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PHASE TRANSITIONS IN SIMPLE SYSTEMS WITH ROTATIONAL-LIKE DEGREES OF FREEDOM*

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Phase transitions in one-dimensional systems of hard-rod particles with internal, rotational-like degrees of freedom are studied. The particles interact with each other through the infinite-range, infinitely weak attractive Kac potential and through the nearest-neighbour short-range potential. This also depends on the internal states of the interacting particles. Exact results for the thermodynamic properties and for some correlation functions at zero temperature are obtained. A simple criterion for the existence of phase transitions in internal degrees of freedom is given. The calculated models seem to suggest that to obtain the rotational first order phase transitions it is necessary to add to the contact hard-core interactions the additional soft interactions, at least between the nearest neighbours.

1. *Introduction*

Phase transitions in one-dimensional models of dense molecular systems with rotational, or some other internal degrees of freedom (IDF) were studied intensively [1–6]. For example, the phase transitions concerning rotation of nonspherical molecules were investigated based on some Ising-type models (cf.e.g. Boccara et al. [7]), or more difficult continuous models [4]. It was shown that molecules having a highly nonsymmetric form (especially needlelike forms) have a tendency toward liquid-crystalline behaviour [1, 3]. On the other hand, the mildly nonspherical molecules behave in a completely different way. With such molecules it may happen that thermal motion produces a (cooperative) destruction of orientational correlations [4, 8]. Another type of the systems, which can be analysed on the basis of an interaction which depends on IDF are those with isostructural phase transitions [9–11].

The phenomenon of isostructural phase transitions is caused by the collapse of the hard core of spherically symmetric molecules under the influence of very high external pressures. The collapsing properties of molecules can be described by IDF [10].

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All the papers mentioned above deal with the phase transitions in the specific systems. The purpose of this paper is to present a general analysis of what is the dependence of the phase transitions (in IDF) on the shape of arbitrary nearest-neighbour interactions. The problem is reduced to the study of equation of state and order parameters at zero-temperature. All discontinuities of these functions for $T = 0$ are connected with the phase transitions which can arise at $T > 0$ (see Section 3). Because of the simplicity of the theory presented some of the earlier results obtained for so called two-state model [5] are easily reproduced.

The outline of this paper is a follows. In Section 2, the model is defined and general solutions for equation of state and n-particle probability distribution functions are given. In Section 3, the properties of equation of state and order parameters at zero-temperature are discussed. Section 4 presents the solutions of simple models with and without the rotational phase transitions. Section 5 contains some final conclusions.

2. *Description of the system*

The Gibbs free energy

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

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

$$l_{ij} = \tfrac{1}{2}(l_i + l_j). \tag{1a}$$

Assume that the length, l_i, and the soft part of the potential depend on the value of some internal parameter, s_i:

$$l_i = l(s_i), \qquad a \leqslant s_i \leqslant b \tag{2}$$

$$l_{ij} = l(s_i, s_j), \tag{2a}$$

$$U = U(r - l_{ij}; s_i, s_j). \tag{2b}$$

The thermodynamics of this system is given by the excess Gibbs free energy per particle, $g(p, T)$ [4, 12]:

$$g(p, T) = -kT \lim_{N \to \infty} \frac{1}{N} \ln \left[(b-a)^{-N} \alpha^{N+1} Q_N\right], \tag{3}$$

$$\begin{aligned} Q_N &= \int_0^\infty dL e^{-\alpha L} \int_a^b ds^N \int_0^L dr^N \exp\left[-\beta \sum_{j=0}^{N} V_{j,j+1}(r)\right] \\ &= \int_a^b ds^N \prod_{j=0}^{N} \int_0^\infty dr \exp\left[-\alpha r - \beta V_{j,j+1}(r)\right] \\ &= \int_a^b ds^N \prod_{j=0}^{N} \int_{l_{j,j+1}}^{\infty} dr \exp\left[-\alpha r - \beta U(r - l_{j,j+1})\right] \\ &= \int_a^b ds^N \prod_{j=0}^{N} K(s_j, s_{j+1}), \end{aligned} \tag{4}$$

where

$$K(s_j, s_{j+1}) = \exp\left\{-\tfrac{1}{2}\alpha[l(s_j)+l(s_{j+1})]\right\} \times \int_0^\infty dr e^{-\alpha r} \exp\left[-\beta U(r; s_j, s_{j+1})\right] \tag{5}$$

and where p is the pressure, T is the temperature, k is the Boltzmann constant and $\alpha = \beta p$, $\beta = 1/kT$.

If periodic boundary conditions are imposed ($s_0 \equiv s_{N+1}$), the partition function Q_N can be evaluated by taking the trace of the N-th iterate of the symmetric kernel-K. Hence [4]:

$$g = -kT \ln \lambda_{\max}, \tag{6}$$

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

$$\int_a^b ds_1 K(s_1, s_2) q(s_1) = \lambda q(s_2), \tag{7}$$

$$\int_a^b q^2(s) ds = 1. \tag{8}$$

All physically interesting quantities, such as specific heat, equation of state, etc., are then simply calculated by differentiation of g with respect to p or T. For example, the specific volume is given by the well-known formula

$$v(p, T) = (\partial g/\partial p)_T. \tag{9}$$

The n-particle probability distribution function of Internal Degrees of Freedom

Physically interesting quantities, such as order parameters are the mean values of some functions depending on IDF. Let us suppose that we have a symmetric function $f(s_1, s_2, \ldots, s_n)$ and let us calculate the mean value $\langle f \rangle$:

$$\begin{aligned}\langle f \rangle &= \lim_{N\to\infty} Q_N^{-1} \int_0^\infty dL e^{-\alpha L} \int_a^b ds^N f(s_1, \ldots, s_n) \int_0^L dr^N \exp\left[-\beta \sum_{j=0}^{N} V_{j,j+1}(r)\right] \\ &= \lim_{N\to\infty} Q_N^{-1} \int_a^b ds^N f(s_1, \ldots, s_n) \prod_{j=0}^{N} K(s_j, s_{j+1}) \\ &= -\lim_{N\to\infty} \frac{1}{N} Q_{Nn}^{-1} \left(\frac{1}{\beta} \frac{\partial}{\partial h} \int_a^b L(s_1, s_n; h) L(s_{n+1}, s_{2n}; h) \ldots L(s_{(N-1)n+1}, s_1; h) \right)_{h=0},\end{aligned} \tag{10}$$

where

$$L(s_1, s_n; h) = \int_a^b ds_2 \ldots ds_{n-1} e^{-\beta h f(s_1, \ldots, s_n)} \prod_{i=1}^{n-1} K(s_i, s_{i+1}). \tag{11}$$

If $\lambda_{\max}(h)$ is the maximal eigenvalue of integral equation

$$\int_a^b L(s_1, s_n; h) q(s_n, h) ds_n = \lambda(h) q(s_1, h),$$

$$\int_a^b q^2(s_n, h) ds_n = 1, \tag{12}$$

and periodic boundary conditions ($Nn+i \equiv i-1$) are imposed on the system, then the formula (10) reduces to

$$\langle f \rangle = -\frac{1}{\beta \lambda_{\max}^{n-1}} \frac{\partial}{\partial h} \lambda_{\max}(h)|_{h=0}. \tag{13}$$

The derivative of $\lambda_{\max}(h)$ with respect to h can be calculated from the formula

$$\lambda(h) = \int_a^b ds_1 ds_n L(s_1, s_n; h) q_{\max}(s_1, h) q_{\max}(s_n, h). \tag{14}$$

Because there is no phase transitions in one dimensional systems, the equilibrium state is unique [13], and therefore,

$$\lim_{h \to 0} \lambda_{\max}(h) = \lambda_{\max}^{n-1}, \tag{15}$$

$$\lim_{h \to 0} q_{\max}(s_n, h) = q_{\max}(s_n). \tag{16}$$

The derivative (13) is then given by:

$$\frac{\partial \lambda_{\max}(h)}{\partial h} = \int_a^b ds_1 ds_n \frac{\partial L(s_1, s_n; h)}{\partial h} q_{\max}(s_1, h) q_{\max}(s_n, h)$$

$$+\lambda_{\max} \int_a^b ds_1 q_{\max}(s_1, h) \frac{\partial q_{\max}(s_1, h)}{\partial h} + \lambda_{\max} \int_a^b ds_n q_{\max}(s_n, h) \frac{\partial q_{\max}(s_n, h)}{\partial h}$$

$$= \int_a^b ds_1 ds_n L'(s_1, s_n; h) q_{\max}(s_1, h) q_{\max}(s_n, h) + \lambda_{\max} \frac{\partial}{\partial h} \int_a^b ds_1 q_{\max}^2(s_1, h). \tag{17}$$

The second term is equal to zero since the integral is identically equal to one for all h due to the normalization of the eigenfunctions.

The derivative (13) is then given only by the first term of (17):

$$\frac{\partial \lambda}{\partial h} = \int_a^b ds_1 ds_n L'(s_1, s_n; h) q_{\max}(s_1, h) q_{\max}(s_n, h). \tag{18}$$

It should be noted that this result is similar to the Hellman–Feynman theorem of quantum mechanics, relating the rate of change of the energy to the derivative of the hamiltonian.

The final formula for $\langle f\rangle$ obtained from Eqs. (10), (12), (13), (18) takes the following form:

$$\langle f\rangle = \int_a^b \varrho(s_1, \ldots, s_n) f(s_1, \ldots, s_n) ds_1 \ldots ds_n, \tag{19}$$

where the n-particle probability distribution function is

$$\varrho(s_1, \ldots, s_n) = \frac{q_{\max}(s_1)K(s_1, s_2)K(s_2, s_3) \ldots K(s_{n-1}, s_n)q_{\max}(s_n)}{\lambda_{\max}^{n-1}}. \tag{20}$$

One-dimensional chain in the Kac potential

All physical quantities calculated in the previous two Sections are analytic functions of p, T for all $T > 0$. This is a consequence of the well known fact that there is no true phase transitions in one-dimensional systems with short-range interactions for $T > 0$ [14]. Phase transitions can occur only in the zero-temperature limit. For $T > 0$ there are possible only the so called pseudo-phase transitions [4, 5, 15], i.e., specific heat and order parameters can change sharply but smoothly as functions of temperature. Therefore, if we want to investigate the phase transitions in the systems described by Eq. (1) for $T > 0$, we must introduce additionally some molecular field potential (MFP).

The simplest realization of such MFP is the Kac potential [16, 17]

$$\varphi(|r_i - r_j|) = -a\gamma e^{-\gamma|r_i - r_j|}, \quad a > 0 \tag{21}$$

together with the so-called Van der Waals limit ($\gamma \to 0$ taken after taking the thermodynamic limit).

When every pair of particles interacts through the Kac potential, the Helmholtz free energy and the equation of state are [17]:

$$F(v, T) = \mathrm{CE}\left[f_0(v, T) - \frac{a}{v}\right], \tag{22}$$

$$P(v, T) = \mathrm{MC}\left[p(v, T) - \frac{a}{v^2}\right], \tag{22a}$$

$$f_0 = g - pv, \tag{22b}$$

where CE and MC denote, respectively, the "Convex Envelope" (in v) and the "Maxwell Construction". The $p(v, T)$ and $f_0(v, T)$ in (22) have to be calculated in the absence of the Kac potential. It is interesting to note that in the Van der Waals limit the exponential form in Eq. (21) is irrelevant. The replacement of $\exp(-\gamma r)$ by any positive function $\phi(\gamma r)$ with

$$\int_0^\infty \phi(x)dx = 1$$

does not change the result given by Eqs. (22).

A knowledge of $F(v, T)$ and $P(v, T)$ tells us whether or not the phase transition takes place. It is, however, not sufficient to solve the problem of particle ordering within a given phase.

In order to investigate the structure of different phases we must calculate the order parameters. They must be calculated with the Kac long-range part of the potential switched on. Using formulas (22)–(22b) we obtain

$$F(v, T, h; a) = \mathrm{CE}\left[f_0(v, T; h) - \frac{a}{v}\right] = \mathrm{CE}\left[g(p, T; h) - pv - \frac{a}{v}\right]. \tag{23}$$

Now, the mean value $\langle f \rangle$ can be calculated by differentiating the free energy (23) with respect to h and taking the limit $h \to 0$. However, it is necessary to keep on mind that in the region of coexistence of phases (given by straight-line segments of the CE construction) the mean value $\langle f \rangle$ is not uniquely defined as the function of v. To avoid such ambiguities, let us denote by CRM (Coexistence Region Modification) the procedure of removing of all values of v belonging to the region of coexistence of phases (given by equation of state, $P(v, T)$). The mean value $\langle f \rangle$ will then be given by the formula:

$$\begin{aligned}\langle f \rangle &= \mathrm{CRM}\left[\frac{\partial F(v, T, h; a)}{\partial h}\bigg|_{h=0}\right] \\ &= \mathrm{CRM}\left\{\frac{\partial}{\partial h}\mathrm{CE}\left[g(p, T; h) - pv - \frac{a}{v}\right]\right\} \\ &= \mathrm{CRM}\,\{\int_a^b \varrho(s_1, \ldots, s_n) f(s_1, \ldots, s_n) ds_1 \ldots ds_n\}.\end{aligned} \tag{24}$$

3. *Zero-temperature limit*

In one-dimensional systems described by Eq. (1), the phase transitions can occur only for $T = 0$. The zero-temperature phase transitions are strictly connected with straight-line segments (SLS) which appear in the equation of state and order parameters and are usually separated by discontinuities. The increase of the temperature rounds of all such discontinuities and thermodynamic functions become continuous in all arguments. For example, the equation of state is a monotonically decreasing function of v, for $T > 0$. However, true phase transitions can still be enforced at non-zero temperatures by switching on the Kac potential.

The introduction into the system of the Kac potential modifies all thermodynamic functions in the manner shown by Eqs. (22), (24). The most important is the modification of the equation of state by the term $-a/v^2$. This additional term breaks down the monotonic behaviour of $p(v, 0)$ for some regions on the v-axis and of $p(v, T > 0)$ in the vicinity of $T = 0$ (for arbitrary $a > 0$, the SLS of $p(v, 0)$ form a typical "Van der Waals wiggle"). After performing the Maxwell construction on $p(v, T) - a/v^2$, the SLS obtained form the coexistence regions for various phases. Such regions are terminated by the critical points, T_c ($T_c > 0$).

For the investigation of phase transitions for $T > 0$ we require all the information about the zero-temperature behaviour of the equation of state and about order parameters for the model without the Kac potential.

Equation of state at zero-temperature

At zero-temperature, the equation of state (9) can be obtained by differentiation of $\ln(\lambda_{\max})$ with respect to p.

We will find the exact form of g. The starting point is Eq. (7):

$$\int_a^b ds_1 K(s_1, s_2) q(s_1) = \int_a^b ds_1 e^{-\alpha l(s_1,s_2)} \int_0^\infty dr e^{-\alpha r - \beta U(r;s_1,s_2)} q(s_1)$$

$$= \int_a^b ds_1 e^{-\alpha l(s_1,s_2)} \exp\{\beta[kT \ln \int_0^\infty dr e^{-\alpha r - \beta U(r;s_1,s_2)}]\} q(s_1)$$

$$\sim \int_a^b ds_1 e^{-\alpha l(s_1,s_2)} \exp\{-\beta \operatorname*{Min}_{(r)} [pr + U(r; s_1, s_2)]\} q(s_1, \beta \to \infty)$$

$$= \lambda_{\max}(p, \beta \to \infty) q(s_2). \tag{25}$$

Now, we rewrite Eq. (25) in an equivalent matrix form

$$\lim_{N\to\infty} \sigma_N \sum_{j=1}^{N} K(s_i, s_j) q(s_j) = \lambda_{\max} q(s_i), \tag{26}$$

where

$$\sigma_N = \frac{b-a}{N}, \qquad s_i \in [\sigma_N(i-1), \sigma_N i], \qquad i = 1, \ldots, N.$$

The dominating matrix elements in the equation (26) have the form

$$A = \sigma_N e^{-\beta \operatorname*{Min}_{(s_i,s_j)} [W(p;s_i,s_j)]}, \qquad (N \to \infty)$$

$$W(p; s_i, s_j) = pl(s_i, s_j) + \operatorname*{Min}_{(r)} [pr + U(r; s_i, s_j)],$$

and are symmetrically distributed with respect to the diagonal line, $s_i = s_j$. The ratio of the remaining matrix elements to A tends to zero when $\beta \to \infty$. Thus, at $T \to 0$, all the elements of symmetric matrix, K, are equal either to 0 or to A ($K = K(A, 0)$) and give the following asymptotic form of Eq. (26):

$$\det(K(A, 0) - \lambda \cdot \mathbf{1}) = 0.$$

Because

$$\det(K(A, 0) - kA) = A^{\kappa} \cdot \det[K(1, 0) - k] = 0, \qquad \kappa < N,$$

all the eigenvalues of the last equation are given simply by:

$$\lambda = kA, \qquad (k \text{ — is a real number}).$$

Thus,

$$\lambda_{\max} \sim k_{\max} \cdot A = k_{\max} e^{-\beta \underset{(s_1,s_2)}{\mathrm{Min}} W(p; s_1, s_2)},$$

$$g(p, T = 0) = \underset{(s_1,s_2)}{\mathrm{Min}} W(p; s_1, s_2) + \mathrm{const}$$

and finally,

$$v(p, T = 0) = \frac{\partial}{\partial p} \underset{(s_1,s_2)}{\mathrm{Min}} \{pl(s_1, s_2) + \underset{(r)}{\mathrm{Min}} [pr + U(r; s_1, s_2)]\}. \tag{27}$$

The correlation functions for $T = 0$

The same technique for the equation of state can be used to obtain the zero-temperature behaviour of the correlation functions $\langle f(s_1, \ldots, s_n)\rangle$. The results are as follows:

$$\langle f(s_1)\rangle = \frac{\partial}{\partial h} \underset{(s_1,s_2)}{\mathrm{Min}} \left\{pl(s_1, s_2) + \frac{h}{2}[f(s_1) + f(s_2)] + \underset{(r)}{\mathrm{Min}} [pr + U(r; s_1, s_2)]\right\}, \tag{28}$$

$$\langle f(s_1, s_2)\rangle = \frac{\partial}{\partial h} \underset{(s_1,s_2)}{\mathrm{Min}} \{pl(s_1, s_2) + hf(s_1, s_2) + \underset{(r)}{\mathrm{Min}} [pr + U(r; s_1, s_2)]\}, \tag{29}$$

$$\langle f(s_1, \ldots, s_n)\rangle = \frac{\partial}{\partial h} \underset{(s_1 s_2, \ldots, s_n)}{\mathrm{Min}} \left[p \sum_{i=1}^{n-1} l(s_i, s_{i+1}) \right.$$

$$\left. + hf(s_1, \ldots, s_n) + \sum_{i=1}^{n-1} \underset{(r)}{\mathrm{Min}} (pr + U(r; s_i, s_{i+1}))\right], \quad n \geqslant 3. \tag{30}$$

The useful theorem

Now, we restrict ourselves to the systems for which the phases are characterized only by two order parameters, $\langle f(s_1)\rangle$ and $\langle f(s_1, s_2)\rangle$. Also, we note that for small values of a the term $p(v, T)$ completely dominates over the attraction term $-av^{-2}$ in Eq. (22a). These two facts and the discussion given at the beginning of this Section permit us to formulate the following theorem:

> For an arbitrary $a > 0$, a transition with respect to IDF may occur if and only if the short-range, zero-temperature equation of state $p(v, T = 0)$ possesses a horizontal part $p = \mathrm{const}$ for some $v : v_1 < v < v_2$, and $\varrho(s_1)$, $\varrho(s_1, s_2)$ are not chaotic distributions in this region of v.

4. *Examples*

As an illustration of the theory given in the previous two Sections, we shall investigate the existence of the phase transitions in some of the simplest models.

Two state model

Let us consider first the system with nearest-neighbour pair interactions given by [5]:

$$U(r;\, s_j,\, s_{j+1}) = \left(1 - \frac{r}{d}\right) V(s_j,\, s_{j+1}); \qquad r < d$$

$$= 0; \qquad r > d \tag{31}$$

$$V(s_j,\, s_{j+1}) = w; \qquad s_j,\, s_{j+1} \in (0,\, \varepsilon\sigma)$$

$$= (1-\varrho\delta)w; \qquad s_j \in (\varepsilon\sigma,\, \sigma),\ s_{j+1} \in (0,\, \varepsilon\sigma) \text{ or vice versa}$$

$$= (1-\delta)w; \qquad s_j,\, s_{j+1} \in (\varepsilon\sigma,\, \sigma). \tag{32}$$

Assume that the length of the particle is equal to either d, or $(1-\nu)d$, depending on its actual internal state:

$$l(s) = \begin{cases} d, & 0 < s < \varepsilon\sigma,\ 0 < \varepsilon < 1 \\ (1+\nu)d, & \varepsilon\sigma < s < \sigma. \end{cases} \tag{33}$$

Finally, in order to investigate structure of the phases, we define the order parameters as:

$$\langle f(s_1)\rangle = \langle \theta(\varepsilon\sigma - s_1)\rangle,$$

$$\langle f(s_1,\, s_2)\rangle = \langle \theta(\varepsilon\sigma - s_1)\theta(\varepsilon\sigma - s_2)\rangle,$$

where $\theta(x)$ is the step-function. The simple calculations of equation of state and order parameters, using Eqs. (27), (29), give the following results[1]:

$\langle f(s_1)\rangle$	$\langle f(s_1, s_2)\rangle$	p	$\frac{v}{d} = \tilde{v}$	Restrictions on the values of parameters
ε	ε^2	0	$2 < \tilde{v}$	$\frac{1}{2} < \varrho < 1$
0	0	$\frac{1-\delta}{1-\nu} w$	$1+\nu < \tilde{v} < 2$	$0 < \nu < \delta < 1$
0.5	0	$\frac{2\delta(1-\varrho)}{\nu} w$	$1+\frac{\nu}{2} < \tilde{v} < 1+\nu$	$\frac{1-\delta}{1-\nu} < \frac{2\delta(1-\varrho)}{\nu}$
1.0	1.0	$\frac{2\varrho\delta}{\nu} w$	$1 < \tilde{v} < 1+\frac{\nu}{2}$	$1-\varrho\delta < \frac{2\delta(1-\varrho)}{\nu}$

These results are identical with those obtained earlier [5] and show the possibility of ordering in IDF.

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[1] It should be noted that, to find the values of the order parameters for the low-density phase ($p = 0$), the low density limit ($v \to \infty$ or $p \to 0$) must be calculated prior to the low-temperature limit $T \to 0$. The reversal of the sequence of these limits would result in unphysical values: $\langle f(s_1)\rangle = \langle f(s_1, s_2)\rangle = 1$ for the low density phase.

The model with $U = 0$

This is the model of the system of rigid molecules with pure, hard-core interaction, given by the molecule shape function $l(s)$. The calculations of the zero-temperature equation of state and the order parameters lead to the following results:

$$p = 0 \quad \text{for} \quad v > d,$$
$$p = \infty \quad \text{for} \quad v < d, \tag{34}$$

and (see footnote 1)

$$\langle f(s_1)\rangle = \frac{1}{b-a}\int_a^b dsf(s), \quad v > d \tag{35}$$

$$\langle f(s_1, s_2)\rangle = \frac{1}{(b-a)^2}\int_a^b\int_a^b ds_1ds_2f(s_1, s_2), \quad v > d \tag{35a}$$

These results show that in the one-dimensional systems with pure hard-core interactions there is no phase transitions with respect to IDF.

The simplified model of rigid rotators

The phase transitions from the hindered to the free rotation were often investigated for an interaction depending only on a difference between the values of IDF of neighbouring particles [18]. Now, we shall present the solution of the one-dimensional continuous version of this class of the models.

Let us consider the system of rotators interacting via the potential:

$$U = U(r; |s_{i+1}-s_i|) = U(r; |s_{i+1}-s_i+\pi|); \quad s_i \in [-\pi, \pi] \tag{36}$$

with a constant particle diameter, $l(s) = d$.

For such models, the integral equation (7) can be solved exactly. This integral equation has all eigenvalues doubly degenerated with the exception of λ_0, and

$$\lambda_0 = \int_{-\pi}^{\pi} K(s)ds, \quad q_0(s) = \frac{1}{\sqrt{2\pi}}, \tag{37}$$

$$\lambda_k = \int_{-\pi}^{\pi} K(s)\cos(ks)ds, \tag{37a}$$

$$q_{1,k} = \frac{1}{\sqrt{\pi}}\cos(ks), \quad q_{2,k}(s) = \frac{1}{\sqrt{\pi}}\sin(ks); \quad k = 1, 2, \ldots \tag{37b}$$

Only the maximal eigenvalue λ_0 contains information concerning the thermodynamic properties of a given system. The appropriate eigenvector, $q_0(s)$, describes the one-particle probability distribution of IDF. Keeping this in mind and using Eqs. (6), (20), (37) we obtain:

$$g = -kT \ln \int_{-\pi}^{\pi} K(s)ds, \tag{38}$$

$$\varrho(s_1) = \frac{1}{2\pi}, \tag{38a}$$

$$\varrho(s_1, s_2) = \frac{K(s_1, s_2)}{2\pi \int_{-\pi}^{\pi} K(s)ds}, \tag{38b}$$

where

$$K(s_1, s_2) = K(|s_1-s_2|) = \exp\{-\alpha d\} \int_0^\infty dr e^{-\alpha r-\beta U(r;|s_1-s_2|)}.$$

The chaotic distribution of IDF (Eq. (38)) shows that there is no rotational phase transitions in the systems with interaction given by formula (36).

5. *Final remarks*

The results presented in this paper show that it is possible to find all thermodynamic properties for one-dimensional systems of particles with IDF. The explicit calculations given for the systems with nearest-neighbour interaction, depending on IDF, and with the Kac long-range potential indicate that the problem reduces to the solution of the Fredholm integral equation (7).

The introduction of the Kac potential allows us to investigate the phase transitions for $T > 0$, even in one-dimensional systems. In the case when the short-range part of the potential depends on IDF, we obtain the phase transitions in which ordering of IDF does occur. The appearance of such phase transitions is closely connected with the behaviour of the equation of state and order parameters at $T = 0$.

To obtain all of these results, it is not necessary to specify the character of IDF — it is sufficient that the interaction depends on them. Probably, the simplest identification of the IDF is as the one-dimensional representation of the rotational motion. The calculations performed on specific models seem to suggest that it is difficult to explain the rotational, first order phase transitions (i.e. as in liquid crystals) as the pure geometric effect, that is, only by the contact hard-core interaction. It is necessary to introduce into the system the additional short-range soft interaction, at least between the nearest neighbours. It is, for example, the multipole interaction, or the interaction softening the hard core as as in (31), (32). The above results are generalization of those obtained earlier by Zwanzig [3] for needlelike molecules.

For the third of proposed model, with the potential interaction depending only on difference between the values of IDF of neighbouring particles, the integral equation (7) can be solved exactly. The results are the same as for classical one-dimensional Heisenberg model, i.e., there is no phase transition in IDF. This result remains valid even after switching on of the Kac potential.

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