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One-Dimensional Model with Rotational and Liquid-Crystalline Phase Transitions

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A one-dimensional system of hard-rod particles with rotational-like internal degrees of freedom is considered. Particles interact with each other through the infinite-range, infinitely weak attractive Kac potential, and through a nearest-neighbor short-range potential. The latter depends also on the internal states of the interacting particles. Exact results for thermodynamic properties and for some correlation functions are obtained. It is found that the considered system exhibits several first-order transitions between phases with different "rotational structure," i.e., with different ordering with respect to the internal degrees of freedom. The calculated equation of state seems to suggest that in the solutions of liquid-crystalline substances in neutral solvents there may exist regions in which the coefficient of thermal expansion is negative—an effect similar to that well known in liquid water.

KEY WORDS: One-dimensional systems; liquid crystals; phase transitions; internal degrees of freedom; hard-core softening; rotational order.

1. INTRODUCTION

The first simple one-dimensional models of dense molecular systems with rotational degrees of freedom were proposed by Casey and Runnels$^{(1)}$ (CR). The models consisted of hard, square (planar) particles on a line, allowed to rotate around their centers. Only the hard-core intermolecular interactions were taken into account. In the lattice-gas model (frozen translational motions), a nonanalytic dependence of free energy on lattice separation was found: a cusp in the pressure appears at a lattice spacing corresponding to

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the smallest intermolecular distance at which a molecule may rotate completely if both neighbors cooperate. In models allowing translations (free gas and harmonic models), the singularity disappears, and only some continuous anomalies in thermodynamic quantities (e.g., a peak in the heat capacity at constant pressure) remain. Such anomalies could probably be interpreted as separating two "phases" with different rotational structure, but this point was not investigated by CR.[2] It should also be mentioned that CR were unable to solve their models completely, mainly because of the two-dimensional character of the rotational motion, and were forced to resort to approximate numerical computations.

The phase transitions connected with the shape of molecules have also been investigated on the basis of Ising-type models (see, e.g., Boccara *et al.*(3)).

In this paper we wish to propose a simpler model, which still exhibits the main features of the molecular rotations. This is the one-dimensional system of hard rods with variable length l depending on the actual value of an internal parameter s: $l = l(s)$. The changes of the length, i.e., of the smallest distance between the centers of mass of two neighbor particles, simulate in one dimension the main geometrical effect of rotation of nonspherical molecules. On the other hand, cooperative effects of rotation connected with mutual evasions of elongated parts of molecules are at least partially lost. However, due to this one-dimensional degeneration of the rotation, the model becomes solvable not only for a pure hard-core potential, but also for arbitrary additional nearest-neighbor interactions.

The soft part of the interaction can also be made dependent on the actual values of the internal parameters (s_i, s_j) of two interacting particles (i, j). In this case, there appears a sequence of phase transitions at $T = 0$,[3] separating several differently ordered phases. In our interpretation, this result simulates, in one dimension, the behavior of liquid-crystalline systems.

The outline of the paper is as follows: in Section 2 the model is defined and the general solutions are given. Section 3 contains its simplest realization, equivalent to the CR model. Sections 4 and 5 present the solution and properties of another realization of our model, exhibiting the above-mentioned sequence of phase transitions. In the last section we propose our interpretation of the presented results.

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[2] Such structures were recently found and investigated in detail by Parliński *et al.*,(2) who performed molecular dynamics simulations of the one-dimensional model of the N_2 crystal.

[3] The appearance of true phase transitions at nonzero temperatures is enforced, according to the results of Stell and Hemmer,(4–6) by the addition to the interactions of an infinitely long, infinitely weak potential of the Kac type.(7,8)

2. THE MODEL

Consider a linear chain of classical hard rods with nearest-neighbor pair interactions

$$V_{ij}(r) = V(|r_i - r_j|) = \begin{cases} \infty, & r < l_{ij} \\ U(r - l_{ij}), & r > l_{ij} \end{cases} \tag{1}$$

$l_{ij} = \frac{1}{2}(l_i + l_j)$. Assume that the length l_i of the rod i depends on the value of some internal parameter s_i:

$$l_i = l_i(s_i), \qquad 0 \leqslant s_i \leqslant \sigma$$

and that, in general, the soft part of the potential also depends on s_i and s_j:

$$U = U(r - l_{ij}; s_i, s_j)$$

In other words, the interaction depends not only on the separation of the centers of interacting particles, but also on their internal states.

A simple generalization of known results (1,9) gives the thermodynamics of this system in terms of the excess Gibbs free energy per particle $g(p, T)$, where p is the pressure and T is the temperature (k is Boltzmann's constant, $\alpha = \beta p$, and $\beta = 1/kT$):

$$g(p, T) = -kT \lim_{N \to \infty} \frac{1}{N} (\sigma^{-N} \alpha^{N+1} Q_N) \tag{2}$$

with

$$\begin{aligned} Q_N &= \int_0^\infty dL \exp(-\alpha L) \int_0^\sigma ds^N \int_0^L dr^N \exp\left[-\beta \sum_{j=0}^{N} V_{j,j+1}(r)\right] \\ &= \int_0^\sigma ds^N \prod_{j=0}^{N} \int_0^\infty dr \exp[-\alpha r - \beta V_{j,j+1}(r)] \\ &= \int_0^\sigma ds^N \prod_{j=0}^{N} \int_{l_{j,j+1}}^\infty dr \exp[-\alpha r - \beta U(r - l_{j,j+1})] \\ &= \int_0^\sigma ds^N \prod_{j=0}^{N} f(s_j, s_{j+1}) \end{aligned} \tag{3}$$

where cyclic boundary conditions ($r_0 = r_N$, etc.) have been used, and where

$$f(s_j, s_{j+1}) = \exp\{-\tfrac{1}{2}\alpha[l(s_j) + l(s_{j+1})]\} \times \int_0^\infty dr \exp(-\alpha r) \exp[-\beta U(r; s_j, s_{j+1})] \tag{4}$$

Hence (10)

$$g = -kT \ln \lambda_{\max} \tag{5}$$

where $\lambda_{\max}$ is the maximal eigenvalue of the Fredholm integral equation:

$$\int_0^\sigma ds_1 f(s_1, s_2) q(s_1) = \lambda q(s_2) \tag{6}$$

These results are considerably simplified when the soft part of the interaction $U(r)$ does not depend on the internal states of the interacting particles. In this case the integrations in Eqs. (3) and (4) can be performed independently, and we get

$$g = -kT \ln \frac{1}{\sigma} \int_0^\sigma ds\, e^{-\alpha l(s)} - kT \ln \alpha \int_0^\infty dr\, e^{-\alpha r - \beta U(r)} \tag{7}$$

Although the most general form of our model cannot be completely solved for arbitrary functions $l(s)$ and $U(r; s_j, s_{j+1})$ except at $T = 0$, the eigenvalues of Eq. (6) can be found for some specific forms of these functions, and this is sufficient for the discussion of the appearance of differently ordered phases and of transitions between them. An example will be presented in detail in Sections 4 and 5. A very simple case, corresponding to the CR model, will be discussed in the next section.

3. PSEUDO PHASE TRANSITION

Consider now the simplest possible realization of the considered model:

$$U(r) = 0, \qquad l(s) = \begin{cases} d, & 0 < s < \epsilon\sigma, \quad 0 < \epsilon < 1 \\ (1 + \nu)d, & \epsilon\sigma < s < \sigma \end{cases} \tag{8}$$

Hence, a particle has a length equal to either d or $(1 + \nu)d$, depending on its actual internal state.

Let $x_1 = x(p, T)$ denote the fraction of particles with actual length equal to d:

$$x_1 = \lim_{N \to \infty} \frac{1}{N} \left\langle \sum_{j=1}^{N} \theta(\epsilon\sigma - s_j) \right\rangle \tag{9}$$

where $\langle \cdots \rangle$ is the thermodynamic average, $\theta(y)$ is the step function.

A simple calculation similar to that in the preceding section leads to the result

$$x_1 = \frac{\epsilon}{\epsilon + (1 - \epsilon)\exp(-\nu p_s)} \tag{10}$$

where $p_s = pd/kT$, and, from Eq. (7),

$$\begin{aligned} g(p, T) &= pd + kT \ln(x_1/\epsilon) \\ v(p, T) &= (\partial g/\partial p)_T = [1 + (1 - x_1)\nu]d \\ C_p(p, T) &= -T(\partial^2 g/\partial T^2)_p = k(p_s\nu)^2 x_1(1 - x_1) \\ &\vdots \end{aligned} \tag{11}$$

Hence, all thermodynamic quantities are continuous functions of p and T, and we have no true phase transition. However, the second derivatives, such as C_p, $(\partial v/\partial T)_p$, $(\partial v/\partial p)_T$, exhibit distinct anomalies as functions of T and p (the exception here is the excess heat capacity at constant volume: $C_v = 0$ for all T and p). Figure 1 shows such an anomaly of C_p, together with the corresponding values of x_1. It is seen that the transition resembles one of second order, and that the high-pressure, low-temperature phase is the ordered one: almost all particles in this phase are in internal states with $s \leqslant 1/2$. The anomaly in C_p is very similar to (perhaps even identical with) the anomaly found by CR in their free-translator model. Note that the present model is computationally much simpler than the CR model [formulas (11) vs. numerical solutions of an integral equation], and at the same time it exhibits the same properties as the latter. Moreover, the order parameter x_1 describing the "rotational structure" of both "phases" is easily calculated here. Our result also proves that the pseudo-phase transition obtained is the pure excluded-volume effect.

Similar calculations can be easily performed, from Eq. (7), for other relations between the particle length l and its internal state s, and also for nonzero soft interparticle potentials $U(r)$. Such details, however, change only the quantitative results, the qualitative picture remaining the same. The corresponding lattice model can also be considered. In this case the present model again leads to results similar to those of CR, in the sense that the nonanalytic dependence of the Helmholtz free energy on lattice separation appears. The details, however, seem not to be very interesting.

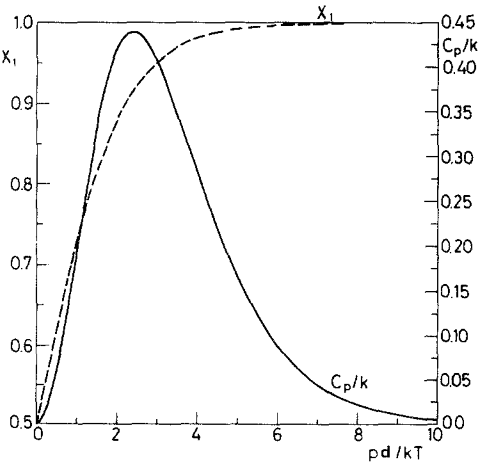

Fig. 1. Anomaly in C_p and the corresponding values of x_1 for $\epsilon = 0.5$.

4. PHASE TRANSITIONS DUE TO THE SOFTENING OF THE HARD CORE

Consider now the system characterized by the following potential (shown in Fig. 2):

$$\begin{aligned} U(r; s_j, s_{j+1}) &= (1 - r/d)W(s_j, s_{j+1}), \qquad & r < d \\ &= 0, & r > d \end{aligned}$$

with

$$\begin{aligned} W(s_j, s_{j+1}) &= w, & s_j, s_{j+1} \in (0, \epsilon\sigma) \\ &= (1 - \rho\delta)w, & s_j \in (\epsilon\sigma, \sigma), \quad s_{j+1} \in (0, \epsilon\sigma) \\ && \text{or vice versa} \\ &= (1 - \delta)w, & s_j, s_{j+1} \in (\epsilon\sigma, \sigma) \end{aligned} \tag{12}$$

$\rho \in \langle 0, 1 \rangle$, with $l(s)$ given by Eq. (8). The calculation of $\lambda_{\max}$ for this potential is rather simple: it is sufficient to note that the integral equation (5) reduces in this case to the following matrix equation:

$$\begin{pmatrix} A & B \\ B & C \end{pmatrix} \begin{pmatrix} q_1 \\ q_2 \end{pmatrix} = \lambda \begin{pmatrix} q_1 \\ q_2 \end{pmatrix}$$

where

$$\begin{aligned} A &= \epsilon E(p_s, w_s, 0, 0) \\ B &= [\epsilon(1 - \epsilon)]^{1/2} \exp(-\nu p_s/2) E(p_s, w_s, \rho, \delta) \\ C &= (1 - \epsilon) \exp(-\nu p_s) E(p_s, w_s, 1, \delta) \\ E(p_s, w_s, \rho, \delta) &= d \exp(-2p_s) \left\{ \frac{\exp[p_s - (1 - \rho\delta)w_s] - 1}{p_s - (1 - \rho\delta)w_s} + \frac{1}{p_s} \right\} \\ w_s &= w/kT, \qquad p_s = pd/kT \end{aligned}$$

The maximal eigenvalue of this equation is

$$\lambda_{\max} = de^{-2p_s}\{A + C + [(A - C)^2 + 4B^2]^{1/2}\}/2 \tag{13}$$

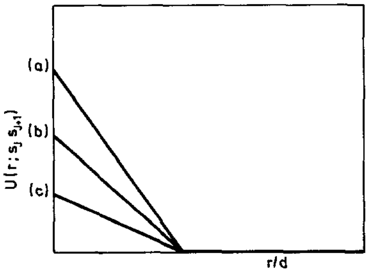

Fig. 2. The shape of the potential $U(r; s_j, s_{j+1})$ for (a) $s_j, s_{j+1} \in (0, \epsilon\sigma)$; (b) $s_j \in (0, \epsilon\sigma)$ and $s_{j+1} \in (\epsilon\sigma, \sigma)$, or vice versa; (c) $s_j, s_{j+1} \in (\epsilon\sigma, \sigma)$.

The equation of state is given by

$$v = (\partial g/\partial p)_T = (kT/\lambda_{\max})\, \partial\lambda_{\max}/\partial p \tag{14}$$

which can be easily analyzed in the zero-temperature limit. Assume that the various parameters of the model satisfy the following set of inequalities:

$$\begin{gathered} \tfrac{1}{2} < \rho < 1, \qquad 0 < \nu < \delta < 1 \\ \frac{1-\delta}{1-\nu} < \frac{2\delta(1-\rho)}{\nu}, \qquad 1 - \rho\delta < \frac{2\delta(1-\rho)}{\nu} \end{gathered} \tag{15}$$

Hence (from now on, we put $d = 1$)

$$\begin{array}{lr} \lim\limits_{T\to 0} v = 1, & p > 2w\rho\delta/\nu \\ \qquad\;\; = 1 + \tfrac{1}{2}\nu, & 2w\delta(1-\rho)/\nu < p < 2w\rho\delta/\nu \\ \qquad\;\; = 1 + \nu, & w(1-\delta)/(1-\nu) < p < 2w\delta(1-\rho)/\nu \\ \qquad\;\; = 2, & 0 < p < (1-\delta)/(1-\nu) \end{array}$$

Inverting the above relations, we get

$$\begin{array}{llr} \lim\limits_{T\to 0} p = 0, & 2 < v & \text{(phase I)} \\ \qquad\;\; = [(1-\delta)/(1-\nu)]w, & 1 + \nu < v < 2 & \text{(phase II)} \\ \qquad\;\; = [2\delta(1-\rho)/\nu]w, & 1 + \tfrac{1}{2}\nu < v < 1 + \nu & \text{(phase III)} \\ \qquad\;\; = (2\rho\delta/\nu)w, & 1 < v < 1 + \tfrac{1}{2}\nu & \text{(phase IV)} \end{array} \tag{16}$$

The above result indicates the appearance of four different phases separated at $T = 0$ by sharp transitions. All these phases can be realized only when all inequalities (15) are fulfilled; if some of them cease to hold, some of the phases described by Eqs. (16) will disappear.

The increase of the temperature rounds off of all discontinuities in Eqs. (16). However, true phase transitions can still be enforced at nonzero temperatures by the introduction into the model of the Kac potential[7,8] $\varphi(r) = -a\gamma e^{-\gamma r}$, $a > 0$, in the so-called van der Waals limit ($\gamma \to 0$ taken after the thermodynamic limit). Namely, when every pair of particles interacts through the Kac potential, the Helmholtz free energy and the equation of state are[8]

$$F(v, T) = \mathrm{CE}[f(v, T) - a/v], \qquad P(v, T) = \mathrm{MC}[p(v, T) - a/v^2] \tag{17}$$

where CE and MC denote, respectively, "convex envelope" (in v) and "Maxwell construction," and where $p(v, T)$ and $f(v, T)$ are calculated in absence of the Kac potential. At $T = 0$, the short-range Helmholtz free energy f as a function of specific volume v is given, for the model (12), by segments separated by singular points (such that $\partial f/\partial v$ is discontinuous), and the function $f - a/v$ becomes nonconvex in some regions. At very low temperatures these singular points are rounded off, but, by continuity, the function $f - a/v$ remains nonconvex in almost the same regions as at $T = 0$ (the term a/v does not change with temperature). Hence, the singularities of the convex envelope of this function are preserved at sufficiently low temperatures. At higher temperatures the phase transitions will disappear successively.

The above reasoning was given by Stell and Hemmer for the case of one additional transition due to the core softening, and it remains valid in the present case.

Assume that, in addition to (15), the following set of inequalities is fulfilled:

$$w\frac{2\rho\delta}{\nu} - \frac{a}{1+\nu/2} > w\frac{2\delta(1-\rho)}{\nu} - \frac{a}{(1+\nu)(1+\nu/2)} > w\frac{1-\delta}{1-\nu} - \frac{a}{2(1+\nu)} > 0 \tag{18}$$

Hence, performing the Maxwell construction on Eq. (17) with p given by Eq. (16), we again obtain four well-separated phase transitions for $T = 0$:

$$\begin{aligned}
\lim_{T\to 0} P(v, T) &= 0, && 2 < v && \text{(I)}\\
&= w\frac{1-\delta}{1-\nu} - \frac{a}{2(1+\nu)}, && 1+\nu < v < 2 && \text{(II)}\\
&= w\frac{2\delta(1-\rho)}{\nu} - \frac{a}{(1+\nu)(1+\nu/2)}, && 1+\frac{\nu}{2} < v < 1+\nu && \text{(III)}\\
&= w\frac{2\delta\rho}{\nu} - \frac{a}{1+\nu/2}, && 1 < v < 1+\frac{\nu}{2} && \text{(IV)}
\end{aligned} \tag{19}$$

For $T > 0$, the equation of state cannot be written directly in closed form: one must calculate the relation $v = v(p, T)$ from Eq. (14), invert it into $p = p(v, T)$, and insert the result into Eq. (17). As an example, a few numerically calculated isotherms are shown in Figs. 3 and 4.

Stell and Hemmer[4-6,11] discussed a similar model of hard rods with a soft repulsion, but without internal degrees of freedom, and found two transitions corresponding to our phases I and IV (if $\epsilon \to 1$) or I and II (if $\epsilon \to 0$). These phases were interpreted by them, respectively, as the van der Waals liquid–gas phase transition (low-density region) and the isostructural one (high-density region). The introduction of rotations coupled

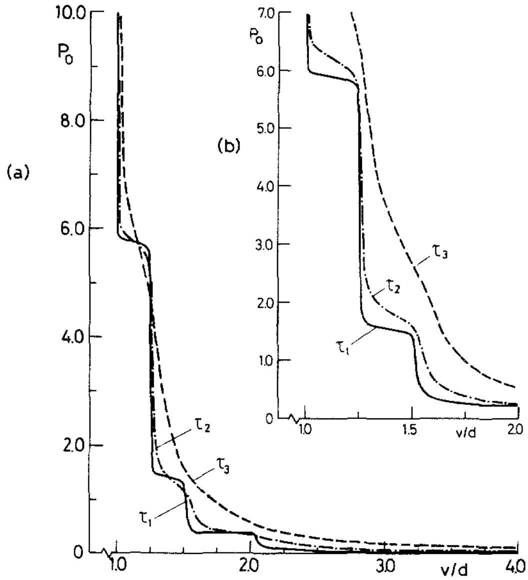

Fig. 3. The isotherms of the system in the absence of the Kac long-range potential for the following parameter sets: (a) $\epsilon = 0.5$, (b) $\epsilon = 0.01$; $\nu = 0.5$, $w/a = 2.0$, $\delta = 0.9$, $\rho = 0.8$, and $\tau_1 = 0.01$, $\tau_2 = 0.05$, $\tau_3 = 0.2$, respectively ($\tau = kdT/a$).

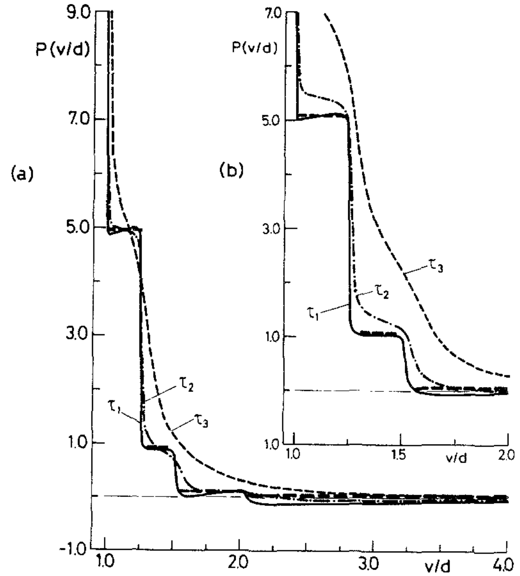

Fig. 4. The isotherms of the system with the Kac long-range potential included, for the parameter sets as in Fig. 3. The dashed straight lines denote the Maxwell construction performed on isotherms τ_1.

with the short-range repulsion leads to the appearance of two new high-density phases and two new transitions. This suggests the interpretation of these new transitions as the rotational ones. This point will be discussed in more detail in the next section.

The critical properties of the present model are not especially interesting. In one-dimensional systems with short-range interactions, phase transitions are possible only in the zero-temperature limit. The well-known device used for the continuation of such transitions to finite temperatures is the Kac potential together with the van der Waals limit. This device is equivalent to the molecular field approach, an approach which becomes exact for one-dimensional systems. However, it is well known that the molecular field approach always leads to classical critical behavior. It is also known that the presence of several transitions with critical points depending on changeable parameters may lead to the confluence of critical points.(4,5) Then, because of the analyticity of a free energy (17) in ρ and T in the one-phase region, the critical exponents are the same as in the Landau general theory of critical behavior applied to a fluid.(12,13)

5. STRUCTURE OF THE PHASES

In order to investigate the structure of the different phases found in the preceding section, we shall calculate two order parameters. The first one, x_1, is given by Eq. (9); the second, x_2, is defined as the fraction of pairs of adjacent particles with both actual lengths equal to d:

$$x_2 = \lim_{N\to\infty} \frac{1}{N} \sum_{j=1}^{N-1} \langle \theta(\epsilon\sigma - s_j)\theta(\epsilon\sigma - s_{j+1})\rangle \tag{20}$$

Both averages, (9) and (20), must now be calculated with the Kac long-range part of the potential switched on. Such calculations cannot be performed in a straightforward way (as in Section 3). Hence we shall make use of another method, a well-known simple version of the functional differentiation: modify the short-range part of the potential by the addition of the term

$$H_e = h_1 \sum_{j=1}^{N} \theta(\epsilon\sigma - s_j) \qquad \text{or} \qquad H_e = h_2 \sum_{j=1}^{N-1} \theta(\epsilon\sigma - s_j)\theta(\epsilon\sigma - s_{j+1})$$

and calculate the appropriate Helmholtz free energy per particle $F(v, T, h; a)$ (h is equal to h_1 or h_2). Using the formula (17), we have

$$F(v, T, h; a) = \mathrm{CE}\left[f(v, T, h) - \frac{a}{v}\right] = \mathrm{CE}\left[g(p, T, h) - pv - \frac{a}{v}\right] \tag{21}$$

Now both order parameters can be calculated by differentiating the appropriate free energy (21) with respect to h, in the limit $h \to 0$.

It is necessary, however, to bear in mind that in the region of coexistence of phases (given by straight-line segments of the CE construction) the order parameters are not defined uniquely as functions of v. To get rid of such ambiguities, denote by CRM (coexistence region modification) the procedure for removing all values of v belonging to the region of coexistence of phases. The order parameters will then be given by

$$\begin{aligned} x_1(v, T; a) &= \mathrm{CRM}\left[\left.\frac{\partial F(v, T, h_1; a)}{\partial h_1}\right|_{h_1=0}\right] \\ &= \mathrm{CRM}\left[\frac{(A - C + L)A + 2B^2}{(A + C + L)L}\right] \end{aligned} \tag{22}$$

$$\begin{aligned} x_2(v, T; a) &= \mathrm{CRM}\left[\left.\frac{\partial F(v, T, h_2; a)}{\partial h_2}\right|_{h_2=0}\right] \\ &= \mathrm{CRM}\left[\frac{(A - C + L)A}{(A + C + L)L}\right] \end{aligned} \tag{23}$$

with $L = [(A - C)^2 + 4B^2]^{1/2}$, A, B, and C being the same as in Section 4. The CRM procedure is equivalent to the switching on of the Kac long-range potential.

When the Kac potential is switched off ($a = 0$), the order parameters are given directly by the expressions within square brackets in Eqs. (22) and (23). It is thus possible to calculate $x_1(v, T; 0)$ and $x_2(v, T; 0)$ for all v and T.

Let us first calculate the zero-temperature limit of the order parameters. Assuming that the inequalities (15) are fulfilled, we get[4]

$$\begin{aligned} \lim_{T\to 0} x_1(v, T; 0) &= \begin{cases} \epsilon & \text{phase I} \\ 0 & \text{phase II} \\ 0.5 & \text{phase III} \\ 1.0 & \text{phase IV} \end{cases} \\ \lim_{T\to 0} x_2(v, T; 0) &= \begin{cases} \epsilon^2 & \text{phase I} \\ 0 & \text{phases II, III} \\ 1.0 & \text{phase IV} \end{cases} \end{aligned} \tag{24}$$

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[4] It is to be noted that, to find the values of the order parameters for the low-density phase I, as given by relations (24), the low-density limit $v \to \infty$ must be performed before the low-temperature limit $T \to 0$. Reversal of this sequence of limits would result in unphysical values $x_1 = x_2 = 1$ for the low-density phase.

The above result shows that, at $T = 0$, the low-density phase (phase I) is characterized by the chaotic distribution of the values of the internal parameters, whereas the remaining phases are ordered, each in a different manner, with respect to the internal states of the particles.

In phases II and IV every particle is in the same internal state, corresponding to the long (phase II) or short (phase IV) particle diameter. In phase III, short and long particles are distributed alternately.

At nonzero temperatures the sharp ordering described above is rounded off a little; however, the qualitative differences remain very distinct.

6. FINAL REMARKS

The results presented in this paper show that the internal states of the molecules, when coupled with the intermolecular potential, can lead to the appearance of new phases. These phases differ in their structure with respect to the internal states of the particles. To obtain these results it is not necessary to specify the character of the internal degrees of freedom—it is sufficient that the intermolecular potential depends on them. Hence the system considered here can serve as an exactly soluble one-dimensional model of several physical systems.[5] Probably the simplest is the identification mentioned in the introduction—of the internal degree of freedom as the one-dimensional representation of the rotational motion. In this case the structure of the phases would differ in the rotational behavior of the constituent particles.

The analogy of our one-dimensional model with liquid-crystalline phases is perhaps a little far-fetched. However, if we imagine one-dimensional cuts through isotropic, nematic, and various smectic phases, the resulting pictures will be somewhat similar to those discussed in the preceding section. This analogy is further supported by the observation that the change of the parameter ν connected with the maximal diameter of the molecule beyond some limits [determined by inequalities (15) and (18)] results in the vanishing of some phase or phases. A similar situation was observed in a homologous series of liquid crystals, where, e.g., the changes of the lengths of end chains of the molecules cause the vanishing of some phases and/or the appearance of other phases.(15,16)

The transitions between real liquid-crystalline phases in pure thermotropic substances depends rather weakly on the density. Thus the present model with its distinct dependence on density will describe the solution of

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[5] A similar, but approximate, discussion was presented by Kuramoto and Furukawa,(14) who attempted to describe isostructural phase transitions by means of a three-dimensional model with a variable shape of the molecules. We are indebted to the Referee for calling our attention to this work.

liquid-crystalline molecules in an inert solvent rather than the pure liquid crystal. The density dependence (together with its critical points) of our model will then correspond to the concentration dependence of the liquid-crystalline solution.

Another nonstandard property of the discussed model is the crossing of isotherms, both for the Kac potential switched on and switched off (cf. Figs. 3 and 4). Such a behavior is found whenever $(\partial v/\partial T)_p$ changes sign. The best-known example is liquid water around its maximum density point. If the analogy between our model and liquid crystals is not completely spurious, this result will indicate the possibility of the observation of regions of negative thermal expansion coefficient in liquid crystals. To our knowledge, such an effect is not known so far, and probably should be sought—according to a preceding remark—in solutions rather than in pure liquid-crystalline substances.

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