discs, the pressure is higher for the mixture to achieve the corresponding volume fraction of the monodisperse system.

Figure 5(a) shows a snapshot of the simulation box at $p^* = 0.7$. Only larger discs in figure 5(a) are displayed in figure 5(b). Figures 5(a) and (b) indicate that large discs are microscopically phase separated to form column clusters.

To examine the dependence of the column formation on the volume fraction, we grouped discs to columns numerically [22] and calculated the average column size for each pressure.

Figure 6 shows the results. The average column size is 1, when all discs are independent from columns. Figure 6 indicates that the column structure of large discs grows when we increase the pressure.

5. Concluding remarks

Though the present results are preliminary and further calculation and analyses are necessary for more detailed examination, they indicate that hard spherical discs show a strong affinity for column formation. In the mixture of large and small spherical discs, microphase separated structures of column clusters of large discs are observed.

In the case of a hard rod–sphere binary mixture, depletion interaction induces layering of rods [12, 13, 23]. We consider for the present case that depletion of small discs from large discs contributes to forming the microphase separated structure. Our results indicate that depletion interaction in systems of disc-like molecules induces column formation of discs.

Acknowledgments

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