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Screening effect and phase transitions in solutions of rodlike dipoles

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A system of rodlike dipoles is investigated by the method of collective coordinates and by the method of Debye-Hückel. The possibility of the appearance of a screening effect is considered. The existence of a first-order isotropic nematic transition in the limit of dilute solutions and in the high-density limit is demonstrated.

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I. INTRODUCTION

There are several approaches to the statistical mechanics of liquid-crystal systems (see, for instance, the review by Vroege and Lekkerkerker [1]). The phase separation in solutions of rodlike molecules interacting via short-range forces was first explained by Onsager [2] using the virial-expansion theory. In that work he already drew attention to electrostatic interactions between the particles. So the effect of the electrostatic repulsion is equivalent to an increase of the effective diameter of rods, and depends on the thickness of the electric double layer and on the ionic strength.

A further development of the Onsager theory of rodlike polyelectrolytes was made by Odijk and co-workers [3,4]. They used the Onsager decomposition of the Debye-Hückel potential and calculated the second virial coefficient. Onsager and his followers restricted themselves to the situation when the electrostatic energy of rods is much greater than the temperature and the rod concentration is much less than unity. So in this case the second-virial-coefficient approximation is quite sufficient to describe the phase transition in solutions of long rods. Furthermore, in this limit it is necessary to know an accurate form of the potential only for the configuration where the outer parts of the double layers overlap. The detailed structure of the potential of the mean force for two charged rods is of no importance in this case. This may be the reason why the subtle effects similar to screening effects in the rod system have not been studied in these works.

The opposite high-density limit has been considered by Deutsch and Goldenfeld [5,6], who presented a systematic way to calculate the free energy of charged needles by means of the collective-coordinate formalism. The authors' efforts were concentrated mainly on determining the phase-transition parameters while analysis of correlation properties of charged needlelike particles remained without attention.

The aim of this paper is to consider some properties of highly concentrated solutions of rodlike dipoles. The consideration is based on the idea of Deutsch and Goldenfeld. The collective-coordinate method may be used to study the system of particles interacting via potential less singular than r^{-3}. Since the needlelike dipole can be represented by two point charges attached to the ends of a rod the electrostatic attraction of polar rodlike particles is essentially Coulombic. Hence the free energy of rodlike dipoles may be derived by means of the collective-coordinates method [7–9]. Cebers [7] performed calculations for the system of needlelike dipoles and obtained the critical temperature and concentration from thermodynamic stability conditions. Kornev and Eskin [8] have generalized his theory by means of introducing the steric interaction between rods. Analysis of phase states has been carried out on the basis of the Maier-Saupe approximation. The formation of the three types of anisotropic structures has been shown.

Neither Cebers nor Kornev and Eskin have clarified a domain of validity of their approximations.

In this paper we discuss correlation properties of rodlike dipoles to throw some light upon the problem. The paper is organized as follows. In Sec. II we briefly review the early works by Cebers [7] and Kornev and Eskin [8]; then we estimate the critical parameters of the isotropic-nematic transitions for polar systems. Here we closely follow the discussions of Kornev and Eskin [8] and present only such formulas which are necessary to elucidate the results being obtained. In Sec. III we present some new results. To find a domain of applicability of the random-phase approximation (RPA) for polar systems in Sec. III we perform a high-density expansion of the effective potential. Such an approach is used as well in the Debye-Hückel theory of electrolytes. The effective potential includes the Debye-Hückel term which expresses the fact that the interactions between particles are screened by the presence of other particles. This effect can be considered as crowding of the neighboring polar molecules around the poles and the formation near each pole of a layer of molecules that are bound to the pole. As a consequence of this effect we derive the limit of validity of the theory. This limit resembles the Debye-Hückel condition.

The conclusions that can be drawn from this work are summarized in Sec. IV.

II. FORMAL CALCULATION

We consider a system of total volume V containing N rods with length l and diameter d. The moment per unit length of rods is m. The microscopic polarization vector $\mathbf{L}$ is given by

$$\mathbf{L}=\sum_{i=1}^{N}\int_{-l/2}^{l/2}\mathbf{n}_i\delta(\mathbf{r}-\mathbf{r}_i-\mathbf{n}_i s)ds\ ,$$

where $\mathbf{n}_i$ is a unit vector parallel to the ith rod and $\mathbf{r}_i$ is the center of mass of the rod. Further, we introduce the collective-coordinate transformation

$$\mathbf{L}_{\mathbf{k}}=\sum_{i=1}^{N}\int_{-l/2}^{l/2}\mathbf{n}_i e^{i\mathbf{k}\cdot(\mathbf{r}_i+\mathbf{n}_i s)}ds\ ,$$

which is the Fourier transform of the microscopic polarization vector. By using $\mathbf{L}_{\mathbf{k}}$ we write the energy of dipole-dipole interaction as

$$U=-\frac{Vm^2}{2}\sum_{i\neq j}\int_{-l/2}^{l/2}\int_{-l/2}^{l/2}(\mathbf{n}_i\cdot\nabla_i)(\mathbf{n}_j\cdot\nabla_i)|\mathbf{r}_i+\mathbf{n}_i s-\mathbf{r}_j-\mathbf{n}_j s'|^{-1}ds\,ds'$$

$$=\frac{m^2}{2V}\sum_{\mathbf{k}}\mathsf{D}(\mathbf{k}):\mathbf{L}_{\mathbf{k}}\mathbf{L}_{-\mathbf{k}}-\frac{m^2}{2V}\sum_{\mathbf{k}}\mathsf{D}(\mathbf{k}):\sum_{i=1}^{N}\mathbf{n}_i\mathbf{n}_i\Delta^2\left(\mathbf{k}\cdot\mathbf{n}_i\frac{l}{2}\right)\ ,$$

where

$$\mathsf{D}(\mathbf{R}-\mathbf{R}')=-\nabla\nabla|\mathbf{R}-\mathbf{R}'|^{-1}$$

$$=\frac{1}{V}\sum_{\mathbf{k}}\mathsf{D}(\mathbf{k})\exp[i\mathbf{k}\cdot(\mathbf{R}-\mathbf{R}')]\ ,$$

$$\Delta^2(\mathbf{k}\cdot\mathbf{n}l/2)=\frac{4\sin^2(\mathbf{k}\cdot\mathbf{n}l/2)}{(\mathbf{k}\cdot\mathbf{n})^2}\ .$$

We then introduce the Onsager artifice, that is, we shall treat particles of different orientation as particles of different kinds [2]. Thus we split the set of all directions in space among elements of solid angles $\omega_1,\ldots,\omega_N$ surrounding the directions $\mathbf{n}_1,\ldots,\mathbf{n}_i$, respectively. Then the free energy of the system takes the form

$$F=-kT\ln\prod_i\frac{(\omega_i)^{M_i}V^N}{M_i!}\frac{Q_0}{V^N}$$

$$\times\int\prod_{\mathbf{k}}d\mathbf{L}'_{\mathbf{k}}\frac{\partial(\{\mathbf{r}_i\})}{\partial(\{\mathbf{L}'_{\mathbf{k}}\})}\exp[-U(\mathbf{L}'_{\mathbf{k}})/kT]\ . \tag{1}$$

Here we denote the rod populations of small solid angle ω_i by M_i. Q_0 is a configuration integral of hard rods,

$$Q_0=V^{-N}\int\exp[-U_0(\mathbf{R})/kT]d\mathbf{R}_1\cdots d\mathbf{R}_N\ ,$$

where U_0 is the energy of steric interaction and $\partial(\{\ \})/\partial(\{\ \})$ is the Jacobian.

The Jacobian of transformation from physical variables to collective ones is obtained as a result of averaging the function

$$J(\mathbf{Lr})=\prod_{\mathbf{k}}\delta(\mathrm{Re}\mathbf{L}'_{\mathbf{k}}-\mathrm{Re}\mathbf{L}_{\mathbf{k}})\delta(\mathrm{Im}\mathbf{L}'_{\mathbf{k}}-\mathrm{Im}\mathbf{L}_{\mathbf{k}})\ ,$$

over a system with short-range interaction (see, for instance, Yukhnovskii and Golovko [10]).

$$\frac{\partial(\{\mathbf{r}_i\})}{\partial(\{\mathbf{L}_{\mathbf{k}}\})}=\frac{1}{Q_0V^N}\int\prod_i d\mathbf{r}_i\exp\left[-\frac{U_0}{kT}\right]J(\mathbf{Lr})\ .$$

The vector $\mathbf{k}$ in the transition function runs over possible values in the half-space $k_3>0$.

The Jacobian cannot be calculated exactly, but in the random-phase approximation (RPA) it becomes a Gaussian (see Appendix).

$$\frac{\partial(\{\mathbf{r}_i\})}{\partial(\{\mathbf{L}_{\mathbf{k}}\})}=\delta\left[\mathrm{Re}\mathbf{L}'_0-\sum_i M_i\mathbf{n}_i l\right]$$

$$\times\prod_{\mathbf{k}\neq0}\frac{\exp(-\frac{1}{2}\mathsf{A}^{-1}(\mathbf{k}):\mathbf{L}_{\mathbf{k}}\mathbf{L}_{-\mathbf{k}})}{\sqrt{2}\pi\det\mathsf{A}(\mathbf{k})}\ , \tag{2}$$

where tensor A means the ordinary average of the tensor $\mathbf{L}_{\mathbf{k}}\mathbf{L}_{-\mathbf{k}}$,

$$\mathsf{A}(\mathbf{k})=\frac{1}{Q_0V^{N-1}}\int\prod_i d\mathbf{r}\exp\left[-\frac{U_0}{kT}\right]\mathbf{L}_{\mathbf{k}}\mathbf{L}_{-\mathbf{k}}\ .$$

As it is shown in the Appendix, tensor A is given by

$$\mathsf{A}(\mathbf{k})=\frac{1}{Q_0}\sum_{u,v}M_uM_v\mathsf{B}_{uv}+\sum_u M_u\mathbf{n}_u\mathbf{n}_u\Delta^2(\mathbf{k}\cdot\mathbf{n}_u l/2)\ ,$$

$$\mathsf{B}_{uv}=-\mathbf{n}_u\mathbf{n}_v\Delta^2(\mathbf{k}\cdot\mathbf{n}_u l/2)\Delta^2(\mathbf{k}\cdot\mathbf{n}_v l/2)$$

$$\times\Delta\left[\mathbf{k}\cdot\frac{\mathbf{n}_u\times\mathbf{n}_v}{|\mathbf{n}_u\times\mathbf{n}_v|}d\right]|\mathbf{n}_u\times\mathbf{n}_v|\ , \tag{3}$$

$$Q_0=1-l^2dV^{-1}\sum_{u,v}M_uM_v|\mathbf{n}_u\times\mathbf{n}_v|\ .$$

Inserting expression (2) into formula (1) we have the Gaussian integral

$$F=-kT\ln\prod_i\frac{(\omega_i)^{M_i}V^N}{M_i!}\frac{Q_0}{V^N}-\frac{m^2}{2V}\sum_{\mathbf{k}}\mathsf{D}(\mathbf{k}):\sum_i M_i\mathbf{n}_i\mathbf{n}_i\Delta^2(\mathbf{k}\cdot\mathbf{n}_i l/2)$$

$$-kT\int\exp\left[-\frac{m^2}{2kTV}\sum_{\mathbf{k}}\mathsf{D}(\mathbf{k}):\mathbf{L}'_{\mathbf{k}}\mathbf{L}'_{\mathbf{k}}\right]\delta\left[\mathrm{Re}\mathbf{L}'_0-\sum_i M_i l\mathbf{n}_i\right]\prod_{\mathbf{k}}\frac{\exp[-\frac{1}{2}A^{-1}(\mathbf{k}):\mathbf{L}'_{\mathbf{k}}\mathbf{L}_{-\mathbf{k}}]}{\sqrt{2}\pi\det A(\mathbf{k})}d\,\mathrm{Re}\mathbf{L}'_0 d\,\mathrm{Re}\mathbf{L}'_{\mathbf{k}}d\,\mathrm{Im}\mathbf{L}'_{-\mathbf{k}}\ .$$

By transition to the continuum limit

$$M_i = Nf(\mathbf{n}_i)\omega_i\ , \quad \sum_{\mathbf{k}} \rightarrow \frac{V}{(2\pi)^3} \int d^3\mathbf{k}\ ,$$

we have the free-energy expression [8]

$$\begin{aligned} F = {} & kTN \ln\varphi + \frac{l^2 d N^2}{V} kT \int\int f(\mathbf{n}) f(\mathbf{n}') |\mathbf{n}\times\mathbf{n}'| d^2\mathbf{n}\, d^2\mathbf{n}' \\ & + kTN \int f(\mathbf{n}) \ln f(\mathbf{n}) d^2\mathbf{n} + \frac{m^2 l^2}{2V} \mathsf{D}(0){:}N^2 \int f(\mathbf{n})\mathbf{n}\, d^2\mathbf{n} \int f(\mathbf{n})\mathbf{n}\, d^2\mathbf{n} \\ & - \frac{kTV}{2(2\pi)^3} \int d^3\mathbf{k} \left\{ \frac{cm^2}{kT} \mathsf{D}(\mathbf{k}){:} \int f(\mathbf{n})\mathbf{n}\mathbf{n}\Delta^2(\mathbf{k}\cdot\mathbf{n}l/2) d^2\mathbf{n} \right. \\ & \qquad - \ln\det\left[\mathsf{I} + \frac{c^2 m^2}{Q_0 kT} \mathsf{D}(\mathbf{k})\cdot \int\int f(\mathbf{n}_u) f(\mathbf{n}_v) \mathsf{B}_{uv} d^2\mathbf{n}_u d^2\mathbf{n}_v \right. \\ & \qquad\qquad \left.\left. + \frac{cm^2}{kT} \mathsf{D}(\mathbf{k})\cdot \int f(\mathbf{n}) \Delta^2 \left[\mathbf{k}\cdot\mathbf{n}\frac{l}{2} \right] \mathbf{n}\mathbf{n}\, d^2\mathbf{n} \right] \right\} . \end{aligned} \tag{4}$$

Here $f(\mathbf{n})$ is the distribution function, $\mathsf{I}_{ij} = \delta_{ij}$, $\mathsf{D}(\mathbf{k}) = 4\pi(\mathbf{k}\mathbf{k}/k^2)$, φ is the volume fraction, $c = N/V$ is the concentration, and $\mathsf{D}(0)$ is the depolarization tensor of the volume,

$$\mathsf{D}(0) = \int \mathsf{D}(\mathbf{R}) d\mathbf{R} = V - \int_S \mathbf{R}\mathbf{n}|\mathbf{R}|^{-3} dS\ ,$$

and S is the boundary surface.

Note that the steric interactions bring the terms of odd order of $\mathbf{n}$ but if the external field is absent the polarization fluctuations do not lead to the formation of state with uncompensated electric flux [9]. This fact may be explained by means of the simplest physical considerations.

Indeed the energy of two rodlike dipoles in antiparallel state is $2m^2 l^2 / l^2 d$ and it is twice as large as energy in parallel state. So the system tends to organize the "antiferroelectric" state. We shall analyze the phase transition to the antiparallel state. In this case the terms of odd order of $\mathbf{n}$ vanish by symmetry and we have the functional differing from that in Ref. [7] by the Onsager term [second term in formula (4)] only. In order to analyze the extremum point of free-energy functional we have to solve the following integral equation which may be obtained as the variation derivative of functional (4),

$$\begin{aligned} & l^2 d c^2 kT \int f(\mathbf{n}') |\mathbf{n}\times\mathbf{n}'| d^2\mathbf{n}' + kTc \ln f(\mathbf{n}) \\ & \quad + \frac{kT}{2} \frac{1}{(2\pi)^3} \int d^3\mathbf{k} \frac{cm^2}{kT} \mathsf{D}(\mathbf{k}){:} \int f(\mathbf{n}')\mathbf{n}'\mathbf{n}'\Delta^2(\mathbf{k}\cdot\mathbf{n}'l/2) d^2\mathbf{n}' \frac{cm^2}{kT} \mathsf{D}(\mathbf{k}){:}\mathbf{n}\mathbf{n}\Delta^2(\mathbf{k}\cdot\mathbf{n}l/2) \\ & \qquad \times \left[1 + \frac{cm^2}{kT} \mathsf{D}(\mathbf{k}){:} \int f(\mathbf{n}')\Delta^2(\mathbf{k}\cdot\mathbf{n}'l/2)\mathbf{n}'\mathbf{n}' d^2\mathbf{n}' \right]^{-1} = \mu\ , \end{aligned} \tag{5}$$

where μ is determined from the condition

$$\int f(\mathbf{n}) d^2\mathbf{n} = 1\ . \tag{6}$$

Note that as well as in the Onsager theory the distribution function of isotropic phase $f = 1$ always satisfies the system of equations (5) and (6). It may be established by simple substitution. Indeed, in the limit of dilute solution the particles have arbitrary orientations ($f = 1$). However, at a certain concentration, the particles begin to be affected by each other so that the system tends to organize a structure with minimum free energy. In other words, the system must be described by means of another solution. The main goal now is to find the critical concentration c^* at which the anisotropic phase may appear.

Following the theory of branching of the solutions of nonlinear equations [11,12] the critical concentration is found as a bifurcation point of the system of equations (5) and (6). Near the spinodal the distribution function can be represented by the Landau–de Gennes form as

$$f = 1 + (c - c^*) a P_2(n) + \cdots\ ,$$

where $P_2(x)$ is the second Legendre polynomial, and a is a constant.

In order to determine the critical concentration we have to linearize the system of equations (5) and (6) in the vicinity of the solution $f = 1$ and to find the smallest eigenvalue of the resulting operator. Omitting the simple but tedious calculations, we write the resulting transcendental equation for determining the critical concentration

$$\frac{\lambda}{\gamma} = \left[\frac{\lambda}{\gamma} \right]^2 \frac{d}{64l} + \lambda^2 h(\lambda)\ , \tag{7}$$

where

$$h(\lambda)=\frac{1}{\pi}\int_0^{\infty}\frac{H^2(\xi)d\xi}{\xi^2\left[1+\frac{\lambda}{\xi^2}\left(1-\frac{\sin\xi}{\xi}\right)\right]^2}\ ,$$

$$H(\xi)=\int_{-1}^{1}P_2(x)\sin^2\left(\frac{\xi x}{2}\right)dx\ ,$$

and

$$\lambda=\frac{8\pi c^* m^2 l^2}{kT}\ ,\quad \gamma=\frac{m^2l^2}{kTl^3}\ ,$$

$$P_2(x)=\tfrac{3}{2}(x^2-\tfrac{1}{3})\ .$$

Cebers [7] has obtained a result similar to that of Eq. (7) using the thermodynamic stability condition and determined the critical temperature and concentration with the help of geometric constructions, namely, as the point of tangency of the line in the left-hand side and the second term in the right-hand side. Below Eq. (7) will be regarded as the branching condition, since it determines the possible number of anisotropic phases. The number of possible phases is defined by the number of roots of Eq. (7). The relationship between the critical concentration and molecular parameters have been discussed by Kornev and Eskin [8] in the general case. They have shown that Eq. (7) has several roots for a range of the molecular parameters.

Since still little is known about the status of the random-phase approximation we cannot interpret these results. So the key objective is the determination of the correct conditions of applicability of the RPA. Then we shall return to the branch equation in order to perform the analysis from the physical viewpoint.

III. PHYSICAL CONSTRUCTION

First we shall restrict our discussion to simple systems in which the particles interact via long-range potentials. We begin with the one-body effective potential acting upon a particle but having its origin in the totality of interactions with all other particles. Let $h(\mathbf{r}-\mathbf{r}',\mathbf{n},\mathbf{n}')$ be the interaction potential between two dipoles in the configurations $(\mathbf{r},\mathbf{n})$ and $(\mathbf{r}',\mathbf{n}')$. It is defined by

$$\begin{aligned}H(\mathbf{r}-\mathbf{r}',\mathbf{n},\mathbf{n}')&=h(\mathbf{R},\mathbf{n},\mathbf{n}')\\&=-\int\int_{-l/2}^{l/2}m\delta(\mathbf{R}-\mathbf{R}''-\mathbf{n}s)\\&\qquad\times\mathbf{n}\cdot\mathbf{E}(\mathbf{R}'')d\mathbf{R}''ds\ ,\end{aligned}\tag{8}$$

where

$$\mathbf{E}=-\nabla\varphi\ ,$$

and φ is the self-consistent potential. It has to satisfy the equation

$$\Delta\varphi=4\pi\nabla\cdot\wp\ ,\tag{9}$$

where $\wp$ is the polarization vector. The polarization vector is defined by

$$\begin{aligned}\wp=&\int\int\int_{-l/2}^{l/2}m\mathbf{n}\delta(\mathbf{R}-\tilde{\mathbf{R}}-\mathbf{n}s)g(\tilde{\mathbf{R}},\mathbf{n},\mathbf{n}')d\tilde{\mathbf{R}}\,d^2\mathbf{n}\,ds\\&+\int_{-l/2}^{l/2}m\mathbf{n}'\delta(\mathbf{R}-\mathbf{n}'s)ds\ ,\end{aligned}\tag{10}$$

where g is the pair distribution function. In equilibrium state the connection between $g(\mathbf{R},\mathbf{n},\mathbf{n}')$ and the interaction potential $h(\mathbf{R},\mathbf{n},\mathbf{n}')$ is given by the Maxwell-Boltzmann formula

$$g(\mathbf{R},\mathbf{n},\mathbf{n}')=cf(\mathbf{n})\exp\left(-\frac{h}{kT}\right)\ ,$$

where $cf(\mathbf{n})$ denotes the concentration at infinity in the configuration $\mathbf{n}$. According to the theory developed by Debye and Hückel we assume that $h/kT\ll1$ then

$$g(\mathbf{R},\mathbf{n},\mathbf{n}')=cf(\mathbf{n})\left(1-\frac{h}{kT}\right)\ .\tag{11}$$

Substituting the expansion (11) into (9) and (10) we have

$$\begin{aligned}\Delta\varphi=&-\frac{4\pi cm}{kT}\nabla\cdot\int\int\int_{-l/2}^{l/2}\mathbf{n}f(\mathbf{n})\delta(\mathbf{R}-\tilde{\mathbf{R}}-\mathbf{n})h(\tilde{\mathbf{R}},\mathbf{n})\\&\qquad\times d\tilde{\mathbf{R}}\,d^2\mathbf{n}\,ds\\&+4\pi m\nabla\cdot\int_{-l/2}^{l/2}\mathbf{n}'\delta(\mathbf{R}-\mathbf{n}'s)ds\ .\end{aligned}\tag{12}$$

To evaluate φ it is convenient to introduce the Fourier transform $\varphi_{\mathbf{k}}$

$$\varphi_{\mathbf{k}}=\int e^{i\mathbf{k}\cdot\mathbf{R}}\varphi(\mathbf{R})d\mathbf{R}\ ,$$

Then Eq. (12) can be solved analytically and solution is expressed as

$$\varphi_{\mathbf{k}}=\frac{i4\pi m\Delta\left(\mathbf{k}\cdot\mathbf{n}'\frac{l}{2}\right)(\mathbf{k}\cdot\mathbf{n}')}{k^2+\frac{4\pi cm^2}{kT}\int f(\mathbf{n})\Delta^2\left(\mathbf{k}\cdot\mathbf{n}\frac{l}{2}\right)(\mathbf{k}\cdot\mathbf{n})^2d^2\mathbf{n}}\ .\tag{13}$$

For the physical interpretation of the results the inverse Fourier transform is necessary. In the general case it cannot be written in closed form and we shall have to select some simple limits:

(a) *Limit of dilute solution.* In the small-λ limit $h\approx U$ and, as it is easy to check, collective properties of the rods are not displayed. There is no local field acting on a given site.

(b) *High-density limit* $\lambda\to\infty$. This is more interesting from the physical viewpoint. We shall consider this case in more detail.

Let us rewrite the right-hand side of Eq. (12) in more convenient form. Notice that the second term may be considered as

$$\begin{aligned}4\pi m\nabla\cdot&\int_{-l/2}^{l/2}\mathbf{n}'\delta(\mathbf{R}-\mathbf{n}'s)ds\\&=4\pi m\frac{\partial}{\partial z}\int_{-l/2}^{l/2}\delta(z-s)ds\,\delta(x)\delta(y)\\&=4\pi m\left[\delta\left(\mathbf{R}+\mathbf{n}'\frac{l}{2}\right)-\delta\left(\mathbf{R}-\mathbf{n}'\frac{l}{2}\right)\right]\end{aligned}\tag{14}$$

(here the z axis is chosen in the direction of $\mathbf{n}'$).

Integrating Eq. (8) by parts and applying to the effective potential the same method as in Eq. (14) we get

$$h(\mathbf{R},\mathbf{n},\mathbf{n}')=-m\int\varphi(\mathbf{R}'',\mathbf{n}')\left[\delta\left[\mathbf{R}-\mathbf{R}''+\mathbf{n}\frac{l}{2}\right]-\delta\left[\mathbf{R}-\mathbf{R}''-\mathbf{n}\frac{l}{2}\right]\right]d\mathbf{R}''\ .$$

After such a calculation the first term on the right-hand side of Eq. (12) can be written as

$$-\frac{4\pi mc}{kT}\nabla\cdot\int\int\int_{-l/2}^{l/2}\mathbf{n}f(\mathbf{n})\delta\left[\mathbf{R}-\tilde{\mathbf{R}}-\mathbf{n}\frac{l}{2}\right]h(\tilde{\mathbf{R}},\mathbf{n},\mathbf{n}')d\tilde{\mathbf{R}}\,d^2\mathbf{n}\,ds$$
$$=\frac{8\pi m^2c}{kT}\left[\varphi(\mathbf{R},\mathbf{n})-\int f(\mathbf{n})[\varphi(\mathbf{R}-\mathbf{n}l,\mathbf{n}')+\varphi(\mathbf{R}+\mathbf{n}l,\mathbf{n}')]d^2\mathbf{n}\right]\ . \qquad (15)$$

Inserting expressions (14) and (15) into (12) we get a new form of Eq. (12),

$$\Delta\varphi=\frac{8\pi m^2c}{kT}\left[\varphi(\mathbf{R},\mathbf{n})-\int f(\mathbf{n})[\varphi(\mathbf{R}-\mathbf{n}l,\mathbf{n}')+\varphi(\mathbf{R}+\mathbf{n}l,\mathbf{n}')]d^2\mathbf{n}\right]+4\pi m\left[\delta\left[\mathbf{R}+\mathbf{n}'\frac{l}{2}\right]-\delta\left[\mathbf{R}-\mathbf{n}'\frac{l}{2}\right]\right]\ . \qquad (16)$$

It is possible to give a physical interpretation of this equation. The first term on the right-hand side of the equation may be treated as an effective charge of the matter. The other terms on the right-hand side denote the charges located at the points $+\mathbf{n}'l/2$ and $-\mathbf{n}'l/2$. In order to analyze the large-scale correlations let us transform the integrodifferential Eq. (16) to the integral equation. To do this we can use the Green function of the Helmholtz equation. Then the solution of the Eq. (16) can be written as

$$\varphi=\varphi_0+\frac{\lambda}{4\pi}\int\frac{\exp(-\sqrt{\lambda}|\mathbf{R}-\mathbf{R}'|/l)}{|\mathbf{R}-\mathbf{R}'|}\left[\int f(\mathbf{n})[\varphi(\mathbf{R}'-\mathbf{n}l)+\varphi(\mathbf{R}'+\mathbf{n}l)]\right]d\mathbf{R}'d^2\mathbf{n}\ , \qquad (17)$$

where

$$\varphi_0=\frac{m\exp(-\sqrt{\lambda}|\mathbf{R}/l-\mathbf{n}/2|)}{|\mathbf{R}-\mathbf{n}l/2|}-\frac{m\exp(-\sqrt{\lambda}|\mathbf{R}/l+\mathbf{n}/2|)}{|\mathbf{R}+\mathbf{n}l/2|)}\ .$$

Let us study the behavior of the potential near the poles. We shall consider the pole located at point $\mathbf{n}'l/2$. The integral on the right-hand side of Eq. (17) can be estimated as

$$J=\frac{\lambda}{4\pi}\int\frac{\exp(-\sqrt{\lambda}|\mathbf{R}-\mathbf{R}'|/l)}{|\mathbf{R}-\mathbf{R}'|}\left[\int f(\mathbf{n})[\varphi(\mathbf{R}'-\mathbf{n}l)+\varphi(\mathbf{R}'+\mathbf{n}l)]\right]d\mathbf{R}'d^2\mathbf{n}$$
$$=\frac{\lambda}{4\pi}\int\frac{\exp(-\sqrt{\lambda}|\mathbf{r}|/l)}{|\mathbf{r}|}\left[\int f(\mathbf{n})[\varphi(\mathbf{R}-\mathbf{r}-\mathbf{n}l)+\varphi(\mathbf{R}-\mathbf{r}+\mathbf{n}l)]\right]d\mathbf{r}\,d^2\mathbf{n}$$
$$\approx\frac{\lambda}{4\pi}\int\frac{\exp(-\sqrt{\lambda}|\mathbf{r}|/l)}{|\mathbf{r}|}\left[\int f(\mathbf{n})[-\varphi(\mathbf{r}+\mathbf{n}l/2)+\varphi(-\mathbf{r}+3\mathbf{n}l/2)]\right]d\mathbf{r}\,d^2\mathbf{n}\ .$$

The vicinity of the point $-\mathbf{n}'l/2$ gives the main contribution to the integral so it can be estimated as

$$J\approx\frac{m\lambda}{2l\pi}\int\int\frac{\exp(-\sqrt{\lambda}|\mathbf{r}|/l)}{|\mathbf{r}|\left|\mathbf{r}+\frac{\mathbf{n}l}{2}\right|}f(\mathbf{n})d\mathbf{r}\,d^2\mathbf{n}$$
$$=O(1)\ .$$

Consequently, the potential in the vicinity $\mathbf{R}=\mathbf{n}'l/2$ can be written as

$$\varphi\approx\frac{m\exp(-\sqrt{\lambda}|\mathbf{R}/l-\mathbf{n}/2|)}{|\mathbf{R}-\mathbf{n}l/2|}\ .$$

The Debye form (exponential form) of the effective potential leads us close to the condition of validity of this approximation

$$\frac{m^2\sqrt{\lambda}}{lkT}\ll 1\quad\text{or}\quad\sqrt{\lambda}\gamma\ll 1\ . \qquad (18)$$

Now we can comment on the results of the asymptotic analysis from the physical viewpoint. The first limit corresponds to the case where the rods behave like solitary dipoles, as in the situation which is typical for pure polar gases. There is no local field with the characteristic scale; nevertheless, this limit contains the important case of low temperature so that a dimensionless coupling constant is

$$\gamma\gg 1\ .$$

Indeed, the high-temperature expansion is correct here because the energy of the order of $U\approx cm^2l^2$ (mean distance between rods is $\approx c^{-1/3}$).

In the high-density limit the long-range effects dominate and rods tend to form the "Debye atmospheres" around the poles. The inequalities (18) are required at high density to ensure that the temperature dominates over the energy of the local field of neighboring rods. The above discussion gives a definite interpretation of the results of branch equation analysis. But first we have to show the equivalence of both approaches. To do it we derive the free-energy expression. The free energy may be written exactly as

$$F=F_{\mathrm{id}}+\frac{cN}{2}\int\int d\mathbf{r}\,d\mathbf{r}'d^2\mathbf{n}\,d^2\mathbf{n}'f(\mathbf{n})f(\mathbf{n}')U(\mathbf{r}-\mathbf{r}')\times\int_0^1 d\alpha\,\tilde{g}(\mathbf{r},\mathbf{r}',\mathbf{n},\mathbf{n}',\alpha)\ , \qquad (19)$$

where α is introduced as a coupling constant for a pair potential. In expression (19) $\tilde{g}(\mathbf{r},\mathbf{r}',\mathbf{n},\mathbf{n}',\alpha)$ is the pair-correlation function for a system with pair potential αU. F_{id} is the ideal-gas part of F. According to the definition of the pair-correlation function we have

$$\tilde{g}=e^{-h(\alpha)/kT}\approx 1-\frac{h(\alpha)}{kT}\ , \qquad (20)$$

where [see expression (13)]

$$h_{\mathbf{k}}(\alpha)=\frac{\dfrac{\alpha m^2}{kT}\mathrm{D}(k):\mathbf{nn}'\Delta\left[\mathbf{k}\cdot\mathbf{n}\dfrac{l}{2}\right]\Delta\left[\mathbf{k}\cdot\mathbf{n}'\dfrac{l}{2}\right]}{1+\dfrac{\alpha c m^2}{kT}\mathrm{D}(k):\int f(\mathbf{n})\mathbf{nn}\Delta^2\left[\mathbf{k}\cdot\mathbf{n}\dfrac{l}{2}\right]d^2\mathbf{n}}\ .$$

Inserting expansion (20) into expression (19) and applying the Fourier transforms, we obtain functional (4) with $d=0$. Consequently the physical construction is equivalent to the formal calculations. From the preceding analysis it follows that the free energy expansion is valid in high-density limit so that the inequality $\lambda^{1/2}\gamma \ll 1$ has to be satisfied.

In order to extend these results to the case of hard-core interactions we have to notice that the effective potential acting upon the particle in the configuration $(\mathbf{R},\mathbf{n})$ due to the particle in the configuration $(0,\mathbf{n}')$ actually depends on a location of the third particle in the configuration $(\tilde{\mathbf{R}},\tilde{\mathbf{n}})$ [see Eq. (12)]. So for a proper definition of the probability we have to take into account the excluded volume of the particles in configurations $(\mathbf{R},\mathbf{n})$ and $(\tilde{\mathbf{R}},\tilde{\mathbf{n}})$. After such modification of the pair distribution function we get functional (4).

IV. DISCUSSION

We shall restrict our discussion to the limit of dilute solution and the high-density limit, in which the RPA is correct.

Let us consider the case $\gamma\to\infty$, $\lambda\to 0$. Within this limit we have de Gennes–Pincus situation [13]. The system of needlelike dipoles has the potential well in the antiparallel state greater than in the parallel state. So the de Gennes–Pincus chains are unstable and particles tend to condense in clusters with compensated polar momentum. Such effect is well known in the colloidal systems (see, for instance, [14]).

A synthesis of ferronematics [15–17], i.e., suspensions of single-domain rodlike ferromagnetic or ferrimagnetic particles in nematic liquid crystals, reveals an interest in deriving the condition of weak clustering.

Initial estimates have been suggested by Brochard and de Gennes [18]. They have obtained the clustering conditions by means of the chain model and used them to determine the critical length of the particle l, above which different grains will tend to form a chain. The minimum concentration, above which the average nematic orientation follows the orientation of the grains, is known and has order d^2/D^2 [18], where D is the sample size.

Let us estimate the threshold from our theory. In the case $\gamma\to\infty$, $\lambda\to 0$ the first term on the right-hand side of the branch equation may be neglected and we have

$$\varphi_c=\frac{105}{8\sigma^2}+O\left[\frac{1}{\gamma^2}\right]\ , \qquad (21)$$

where parameter $\sigma=2m^2l^2/l^2dkT$ is a measure of the ratio of the energy of rodlike dipoles in the antiparallel state and the thermal energy.

Using the experimental parameter values $M_s=4ml/\pi d^2l\approx 340$ G and $d\approx 7\times 10^{-6}$ cm from [15–17] we can find that $\varphi_c\approx 10^{-5}$ at room temperature. In the most experimental situations the volume fraction φ is of the order of $\approx 10^{-6}$, i.e., it is less than the critical value φ_c. Formula (21) may be used to determine the critical size of the particle for different models of the director orientation and magnetization [18,19], i.e., for different φ_c.

Let us now proceed to the high-density limit. It is convenient to rewrite Eq. (7) in the form

$$\frac{1}{\lambda}-\frac{d}{l}\frac{1}{64\gamma}=\gamma h(\lambda)\ .$$

Function $h(\lambda)$ is decreased and has a maximum at $\lambda=0$, $h(0)=\frac{1}{105}$. So Eq. (7) has a unique solution in the vicinity $\gamma=0$, which may be found by the point of intersection of the hyperbola and the integral curve. In the asymptotic limit we have

$$\varphi_c=2\frac{d}{l}-128\gamma^2h(32\sigma)\ .$$

Hence the instability appears earlier than that in the Onsager case [11], but the contribution to the critical concentration by the electrostatic interactions is weak.

In conclusion, we note that the free-energy functional may be used for solving an electrolytic problem. Indeed after substituting $4\pi/k^2$ for $\mathrm{D}(\mathbf{k}):\mathbf{nn}$ in formula (4) we shall get a free energy of the system with Coulombic interactions. The functional of Deutsch and Goldenfeld differs from this by the term

$$-\frac{kTV}{2(2\pi)^3}\int d^3\mathbf{k}\frac{cm^2}{kT}\mathrm{D}(\mathbf{k}):\int f(\mathbf{n})\mathbf{nn}\Delta^2(\mathbf{k}\cdot\mathbf{n}l/2)d^2\mathbf{n}\ .$$

This contribution can be treated as the energy of rods placed in their own fields. This term can be added to the functional of Deutsch and Goldenfeld in order to eliminate a divergence. Such procedure is widely used (see, for instance, Lifshitz [20] where a similar term is referred to the vacuum fluctuations). So this divergence is of no physical consequence and we can say that the "electrolytic" modification of functional (4) is the same as that of the functional of Deutsch and Goldenfeld. This form is the regularization of their functional only. In the next paper we shall study the electrolytic problem and consider the problem of counterion condensation on the rodlike molecules.

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APPENDIX: CALCULATION OF THE JACOBIAN

We shall evaluate the integral

$$\frac{\partial(\{\mathbf{r}_i\})}{\partial(\{\mathbf{L}_\mathbf{k}\})}=\frac{1}{Q_0 V^N}\int \prod_i d\mathbf{r}_i \exp\left[-\frac{U_0}{kT}\right] J(\mathbf{L}\mathbf{r}) \; .$$

Using the integral representation of the δ function

$$\delta(x)=\frac{1}{2\pi}\int_{-\infty}^{\infty} \exp i\omega x \, d\omega \; ,$$

we have

$$\frac{\partial(\{\mathbf{r}_i\})}{\partial(\{\mathbf{L}_\mathbf{k}\})}=\int \prod_\mathbf{k} \frac{1}{2\pi} e^{i\omega_\mathbf{k}\cdot\mathbf{L}'_\mathbf{k}} \left\langle \exp\left[-i\sum_\mathbf{k} \omega_\mathbf{k}\cdot\mathbf{L}'_\mathbf{k}\right]\right\rangle d\,\mathrm{Re}\,\omega_\mathbf{k} \, d\,\mathrm{Im}\,\omega_\mathbf{k} \; ,$$

where brackets denote the average with respect to function $\exp(-U_0/kT)$.

Expanding the exponent inside the brackets and retaining the products of term $\langle \mathbf{L}_\mathbf{k}\mathbf{L}_{-\mathbf{k}}\rangle$ only, we get

$$\frac{\partial(\{\mathbf{r}_i\})}{\partial(\{\mathbf{L}_\mathbf{k}\})}=\delta\left[\mathbf{L}'_0-\sum_i M_i \mathbf{n}_s l\right]\int \prod_{\mathbf{k}(\neq 0)} \frac{1}{2\pi} e^{i\omega_\mathbf{k}\cdot\mathbf{L}'_\mathbf{k}} \exp\left[-\tfrac{1}{2}\sum_{\mathbf{k}(\neq 0)} \omega_\mathbf{k}\omega_{-\mathbf{k}}:\mathsf{A}(\mathbf{k})\right] d\,\mathrm{Re}\,\omega_\mathbf{k} \, d\,\mathrm{Im}\,\omega_\mathbf{k} \; .$$

Calculating the Gaussian integral we have Eq. (2).

To evaluate the cumulant average

$$\begin{aligned}\mathsf{A}(\mathbf{k})&=\frac{1}{Q_0 V^N}\sum_{u\neq v} M_u M_v \mathbf{n}_u\mathbf{n}_v \Delta(\mathbf{k}\cdot\mathbf{n}_u l/2)\Delta(\mathbf{k}\cdot\mathbf{n}_v l/2)\int e^{-U_0/kT} e^{-i\mathbf{k}\cdot(\mathbf{r}_u-\mathbf{r}_v)} d\mathbf{r}_1 \ldots d\mathbf{r}_N+\sum_u M_u \mathbf{n}_u\mathbf{n}_u \Delta^2(\mathbf{k}\cdot\mathbf{n}_u l/2)\\ &=\frac{1}{Q_0}\sum_{u,v} M_u M_v \mathsf{B}_{uv}+\sum_u M_u \mathbf{n}_u\mathbf{n}_u \Delta^2(\mathbf{k}\cdot\mathbf{n}_u l/2) \; .\end{aligned} \tag{A1}$$

We introduce the Mayer function f [21,2,1] as

$$e^{-U_0/kT}=1+f \; .$$

To make the calculation possible we retain the first term in the cluster integral only. It is convenient to express the relative position vector $\mathbf{r}$ between the center of mass of rods in terms of the variables suggested by Straley [22]

$$\mathbf{r}=\alpha\mathbf{n}_u+\beta\mathbf{n}_v+\gamma\frac{\mathbf{n}_u\times\mathbf{n}_v}{|\mathbf{n}_u\times\mathbf{n}_v|} \; .$$

The volume element $d\mathbf{r}$ is expressed as

$$d\mathbf{r}=|\mathbf{n}_u\times\mathbf{n}_v|\,d\alpha\, d\beta\, d\gamma \; .$$

Then the integral in formula (A1) is written as

$$V^{N-1}\int f e^{-\mathbf{k}\cdot\mathbf{r}} d\mathbf{r}=V^{N-1}\int_{-l/2}^{l/2}\int_{-l/2}^{l/2}\int_{-d}^{d} \exp\left[i\left[\alpha\mathbf{k}\cdot\mathbf{n}_u+\beta\mathbf{k}\cdot\mathbf{n}_v+\gamma\mathbf{k}\cdot\frac{\mathbf{n}_u\times\mathbf{n}_v}{|\mathbf{n}_u\times\mathbf{n}_v|}\right]\right]|\mathbf{n}_u\times\mathbf{n}_v|\,d\alpha\, d\beta\, d\gamma \; .$$

Calculating these integrals and inserting the result into the formula (A1) we get

$$\mathbf{B}_{uv}=-\mathbf{n}_u\mathbf{n}_u\Delta^2(\mathbf{k}\cdot\mathbf{n}_v l/2)\Delta^2(\mathbf{k}\cdot\mathbf{n}_v l/2)\Delta\left[\mathbf{k}\cdot\frac{\mathbf{n}_u\times\mathbf{n}_v}{|\mathbf{n}_u\times\mathbf{n}_v|}d\right]|\mathbf{n}_u\times\mathbf{n}_v| \; ,$$

$$Q_0=1-l^2 d V^{-1}\sum_{u,v} M_u M_v |\mathbf{n}_u\times\mathbf{n}_v| \; .$$

which are Eq. (3).

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