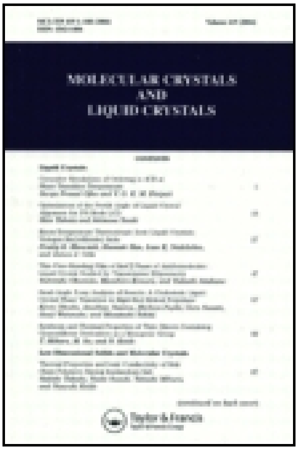

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Estimation of the Chemical Potential of the System of Hard Molecules

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Estimation of the Chemical Potential of the System of Hard Molecules

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For the estimation of the chemical potential of the system of hard rod-like molecules, insertion probability of a molecule into the system is obtained through Monte Carlo simulation. The growth probability of a test molecule from one size to the other size is accumulated to give rough estimation of insertion probability of a molecule into the system of hard spherocylinders. The chemical potential is then obtained as a logarithm of the insertion probability.

Keywords: chemical potential; Monte Carlo simulation

INTRODUCTION

Hard repulsive interaction between molecular cores plays an essential role for the appearance of microscopic structures of condensed molecular systems. In fact, computer simulations[1,2] and experiments[3,4] have indicated that the systems of hard rod-like molecules without attractive molecular interaction show variety of phases: nematic phase, smectic-A phase, rotator phase, and so forth.

In our previous studies[5, 6], we have considered a binary mixture of hard parallel rod-like molecules and hard spherical molecules. Constant pressure Monte Carlo (MC) simulation showed that in the mixture the smectic-A phase is induced as a microphase separation between rod-like molecules and spherical molecules.

Molecular simulations are often accompanied by the problem of finite system size. Smallness of the system size with periodic boundary conditions sometimes realizes a state which is unstable for larger systems. Thus the states appearing in simulations are often exposed to the stability problem.

One of the quantities which is useful to discuss the stability of phases is the chemical potential. In the present study, we consider an estimation of chemical potential of the system of hard spherocylinders.

THEORY FOR CHEMICAL POTENTIAL

In this section we follow the conventional theory of thermodynamic functions of fluids[7].

We denote the position of j-th molecule by $\boldsymbol{r}_j$. The potential energy of the system of N molecules U_N is related to the pair potential energy u between i-th and j-th molecule as

$$U_N = \sum_{i<j}^{N} u(\boldsymbol{r}_i, \boldsymbol{r}_j). \tag{1}$$

For the present system of hard molecules we have

$$u = \begin{cases} \infty, & \text{if the molecules intersect to each other,} \\ 0, & \text{otherwize.} \end{cases} \tag{2}$$

The Helmholtz free energy F_N of the system of N molecules is given by

$$F_N = 3k_{\mathrm{B}}TN \ln \Lambda - k_{\mathrm{B}}T \ln Z_N. \tag{3}$$

where Λ is the de Broglie thermal wavelength, k_B Boltzmann's constant and Z_N is the configuration part of the partition function of the system. It is defined as

$$Z_N = \frac{1}{N!}\int d\boldsymbol{r}^N \exp[-\beta U_N], \tag{4}$$

where $\beta = (k_B T)^{-1}$. The chemical potential μ is given by

$$\begin{aligned} \mu &= F_{N+1} - F_N \\ &= \mu_0 - k_B T \ln P, \end{aligned} \tag{5}$$

where μ_0 is the chemical potential of an ideal gas, and

$$P = \frac{\int d\boldsymbol{r}^{N+1} \exp\left[-\beta U_N - \beta \sum_{j=1}^{N} u(\boldsymbol{r}_j, \boldsymbol{r}_{N+1})\right]}{\int d\boldsymbol{r}^{N+1} \exp[-\beta U_N]}. \tag{6}$$

GRADUAL INSERTION OF A MOLECULE

To obtain the chemical potential μ of Eq. (5) we have to estimate P of Eq. (6). Equation (6) indicates that P for the system of hard core molecules is the probability of the insertion of a molecule into the system. In the present study, we would like to estimate P through MC simulation. However for the dense fluid of hard molecules, the insertion probability is extremely low. Then the simulation does not give reliable statistics during a realistic simulation time.

Gradual insertion method is considered to deal with this difficulty[8]. We introduce here a parameter λ which scales the size of a test molecule. We define a rule that $\lambda = 0$ corresponds to an ideal molecule which takes a position without interacting with other molecules, and that $\lambda = W$ corresponds to the entire molecule. Putting an ideal molecule as a test molecule in the system we consider to grow it step by step to the entire molecule. Letting λ_j be the shape parameter λ of j-th growth stage, the partial insertion probability $\rho(\lambda_j|\lambda_{j+1})$ that the molecule of the j-th stage can grow up to the molecule of the $(j+1)$-th stage is described as

$$\rho(\lambda_j|\lambda_{j+1}) = \frac{\int \mathrm{d}\boldsymbol{r}^{N+1} \exp\left[-\beta U_N - \beta \sum_{j=1}^{N} \phi(\boldsymbol{r}_j, \boldsymbol{r}_{N+1}; \lambda_{j+1})\right]}{\int \mathrm{d}\boldsymbol{r}^{N+1} \exp\left[-\beta U_N - \beta \sum_{j=1}^{N} \phi(\boldsymbol{r}_j, \boldsymbol{r}_{N+1}; \lambda_j)\right]}, \tag{7}$$

where $\phi(\boldsymbol{r}, \boldsymbol{r}'; \lambda)$ is the pair potential energy between an ordinary molecule at position $\boldsymbol{r}$ and the test molecule of the shape indicated by λ at position $\boldsymbol{r}'$. The case $\lambda = 0$ of the ideal molecule gives

$$\phi(\boldsymbol{r}, \boldsymbol{r}'; 0) = 0, \tag{8}$$

and $\lambda = W$ of the entire molecule gives

$$\phi(\boldsymbol{r}, \boldsymbol{r}'; W) = u(\boldsymbol{r}, \boldsymbol{r}'). \tag{9}$$

The P of Eq. (6) is then rewritten to

$$P = \rho(0|W) = \prod_{j=0}^{n-1} \rho(\lambda_j|\lambda_{j+1}), \tag{10}$$

where $\lambda_0 = 0$ and $\lambda_n = W$.

Though the probability P or $\rho(0|W)$ of a dense system is too low for statistical average, we can choose λ_j's as the $\rho(\lambda_j|\lambda_{j+1})$ appropriately gets large. Estimations of $\rho(\lambda_j|\lambda_{j+1})$'s for $0 \leq j \leq n$ reproduce P according to Eq. (10).

If the molecule is a deformable molecule, we have to consider the contribution of number of molecular conformations. For such cases. Frenkel, Mooij and Smit have proposed a type of gradual insertion method which grows a deformable chain molecule step by step in MC simulation[9]. Their method is a possible alternative for the method we use in the present study.

ESTIMATION FOR THE SYSTEM OF SPHEROCYLINDERS

MC simulation

In the present study we test the gradual insertion into the system of hard spherocylinders. Spherocylinder is a cylinder each end of which is capped with a hemisphere. In the present system, long axes of all the spherocylinders are aligned parallel to z-direction. Intermolecular interaction is the hard repulsive interaction described by Eq. (2). The length l to diameter d ratio of the present spherocylinder is $l/d = 5$. Phase behavior of the spherocylinders of $l/d = 5$ has been studied well by computer simulations[1,2].

In the present study, isobaric MC simulation was performed for the system of 1440 spherocylinders at normalized pressure $pd^3/k_BT = 0.6$ where p is the pressure with an actual unit. At this pressure, we have confirmed through the simulation that the system shows smectic-A phase with volume fraction $\eta = 0.48$. This agrees the reported simulation results[1]. We should note that the volume fraction η we use here is defined as

$$\eta = Nv_0/V,$$

where v_0 is the molecular volume and V the volume of the system.

Initial configuration of the simulation was produced according to the procedure which expands a closed packed structure[1].

During the simulation, sequential trials are made to move molecular positions and system size. After the system goes to the stable configuration, we put a test molecule into the system for the estimation of $\rho(\lambda_j|\lambda_{j+1})$.

Scaling parameter λ

For the gradual insertion, we define the relation between the scaling parameter λ and the size of the growing spherocylinder. As described by Figure 1, we denote the length of the cylinder of the growing

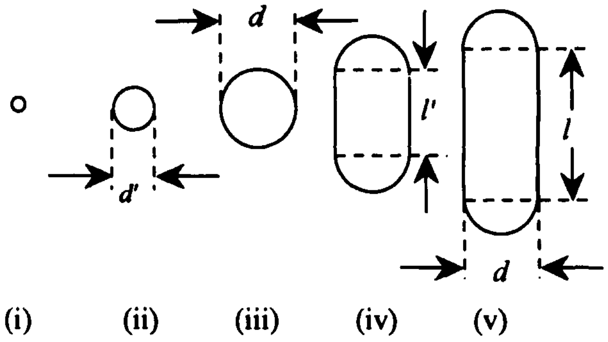

FIGURE 1 Growth stages of the spherocylinder.

spherocylinder by l' and the diameter by d'. We let d and l be the length and diameter of the entire spherocylinder.

We divide the growth stages to spherical stages and cylindrical stages. In the spherical stages, the growing molecule is a sphere which satisfies $d' \leq d$. Stages (i), (ii) and (iii) of Figure 1 correspond to the spherical stages. After the diameter of the test sphere grows up to d which is the diameter of the entire spherocylinder, the test molecule goes to the cylindrical stages. At cylindrical stages, the molecule is spherocylinder of diameter d with length l' which satisfies $0 < l' \leq l$.

We define the following relation between the scaling parameter λ and the shape of the growing test molecule. When $\lambda \leq 1$, the test molecule is on one of spherical stages and the diameter of the molecule is given by $d' = \lambda d$, while when $\lambda > 1$, it is a spherocylinder of diameter d with length $l' = (\lambda - 1)d$.

Estimation of partial insertion probability

Here we propose a procedure to obtain the estimation of $p(\lambda_j|\lambda_{j+1})$. After the MC simulation relaxes the system configuration, we try to insert a test molecule of infinitesimal size into the system. We denote the shape scaling parameter λ of such infinitesimal hard sphere as δ. It is a point which can not exist within cores of other molecules.

The probability of insertion of the infinitesimal hard sphere and the volume fraction η are related as

$$\rho(0|\delta) = (1 - \eta). \tag{11}$$

After the insertion is succeeded, the position of the test molecule is tried to move in ordinary MC cycles. At this stage, the test particle with $\lambda = \delta$ is realized.

When the test particle of the scale λ_j is realized, we calculate $\rho(\lambda_j|\lambda_{j+1})$ with the following manner. During the MC process, we can obtain the maximum growth size of the test molecule to which the test molecule can grow without touching other molecules. This maximum growth size changes as molecules around the test particle move. Statistical samplings of the maximum growth size enables us to obtain $\rho(\lambda_j|\lambda)$ as a function of λ. Each curve in Figure 2 shows insertion probability obtained from 10^3 samplings of the maximum growth size. The λ_{j+1} is then chosen as $\rho(\lambda_j|\lambda_{j+1})$ is large appropriately to obtain reliable ρ. The test molecule of $(j + 1)$-th stage with thus determined λ_{j+1} is easily obtained from the expansion of the test molecule of j-th stage. Repeating the above procedure we finally reach $\rho(\lambda_{n-1}|W)$. Then Eqs. (5) and (10) reproduce the chemical potential.

Results

Figure 3 shows results obtained from various runs of MC simulation. Different timings of the start of the gradual insertion makes differences among results. These differences result from fluctuation of positions of molecules. We expect that enough number of samplings will diminish the differences. In the present simulation with spherocylinders of length to diameter ratio $l/d = 5$, $\lambda = 6$ corresponds to the entire molecule. From four runs indicated by Figure 3 we have obtained the present estimation of the chemical potential as

$$\beta\mu - \beta\mu_0 = -\ln \rho(0|6) = 9.3 \pm 0.8. \tag{12}$$

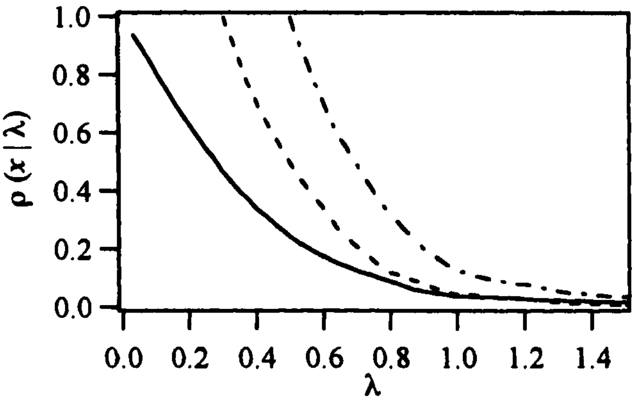

FIGURE 2 Partial insertion probability. Solid line: $x = \delta$. Dashed line: $x = 0.3$. Dot-dashed line: $x = 0.5$.

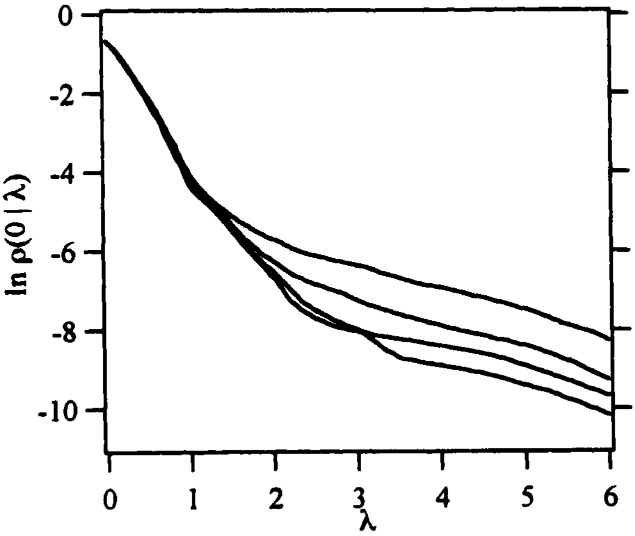

FIGURE 3 Logarithm of insertion probability obtained from several runs of MC simulation.

CONCLUDING REMARKS

We have estimated the chemical potential of the system of spherocylinder with the length to diameter ratio $l/d = 5$ at pressure $pd^3/(k_BT) = 0.6$.

The chemical potential is the Gibbs free energy per particle. It is also obtained by integrating the equation of state of the system. We define a normalized pressure as $p^* = pv_0/(k_BT)$. We should note that we have used another definition $pd^3/(k_BT)$ as the normalized pressure in the description of the condition of the present MC simulation.

The chemical potential at volume fraction η is given by

$$\beta\mu(\eta) - \beta\mu_0(\eta) = \int_0^\eta [p^*(\eta') - \eta'] \frac{d\eta'}{\eta'^2} + p^*(\eta)\eta - 1. \qquad (13)$$

For the determination of the phase transition density, the expansion coefficients of the equation of state of the system of spherocylinders have already been determined by MC simulation[1]. For low density the equation of state is given by virial expansion:

$$p^* = \eta + 4\eta^2 + 16B_3^*\eta^3 + 64B_4^*\eta^4 + 256B_5^*\eta^5, \qquad (14)$$

where B_n^* is a modified virial coefficient. For rather higher density, another expansion called y expansion gives good approximation for the equation of state;

$$p^* = C_1^*y + C_2^*y^2 + C_3^*y^3. \qquad (15)$$

where $y = \eta/(1-\eta)$. Stroobants, Lekkerkerker and Frenkel have given estimation of the coefficients of Eqs. (14) and (15)[1]. For the system of spherocylinders of $l/d = 5$, they have shown that $B_3^* = 0.5968$, $B_4^* = 0.2362$, $B_5^* = 0.0618$, $C_1^* = 2.141$, $C_2^* = 1.065$ and $C_3^* = 0.460$. Using Eq. (14) for $0 \leq \eta \leq 0.35$ and Eq. (15) for $0.35 < \eta$ with the above values of coefficients, we can obtain another estimation of μ as

$$\beta\mu(0.48) - \beta\mu_0(0.48) = 9.40. \qquad (16)$$

where $\eta = 0.48$ is put as the average value of η of the present MC simulation. The value of Eq. (16) encourage the estimation of Eq. (12) obtained with the present MC simulation.

Acknowledgments

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