Scaling properties of soft-core parallel spherocylinders near the crystal–smectic-phase transition

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By carrying out constant-pressure molecular-dynamics simulations near the melting transition from crystal to smectic liquid crystal, we characterize the scaling properties of systems composed of soft-core parallel spherocylinders. Properties at the transition have a clear dependence on the length-to-width ratio of the cylinder. These scaling properties are explained by introducing the concept of the temperature dependence of the effective core of the spherocylinders. Utilizing these scaling properties, the equations of state of systems with different anisotropy can be scaled onto one another.

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The seminal computer simulation studies of Alder and Wainright [1] and Wood and Jacobson [2] showed that a solid–fluid-phase transition exists even for a system of hard-core spheres. Later, extensive work was done for the so-called *soft* spheres [3–5] which interact through inverse power pair potentials $\phi(r) = \varepsilon(\sigma/r)^n$ where r is the distance between the two particles and σ can be defined as the diameter of the spheres. The soft-sphere model includes hard spheres as its limit when $n = \infty$ [6,7]. These systems are known to have scaling properties and the equation of state depends only on the single variable $\rho^* = \frac{N}{V}\left(\frac{\varepsilon}{kT}\right)^{3/n}$ defined by temperature T and the number density N/V, where N is the total number of particles and V is the volume of the system, which we will call the reduced density [4,8,9]. Properties such as the transition densities ρ_m^* (melting) and ρ_f^* (freezing) of the systems composed of soft-core spheres change systematically depending on the power n [5].

Recently, systems of anisotropic particles have been widely studied by computer simulations. From these simulations of anisotropic particles, such as hard ellipsoids of revolution [10], hard parallel spherocylinders [11,12], hard spherocylinders [13], and disklike hard cores [14], it has been shown that a wide variety of liquid crystalline phase appears. It has also been established that the anisotropic shape of the repulsive force of the particles plays an indispensable role for these phases to be stable.

In this work, we choose systems composed of *soft-core* parallel spherocylinders and elucidate the existence of the scaling properties of these systems. The study of anisotropic particles is interesting not only in relation to liquid crystals but also in its own right. In particular, it is important to clarify the effect of anisotropy on the physical properties at the melting temperature. The pair potential defining our parallel soft-core spherocylinders is given by

$$\phi(r_{ij}) = \varepsilon\left(\frac{D}{r_{ij}}\right)^n,$$

with

$$r_{ij}^2 = \begin{cases} x_{ij}^2 + y_{ij}^2, & -L < z_{ij} < L \\ x_{ij}^2 + y_{ij}^2 + (|z_{ij}| - L)^2, & \text{otherwise,} \end{cases} \quad (1)$$

where r_{ij} is the minimum distance between the ith and jth particles. The long axis of the spherocylinders is confined to the z axis ($L_z \equiv L_{\|}$) of the simulation box. To get an intuitive conception of this potential, imagine a hard line of length L covered all over with a blanket of uniform thickness (which is $D/2$ at the contour of energy ε) which becomes a spherocylinder as a result. We choose the inverse power n to be 14 which corresponds to a rather "hard" blanket. In this paper, the effect of the anisotropy of these systems is investigated by changing the length-to-width ratio (L/D) of the cylinder. Note that the potential described by Eq. (1) includes soft sphere as the limiting case, $L = 0$. The energy is measured in units of ε, the length in units of D, and k is set equal to unity.

From our experience in simulating systems of anisotropic molecules, we know that the conventional molecular-dynamics (MD) method leads to a special situation with an imbalance in the stress tensor. Especially in a case when extremely high pressure is acting on the direction perpendicular to the molecular axis compared to the pressure along the director, the columnar phase appears between the solid and the smectic phases [15] even for systems with only repulsive interaction (though the columnar phase in such case is not stable under hydrostatic pressure). There is a higher probability to be caught in artifacts when the molecules get longer. It is important to adopt a method which simulates a situation under true hydrostatic constant-pressure. The constant-pressure MD simulation method of Parrinello and Rahman [16] gives a correct melting path where the main data for this work are obtained. After the system melts and starts diffusing anisotropically, alternative means are necessary. Methods to overcome this problem have been proposed in our previous paper [17], where we use method (i) in this work. The results reported here are for system size $N = 600$.

In the $L = 0$ limit, where the particles are soft-core

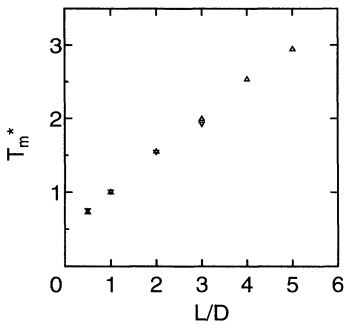

FIG. 1. The reduced transition temperature $T_m^* \equiv T_m/T_m(L/D=1)$ plotted against the length-to-width ratio L/D of the cylinder for systems of soft-core parallel spherocylinders.

spheres described by inverse power potentials of $n = 14$, the solid melts at $\rho_m^* = 1.094$ with $(PV/NT)_m = 16.46$. At the transition, the density is $\rho_f^* = 1.049$ in the fluid phase. These results fit well with the systematic results known for other soft-core spheres; these values fall in the region between the value $\rho_m^* = 1.194$ for the twelfth-inverse-power potentials and the value $\rho_m = 1.041$ for hard spheres ($n = \infty$) [3].

The structure of the smectic phase which we observe in systems of soft-core parallel spherocylinders has been studied [17,18], but there is still some question as to how to relate the phase directly to one of the smectic phases known in real liquid crystalline material; more extensive studies need to be carried out.

We first report the transition temperature $T_m^* = T_m/\ T_m(L/D=1)$ where $T_m(L/D=1)$ is the melting temperature for a system of particles of $L/D = 1$, as a function of the degree of anisotropy, L/D, of the cylinder (Fig. 1). The upright triangles ($\triangle$) denote the data of the melting temperature obtained from the Parrinello and Rahman method. There exists a rather small hysteresis in this transition from crystal-solid to smectic liquid-crystal which we denote by the inverted triangles ($\triangledown$) for comparison. For molecules of $L/D = 4$ and 5, we only present the melting point. As seen in Fig. 1, a linear relation between T_m^* and L/D is well maintained for systems consisting of particles of $L/D \geq 0.5$. This relation can be written as

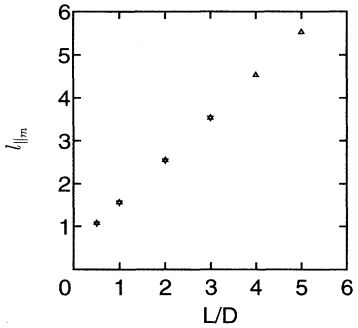

FIG. 2. The anisotropy (L/D) dependence of the specific length $l_{\|m}$ parallel to the long axis of the particle at the melting transition.

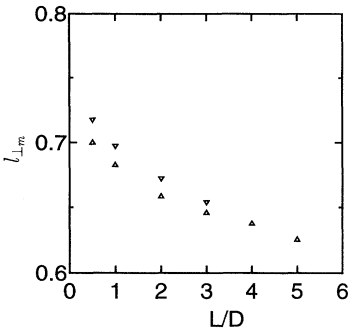

FIG. 3. The anisotropy (L/D) dependence of the specific length $l_{\perp m}$ perpendicular to the long axis of the particle at the melting transition.

$$T_m^* = \alpha L + T_m^*(0), \tag{2}$$

where $\alpha \simeq 0.5$, $T_m^*(0) \simeq 0.5$. When the anisotropy becomes close to the limit $L/D \to 0$, the T_m^* vs L/D relation deviates from Eq. (2). It is well known from real liquid crystalline materials that longer molecules have higher melting temperatures.

It is interesting to introduce the specific lengths $l_{\|}$ and $l_{\perp}$—which are, respectively, the average interparticle distances parallel and perpendicular to the long axis of the particles—by the definitions $l_{\|} = L_{\|}/n_{\|}$ and $l_{\perp} = (L_{\perp}^2/n_{\perp})^{\frac{1}{2}}$, with $n_{\|}$ being the number of layers and $n_{\perp} = N/n_{\|}$ being the number of particles in a layer. These values are related to the specific volume by $V/N = l_{\|} l_{\perp}^2$.

In Fig. 2 we plot the dependence of the specific length $l_{\|m}$ at the transition on the degree of anisotropy. A linear relation is obtained (see Fig. 2) which can be expressed as

$$l_{\|m} = L + l_{\|m}(0). \tag{3}$$

These results come from the fact that the potential of the particles has a hard line of length L as the long axis. This shows that the melting starts if there is enough space, which is about $l_{\|m}(0)$ between the cylinders.

The specific length $l_{\perp m}$ at the transition is drawn against L/D in Fig. 3. Note that the specific length $l_{\perp m}$ gets smaller when the particles get more anisotropic. Here we introduce the concept of the effective core and

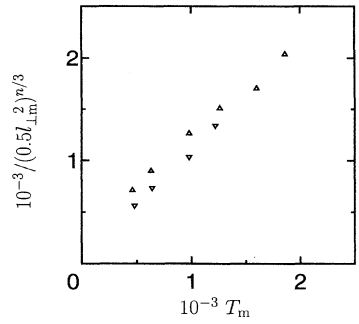

FIG. 4. The value $1/[l_{\|m}(0) l_{\perp m}^2]^{n/3}$ drawn against T_m for different anisotropies where $l_{\|m}(0) = 0.5$.

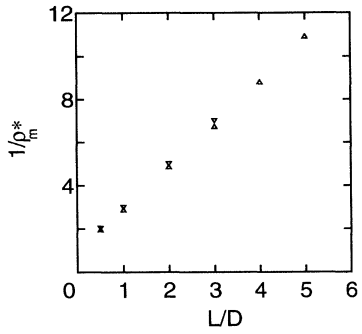

FIG. 5. The inverse of the reduced transition density $1/\rho_m^*$ plotted for systems with different anisotropy (L/D).

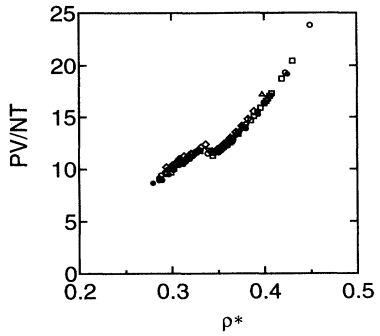

FIG. 6. The equations of state of soft-core parallel spherocylinders $L/D = 0.5(\circ)$, $2.0(\square)$, $3.0(\diamond)$, $4.0\ (\triangle)$, $5.0(\triangledown)$ scaled on the case for $L/D = 1(\bullet)$.

relate it to specific lengths. When the temperature of the system is T, the effective core d_Φ of a particle is defined as the distance at which the neighboring particle feels the potential energy $\Phi(d_\Phi)$. It is expected that melting takes place when $T \simeq \Phi(d_\Phi)$ which leads to the relation

$$T = \left(\frac{1}{d_\Phi}\right)^n . \tag{4}$$

In other words, we assert that, on the average, neighboring particles can go up the potential wall where the energy barrier equals the kinetic energy which is T and the distance at that point is the effective core d_Φ. We assume that the effective core diameter in the direction of the long axis of the particle is determined only by the sphere cap at the end of the spherocylinder. Then it is natural to relate the specific lengths $l_\parallel$ and $l_\perp$ to the effective core d_Φ by the equation

$$d_\Phi = \left[(l_\parallel - L)l_\perp^2\right]^{1/3} . \tag{5}$$

At the transition, Eqs. (4) and (5) lead to the relation

$$T_m = \left(\frac{1}{[(l_{\parallel m} - L)l_{\perp m}^2]^{1/3}}\right)^n . \tag{6}$$

To show that this relation is satisfied, we draw $1/[l_{\parallel m}(0)l_{\perp m}^2]^{n/3}$ against T_m for different anisotropies in Fig. 4, where we have used $l_{\parallel m}(0) = 0.5$, and recall from Eq. (3) that $l_{\parallel m} - L = l_{\parallel m}(0)$. It is seen in Fig. 4 that Eq. (6) is well fulfilled and our analysis is appropriate.

Finally the inverse of the reduced transition density $1/\rho_m^*$ is plotted as a function of anisotropy in Fig. 5. A clear linear dependence is observed which can be written as

$$\frac{1}{\rho_m^*} = \beta L + \frac{1}{\rho_m^*(0)}, \tag{7}$$

where $\beta \simeq 2.0$. If we recollect that $\rho^* = \frac{N}{V}\left(\frac{\epsilon}{kT}\right)^{3/n}$ and $V/N = l_\parallel l_\perp^2$, Eqs. (3) and (6) will require the coefficients to be $\beta = 1/l_{\parallel m}(0)$ and $\rho_m^*(0) = 1.0$. Figure 5 ascertains that these requirements for the coefficients are met.

Utilizing Eq. (7), we are able to scale the equation of state for $L/D = 0.5, 2.0, 3.0, 4.0, 5.0$ on the plot for $L/D = 1$. The results are shown in Fig. 6 where the values $\beta = 2.0$ and $\rho_{\parallel m}(0) = 1.0$ are adopted.

By making use of these scaling properties we find here, it becomes possible to derive, from knowledge concerning the properties of a system composed of soft-core spherocylinders with an arbitrary degree of anisotropy, the behavior of a system characterized by any other degree of anisotropy.

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