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Pressure Dependence of Phase Transition Behaviour in Nematic and Isotropic Phases for the Gay–Berne Discogens

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We investigated pressure dependence of phase transition behaviour in the nematic–isotropic phase transition with molecular dynamics simulations of the Gay-Berne disc model over a range of pressures from 5.0 to 30.0 before investigating molecular and director dynamics of the system. The nematic–isotropic transition temperature changes non-linearly, which is similar to the change in real nematics. The change in the transition temperature can be fitted with a second order polynomial function. Moreover, the Clapeyron relationship between the systems at two different pressures is also reasonably valid.

Keywords Discotic; Gay-Berne model; molecular dynamic simulations; nematic; pressure dependence

1. Introduction

Liquid crystals are currently used widely for electronic devices in applications and studied in many areas of basic scientific research [1–3]. Although numerous studies have been conducted on these fascinating materials, further studies focussing on applications, such as chemical sensors [4] and semiconductors [5–7], and other basic research, are still being conducted.

Similar to rod-like molecules, discotic molecules also take on a variety of liquid crystalline phases and characteristic dynamics with changing pressure and temperature. In conjunction with experiment, computer simulation is a very powerful tool to discover not only phase diagrams and structures but also properties of molecular and director dynamics [8].

In our previous paper [9], we found characteristic rotational motion near the nematic–isotropic phase transition temperature for rod-like molecules through the Gay–Berne (GB) model. A rough sketch of the characteristic molecular motion was presented. Free volume is one of the important factors to understand the molecular motion in this sketch. We, therefore, focus on the properties of molecular and

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director dynamics in the nematic–isotropic phase transition region and nematic phase by altering both the system pressure and molecular shape. However, before a detailed discussion on dynamics properties, we must first explore the phase transition behaviour of the model systems. As a part of this series of our research and as preliminary results, we have reported pressure dependence of the phase transition behaviour and some dynamics properties for the Gay–Berne discogen under two pressure conditions [10]. The systems at two pressures show the same phase sequences: isotropic, discotic nematic and columnar phases. In addition, an apparent jump in the relaxation time of the first-rank orientational time autocorrelation function was found for both cases. On the other hand, a clear difference by pressure was revealed in the retardation factor $g_{\|}$ as a function of the reduced temperature T^*/T^*_{NI}, even after considering the value of the second rank orientational order parameter. This previous study also shows that a wider range of pressures would be needed to investigate the phase transition behaviour and dynamics in depth. In this paper, we report pressure dependence on the phase transition behaviour of the nematic–isotropic phase for the Gay–Berne discotic model with a wider range of pressures.

2. Computational Details

To investigate pressure effects on the phase transition behaviour more precisely, we studied extensive system that we studied before [10]. In this study, the phase transition of the isotropic and nematic phases are considered over a wider range of pressure values P^* of 5.0 to 30.0. As in the previous simulation, isothermal–isobaric molecular dynamics simulations were used to monitor the phase transition behaviour in the isotropic and nematic phases. The detailed procedure of the molecular dynamics simulation technique used was the same as in a previous study [11]. To solve the equations of numerical integration for the case of the isothermal–isobaric ensemble, we applied the implicit leap-frog scheme. We also used the generic Gay–Berne model, GB (0.345, 0.2, 1, 3) [12]. The parameter set was chosen because it accurately models a wide range of the nematic phase. In the GB pair potential [13], the molecules i and j interact by

$$U_{ij}^{GB}(\mathrm{r}_{ij}, \mathrm{u}_i, \mathrm{u}_j) = 4\varepsilon(\hat{\mathrm{r}}_{ij}, \mathrm{u}_i, \mathrm{u}_j)(d_{ij}^{-12} - d_{ij}^{-6}), \tag{1}$$

where

$$d_{ij} = \frac{r_{ij} - \sigma(\hat{\mathrm{r}}_{ij}, \mathrm{u}_i, \mathrm{u}_j) + \sigma_0}{\sigma_0}. \tag{2}$$

Here r_{ij} is the distance between the centres of mass of molecules i and j, and $\hat{\mathrm{r}}_{ij} = \mathrm{r}_{ij}/r_{ij}$ is a unit vector along the intermolecular separation vector r_{ij}. In particular, σ_0 is the diameter of the molecule. In the case of discotic molecules, it is appropriate to use subscripts f and e. The length parameters, σ_f and σ_e, and energy parameters, ε_f and ε_e, correspond to two configurations of the thickness (face-to-face separation) and the diameter (edge-to-edge separation) of a disc. In this study, the two parameters σ_0 and ε_0 indicate σ_e and ε_e, respectively. The molecular shape parameter σ_0 and the energy parameter ε_0 depend on the unit vectors u_i and u_j as well as $\hat{\mathrm{r}}_{ij}$, as given by the following set of equations:

$$\sigma(\hat{\mathrm{r}}_{ij}, u_i, \mathrm{u}_j) = \sigma_0\left[1 - \frac{\chi}{2}\left\{\frac{(\mathrm{u}_i \cdot \hat{\mathrm{r}}_{ij} + \mathrm{u}_j \cdot \hat{\mathrm{r}}_{ij})^2}{1 + \chi(\mathrm{u}_i \cdot \mathrm{u}_j)} + \frac{(\mathrm{u}_i \cdot \hat{\mathrm{r}}_{ij} - \mathrm{u}_j \cdot \hat{\mathrm{r}}_{ij})^2}{1 - \chi(\mathrm{u}_i \cdot \mathrm{u}_j)}\right\}\right]^{-\frac{1}{2}}, \tag{3}$$

where $\chi = (\kappa^2 - 1)/(\kappa^2 + 1)$, and

$$\varepsilon(\hat{\mathrm{r}}_{ij}, \mathrm{u}_i, \mathrm{u}_j) = \varepsilon_0[\varepsilon_1(\mathrm{u}_i, \mathrm{u}_j)]^{\nu}[\varepsilon_2(\hat{\mathrm{r}}_{ij}, \mathrm{u}_i, \mathrm{u}_j)]^{\mu}, \tag{4}$$

where the exponents μ and ν are adjustable.

$$\varepsilon_1(\mathrm{u}_i, \mathrm{u}_j) = [1 - \chi^2(\mathrm{u}_i \cdot \mathrm{u}_j)^2]^{-1/2}, \tag{5}$$

and

$$\varepsilon(\hat{\mathrm{r}}_{ij}, \mathrm{u}_i, \mathrm{u}_j) = 1 - \frac{\chi'}{2}\left\{\frac{(\mathrm{u}_i \cdot \hat{\mathrm{r}}_{ij} + \mathrm{u}_j \cdot \hat{\mathrm{r}}_{ij})^2}{1 + \chi'(\mathrm{u}_i \cdot \mathrm{u}_j)} + \frac{(\mathrm{u}_i \cdot \hat{\mathrm{r}}_{ij} - \mathrm{u}_j \cdot \hat{\mathrm{r}}_{ij})^2}{1 - \chi'(\mathrm{u}_i \cdot \mathrm{u}_j)}\right\}, \tag{6}$$

where $\chi' = (\kappa'^{1/\mu} - 1)/(\kappa'^{1/\mu} + 1)$. $\kappa = \sigma_f/\sigma_e$ is the aspect ratio of the molecule, and $\kappa' = \varepsilon_e/\varepsilon_f$ is the anisotropy of the energy well depth. ε_0 and σ_0 are units of energy and length, respectively. All quantities are scaled by their respective units in this study. The reduced time step, $\Delta t^*(\Delta t(\varepsilon_0/m\sigma_0^2)^{1/2})$, was taken to be 0.001. Here m is the mass of a particle, and σ_0 and ε_0 are parameters for length and energy in the Gay–Berne potential function. We set the reduced moment of inertia, $I_\perp^*(\equiv I_\perp/m\sigma_0^2)$, of the particles equal to 0.06. The reduced pressure, $P^*(\equiv P\sigma_0^3/\varepsilon_0)$, was set equal to 5.0 to 30.0, at which point the system undergoes a transition from the isotropic to the nematic phase. We performed the simulation at reduced temperatures, $T^*(\equiv k_BT/\varepsilon_0)$, of 1.9 to 5.0 for the system. The cut-off distance, $r_c^*(\equiv r_c/\sigma_0)$, for the potential energy calculation was set equal to 1.6, and a Verlet neighbour list was used in order to improve the efficiency of the simulation. The second rank orientational order parameter $<P_2>$ was determined via the Q-tensor [14]

$$Q_{\alpha\beta} = N^{-1}\sum_i (3u_\alpha^i u_\beta^i - \delta_{\alpha\beta})/2, \tag{7}$$

where u_α^i is a component, $\alpha = x, y$, or z, of the unit vector giving the orientation of the symmetry axis for molecule i, and N is the number of molecules. We defined the second rank orientational order parameter $<P_2>$ as the maximum eigenvalue obtained by diagonalising the Q-tensor; its eigenvector is then identified as the director. Typically, 1.0 to 3.0×10^6 time steps were used for equilibration, and then 2.0×10^6 steps were taken to examine the dynamics. We used a large system with 8,788 particles.

3. Results and Discussion

Figure 1 shows the pressure dependence of the nematic–isotropic transition temperature T^*_{NI} obtained from the simulation. These transition temperatures were obtained during the cooling process from the isotropic phase. As seen in the figure, the dependency is not obviously a linear relationship but instead appears quadratic. In fact, many experiments show that the nematic–isotropic transition temperature T^*_{NI} as a function of pressure is proportional to the polynomial function [15].

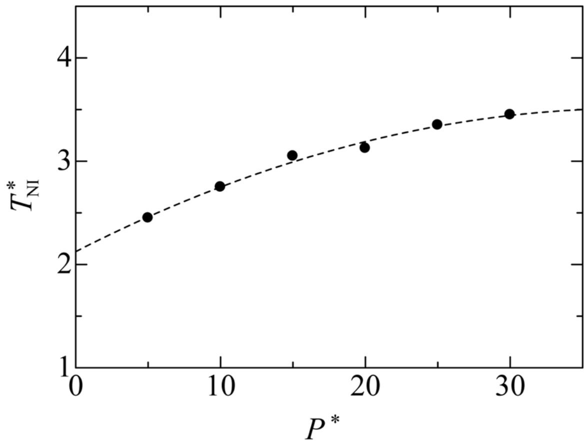

Figure 1. Pressure dependence of the nematic–isotropic transition temperature T^*_{NI} for the Gay–Berne disc system.

We successfully fitted the available data with the second order polynomial function as follows:

$$T_{\mathrm{NI}}/\mathrm{K} = \mathrm{a} + \mathrm{b} \cdot (P/\mathrm{bar}) + \mathrm{c} \cdot (P/\mathrm{bar})^2, \tag{8}$$

where a corresponds to T_{NI}, the sign of b is positive and its magnitude is $\sim 10^{-2}$, and the sign of c is negative and its magnitude is $\sim 10^{-6}$ [15]. Many typical nematic compounds of rod-like shaped molecules, such as cyanobiphenyls, cyclohexylphenyls and Schiff base compounds, follow this relationship. Although there is no available data for compounds, which have a discotic nematic–isotropic phase transition, many compounds having nematic–isotropic phase transitions demonstrate this relationship. Thus, they can be expected to have the same tendency for the compounds with disc shapes. Surprisingly, the coefficients b and c are almost constant values with small uncertainties for many real nematogens. Therefore, this fact may be used to verify the validity of the mesogenic model in our simulation. The results of the simulation of the GB discogen clearly show the same trend. The temperature just below the nematic–isotropic transition temperature for the GB (0.345, 0.2, 1, 3) system studied can also be fitted by the second order polynomial function, corresponding with the experimental data. Therefore, the mesogenic system can reproduce quantitatively realistic behaviour of the relationship, although we do not expect quantitative agreement with data from real systems because of the simple mesogenic model. The best fit in a non-dimensional unit for the system is as follows:

$$T^* = 2.125 + 7.18 \times 10^{-2} \cdot P^* - 9.29 \times 10^{-4} \cdot P^{*2}. \tag{9}$$

The non-linear P–T relationship means that evaluation of the Clapeyron relationship in thermodynamics has to be verified at each point. Therefore, we will now attempt to evaluate the Clapeyron relationship with different two pressures.

$$\frac{dP}{dT} = \frac{\Delta H}{T \Delta V}. \tag{10}$$

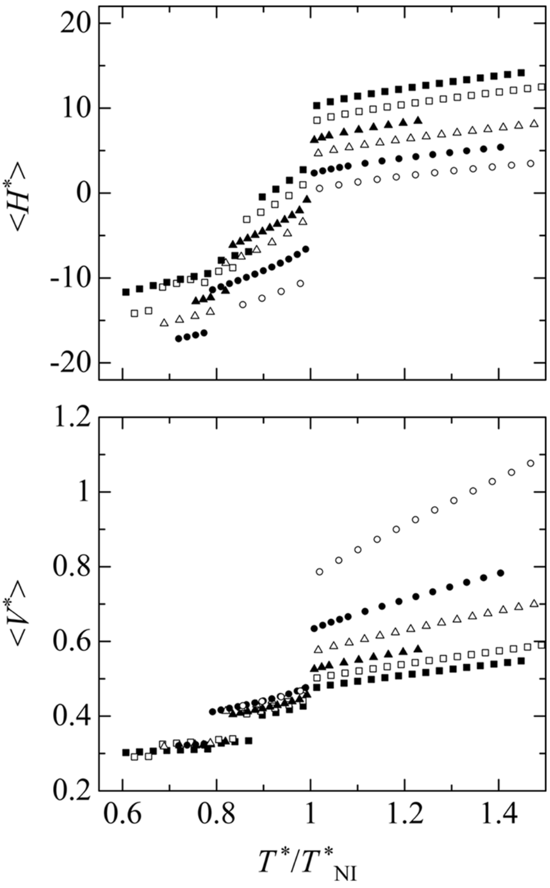

Figure 2. The values of enthalpy <H^*> and volume <V^*> per particle as a function of the scaled temperature T^*/T^*_{NI} for the Gay–Berne disc system at the pressure P^* values of 5.0 (open circle), 10.0 (closed circle), 15.0 (open triangle), 20.0 (closed triangle), 25.0 (open square), and 30.0 (closed square).

In order to verify the validity of the relationship, the enthalpy <H^*> and the volume <V^*> per particle as functions of the scaled temperature T^*/T^*_{NI} are shown in Figure 2. Although all systems at different pressures show other highly ordered phases, it is complicated but interesting to assign the phases in the lower temperature region. Next we focus on only the nematic–isotropic transition point. The jump in enthalpy per particle <H^*> for the system at lower pressure was larger than those for systems at higher pressure. This trend was also the same for the change in volume per particle <V^*>.

These trends are caused by the value of the second rank orientational order parameter <P_2> from the isotropic phase. The <P_2> value for the system at lower pressure jumps to a higher ordered state than that for the higher pressure system. The validity of the Clapeyron relationship was evaluated with these data. Here we calculated the difference of enthalpy ΔH^* and volume ΔV^* from a cross point of extrapolated lines for both the nematic and isotropic regions. Table 1 shows the evaluated values obtained from two systems at different pressures. Because of the

Table 1. Clapeyron relation for the GB disc system

P^*	$\frac{dP^*}{dT^*}$	$\frac{dH^*}{T^*_{\mathrm{NI}}dV^*}$
5.0–10.0	18.4	13.6 ($P^* = 5.0$) 20.6 ($P^* = 10.0$)
10.0–15.0	20.6	20.6 ($P^* = 10.0$) 25.3 ($P^* = 15.0$)
15.0–20.0	25.5	25.3 ($P^* = 15.0$) 32.1 ($P^* = 20.0$)
20.0–25.0	33.3	32.1 ($P^* = 20.0$) 37.8 ($P^* = 25.0$)
25.0–30.0	48.3	37.8 ($P^* = 25.0$) 44.9 ($P^* = 30.0$)

non-linear behaviour of the P–T relationship, the dP^*/dT^* value increases as pressure increases. The largest value was more than 2.5 times than that of the smaller one. However, $dH^*/T^*_{\mathrm{NI}}dV^*$ values also change similarly. Although the value for the system at lower pressure is always smaller, the Clapeyron relationship as a whole is reasonably valid. This tendency is likely to be the same for the system of the GB rod-like model as well [16].

4. Summary

In order to investigate phase transition behaviour at the nematic–isotropic phase transition point for the system of disc-like molecules, we performed molecular dynamics simulations at various pressures for the GB disc model. In this study, pressure dependence of the nematic–isotropic transition was investigated using a relatively large system composed of 8,788 molecules. We used a wider range of pressures, P^* of 5.0 to 30.0, in these simulations. The nematic–isotropic phase transition temperature T^*_{NI} increased non-linearly with increasing pressure. Since many real nematics behave similarly, this result is very realistic. Considering the non-linear behaviour, we verified the validity of the Clapeyron relationship in the systems and found that the relationship between the two systems at different pressures was reasonably valid.

We have been studying about properties of molecular and director dynamics in the nematic phase and near the nematic–isotropic phase transition temperature for future studies. In particular, we are focusing on the rotational motion of molecules, which is evaluated from first- and second-rank orientational time correlation functions.

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