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Theory of the Spontaneous Polarization of the Adsorbed Monolayer of Polar Molecules. The Collective Variables Method

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The theory of the spontaneous polarization of the adsorbed monolayer of polar molecules is developed using the collective variables method. The total potential of the system is represented as the sum of the one-body and two-body interaction potentials. The one-body potential depends on the orientation of the molecular dipoles in the external electric field and on the interactions between the molecules and the substrate. The two-body potential consists of the sum of intermolecular potentials which can be separated into the "short-range" part describing the orientation-independent interaction at distances, and the long-range part dependent on both the coordinates and the orientations of the interacting species. The variation of the configurational Helmholtz free energy of the system related to the long-range orientational interactions is shown to consist of three terms describing different modes of interactions of density fluctuations: (a) neglect of particle's density fluctuation or self-consistent mean field approximation (SCMF), (b) harmonic oscillations of the particle's density—the random phases approximation (RPA), and (c) various unharmonic interactions of the fluctuation waves. In the SCMF approximation using the assumption of the multiplicative separation of the high-order distribution function the singlet distribution function is calculated and the polarization vector of the adsorbed monolayer is determined. The corrections to the singlet distribution function arising from the terms (b) and (c) of the free energy are calculated. It is shown that the spontaneous polarization of the adsorbed monolayer of polar molecules may be regarded as the first-order phase transition.

KEY WORDS: Spontaneous polarization; adsorbed monolayer; configurational integral; phase transitions; collective variables.

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1. INTRODUCTION

In the previous paper$^{(1)}$ the spontaneous polarization of the adsorbed monolayer of polar molecules was treated using the dipole–dipole pair interaction potential and the SCMF approximation for the polarization, and the conditions of the formation of the polydomain structure of the surface polarization were considered.

In this paper we present the general theory of the spontaneous polarization of an adsorbed monolayer of polar molecules with the pair interaction potential dependent on the distance between the molecules and on their mutual orientations. The pair interaction potential can be separated into two parts, (1) the "short-range" term describing the interactions at short distances and independent on the molecular orientations and (2) the long-range part, which is orientation dependent. This separation is in fact conventional, and in all of what follows the terms independent on the molecular orientations will be attributed for convenience to the "short-range" part.

We calculate the variation of the configurational Helmholtz free energy associated with the long-range interactions using the method of the collective variables described in Refs. 2 and 3. The long-range interaction is treated against the "short-range" background, i.e., using this short-range part as a basis with the various account for the interaction of the density oscillation modes, which are the collective variables. As the result the variation of the configurational free energy can be expanded into the (infinite) series with the successive terms accounting for different character of the interaction of the density fluctuations in the long-range interaction, that is, for the different degrees of screening of the initial long-range interaction. It is convenient to represent each term of the series as a diagram involving both complex vertices which describe the correlators of the products of spherical functions with variables dependent on the molecular orientations in the adsorbed monolayer, and lines denoting the pair correlation function of the system. Under certain statistical assumptions (the multiplicative separation of the higher-order correlation functions in the SCMF approximation and low values of the polarization vector) one can restrict oneself to the calculation of the first few terms in the expansions of the free energy to evaluate the singlet distribution function and the polarization of the system. The character of the dependence of the polarization on the external electric field shows that the spontaneous polarization arises as a first-order phase transition.

The approach$^{(2,3)}$ taken as a principle of the present work can be compared with the expansion of the molecular distributions and the Helmholtz free energy in the long-range part of the interaction potential.$^{(4-10)}$ The first few terms of this expansion give results identical to the one obtained using our approach, leading to the known SCMF and RPA. In this work the diagrams are used to account for the higher-order terms of the expansion and in the most simple cases (e.g., homogeneous systems without ordering) some infinite classes of these diagrams can be grouped into closed-form expressions giving the corrections to the SCMF and RPA methods.(3)

The alternative to the method described in the present paper is the approach which treats the long-range interactions "against the background" of the reference system.(11) The collective variables are introduced by Gaussian transformation; however, the expressions for thermodynamic potentials and correlation functions have not been studied in detail (cf. with Ref. 3).

2. BASIC EQUATIONS

We consider the structure and correlation properties of the polar molecules in the adsorbed submonolayer. The limitation to a single monolayer (instead of the more general discussion on the multilayer filling of the substrate surface) is justified, perhaps, for the adsorbents of the high expressed chemical interactions with the adsorbate molecules. In this case the monolayer of the molecules is formed with the mobility and orientation sharply different from the corresponding properties of volume phase (see below). The monolayer limited by the substrate on one side is submerged in the "solvent," consisting of the molecules of the monolayer itself as well as the molecules of different nature which are in the space above the monolayer.

Consider the calculation of the configurational integral

$$Q_N(T, S) = \frac{1}{S^N} \int \exp(-\beta_B U_N)(d\Gamma) \tag{1}$$

for a system of interacting molecules in an adsorbtion monolayer with surface area S. Here $\beta_B = 1/k_B T$, Boltzmann's constant k_B and Kelvin temperature T, the integration in (1) extends over the configurational space of N molecules, $(d\Gamma) = \prod_{i=1}^{N} d\Gamma_i$ where $d\Gamma_i = d\mathbf{R}_i\, d\zeta_i$, $d\mathbf{R}_i$ the surface element and $d\zeta_i$ is related to the element of space angle $d\Omega_i$ with the relation $d\zeta_i = d\Omega_i/2\pi$.

The total potential energy of the system may be represented as

$$U_N = \mathscr{U}(\Omega) + U(\mathbf{R}, \Omega) \tag{2}$$

where the first term is the sum of one-body interactions, including the energy of the molecule possessing the dipole moment d_i and locayed at point i of the surface in the external electric field E_0, and the energy of interaction between the molecule and the surface

$$\mathscr{U}(\Omega)=\sum_{i=1}^{N} u(\Gamma_i)=\sum_{i=1}^{N}\left[-E_0 d_i+u_0(\Omega_i)\right] \tag{3}$$

the second term results from the two-body interactions of the particles located at points i, j,

$$U(R,\Omega)=\sum_{u<j} v(\Gamma_i,\Gamma_j)=\sum_{i<j} v(\mathbf{R}_{ij},\Omega_i,\Omega_j) \tag{4}$$

with $\mathbf{R}_{ij}=\mathbf{R}_j-\mathbf{R}_i$.

For this last term the following standard-form expansion is valid:

$$v(R_{ij},\Omega_i,\Omega_j)=\sum_{m_1,m_2,\lambda} v^{\mu_1\mu_2}_{m_1,m_2,\lambda}(R_{ij})\, Y^{\mu_1}_{m_1}(\Omega_i)\, Y^{\mu_2}_{m_2}{}^*(\Omega_j)\, \phi_\lambda(\varphi_{\mathbf{R}_{ij}}) \tag{5}$$

with $\phi_\lambda(\varphi_{\mathbf{R}_{ij}})=\exp(i\lambda\varphi_{\mathbf{R}_{ij}})$, $\varphi_{\mathbf{R}_{ij}}$ is the azimuth angle of radius vector $\mathbf{R}_{ij}$, $Y^{\mu_1}_{m_1}(\Omega_i)$ the spherical function dependent on the molecular orientation, and an asterisk denotes the complex conjugated value. The coefficients of expansion (5) are

$$v^{\mu_1\mu_2}_{m_1m_2\lambda}(R_{ij})=(2\pi)^{-1}\int v(\mathbf{R}_{ij},\Omega_i,\Omega_j)\, Y^{\mu_1}_{m_1}{}^*(\Omega_i)\, Y^{\mu_2}_{m_2}(\Omega_j)\, \phi^*_\lambda(\varphi_{R_{ij}})\, d\varphi_{\mathbf{R}_{ij}}\, d\Omega_i\, d\Omega_j$$

The requirement of the spatial uniformity implies the following symmetry restrictions on the function $v(\mathbf{R}_{ij},\Omega_i,\Omega_j)$:

(i) It must be invariant with respect to translations.

(ii) It must be rotation invariant with respect to the simultaneous variations of the azimuth angles φ_i, φ_j, which determine the orientations of ith and jth molecules, and the variation of anfle $\varphi_{R_{ij}}$, if these variations are equal to each other.

(iii) It must be invariant with respect to transpositions of two molecules.

(iv) The expression (5) must be real.

Here we consider the axial-symmetric molecules possessing the dipole moment directed along the axis which can be inclined to the adsorbent surface. In other words, we investigate the orientational ordering due to the pair interactions, dependent on the orientations of the molecule (e.g., the dipole–dipole potential) and independent of the geometrical shape of the molecules. Otherwise, when the "irregular shape" of the molecules is to be considered, the above symmetry conditions must be attended with the requirement of the invariance of expressions (5) with respect to the symmetry group of an adsorbed molecule. This case, which seems to be the most general one, corresponds to the interference of ordering effects due to both the tenzor character of the orientational dependence of intermolecular orientational potential and the geometrical shape of the molecules.

Assuming the above symmetry conditions, one can transform the expression (5) to

$$v(R_{ij}, \Omega_i, \Omega_j) = \sum_{\substack{m_1, m_2 \\ \mu_1, \mu_2}} v_{m_1 m_2}^{\mu_1 \mu_2}(R_{ij})\, Y_{m_1}^{\mu_1}(\Omega_i)\, Y_{m_2}^{\mu_2 *}(\Omega_j)\, \phi_{\mu_2 - \mu_1}(\varphi_{\mathbf{R}_{ij}}) \tag{6}$$

with the following relations valid for the coefficients:

$$\begin{aligned} v_{m_1 m_2}^{\mu_1 \mu_2}(R_{12}) &= v_{m_2 m_1}^{-\mu_2, -\mu_1}(R_{12}) \\ v_{m_1 m_2}^{\mu_1 \mu_2}(R_{12}) &= (-1)^{\mu_1 - \mu_2} v_{m_1 m_2}^{-\mu_1, -\mu_2 *}(R_{12}) \end{aligned} \tag{7}$$

For the dipole–dipole interaction between the adsorbed molecules, for example,

$$v_{dd}(R_{12}, \Omega_1, \Omega_2) = -\frac{1}{\varepsilon_1 R_{12}^3} \{[3(\mathbf{d}_1 \mathbf{n})(\mathbf{d}_2 \mathbf{n}) - \mathbf{d}_1'' \mathbf{d}_2''](1-\kappa) - d_1^{\perp} d_2^{\perp}(1+\kappa)\} \tag{8}$$

the nonzero coefficients of expansion (6) are

$$\begin{gathered} v_{11}^{00}(R_{12}) = \frac{8\pi\varepsilon_2 d^2}{3\varepsilon_1(\varepsilon_1 + \varepsilon_2) R_{12}^3}, \qquad v_{11}^{-1,1}(R_{12}) = v_{11}^{1,-1}(R_{12}) = \frac{4\pi d^2}{(\varepsilon_1 + \varepsilon_2) R_{12}^3} \\ v_{11}^{11}(R_{12}) = v_{11}^{-1,-1}(R_{12}) = -\frac{4\pi d^2}{3(\varepsilon_1 + \varepsilon_2) R_{12}^3} \end{gathered} \tag{9}$$

with $\mathbf{d}_i''$, $\mathbf{d}_i^{\perp}$ $(i = 1, 2)$ the lateral and transverse component of the dipole moment $\mathbf{d}$ of molecule, respectively, $\mathbf{n}$ the unit vector directed along the radius vector $\mathbf{R}_{12}$, $\kappa = (\varepsilon_2 - \varepsilon_1)/(\varepsilon_2 + \varepsilon_1)$, ε_1, ε_2 the permittivities of the media adjacent to the interface from the adsorbed phase and the substrate, respectively.

The relations (7) are clearly valid for the coefficients of (9). As to expression (8), its validity requires not only the condition $R_{12} \gg l$ (l is the dipole lever), but also the condition $R_{12} \gg h$ (h is the distance between the dipole and interface) is to hold. Note that besides the dipole–dipole pair interaction, a self-image potential on a dipole given by Ref. 12

$$u_{im}(\Omega) = -\frac{\kappa d^2}{2\varepsilon_1 (2h)^3} (1 + \cos^2 \vartheta) \tag{8a}$$

has to contribute into $u_0(\Omega)$ in (3).

Because of the chemical interaction of the molecular dipole with the surface of the noninert adsorbent, the dipole can be directed either "to" or "from" the surface, the orientation depends on the structure of the surface and the type of the molecule. For example on the surface formed by protons, the dipole moment of the water molecule is directed from the surface. This unipolar orientation of the molecular dipoles near the surface is shown to exist by the measurements of the potential jump with the adsorbtion of polar molecules.(13)

The preferential orientation of the dipoles at the absorbent surface results in the ranging of the polar angle ϑ of the dipole orientation between 0 and $\pi/2$ (see Section 5). (Note that the interval $0 \leqslant \vartheta \leqslant \pi$ would correspond to the account of all possible orientations of the dipole). The potential $u_0(\vartheta)$ is to be symmetric about $\vartheta = 0$ due to the homogeneity of the surface. We approximate the behavior of $u_0(\vartheta)$ by some function (see Section 5) which takes into account the restriction of the angle ϑ, and accumulates the contributions of both the orienting effect of the surface and the expression (8a).

Perhaps the term *spontaneous polarization* is not quite correct in this case as the change in symmetry of the molecules–dipoles arrangement occur not in free but in partially oriented admonolayer ($0 \leqslant \vartheta \leqslant \pi/2$). Although the appearence of surface component of polarization is obliged to interactions between admolecules in the system.

It is to be noted that the proposed model of the adsorbed monolayer of polar molecules is by no means general. One can consider the alternative model of the adsorbtion of polar molecules on the inert substrate with the interaction energy between the surface and the moleculare dipole independent of whether the dipole is oriented "to" or "from" the surface. In this case the potential $u_0(\vartheta)$ will symmetrical about $\vartheta = \pi/2$ [see Eq. (8a)]. The corresponding treatment can be performed about for such a model following the lines of the present paper, the differences between them will arise in Section 5, where the numerical estimates are obtained. The ranging of the polar angle of dipole orientation between 0 and π, and the symmetry of the potential $u_0(\vartheta)$ about $\vartheta = \pi/2$ would lead, as it seems, to the "antiferromagnetic" type of ordering of the molecules instead of the "ferromagnetic" one, obtained below for the present model.

As mentioned at the beginning of Section 1, the pair interaction potential can always be conventionally divided into two parts,

$$v(\mathbf{R}_{ij}, \Omega_i, \Omega_j) = \varphi(R_{ij}) + \Phi(\mathbf{R}_{ij}, \Omega_i, \Omega_j) \tag{10}$$

with $\varphi(R_{ij})$ the short-range pair interaction independent of the orientation and decreasing quite rapidly with distance (see below) and $\Phi(\mathbf{R}_{ij}, \Omega_i, \Omega_j)$ the long-range part which determines the orientational properties of the system.

The expression (6) together with the relations (7) is valid for the long-range part of the potential,

$$\Phi(\mathbf{R}_{ij}, \Omega_i, \Omega_j) = \sum_{\substack{m_1, m_2 \\ \mu_1, \mu_2}} \phi^{\mu_1 \mu_2}_{m_1 m_2}(R_{ij})\, Y^{\mu_1}_{m_1}(\Omega_i)\, Y^{\mu_2 *}_{m_2}(\Omega_j)\, \phi_{\mu_2 - \mu_1}(\varphi_{\mathbf{R}_{ij}}) \tag{11}$$

where

$$\phi^{\mu_1 \mu_2}_{m_1 m_2}(R_{ij}) = (2\pi)^{-1} \int \Phi(\mathbf{R}_{ij}, \Omega_i, \Omega_j)\, Y^{\mu_1 *}_{m_1}(\Omega_i)\, Y^{\mu_2}_{m_2}(\Omega_j)\, \phi^{*}_{\mu_2 - \mu_1}(\varphi_{R_{ij}}) \times d\Omega_i\, d\Omega_j\, d\varphi_{R_{ii}} \tag{12}$$

and

$$\phi^{\mu_1 \mu_2}_{m_1 m_2}(R_{12}) = \phi^{-\mu_2, -\mu_1}_{m_2 m_1}(R_{12}), \qquad \phi^{\mu_1 \mu_2}_{m_1 m_2}(R_{12}) = (-1)^{\mu_1 - \mu_2} \phi^{-\mu_1, -\mu_2}_{m_1 m_2}(R_{12}) \tag{13}$$

To introduce the collective variables we now proceed to the Fourier representation of the function $\Phi(\mathbf{R}_{ij}, \Omega_i, \Omega_j)$. Using the familiar relation

$$\exp(i\mathbf{k}\mathbf{R}_{ij}) = \sum_{s=-\infty}^{\infty} i^s \mathscr{E}_s(kR_{ij}) \exp[i(\varphi_{\mathbf{k}} - \varphi_{\mathbf{R}_{ij}})s]$$

with $\mathscr{E}_s(kR_{ij})$ the Bessel function of sth order, φ_k the azimuth angle of vector k, one can transform (11) into the expression

$$\phi(R_{ij}, \Omega_i, \Omega_j) = \frac{1}{S} \sum_k \exp(-i\mathbf{k}\mathbf{R}_{ij}) \sum_{\substack{m_1, m_2 \\ \mu_1, \mu_2}} \phi^{\mu_1 \mu_2}_{m_1, m_2}(k)\, Y^{\mu_1}_{m_1}(\Omega_i) \times Y^{\mu_2 *}_{m_2}(\Omega_j)\, \phi_{\mu_2 - \mu_1}(\varphi_{\mathbf{k}}) \tag{14}$$

$$\phi^{\mu_1 \mu_2}_{m_1 m_2}(k) = 2\pi i^{\mu_2 - \mu_1} \int_0^\infty \mathscr{E}_{\mu_2 - \mu_1}(kR)\, \phi^{\mu_1 \mu_2}_{m_1 m_2}(R) R\, dR$$

where the summation extends over all wave vector components of the system.

The total long-range interaction potential can now be expressed in the form

$$\begin{aligned} \phi(R, \Omega) &= \sum_{i<j} \Phi(\mathbf{R}_{ij}, \Omega_i, \Omega_j) \\ &= \frac{1}{2\beta_B} \sum_{k \neq 0} \Bigg[\sum_{\substack{m_1, m_2 \\ \mu_1, \mu_2}} \alpha^{\mu_1 \mu_2}_{m_1 m_2}(k)\, \hat{\rho}^{\mu_1}_{m_1}(\mathbf{k})\, \hat{\rho}^{\mu_2 *}_{m_2}(\mathbf{k}) \\ &\quad - \frac{1}{N} \sum_{\substack{m_1, m_2 \\ \mu_1, \mu_2}} \alpha^{\mu_1 \mu_2}_{m_1 m_2}(k)\, Y^{\mu_1}_{m_1}(\Omega_i)\, Y^{\mu_2 *}_{m_2}(\Omega_j)\, \phi_{\mu_2 - \mu_1}(\varphi_{\mathbf{k}}) \Bigg] + \frac{1}{S} \sum_{i<j} \phi(\Omega_i, \Omega_j) \end{aligned} \tag{15}$$

where

$$\phi(\Omega_i, \Omega_j) = \int \Phi(\mathbf{R}_{12}, \Omega_i, \Omega_j)\, d\mathbf{R}_{12}, \qquad \alpha^{\mu_1\mu_2}_{m_1m_2}(k) = \beta_B \rho_0 \phi^{\mu_1\mu_2}_{m_1m}(k)$$

$$\hat{\rho}^{\mu_1}_{m_1}(\mathbf{k}) = \frac{1}{\sqrt{N}} \sum_{i=1}^{N} \exp(i\mathbf{k}\mathbf{R}_i)\, Y^{\mu_1}_{m_1}(\Omega_i)\, \phi_{-\mu_1}(\varphi_{\mathbf{k}})$$

is the Fourier transformant of the fluctuation of density operator, $\rho_0 = N/S$ is the density of molecules in the adsorbed monolayer. The last term in (15) is due to the large-scale fluctutions in the system.

Separating the real and imaginary parts of the Fourier transformant $\rho^{\mu}_{m}(\mathbf{k})$, one can represent the function for transfer form (R)—to (ρ)—space of the collective variables as follows[2,3]:

$$\begin{aligned}
\mathscr{E}(\rho, R, \Omega) &= \prod_{k \neq 0} \prod_{m,\mu} \delta(\rho^{\mu}_{m}(\mathbf{k}) - \hat{\rho}^{\mu}_{m}(\mathbf{k})) \\
&= \int \exp\left[2\pi i \sum_{k \neq 0}{}' \sum_{m,\mu} \omega^{\mu c}_{m}(\mathbf{k})(\rho^{\mu c}_{m}(\mathbf{k}) - \hat{\rho}^{\mu c}_{m}(\mathbf{k}))\right. \\
&\quad \left. + \, \omega^{\mu s}_{m}(\mathbf{k})(\rho^{\mu s}_{m}(\mathbf{k}) - \hat{\rho}^{\mu s}_{m}(\mathbf{k}))\right] (d\omega) \\
&= \int \exp\left[\pi i \sum_{\mathbf{k} \neq 0} \sum_{m,\mu} \omega^{\mu}_{m}(\mathbf{k})(\rho^{\mu}_{m}(\mathbf{k}) - \hat{\rho}^{\mu}_{m}(\mathbf{k}))\right] (d\omega)
\end{aligned} \tag{16}$$

where $(d\omega)$ stands for the phase space elemental volume of variables ω, $\prod'_{\mathbf{k}\neq 0} \prod_{m,\mu} d\omega^{\mu c}_{m}(\mathbf{k})\, d\omega^{\mu s}_{m}(\mathbf{k})$, the Fourier transformant $\hat{\rho}^{\mu}_{m}(\mathbf{k})$, the collective variable $\rho^{\mu}_{m}(k)$ and an auxiliary variable $\omega^{\mu}_{m}(\mathbf{k})$ are split into the real and imaginary parts

$$\hat{\rho}^{\mu}_{m}(\mathbf{k}) = \hat{\rho}^{\mu c}_{m}(\mathbf{k}) - i\hat{\rho}^{\mu s}_{m}(\mathbf{k})$$

$$\rho^{\mu}_{m}(\mathbf{k}) = \rho^{\mu c}_{m}(\mathbf{k}) - i\rho^{\mu s}_{m}(\mathbf{k})$$

$$\omega^{\mu}_{m}(\mathbf{k}) = \omega^{\mu c}_{m}(\mathbf{k}) + i\omega^{\mu s}_{m}(\mathbf{k})$$

the primed sum and product extend over the upper half-space. When deriving (16) we used the requirement of reality of the scalar products $\sum_{\mathbf{k}\neq 0} \sum_{m,\mu} \hat{\rho}^{\mu}_{m}(\mathbf{k})\, \omega^{\mu}_{m}(\mathbf{k})$ and $\sum_{k\neq 0} \sum_{m,\mu} \rho^{\mu}_{m}(\mathbf{k})\, \omega^{\mu}_{m}(\mathbf{k})$ leading to the following relations:

$$\begin{aligned}
(-1)^M \omega^{-\mu}_{m}(-\mathbf{k}) &= \omega^{\mu}_{m}{}^{*}(\mathbf{k}) \\
(-1)^M \hat{\rho}^{-\mu}_{m}(-\mathbf{k}) &= \hat{\rho}^{\mu}_{m}{}^{*}(\mathbf{k}) \\
(-1)^M \rho^{-\mu}_{m}(-\mathbf{k}) &= \rho^{\mu}_{m}{}^{*}(\mathbf{k})
\end{aligned} \tag{17}$$

Introducing the expressions (2)–(4), (10), (15), (16) into (1), one obtains

$$Q_N(T,S)=\frac{1}{S^N}\int \mathscr{E}(\rho,R,\Omega)\exp[-\beta_B U_0(R)-\beta_B\phi(\rho,\Omega)-\beta_B\mathscr{U}(\Omega)] \times (dR)(d\zeta)(d\rho) \qquad (18)$$

$$\begin{aligned}\phi(\rho,\Omega)=\frac{1}{2\beta_B}\sum_{\mathbf{k}\neq 0}\Bigg[&\sum_{\substack{m_1,m_2\\ \mu_1,\mu_2}} \alpha^{\mu_1\mu_2}_{m_1m_2}(k)\,\rho^{\mu_1}_{m_1}(\mathbf{k})\,\rho^{\mu_2 *}_{m_2}(\mathbf{k})\\ &-\frac{1}{N}\sum_{\substack{m_1,m_2\\ \mu_1,\mu_2}}\sum_{i=1}^{N}\alpha^{\mu_1\mu_2}_{m_1m_2}(k)\,Y^{\mu_1}_{m_1}(\Omega_i)\,Y^{\mu_2 *}_{m_2}(\Omega_j)\,\phi_{\mu_2-\mu_1}(\varphi_{\mathbf{k}})\Bigg]\\ &+\frac{1}{S}\sum_{i<j}^{N}\phi(\Omega_i,\Omega_j)\end{aligned}$$

for the configurational integral of the system. Here $U_0(R)=\sum_{i<j}^{N}\varphi(R_{ij})$ is the net potential from short-range interaction, $(dR)=\prod_{i=1}^{N}dR_i$, $(d\zeta)=\prod_{i=1}^{N}d\zeta_i$, $(d\rho)=\prod'_{k\neq 0}\prod_{m,\mu}d\rho^{\mu c}_{m}(\mathbf{k})\,d\rho^{\mu s}_{m}(\mathbf{k})$ the elemental volume of the collective variables phase space.

In fact, the expression (16) for the configurational integral seems to be much more involved than the original formula (1) since it contains the integration in the collective variables phase space in addition to the integration in the configurational space. If, however, one restricts oneself to the calculation of the variation of configurational integral due to the long-range orientational interactions in the system, without the calculation of the integral itself, the expression (18) turns out to be very useful.

Define first the reference system, relative to which the ordering will be considered:

$$Q_{SF}=\frac{1}{S^N}\int\exp\left[-\beta_B U_0(R)-\beta_B\mathscr{U}(\Omega)-\frac{\beta_B}{S}\sum_{i<j}^{N}\phi(\Omega_i,\Omega_j)\right](dR)(d\zeta) \qquad (19)$$

where the net potential in addition to the terms describing the one-body and two-body short-range interactions contains the term describing the long-range fluctuations.

The configurational integral (19) can be used as a basis for the calculation of the distribution functions of the system. First it should be noted that these functions may be separated into coordinate and angular parts

$$\rho^{(n)}(R_1,\dots,R_n,\Omega_1,\dots,\Omega_n)=\rho^{(n)}(R_1,\dots,R_n)\,F^{(n)}(\Omega_1,\dots,\Omega_n) \qquad (20)$$

$$\rho^{(n)}(\mathbf{R}_1,\dots,\mathbf{R}_n)=N(N-1)\cdots(N-n+1)\frac{\int \exp[-\beta_B U_0(R)]\,dR_{n+1}\cdots dR_N}{\int \exp[-\beta_B U_0(R)](dR)}$$

$$F^{(n)}(\Omega_1,\dots,\Omega_n)=\frac{\int \exp[-\beta_B \mathscr{U}(\Omega)-(\beta_B/S)\sum_{i<j}^N \phi(\Omega_i,\Omega_j)]\,d\zeta_{n+1}\cdots d\zeta_N}{\int \exp[-\beta_B \mathscr{U}(\Omega)-(\beta_B/S)\sum_{i<j}^N \phi(\Omega_i,\Omega_j)](d\zeta)}$$

We shall calculate the correlation function $F^{(n)}(\Omega_1,\dots,\Omega_n)$ (up to the arbitrary high order) using the multiplicative splitting approximation:

$$F_0^{(n)}(\Omega_1,\dots,\Omega_n)=\prod_{i=1}^{n} F_0^{(n)}(\Omega_i) \tag{21}$$

Assuming this approximation to be valid, one can perform the integration in the equation for the singlet correlation function

$$\frac{\partial \ln F^{(1)}(\Omega_1)}{\partial \vartheta_1}=-\beta_B\frac{\partial \mathscr{U}(\Omega_1)}{\partial \vartheta_1}-\beta_B\rho_0\int \frac{F^{(2)}(\Omega_1,\Omega_2)}{F^{(1)}(\Omega_1)}\frac{\partial \phi(\Omega_1,\Omega_2)}{\partial \vartheta_1}\,d\Omega_2 \tag{22}$$

(where ϑ_1 is the polar angle which determines the molecular orientation), to obtain

$$F_0^{(1)}(\Omega_1)=\frac{\exp[-\beta_B\mathscr{U}(\Omega_1)-\beta_B\rho_0\int \phi(\Omega_1,\Omega_2)F_0^{(1)}(\Omega_1)\,d\Omega_2]}{\int \exp[-\beta_B\mathscr{U}(\Omega_1)-\beta_B\rho_0\int \phi(\Omega_1,\Omega_2)F_0^{(1)}(\Omega_2)\,d\Omega_2]\,d\Omega_1} \tag{23}$$

The expression (23) is the transcendental equation which can be used to determine the constants characteristic to the singlet correlation function. Some examples of its usage will be given below.

Using Eqs. (18), and (19) the configurational integral can be expressed as

$$Q_N(T,S)=Q_{SF}\int \mathscr{E}(\rho)\exp\left[-\frac{1}{2}\sum_{k\neq 0}\sum_{\substack{m_1,m_2\\ \mu_1,\mu_2}} \alpha_{m_1m_2}^{\mu_1\mu_2}(k)\,\rho_{m_1}^{\mu_1}(\mathbf{k})\,\rho_{m_2}^{\mu_2}{}^*(\mathbf{k})\right](d\rho) \tag{24}$$

$$\begin{aligned}\mathscr{E}(\rho)=\frac{1}{S^N Q_{SF}}\int \mathscr{E}(\rho,R,\Omega)\exp\Bigg[&-\beta_B U_0(R)-\beta_B\mathscr{U}(\Omega)\\ &+\frac{1}{2N}\sum_{k\neq 0}\sum_{\substack{m_1,m_2\\ \mu_1,\mu_2}}\sum_{i=1}^{N}\alpha_{m_1m_2}^{\mu_1\mu_2}(k)\,Y_{m_1}^{\mu_1}(\Omega_i)\,Y_{m_2}^{\mu_2}{}^*(\Omega_i)\,\phi_{\mu_2-\mu_1}(\varphi_{\mathbf{k}})\\ &-\frac{\beta_B}{S}\sum_{i<j}^{N}\phi(\Omega_i,\Omega_j)\Bigg](dR)(d\zeta)\end{aligned} \tag{25}$$

and, of course, the crucial point in the calculation of the configuration integral is the accuracy in determining the Jacobian for the transfer to the collective variables space.

Using Eq. (16) one obtains for the Jacobian an expression

$$\begin{aligned}\mathscr{E}(\rho) = {} & \frac{1}{S^N Q_{SF}} \int (d\omega) \exp\left[i\pi \sum_{\mathbf{k}\neq 0} \sum_{m,\mu} \omega_m^\mu(\mathbf{k})\, \rho_m^\mu(\mathbf{k}) \right] \\ & \times \int (dR)(d\zeta) \exp\Bigg[-\beta_B U_0(R) - \beta_B \mathscr{U}(\Omega) \\ & + \frac{1}{2N} \sum_{\mathbf{k}\neq 0} \sum_{\substack{m_1, m_2 \\ \mu_1, \mu_2}} \sum_{i=1}^{N} \alpha_{m_1 m_2}^{\mu_1 \mu_2}(k)\, Y_{m_1}^{\mu_1}(\Omega_i)\, Y_{m_2}^{\mu_2 *}(\Omega_i)\, \phi_{\mu_2-\mu_1}(\varphi_{\mathbf{k}}) \\ & - \frac{\beta_B}{S} \sum_{i<j}^{N} \phi(\Omega_i, \Omega_j) - i\pi \sum_{\mathbf{k}\neq 0} \sum_{m,\mu} \omega_m^\mu(\mathbf{k})\, \hat{\rho}_m^\mu(\mathbf{k}) \Bigg]\end{aligned}$$

where the second integral represents the Fourier transformant of $\mathscr{E}(\rho)$; it follows then that

$$\mathscr{E}(\rho) = \int \mathscr{E}(\omega) \exp\left[i\pi \sum_{\mathbf{k}\neq 0} \sum_{m,\mu} \omega_m^\mu(\mathbf{k})\, \rho_m^\mu(\mathbf{k}) \right] (d\omega) \tag{26}$$

$$\begin{aligned}\mathscr{E}(\omega) = {} & \frac{1}{S^N Q_{SF}} \int \exp\Bigg[-\beta_B U_0(R) - \beta_B \mathscr{U}(\Omega) \\ & - \frac{1}{2N} \sum_{\mathbf{k}\neq 0} \sum_{m_1 m_2} \sum_{i=1}^{N} \alpha_{m_1 m_2}^{\mu_1 \mu_2}(k)\, Y_{m_1}^{\mu_1}(\Omega_i)\, Y_{m_2}^{\mu_2 *}(\Omega_i)\, \phi_{\mu_2-\mu_1}(\varphi_{\mathbf{k}}) \\ & - \frac{\beta_B}{S} \sum_{i<j=1}^{N} \phi(\Omega_i \Omega_j) - i\pi \sum_{\mathbf{k}\neq 0} \sum_{m,\mu} \omega_m^\mu(\mathbf{k})\, \hat{\rho}_m^\mu(\mathbf{k}) \Bigg] (dR)(d\zeta)\end{aligned} \tag{27}$$

One can define the semi-invariant expansions of the exponent argument in (27)(14)

$$\left\langle \exp\left(\sum_{i=1}^{N} \xi_i x_i \right) \right\rangle = \exp\left[\sum_{\nu_1, \dots, \nu_N} \left(\prod_i \frac{1}{\nu_i !} \xi_i^{\nu_i} \right) \langle x_1^{\nu_1} \cdots x_N^{\nu_N} \rangle_s \right] \tag{28}$$

introducing the semi-invariants $\langle x_1^{\nu_1} \cdots x_N^{\nu_N} \rangle_s$, the term with $\nu_1 = \cdots = \nu_N = 0$ is to be excluded from the sum in (28). The averaging in (28) is performed with respect to the distribution determined by the SCMF approximation (19). The first few semi-invariants are

$$\langle x_1 \rangle_s = \langle x_1 \rangle, \qquad \langle x_1 x_2 \rangle_s = \langle x_1 x_2 \rangle - \langle x_1 \rangle \langle x_2 \rangle,$$

$$\begin{aligned}\langle x_1 x_2 x_3 \rangle_s = {} & \langle x_1 x_2 x_3 \rangle - [\langle x_1 x_2 \rangle \langle x_3 \rangle + \langle x_1 x_3 \rangle \langle x_2 \rangle + \langle x_2 x_3 \rangle \langle x_1 \rangle] \\ & + 2 \langle x_1 \rangle \langle x_2 \rangle \langle x_3 \rangle\end{aligned}$$

Using Eq. (28) one can transform (27) to obtain the following exponential form:

$$\mathscr{E}(\omega) = \exp\left[\frac{1}{2}\sum_{\mathbf{k}\neq 0}\sum_{\substack{m_1 m_2\\ \mu_1\mu_2}} \alpha^{\mu_1\mu_2}_{m_1 m_2}(k)\langle Y^{\mu_1}_{m_1} Y^{\mu_2}_{m_2}{}^{*}\rangle\, \Phi_{\mu_2-\mu_1}(\varphi_{\mathbf{k}}) + \sum_{n\geqslant 2}\mathscr{D}_n(\omega)\right] \tag{29}$$

where

$$\mathscr{D}_n(\omega) = \frac{(-i\pi)^n}{n!\,(N^n)^{1/2}}\sum_{\mathbf{k}_1,\ldots,\mathbf{k}_n}\sum_{\substack{m_s,\mu_s\\ (1\leqslant s\leqslant n)}} \omega^{\mu_1}_{m_1}(\mathbf{k}_1)\cdots\omega^{\mu_n}_{m_n}(\mathbf{k}_n)\,\mathscr{M}^{\mu_1\cdots\mu_n}_{m_1\cdots m_n}(\mathbf{k}_1,\ldots,\mathbf{k}_n) \tag{30}$$

$$\frac{N}{(N^n)^{1/2}}\mathscr{M}^{\mu_1\cdots\mu_n}_{m_1\cdots m_n}(\mathbf{k}_1,\ldots,\mathbf{k}_n) = \langle\hat\rho^{\mu_1}_{m_1}(\mathbf{k}_1)\cdots\hat\rho^{\mu_n}_{m_n}(\mathbf{k}_n)\rangle_s$$

The first term in the exponent in (29) implies the multiplicative approximation for the orientational correlational function. Otherwise it should involve the infinite sum over the semi-invariants defined in (28). The value of $\mathscr{M}^{\mu_1\cdots\mu_n}_{m_1\cdots m_n}(\mathbf{k}_1,\ldots,\mathbf{k}_n)$ which is the nth order semi-invariant resulting from the averaging of the expression $\exp[-i\pi\sum_{\mathbf{k}\neq 0}\sum_{m,\mu}\omega^{\mu}_{m}(\mathbf{k})\hat\rho^{\mu}_{m}(\mathbf{k})]$ in $\mathscr{E}(\omega)$ represents the tensor component of the structure factor of the system.

Using formula (30) one can calculate the tensor components for some structure factors:

$$\begin{aligned}\mathscr{M}^{\mu_1\mu_2}_{m_1 m_2}(\mathbf{k}_1,\mathbf{k}_2) &= \frac{1}{N}\left[\langle Y^{\mu_1}_{m_1} Y^{\mu_2}_{m_2}\rangle\sum_{j=1}^{N}\exp[i(\mathbf{k}_1+\mathbf{k}_2)\mathbf{R}_j]\right.\\ &\quad\left. + \langle Y^{\mu_1}_{m_1}\rangle\langle Y^{\mu_2}_{m_2}\rangle\sum_{l\neq j}^{N}\langle\exp[i(\mathbf{k}_1\mathbf{R}_l+\mathbf{k}_2\mathbf{R}_j)]\rangle_s\right]\phi_{-\mu_1-\mu_2}(\varphi_{\mathbf{k}}) \qquad (31)\\ &= \left[\langle Y^{\mu_1}_{m_1} Y^{\mu_2}_{m_2}\rangle\delta_{\mathbf{k}_1+\mathbf{k}_2,0} + \frac{1}{N}\rho_0^2\langle Y^{\mu_1}_{m_1}\rangle\langle Y^{\mu_2}_{m_2}\rangle\, h^{(2)}(\mathbf{k}_1,\mathbf{k}_2)\right]\phi_{-\mu_1}(\varphi_{\mathbf{k}_1})\,\phi_{-\mu_2}(\varphi_{\mathbf{k}_2})\end{aligned}$$

$$\begin{aligned}\mathscr{M}^{\mu_1\mu_2\mu_3}_{m_1 m_2 m_3}(\mathbf{k}_1,\mathbf{k}_2,\mathbf{k}_3) = \Bigg\{&\left\langle\prod_{i=1}^{3} Y^{\mu_i}_{m_i}\right\rangle\ \delta_{\mathbf{k}_1+\mathbf{k}_2+\mathbf{k}_3,0}\\ &+\frac{1}{N}\rho_0^2[\langle Y^{\mu_1}_{m_1}\rangle\langle Y^{\mu_2}_{m_2} Y^{\mu_3}_{m_3}\rangle\, h^{(2)}(\mathbf{k}_1,\mathbf{k}_2+\mathbf{k}_3)\\ &+\langle Y^{\mu_2}_{m_2}\rangle\langle Y^{\mu_1}_{m_1} Y^{\mu_3}_{m_3}\rangle\, h^{(2)}(\mathbf{k}_2,\mathbf{k}_1+\mathbf{k}_3)\\ &+\langle Y^{\mu_3}_{m_3}\rangle\langle Y^{\mu_1}_{m_1} Y^{\mu_2}_{m_2}\rangle\, h^{(2)}(\mathbf{k}_3,\mathbf{k}_1+\mathbf{k}_2)]\\ &+\frac{1}{N}\rho_0^3 h^{(3)}(\mathbf{k}_1,\mathbf{k}_2,\mathbf{k}_3)\prod_{i=1}^{3}\langle Y^{\mu_i}_{m_i}\rangle\Bigg\}\ \prod_{i=1}^{3}\phi_{-\mu_i}(\varphi_{\mathbf{k}_i})\end{aligned} \tag{32}$$

where

$$j^{(2)}(\mathbf{k}_1,\mathbf{k}_2)=\int h^{(2)}(\mathbf{R}_1,\mathbf{R}_2)\exp[i(\mathbf{k}_1\mathbf{R}_1+\mathbf{k}_2\mathbf{R}_2)]\,d\mathbf{R}_1\,d\mathbf{R}_2$$

$$h^{(3)}(\mathbf{k}_1,\mathbf{k}_2,\mathbf{k}_3)=\int h^{(3)}(\mathbf{R}_1,\mathbf{R}_2,\mathbf{R}_3)\exp[i(\mathbf{k}_1\mathbf{R}_1+\mathbf{k}_2\mathbf{R}_2+\mathbf{k}_3\mathbf{R}_3)]\,d\mathbf{R}_1\,d\mathbf{R}_2\,d\mathbf{R}_3$$

are the Fourier representations of binary and ternary coordinate correlation functions (20):

$$\begin{aligned}
h^{(2)}(\mathbf{R}_1,\mathbf{R}_2)&=g^{(2)}(\mathbf{R}_1,\mathbf{R}_2)-1\\
h^{(3)}(\mathbf{R}_1,\mathbf{R}_2,\mathbf{R}_3)&=g^{(3)}(\mathbf{R}_1,\mathbf{R}_2,\mathbf{R}_3)-g^{(2)}(\mathbf{R}_1,\mathbf{R}_2)-g^{(2)}(\mathbf{R}_1,\mathbf{R}_3)\\
&\quad-g^{(2)}(\mathbf{R}_2,\mathbf{R}_3)+2\\
\rho_0^{(n)}g^{(n)}(\mathbf{R}_1,\ldots,\mathbf{R}_n)&=\rho^{(n)}(\mathbf{R}_1,\ldots,\mathbf{R}_n)
\end{aligned}$$

The obvious generalization of (3), (31), (32) for the *n*th order semi-invariant $\mathscr{M}^{\mu_1\cdots\mu_n}_{m_1\cdots m_n}(\mathbf{k}_1,\ldots,\mathbf{k}_n)$ is

$$\begin{aligned}
\mathscr{M}^{\mu_1\cdots\mu_n}_{m_1\cdots m_n}(\mathbf{k}_1,\ldots,\mathbf{k}_n)&=\Bigg\{\left\langle\prod_{i=1}^{n}Y^{\mu_i}_{m_i}\right\rangle\delta_{\mathbf{k}_1+\cdots+\mathbf{k}_n,0}\\
&\quad+\frac{1}{2!N}\rho_0^2\sum_{n_1\geqslant1}\sum_{\substack{1\leqslant i_1<\cdots<i_{n_1}\\ i_{n_1+1}<\cdots<i_n}}\left\langle\prod_{j=i_1}^{i_{n_1}}Y^{\mu_j}_{m_j}\right\rangle\left\langle\sum_{j=i_{n_1+1}}^{i_n}Y^{\mu_j}_{m_j}\right\rangle\\
&\quad\times h^{(2)}(\mathbf{k}_{i_1}+\cdots+\mathbf{k}_{i_{n_1}},\mathbf{k}_{i_{n_1+1}}+\cdots+\mathbf{k}_{i_n})\\
&\quad+\frac{1}{3!N}\rho_0^3\sum_{\substack{n_1\geqslant1,n_2\geqslant1\\ n-n_1-n_2\geqslant1}}\sum_{\substack{1\leqslant i_1<\cdots<i_{n_1}\\ i_{n_1+1}<\cdots<i_{n_2}\\ i_{n_2+1}<\cdots<i_n}}\left\langle\prod_{j=i_1}^{i_{n_1}}Y^{\mu_j}_{m_j}\right\rangle\\
&\quad\times\left\langle\prod_{j=i_{n_1+1}}^{i_{n_2}}Y^{\mu_j}_{m_j}\right\rangle\left\langle\prod_{j=i_{n_2+1}}^{i_n}Y^{\mu_j}_{m_j}\right\rangle\\
&\quad\times h^{(3)}(\mathbf{k}_{i_1}+\cdots+\mathbf{k}_{i_{n_1}},\mathbf{k}_{i_{n_1+1}}+\cdots+\mathbf{k}_{i_{n_2}},\mathbf{k}_{i_{n_2+1}}+\cdots+\mathbf{k}_{i_n})+\cdots\\
&\quad+\frac{1}{N}\rho_0^n\prod_{j=1}^{n}\langle Y^{\mu_j}_{m_j}\rangle h^{(n)}(\mathbf{k}_1,\ldots,\mathbf{k}_n)\Bigg\}\prod_{i=1}^{n}\phi_{-\mu_i}(\varphi_{k_i})
\end{aligned}\tag{33}$$

where

$$h^{(n)}(\mathbf{k}_1,\ldots,\mathbf{k}_n)=\int h^{(n)}(\mathbf{R}_1,\ldots,\mathbf{R}_n)\exp[i(\mathbf{k}_1\mathbf{R}_1+\cdots+\mathbf{k}_n\mathbf{R}_n)]\,d\mathbf{R}_1\cdots d\mathbf{R}_n$$

is the Fourier representation of the nth-order coordinate correlation function, and function $h^{(n)}(\mathbf{R}_1,\ldots,\mathbf{R}_n)$ is defined by

$$h^{(n)}(\mathbf{R}_1,\ldots,\mathbf{R}_n)=\sum_{\substack{\{n_i\}\\(\sum_{i=1}^{k}n_i=n)}}(-1)^{k-1}(k-1)!\prod_{i=1}^{k}g^{(n_i)}(\mathbf{R}_{i_1},\ldots,\mathbf{R}_{i_{n_j}})$$

where the sum extends over all possible unconnected subsets of the whole set of variables $\mathbf{R}_1,\ldots,\mathbf{R}_n$, and the product extends over k subsets.

Using (29), (26) can be written in the following operator form[3]:

$$\mathscr{E}(\rho)=\exp\left[\sum_{n\geqslant 3}\hat{\mathscr{D}}_n\left(\frac{\partial}{\partial\rho}\right)\right]\mathscr{E}_G(\rho) \tag{34}$$

where

$$\mathscr{E}_G(\rho)=\int\exp\left[i\pi\sum_{\mathbf{k}\neq 0}\sum_{m,\mu}\omega_m^{\mu}(\mathbf{k})\,\rho_m^{\mu}(\mathbf{k})\right]\mathscr{E}_G(\omega)(d\omega) \tag{35}$$

$$\mathscr{E}_G(\omega)=\exp\left[\frac{1}{2}\sum_{\mathbf{k}\neq 0}\sum_{\substack{m_1m_2\\\mu_1\mu_2}}\alpha_{m_1m_2}^{\mu_1\mu_2}(k)\langle Y_{m_1}^{\mu_1}Y_{m_2}^{\mu_2 *}\rangle\,\phi_{\mu_2-\mu_1}(\varphi_{\mathbf{k}})+\mathscr{D}_2(\omega)\right] \tag{36}$$

$$\hat{\mathscr{D}}_n\left(\frac{\partial}{\partial\rho}\right)=\frac{(-1)^nN}{n!(N^n)^{1/2}}\sum_{\mathbf{k}_1,\ldots,\mathbf{k}_n}\sum_{\substack{m_s,\mu_s\\(1\leqslant s\leqslant n)}}\mathscr{M}_{m_1\cdots m_n}^{\mu_1\cdots\mu_n}(\mathbf{k}_1,\ldots,\mathbf{k}_n)\frac{\partial^n}{\partial\rho_{m_1}^{\mu_1}(\mathbf{k}_1)\cdots\partial\rho_{m_n}^{\mu_n}(\mathbf{k}_n)} \tag{37}$$

The advantage of this form for the Jacobian for the transfer to collective variables is the possibility to calculate the zero approximation to the function $\mathscr{E}(\rho)$ assuming the Gaussian distribution for Fourier components of density fluctuations. In subsequent sections we shall work out the procedure to determine $\mathscr{E}(\rho)$ with respect to $\mathscr{E}_G(\varepsilon)$, the transfer Jacobian in Gaussian approximation.[3]

3. RANDOM PHASES APPROXIMATION

One of the remarkable features of the collective variables method in the form, first proposed in Ref. 2 and developed further in Ref. 3, is the possibility to calculate the configurational integral in the Gaussian approximation, termed RPA.

With the exponent in (34) being omitted, the zero-order approximation is

$$Q_N(T,S)=Q_{SF}\,Q_{RP} \tag{38}$$

with

$$Q_{RP}=\int\mathscr{E}_G(\rho)\exp\left[-\frac{1}{2}\sum_{\mathbf{k}\neq 0}\sum_{\substack{m_1,m_2\\\mu_1,\mu_2}}\alpha_{m_1m_2}^{\mu_1\mu_2}(k)\,\rho_{m_1}^{\mu_1}(\mathbf{k})\,\rho_{m_2}^{\mu_2 *}(\mathbf{k})\right](d\rho) \tag{39}$$

and $\mathscr{E}_G(\rho)$ follows from (35), (36) with the coefficient $D_2(\omega)$, which can be represented using the expressions (17), (31) in the symmetrical form

$$D_2(\omega) = -\frac{\pi^2}{2} \sum_{k \neq 0} \sum_{\substack{m_1, m_2 \\ \mu_1, \mu_2}} \mathscr{M}^{\mu_1, \mu_2}_{m_1, m_2}(k)\, \omega^{\mu_1}_{m_1}(\mathbf{k})\, \omega^{\mu_2 *}_{m_2}(\mathbf{k}) \tag{40}$$

$$\mathscr{M}^{\mu_1 \mu_2}_{m_1 m_2}(k) = [\langle Y^{\mu_1}_{m_1} Y^{\mu_2 *}_{m_2} \rangle + \rho_0 \langle Y^{\mu_1}_{m_1} \rangle \langle Y^{\mu_2 *}_{m_2} \rangle\, h^{(2)}(k)]\, \phi_{\mu_2 - \mu_1}(\varphi_{\mathbf{k}}) \tag{41}$$

Here $h^{(2)}(k) = \int \exp(i\mathbf{k}\mathbf{R}_{12})\, h^{(2)}(\mathbf{R}_{12})\, d\mathbf{R}_{12}$ is the Fourier representation of the coordinate correlation function which for the uniform systems is dependent on the radius vector of the distance between two molecules.

Diagonalizing the quadratic form (40) and reducing the expression (36) to the product of Gaussian integrals one obtains

$$\begin{aligned} \mathscr{E}_G(\rho) = \exp &\left[-\frac{1}{2} \sum_{k \neq 0} \sum_{\substack{m_1, m_2 \\ \mu_1, \mu_2}} (\mathscr{M}^{-1}(k))^{\mu_1 \mu_2}_{m_1 m_2} \rho^{\mu_1}_{m_1}(\mathbf{k})\, \rho^{\mu_2 *}_{m_2}(\mathbf{k}) \right] \\ \times \exp &\left\{ \frac{1}{2} \sum_{\mathbf{k} \neq 0} \left[\sum_{\substack{m_1, m_2 \\ \mu_1, \mu_2}} \alpha^{\mu_1, \mu_2}_{m_1, m_2}(k) \langle Y^{\mu_1}_{m_1} Y^{\mu_2 *}_{m_2} \rangle\, \phi_{\mu_2 - \mu_1}(\varphi_{\mathbf{k}}) \right.\right. \\ &\left.\left. - \ln(\det \pi \mathscr{M}^{\mu_1 \mu_2}_{m_1 m_2}(k)) \right] \right\} \end{aligned} \tag{42}$$

for this expression, where $\det \mathscr{M}^{\mu_1 \mu_2}_{m_1 m_2}(k)$ and $(\mathscr{M}^{-1}(k))^{\mu_1 \mu_2}_{m_1 m_2}$ are the determinant and the matrix inverse to $\mathscr{M}^{\mu_1 \mu_2}_{m_1 m_2}(k)$, respectively. Introducing the expression (42) into (39) and performing the integration one obtains the expression for the Helmholtz free energy,

$$\begin{aligned} \beta_B \mathscr{F} &= -\ln \frac{S^N Q_N(T, S)}{N!} = \beta_B(\mathscr{F}_{id} + \mathscr{F}_{SF} + \mathscr{F}_{RP}) \\ \beta_B \mathscr{F}_{id} &= -\ln \frac{S^N}{N!} \\ \beta_B \mathscr{F}_{SF} &= -\ln Q_{SF} \\ \beta_B \mathscr{F}_{RP} &= -\ln Q_{RP} \\ &= \frac{1}{2} \sum_{\mathbf{k} \neq 0} \left[\ln \det(\hat{I} + \hat{\mathscr{M}}(k)\, \hat{\alpha}(k)) \right. \\ &\quad \left. - \sum_{\substack{m_1, m_2 \\ \mu_1, \mu_2}} \alpha^{\mu_1 \mu_2}_{m_1 m_2}(k) \langle Y^{\mu_1}_{m_1} Y^{\mu_2 *}_{m_2} \rangle\, \phi_{\mu_2 - \mu_1}(\varphi_{\mathbf{k}}) \right] \end{aligned} \tag{43}$$

where $\mathscr{F}_{id}$, $\mathscr{F}_{SF}$, $\mathscr{F}_{RP}$ are the components of the free energy for the classic ideal gas, the SCMF approximation, and the RPA, respectively; $Q_N(T, S)$ in (43) is represented in the form (38); $\hat{\mathscr{M}}(k)$; $\hat{\alpha}(k)$ are the matrices written as operators; $\hat{I}$ is the unit tensor.

The second-order distribution function which is determined by the long-range order interactions in the system can be obtained by differentiating expression (43) with respect to the potential (11):

$$
\begin{aligned}
&\rho_2(R_{12}, \Omega_1, \Omega_2) \\
&\quad = \frac{\delta(\beta_B \mathscr{F}_{SF} + \beta_B \mathscr{F}_{RP})}{\delta\beta_B \Phi(\mathbf{R}_{12}, \Omega_1, \Omega_2)} = \rho_0^2 F_0^{(1)}(\Omega_1)\, F_0^{(1)}(\Omega_2) \\
&\quad + \frac{\rho_0^2}{N} \sum_{\mathbf{k} \neq 0} \sum_{\substack{m_1, m_2 \\ \mu_1, \mu_2}} \exp(-i\mathbf{k}\mathbf{R}_{12})\, Y_{m_1}^{\mu_1 *}(\Omega_1)\, Y_{m_2}^{\mu_2}(\Omega_2) \phi_{\mu_1 - \mu_2}(\varphi_{\mathbf{k}}) \\
&\quad \times \left\{ \frac{\partial}{\partial \alpha_{m_1 m_2}^{\mu_1 \mu_2}(k)} \ln \det(\hat{I} + \hat{\mathscr{M}}(k)\, \hat{\alpha}(k)) - \langle Y_{m_1}^{\mu_1} Y_{m_2}^{\mu_2 *} \rangle\, \phi_{\mu_2 - \mu_1}(\varphi_{\mathbf{k}}) \right\} \qquad (44) \\
&\quad + \frac{1}{2} \sum_{\mathbf{k} \neq 0} \sum_{\substack{m_1, m_2 \\ \mu_1, \mu_2}} \Bigg[\frac{\delta \mathscr{M}_{m_1 m_2}^{\mu_1 \mu_2}(k)}{\delta\beta_B \Phi(\mathbf{R}_{12}, \Omega_1, \Omega_2)} \frac{\partial}{\partial \mathscr{M}_{m_1 m_2}^{\mu_1 \mu_2}(k)} \ln \det(\hat{I} + \hat{\mathscr{M}}(k)\, \hat{\alpha}(k)) \\
&\quad - \alpha_{m_1 m_2}^{\mu_1 \mu_2}(k)\, \phi_{\mu_2 - \mu_1}(\varphi_{\mathbf{k}}) \frac{\delta \langle Y_{m_1}^{\mu_1} Y_{m_2}^{\mu_2 *} \rangle}{\delta\beta_B \Phi(\mathbf{R}_{12}, \Omega_1, \Omega_2)} \Bigg]
\end{aligned}
$$

where

$$
\begin{aligned}
\frac{\delta \langle f(\Omega) \rangle}{\delta\beta_B \Phi(\mathbf{R}_{12}, \Omega_1, \Omega_2)} = \frac{2\rho_0^2}{N} \Bigg\{ \Bigg(& \langle f(\Omega) \rangle \int F_0^{(1)}(\Omega_i)\, F_0^{(1)}(\Omega_j)\, \phi(\Omega_i, \Omega_j)\, d\Omega_i\, d\Omega_j \\
& - \int f(\Omega_i)\, F_0^{(1)}(\Omega_i)\, F_0^{(1)}(\Omega_j)\, \phi(\Omega_i, \Omega_j)\, d\Omega_i\, d\Omega_j \\
& - \frac{1}{2} \Bigg\{ \langle f(\Omega) \int F_0^{(1)}(\Omega_i) [\phi(\Omega_i, \Omega_1) + \phi(\Omega_i, \Omega_2)]\, d\Omega_i \\
& - \int f(\Omega_i)\, F_0^{(1)}(\Omega_i) [\phi(\Omega_i, \Omega_1) + \phi(\Omega_i, \Omega_2)]\, d\Omega_i \Bigg\} \\
& + \langle f(\Omega) - \frac{1}{2} [f(\Omega_1) + f(\Omega_2)] \Bigg)\, F_0^{(1)}(\Omega_1)\, F_0^{(1)}(\Omega_2)
\end{aligned}
$$

and $f(\Omega)$ is an arbitrary function dependent on the molecular orientations.

The total distribution function consists of the distribution function which is due to the short-range interaction [Eq. (20) for the second order] and the function due to the long-range interactions

$$\mathscr{R}^{(2)}(\mathbf{R}_{12}, \Omega_1, \Omega_2) = \rho^{(2)}(\mathbf{R}_{12}, \Omega_1, \Omega_2) + \rho_2(\mathbf{R}_{12}, \Omega_1, \Omega_2) \tag{45}$$

and the condition for the function (45) to vanish for $R_{12} < \sigma$ (σ is the hard-sphere diameter) yields the restriction to be put upon the long-range interaction potential domain of definition

$$\Phi(\mathbf{R}_{12}, \Omega_1, \Omega_2) = 0 \qquad \text{if} \quad R_{12} < \sigma \tag{46}$$

Thus the condition

$$\rho_2(\mathbf{R}_{12}, \Omega_1, \Omega_2) = 0 \qquad \text{if} \quad R_{12} < \sigma \tag{47}$$

is to attend to the formula (44), which now completely defines the distribution function for the long-range interactions.

The expressions (46), (47) are the consequences of the additional assumption of $\rho^{(2)}(\mathbf{R}_{12}, \Omega_1, \Omega_2) = 0$ when $R_{12} < \sigma$ used in (45) and satisfies the condition of potential minimum $\beta_B(\mathscr{F}_{SF} + \mathscr{F}_{RP})$ in respect to $\beta_B \Phi(\mathbf{R}_{12}, \Omega_1, \Omega_2)$ in the domain $R_{12} < \sigma$.[15,16] In the more general case without using the approximation with respect to $\rho^{(2)}(\mathbf{R}_{12}, \Omega_1, \Omega_2)$ the condition of the optimal separation of interactions leads to self-consistent determination of $\beta_B \Phi(\mathbf{R}_{12}, \Omega_1, \Omega_2)$ potential in domain $R_{12} < \sigma$ with condition $\mathscr{R}^{(2)}(\mathbf{R}_{12}, \Omega_1, \Omega_2) = 0$ at $R_{12} < \sigma$ (mean-spherical approximation).

Using the expression (43) one can calculate the singlet distribution function which describes the ordering in the system

$$F^{(1)}(\Omega_1) = \frac{1}{\mathscr{N}} \frac{\delta \beta_B \mathscr{F}}{\delta \beta_B u_0(\Omega_1)} = F_0^{(1)}(\Omega_1) + F_{RP}^{(1)}(\Omega_1) \tag{48}$$

where

$$F_{RP}^{(1)}(\Omega_1) = \frac{1}{2N} \sum_{\mathbf{k} \neq 0} \sum_{\substack{m_1 m_2 \\ \mu_1 \mu_2}} \left[\frac{\delta \mathscr{M}_{m_1 m_2}^{\mu_1 \mu_2}(\mathbf{k})}{\delta \beta_B u(\Omega_1)} \frac{\partial \ln \det [\hat{I} + \hat{\mathscr{M}}(\mathbf{k})\, \hat{\alpha}(k)]}{\partial \mathscr{M}_{m_1 m_2}^{\mu_1 \mu_2}(\mathbf{k})} \right.$$

$$\left. - \alpha_{m_1 m_2}^{\mu_1 \mu_2}(k)\, \phi_{\mu_2 - \mu_1}(\varphi_{\mathbf{k}}) \frac{\delta \langle Y_{m_1}^{\mu_1} Y_{m_2}^{\mu_2 *} \rangle}{\delta \beta_B u(\Omega_1)} \right] \tag{49}$$

$$
\begin{aligned}
\frac{\delta\langle f(\Omega)\rangle}{\delta\beta_B u(\Omega_1)} = \Bigg[& \langle f(\Omega)\rangle \int F_0^{(1)}(\Omega_i)\, F_0^{(1)}(\Omega_j)\, \phi(\Omega_i \Omega_j)\, d\Omega_i\, d\Omega_j \\
& - \int f(\Omega_i)\, F_0^{(1)}(\Omega_i)\, F_0^{(1)}\, \phi(\Omega_i \Omega_j)\, d\Omega_i\, d\Omega_j \\
& - \langle f(\Omega)\rangle \int F_0^{(1)}(\Omega_i)\, \phi(\Omega_i \Omega_1)\, d\Omega_i \\
& + \int f(\Omega_i)\, F_0^{(1)}(\Omega_i)\, \phi(\Omega_i \Omega_j)\, d\Omega_i + \langle f(\Omega)\rangle - f(\Omega_1) \Bigg] F_0^{(1)}(\Omega_1)
\end{aligned}
\tag{50}
$$

and from Eqs. (49), (50) it is seen that the addend $F_{RP}^{(1)}(\Omega_1)$ does not affect the normalization of the function $F^{(1)}(\Omega_1)$.

The form of Eq. (50) implies that the semi-invariant-like expressions combine into the function $F_{RP}^{(1)}(\Omega_1)$. Thus this addend will be small if either the deviations from the mean value, or the absolute values of polarization will be small. We refer the numerical estimations of the polarization according to formula (48) to the last section.

4. THE CORRECTIONS TO THE RANDOM PHASES APPROXIMATION

We now proceed to the most important part of the problem, the estimation of the exponential terms in Eq. (34) and the calculation of the configurational integral (24) using the value of $\mathscr{E}(\rho)$. This approach in fact generalizes the results obtained in Ref. 3 for the order appearing in the system.

Note that the contribution of the diagrams expressing the corrections to the RPA is negligible provided the assumption of small polarization is adopted in Section 5, so that the reader interested in the physically relevant results can skip this section.

The corrections to $\mathscr{E}_G(\rho)$ can be obtained by acting the operators $\hat{\mathscr{D}}_n(\partial/\partial\rho)$ and their products on this function, but for the result of the integration to be nonzero, it is necessary to separate the terms which are in the form $\rho_{m_1}^{\mu_1}(\mathbf{k})\, \rho_{m_2}^{\mu_2}(\mathbf{k})$.

Some definitions from Ref. 3 are useful to introduce. The sum over the vectors $\mathbf{k}_1 + \cdots + \mathbf{k}_n$ will be termed the closed one if $\mathbf{k}_1 + \cdots + \mathbf{k}_n = 0$, and the irreducible one, if it can not be separated into the closed patterns (for instance, $\mathbf{k}_1 + \cdots + \mathbf{k}_4 = 0$, $\mathbf{k}_5 + \cdots + \mathbf{k}_8 = 0$, $\mathbf{k}_9 + \cdots + \mathbf{k}_n = 0$, etc.).

The simplest term describing the contribution of the exponential operators in (34) with all the sums closed and irreducible, is the product of two paired operators

$$\frac{1}{2}\hat{D}_3\left(\frac{\partial}{\partial\rho}\right)\hat{D}_3\left(\frac{\partial}{\partial\rho}\right)\mathscr{E}_G(\rho)=\frac{3!}{2(3!)^2}\frac{N^2}{N^3}\sum_{\substack{m_1,\ldots,m'_3\\ \mu_1,\ldots,\mu'_3}}\mathscr{M}^{\mu_1\mu_2\mu_3}_{m_1m_2m_3}(\mathbf{k}_1,\mathbf{k}_2,\mathbf{k}_3)$$
$$\times\mathscr{M}^{\mu'_1\mu'_2\mu'_3}_{m'_1m'_2m'_3}{}^{*}(\mathbf{k}_1,\mathbf{k}_2,\mathbf{k}_3)\frac{\partial^2}{\partial\rho^{\mu_1}_{m_1}(\mathbf{k}_1)\,\partial\rho^{\mu'_1}_{m'_1}{}^{*}(\mathbf{k}_1)}$$
$$\times\frac{\partial^2}{\partial\rho^{\mu_2}_{m_2}(\mathbf{k}_2)\,\partial\rho^{\mu'_2}_{m'_2}{}^{*}(\mathbf{k}_2)}\frac{\partial^2}{\partial\rho^{\mu_3}_{m_3}(\mathbf{k}_3)\,\partial\rho^{\mu'_3}_{m'_3}(\mathbf{k}_3)}\mathscr{E}_G(\rho)\tag{51}$$

the combinatorial factor 3! in the numerator arising from different pairings of derivatives in each of the operators $D_3(\partial/\partial\rho)$. The paired differentiation of $\mathscr{E}_G(\rho)$ yields

$$\frac{\partial^2\mathscr{E}_G(\rho)}{\partial\rho^{\mu}_{m}(\mathbf{k})\,\partial\rho^{\mu'}_{m'}{}^{*}(\mathbf{k})}=\Bigg[\sum_{\substack{m_1,m_2\\ \mu_1,\mu_2}}(\mathscr{M}^{-1}(k))^{\mu\mu_2}_{mm_2}(\mathscr{M}^{-1}(k))^{\mu_1\mu'}_{m_1m'}\rho^{\mu_1}_{m_1}(\mathbf{k})$$
$$\times\rho^{\mu_2}_{m_2}{}^{*}(\mathbf{k})-(\mathscr{M}^{-1}(k))^{\mu\mu'}_{mm'}\Bigg]\mathscr{E}_G(\rho)\tag{52}$$

The contribution from the pairing of two operators into the configurational integral can be calculated by introducing (51) and (52) into (24), integrating over the collective variables and transforming to the coordinate representation. With the factor $Q_{SF}\,Q_{RP}$ omitted, one obtains

$$\frac{1}{2\cdot 3!}\sum_{\substack{m_1,\ldots,m'_3\\ \mu_1,\ldots,\mu'_3}}\int q^{\mu_1\mu_2\mu_3}_{m_1m_2m_3}(\mathbf{R}_1,\mathbf{R}_2,\mathbf{R}_3)\,q^{\mu'_1\mu'_2\mu'_3}_{m'_1m'_2m'_3}(\mathbf{R}'_1,\mathbf{R}'_2,\mathbf{R}'_3)$$
$$\times\prod_{i=1}^{3}g^{\mu_i\mu'_i}_{m_jm'_j}(\mathbf{R}_i-\mathbf{R}_{i'})\,d\mathbf{R}_1\cdots d\mathbf{R}'_3\tag{53}$$

where

$$q^{\mu_1\mu_2\mu_3}_{m_1m_2m_3}(\mathbf{R}_1,\mathbf{R}_2,\mathbf{R}_3)=\frac{N}{S^3}\sum_{k_1,k_2,k_3}\mathscr{M}^{\mu_1\mu_2\mu_3}_{m_1m_2m_3}(\mathbf{k}_1,\mathbf{k}_2,\mathbf{k}_3)$$
$$\times\exp[-i(\mathbf{k}_1\mathbf{R}_1+\mathbf{k}_2\mathbf{R}_2+\mathbf{k}_3\mathbf{R}_3)]\tag{54}$$

$$g^{\mu\mu'}_{mm'}(\mathbf{R}'-\mathbf{R})=\frac{1}{N}\sum_{\mathbf{k}}[\hat{a}(k)(\hat{I}+\hat{\mathscr{M}}(k)\,\hat{a}(k))^{-1}]^{\mu\mu'}_{mm'}\exp[i\mathbf{k}(\mathbf{R}'-\mathbf{R})]\tag{55}$$

It should be noted that the tensor component of the correlation function (55), which is the tensor analog of the screened potential, does not coincide with the corresponding component of the correlation function resulting from Eq. (44).

The definition (54) can be generalized

$$q^{\mu_1\cdots\mu_n}_{m_1\cdots m_n}(\mathbf{R}_1,\dots,\mathbf{R}_n)=\frac{N}{S^N}\sum_{k_1,\dots,k_n}\mathscr{M}^{\mu_1\cdots\mu_n}_{m_1\cdots m_n}(\mathbf{k}_1,\dots,\mathbf{k}_n)\times\exp[-i(\mathbf{k}_1\mathbf{R}_1+\cdots+\mathbf{k}_n\mathbf{R}_n)] \tag{56}$$

The detailed calculation of the function (54)

$$\begin{aligned}&q^{\mu_1\mu_2\mu_3}_{m_1m_2m_3}(\mathbf{R}_1,\mathbf{R}_2,\mathbf{R}_3)\\&\quad=\frac{1}{S^3}\sum_{\mathbf{k}_1,\mathbf{k}_2,\mathbf{k}_3}\exp[-i(\mathbf{k}_1\mathbf{R}_1+\mathbf{k}_2\mathbf{R}_2+\mathbf{k}_3\mathbf{R}_3)]\left\{\left\langle\prod_{i=1}^{3}Y^{\mu_i}_{m_i}\right\rangle N\delta_{\mathbf{k}_1+\mathbf{k}_2+\mathbf{k}_3,0}\right.\\&\qquad+\rho_0^2[\langle Y^{\mu_1}_{m_1}\rangle\langle Y^{\mu_2}_{m_2}Y^{\mu_3}_{m_3}\rangle\,h^{(2)}(\mathbf{k}_1,\mathbf{k}_2+\mathbf{k}_3)\\&\qquad+\langle Y^{\mu_2}_{m_2}\rangle\langle Y^{\mu_1}_{m_1}Y^{\mu_3}_{m_3}\rangle\,h^{(2)}(\mathbf{k}_2,\mathbf{k}_1+\mathbf{k}_3)\\&\qquad+\langle Y^{\mu_3}_{m_3}\rangle\langle Y^{\mu_1}_{m_1}Y^{\mu_2}_{m_2}\rangle\,h^{(2)}(\mathbf{k}_3,\mathbf{k}_1+\mathbf{k}_2)]\\&\qquad\left.+\rho_0^3\prod_{i=1}^{3}\langle Y^{\mu_i}_{m_i}\rangle\,h^{(3)}(\mathbf{k}_1,\mathbf{k}_2,\mathbf{k}_3)\right\}\prod_{i=1}^{3}\phi_{-\mu_i}(\varphi_{\mathbf{k}_i})\end{aligned} \tag{57}$$

is as follows. Within the continuous distribution of wave vectors, the first term in (57) can be represented as

$$\begin{aligned}&\left\langle\prod_{i=1}^{3}Y^{\mu_i}_{m_i}\right\rangle\frac{N}{S^3}\sum_{k_1,k_2,k_3}\exp[-i(\mathbf{k}_1\mathbf{R}_1+\mathbf{k}_2\mathbf{R}_2+\mathbf{k}_3\mathbf{R}_3)\\&\qquad-i(\mu_1\varphi_{\mathbf{k}_1}+\mu_2\varphi_{\mathbf{k}_2}+\mu_3\varphi_{\mathbf{k}_3})]\,\delta_{\mathbf{k}_1+\mathbf{k}_2+\mathbf{k}_3,0}\\&\quad=\left\langle\prod_{i=1}^{3}Y^{\mu_i}_{m_i}\right\rangle(2\pi)^{-6}\rho_0\lim_{\varepsilon\to+0}\int d\mathbf{R}\,d\mathbf{k}_1\,d\mathbf{k}_2\,d\mathbf{k}_3\\&\qquad\times\exp\{-i[\mathbf{k}_1(\mathbf{R}_1-\mathbf{R})+\mathbf{k}_2(\mathbf{R}_2-\mathbf{R})+\mathbf{k}_3(\mathbf{R}_3-\mathbf{R})]\}\\&\qquad\times\exp\{-i(\mu_1\varphi_{\mathbf{k}_1}+\mu_2\varphi_{\mathbf{k}_2}+\mu_3\varphi_{\mathbf{k}_3})\}\exp[-\varepsilon(k_1+k_2+k_3)]\end{aligned} \tag{58}$$

Performing the threefold integration over the wave numbers one obtains the product of three independent integrals, each of them equal to

$$\mathscr{P}_\mu(\mathbf{r})=(2\pi)^{-2}\lim_{\varepsilon\to+0}\int\exp(-i\mathbf{k}\mathbf{r}-\varepsilon k-i\mu\varphi_{\mathbf{k}})\,d\mathbf{k}$$

and integrating over $\varphi_{\mathbf{k}}$ yields

$$\begin{aligned}\mathscr{P}_\mu(\mathbf{r}) &= (2\pi)^{-1} i^{-\mu} e^{-i\mu\varphi_{\mathbf{r}}} \lim_{\varepsilon\to+0} \int_0^\infty e^{-\varepsilon k}\, \mathscr{E}_\mu(kr) k\, dk \\ &= i^{-\mu} e^{-i\mu\varphi_{\mathbf{r}}} \times \begin{cases} \delta(\mathbf{r}), & \mu = 0 \\ \dfrac{1}{2\pi r^2} \dfrac{\Gamma(|\mu|+2)\,\Gamma(1/2)}{2^{|\mu|}\,\Gamma(|\mu|-2)/2)\,\Gamma(|\mu|/2)} \times \begin{cases} 1, & \mu > 0 \\ (-1)^\mu, & \mu < 0 \end{cases} \end{cases}\end{aligned} \tag{59}$$

with $\Gamma(x)$ the Γ-function. Here to obtain the final form of the integral (59) the tabular value(17) for the integral

$$\begin{aligned}\int_0^\infty e^{-\varepsilon x}\, \mathscr{E}_\mu(rx) x\, dx = \frac{(r/2\varepsilon)^\mu\, \Gamma(\mu+2)}{\varepsilon^2\, \Gamma(\mu+1)} \left(1 + \frac{r^2}{\varepsilon^2}\right)^{-3/2} \\ \times F\left(\frac{\mu-1}{2}, \frac{\mu}{2}, \mu+1, -\frac{r^2}{\varepsilon^2}\right), \qquad \varepsilon > 0,\ \mu \geqslant 0\end{aligned}$$

and the relation between the hypergeometric function

$$\begin{aligned}&F\left(\frac{\mu-1}{2}, \frac{\mu}{2}; \mu+1; -\frac{r^2}{\varepsilon^2}\right) \\ &\quad = \frac{\Gamma(\mu+1)\,\Gamma(1/2)}{\Gamma(\mu/2)\,\Gamma((\mu+3)/2)} (-1)^{(\mu-1)/2} \left(-\frac{r^2}{\varepsilon^2}\right)^{-(\mu-1)/2} \\ &\quad\quad \times F\left(\frac{\mu-1}{2}, -\frac{\mu+1}{2}; \frac{1}{2}; -\frac{\varepsilon^2}{r^2}\right) \\ &\quad\quad + \frac{\Gamma(\mu+1)\,\Gamma(-1/2)}{\Gamma((\mu-1)/2)\,\Gamma((\mu+2)/2)} (-1)^{\mu/2} \left(-\frac{r^2}{\varepsilon^2}\right)^{-\mu/2} \\ &\quad\quad \times F\left(\frac{\mu}{2}, -\frac{\mu}{2}; \frac{3}{2}; -\frac{\varepsilon^2}{r^2}\right)\end{aligned}$$

were used.

Using the value of (59), one obtains for the contribution of (58) the following expression:

$$\rho_0 \left\langle \prod_{i=1}^{3} Y_{m_i}^{\mu_i} \right\rangle \int \prod_{i=1}^{3} \mathscr{P}_{\mu_i}(\mathbf{R}_i - \mathbf{R})\, d\mathbf{R} \tag{60}$$

Note that the angular dependence of the function $\mathscr{P}_\mu(\mathbf{r})$ do not lead to the divergence of the integral at $r \to 0$.

The typical term in square brackets in (57) being integrated, transforms into

$$(2\pi)^{-6}\rho_0^2\langle Y^{\mu_1}_{m_1}\rangle\langle Y^{\mu_2}_{m_2}Y^{\mu_3}_{m_3}\rangle \lim_{\varepsilon\to+0}\int d\mathbf{k}_1\,d\mathbf{k}_2\,d\mathbf{k}_3\,d\mathbf{r}_1\,d\mathbf{r}_2\,h^{(2)}(\mathbf{r}_1,\mathbf{r}_2)$$

$$\times\exp\left[-i\sum_{j=1}^{3}(\mathbf{k}_j\mathbf{R}_j+\mu_j\varphi_{R_j})-\varepsilon\sum_{j=1}^{3}k_j+i(\mathbf{k}_1\mathbf{r}_1+(\mathbf{k}_2+\mathbf{k}_3)\mathbf{r}_2)\right]$$

$$=\langle Y^{\mu_1}_{m_1}\rangle\langle Y^{\mu_2}_{m_2}Y^{\mu_3}_{m_3}\rangle\rho_0^2\int h^{(2)}(\mathbf{r}_1,\mathbf{r}_2)\,\mathscr{P}_{\mu_1}(\mathbf{R}_1-\mathbf{r}_1)\prod_{i=2}^{3}\mathscr{P}_{\mu_i}(\mathbf{R}_i-\mathbf{r}_2)\,d\mathbf{r}_1\,d\mathbf{r}_2 \qquad (61)$$

and the last term in (57) transforms into

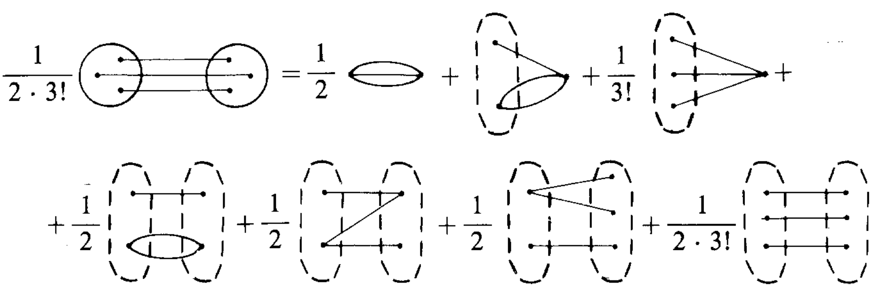
$$(2\pi)^{-6}\rho_0^3\prod_{j=1}^{3}\langle Y^{\mu_j}_{m_j}\rangle \lim_{\varepsilon\to+0}\int d\mathbf{k}_1\,d\mathbf{k}_2\,d\mathbf{k}_3\,d\mathbf{r}_1\,d\mathbf{r}_2\,d\mathbf{r}_3\,h^{(3)}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)$$

$$\times\exp\left[-i\sum_{j=1}^{3}\mathbf{k}_j(\mathbf{R}_j-\mathbf{r}_j)+\mu_j\varphi_{\mathbf{k}_j}-\varepsilon\sum_{j=1}^{3}k_j\right]$$

$$=\rho_0^3\prod_{j=1}^{3}\langle Y^{\mu_j}_{m_j}\rangle\int h^{(3)}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)\prod_{j=1}^{3}\mathscr{P}_{\mu_j}(\mathbf{R}_j-\mathbf{r}_j)\,d\mathbf{r}_1\,d\mathbf{r}_2\,d\mathbf{r}_3 \qquad (62)$$

The contribution from pairing of two operators $D_3(\partial/\partial\rho)$ is convenient to represent using the graphical notation introduced in Ref. 3. The function $q^{\mu_1\mu_2\mu_3}_{m_1m_2m_3}(\mathbf{R}_1,\mathbf{R}_2,\mathbf{R}_3)$ corresponds to the complex vertex[6] that includes the field vertices upon which the integration is performed and the correlators of the spherical functions products [see Eqs. (60)–(62)]. The field vertices are connected with each other by the lines which represent the tensor components of the correlation function (55).

Thus the formula (53) can be expressed in the form[3]



(63)

Here the diagram with the complex vertices in lhs represents the contribution resulting from the pairing of two irreducible operators $D_3(\partial/\partial\rho)$. The first diagram on the right-hand side corresponds to the pairing of the vertex determined by Eq. (60) to its conjugated vertex. The function (60) corresponds to the filled field vertex, at which the three lines end off. The line corresponds to the function (55), with its arbitrarily defined end corresponding to the second indices of the tensor (55) and the conjugated values of the spherical functions in the correlators.

The next diagram in the rhs of Eq. (63) represents the bonding of the vertex (60) with the vertex of type (61). The function (61) corresponds to two field vertices enclosed into the dashed contour and emitting one and two lines. The rest of diagrams on the right-hand side of Eq. (63) corresponds to the bonding of the vertices (61) and (62) with each other.

One can generalize the above definitions for the case of pairing of two irreducible operators $\hat{D}_n(\partial/\partial\rho)$ with $n > 3$, the case when the complex vertices arise, containing m field vertices ($m \geqslant 1$). If the number of the vertices exceeds one, they are to be enclosed into the dashed contour. The function

$$\rho_0 \left\langle \prod_{i=1}^{n} Y_{m_i}^{\mu_i} \right\rangle = \prod_{i=1}^{n} \mathscr{P}_{\mu_i}(\mathbf{R}_i - \mathbf{R})\, d\mathbf{R} \qquad \text{if} \quad m = 1 \tag{64}$$

or

$$\begin{aligned} &\rho_0^m \prod_{j=1}^{m} \left\langle \prod_{i=n_1+\cdots+n_{j-1}+1}^{n_1+\cdots+n_j} Y_{m_i}^{\mu_i} \right\rangle \int h^{(m)}(\mathbf{r}_1, \dots, \mathbf{r}_m) \\ &\quad \times \prod_{j=1}^{m} \prod_{i=n_1+\cdots+n_{j-1}+1}^{n_1+\cdots n_j} \mathscr{P}_{\mu_i}(\mathbf{R}_i - \mathbf{r}_j)\, d\mathbf{r}_1 \cdots d\mathbf{r}_m \qquad \text{if} \quad m \geqslant 2 \end{aligned} \tag{65}$$

corresponds to every complex vertex with m field vertices emitting $n_1, \dots, n_m$ lines.

Every diagram Δ with its topological properties contributes to the expansion of two pairing operators $\hat{D}_n(\partial/\partial\rho)$ with the weight

$$\mathscr{D}(\Delta) = \frac{1}{n!} \frac{n!}{\sigma(\Delta)} = \frac{1}{\sigma(\Delta)} \tag{66}$$

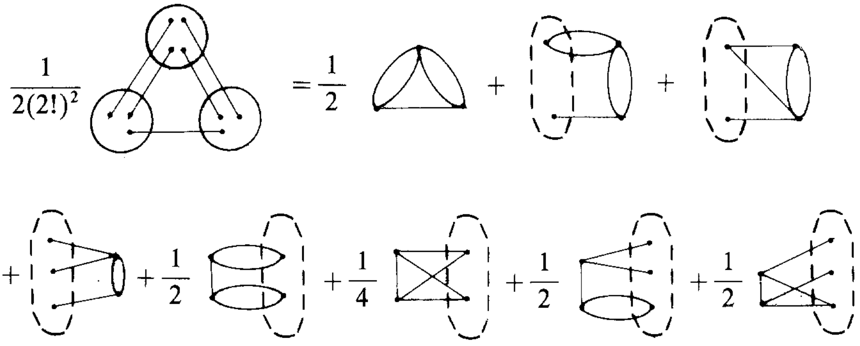
where the symmetry number $\sigma(\Delta)$ of the diagram is equal to the number of permutations of bonds and of the transformations of the diagram which remains its topological properties unchanged. In the formula (66) the factor $n!$ in the denominator is related to the coefficient remaining after the pairing in the operators $\hat{D}_n(\partial/\partial\rho)$ and the one in the numerator results from permutations of the bonds. The inverse factorial $1/n!$ corresponds to the total of the lines connecting the pair of field vertices of the diagram.

It can be readily shown that the factors before each of the diagrams from (63) correspond to the above rules. Thus for instance for the first diagram on the right-hand side of (63),

$\sigma\Big($  $\Big) = 2 \cdot 3!$

with the coefficient 3! corresponds to all possible permutations of the bonds, and the factor 2 is related to the transformation of the diagram into itself by the rotation through the angle of π around the vertical axis.

The pairing of three (or more) irreducible operators can be performd in the similar manner. For the case of three operators paired, the lowest order will be characteristic to the term $\hat{D}_3^2(\partial/\partial\rho)\,\hat{D}_4(\partial/\partial\rho)$ the corresponding contribution is



(67)

The diagrams on the right-hand side of Eq. (67) follow the "complication" of the signle vertex with three and four lines; the diagrams corresponding to the simultaneous complication of these two vertices are omitted. As before, the contribution arising from every vertex corresponds to the expressions (64), (65), and the weights of each of the diagrams are in agreement with the final form of Eq. (66).

The contribution of the irreducible operators (34) to the configurational integral (24) is to be attend with the contribution from the derivatives paired in each operator $\hat{D}_n(\partial/\partial\rho)$.(13) Only the operators with even n will contribute to the final expression.

Consider the value resulting from the operator $\hat{D}_6(\partial/\partial\rho)$ with all internal derivatives paired. Performing first the pairing in the Eq. (37) with the factor of $h^{(2)}(\mathbf{k}_1 + \mathbf{k}_2 + \mathbf{k}_3, \mathbf{k}_4 + \mathbf{k}_5 + \mathbf{k}_6)$ [see Eq. (24), (33)] one obtains

$$\frac{6!}{3!\,3!}\,\frac{3!}{2!}\,\frac{N}{6!\,N^3}\,\frac{\rho_0^2}{N}\sum_{\substack{m_1,\dots,m'_3\\ \mu_1,\dots,\mu'_3}}\left\langle\prod_{i=1}^{3}Y_{m_i}^{\mu_i}\right\rangle\left\langle\prod_{i=1}^{3}Y_{m'_i}^{\pi'_i *}\right\rangle$$

$$\times\sum_{\mathbf{k}_1,\mathbf{k}_2,\mathbf{k}_3}h^{(3)}(\mathbf{k}_1+\mathbf{k}_2+\mathbf{k}_3,-\mathbf{k}_1-\mathbf{k}_2-\mathbf{k}_3)\prod_{i=1}^{3}\phi_{-\mu_i}(\varphi_{\mathbf{k}_i})\prod_{i=1}^{3}\phi^{*}_{-\mu'_i}(\varphi_{\mathbf{k}_i})$$

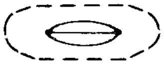
$$\times\frac{1}{Q_{RP}}\int(d\rho)\exp\left[-\frac{1}{2}\sum_{\mathbf{k}\neq 0}\sum_{\substack{m_1,m_2\\ \mu_1,\mu_2}}\alpha_{m_1,m_2}^{\mu_1\mu_2}(k)\,\rho_{m_1}^{\mu_1}(\mathbf{k})\,\rho_{m_1}^{\mu_2 *}(\mathbf{k})\right]$$

$$\times\frac{\partial^2}{\partial\rho_{m_1}^{\mu_1}(\mathbf{k}_1)\,\partial\rho_{m'_1}^{\mu'_1 *}(\mathbf{k}_1)}\,\frac{\partial_2}{\partial\rho_{m_2}^{\mu'_2}(\mathbf{k}_2)\,\partial\rho_{m'_2}^{\mu'_2 *}(\mathbf{k}_2)}\,\frac{\partial^2}{\partial\rho_{m_3}^{\mu_3}(\mathbf{k}_3)\,\partial\rho_{m'_3}^{\mu'_3 *}(\mathbf{k}_3)}\,\mathscr{E}_G(\rho)$$

$$=\frac{1}{2\cdot 3!}\rho_0^2\sum_{\substack{m_1,\dots,m'_3\\ \mu_1,\dots,\mu'_3}}\left\langle\prod_{i=1}^{3}Y_{m_i}^{\mu_i}\right\rangle\left\langle\prod_{i=1}^{3}Y_{m'_i}^{\mu'_i *}\right\rangle\int d\mathbf{r}_1\,d\mathbf{r}_2\,d\mathbf{R}_1\cdots d\mathbf{R}'_3\,h^{(2)}(\mathbf{r}_1,\mathbf{r}_2)$$

$$\times\prod_{i=1}^{3}\mathscr{P}_{\mu_i}(\mathbf{R}_i-\mathbf{r}_1)\,\mathscr{P}^{*}_{\mu'_i}(\mathbf{R}'_i-\mathbf{r}_2)\,g_{m_i m'_i}^{\mu_i\mu'_i}(\mathbf{R}_i-\mathbf{R}'_i)$$

$$=\frac{1}{2}$$



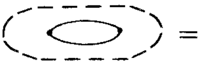
(68)

The combinatorial factor in the lhs arises from the partition of the wave vectors into two groups consisting of three vectors and their subsequent pairing inside the groups.

The diagrammatic form of the expression (68) corresponds to the first diagram on the right-hand side of Eq. (63). Performing the detailed calculation one can prove that with the derivatives in the operator $\hat{D}_6(\partial/\partial\rho)$ being paired, the diagrams arises possessing the topology similar to diagrams in (63) with the dashed contour enclosing them. These diagrams contain the correlation function with the order equal to the number of the field vertices of diagram enclosed with the dashed contour. It is to be noted that the pairing of the derivatives inside the operators, i.e., the account for the reducible sums in the expression (37) results in the manifold of the diagrams more than sufficient for the correspondence with the irreducible diagrams to be stated.

Among the omitted reducible diagrams the one possessing the lowest vertices and bonds number is

$$\frac{1}{2}$$

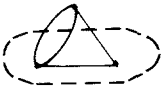


$$=\frac{1}{4}\rho_0^2\sum_{\substack{m_1,\dots,m'_2\\ \mu_1,\dots,\mu'_2}}\langle Y_{m_1}^{\mu_1}Y_{m_2}^{\mu_2}\rangle\langle Y_{m'_1}^{\mu'_1 *}Y_{m'_2}^{\mu'_2 *}\rangle$$

$$\times\int d\mathbf{r}_1\,d\mathbf{r}_2\,d\mathbf{R}_1\cdots d\mathbf{R}'_2 h^{(2)}(\mathbf{r}_1,\mathbf{r}_2)$$

$$\times\prod_{i=1}^{2}\mathscr{P}_{\mu_i}(\mathbf{R}_i-\mathbf{r}_1)\,\mathscr{P}^{*}_{\mu_i}(\mathbf{R}'_i-\mathbf{r}_2)\,g_{m_i m'_i}^{\mu_i\mu'_i}(\mathbf{R}_i-\mathbf{R}'_i)\qquad(69)$$

The terms representing different compositions of the irreducible and reducible operators will contribute to the configurational integral too. Among them the term with the lowest order of vertices and bonds number is



$$= \frac{1}{2}\rho_0^3 \sum_{\substack{m_1,\ldots m'_4 \\ \mu_1,\ldots,\mu'_4}} \left\langle \prod_{i=1}^{3} Y_{m_i}^{\mu_i} \right\rangle \langle Y\mu'_{3_{m'_3}} * Y_{m_4}^{\mu_4} \rangle \langle Y_{m'_1}^{\mu'_1} * Y_{m'_2}^{\mu'_2} * Y_{m'_4}^{\mu'_4} * \rangle$$

$$\times \int d\mathbf{R}\, d\mathbf{r}_1\, d\mathbf{r}_2\, d\mathbf{R}_1 \cdots d\mathbf{R}'_4\, h^{(2)}(\mathbf{r}_1, \mathbf{r}_2)$$

$$\times \prod_{i=1}^{3} \mathscr{P}_{\mu_i}(\mathbf{R}_i - \mathbf{r}_1)\, \mathscr{P}_{\mu_4}(\mathbf{R}_1 - \mathbf{r}_2) \prod_{i=1}^{3} \mathscr{P}_{\mu_i}^{*}(\mathbf{R}'_i - \mathbf{R})$$

$$\times \mathscr{P}_{\mu'_3}^{*}(\mathbf{R}'_3 - \mathbf{r}_2)\, \mathscr{P}_{\mu'_4}^{*}(\mathbf{R}'_4 - \mathbf{R}) \prod_{i=1}^{4} g_{m_i m'_i}^{\mu_i \mu'_i}(\mathbf{R}_i - \mathbf{R}'_i)$$

so far only the connected diagrams were considered. The disconnected diagrams will of cource contribute into (24) in the form of all possible powers of the connected diagrams muliplicated, each of them divided by the factorial of the pover value.[3] This results in the total contribution into the configurational integral equal to the exponential function of the sum of contributions of all connected diagrams. The thermodynamic potentials, in particular the Helmholtz free energy (43) is represented by then sum of the contributions of all the connected diagrams described above [with the inverted sign, see Eq. (43)].

The calculation of connected integrals defined by the formulas (63), (67), (69), (70), even for the case of low orders, requires the compicated integration in the configurational space of some molecules to be performed, involving the correlation functions of more than second order with the short-range interactions.

5. NUMERICAL CALCULATIONS AND DISCUSSION

We now proceed to the calculation of the singlet correlation function defined by the Eqs. (48)–(50) and with all the connected diagrams described above with inverted sign to determine the polarization of the system. Restricting ourselves to the calculation of the mean value of polarization for small deviations of the dipoles of molecules from the vertical position (at the value of the polar angle $\vartheta = 0$), we rewrite the expression (8) for the model dipole–dipole potential in the form of the expansion in spherical functions $\overline{Y}_1^0 = Y_1^0(\Omega) - (3/4\pi)^{1/2}$ [instead of $Y_1^0(\Omega)$], and $Y_1^{\pm 1}(\Omega)$. This results in in the trivial substitution of $\overline{Y}_1^0(\Omega)$ instead of $Y_1^0(\Omega)$ into the above expressions; the additional orientational-independent term arising in the pair interaction potential can be introduced into its short-range part.

With these modifications being performed, the short-range potential becomes

$$\varphi(R_{ij})=\begin{cases}\infty, & \text{if } R_{ij}<\sigma\\[4pt] \dfrac{2\varepsilon_2 d^2}{\varepsilon_1(\varepsilon_1+\varepsilon_2)R_{ij}^3}, & \text{if } R_{ij}>\sigma\end{cases}\tag{71}$$

From the Eqs. (8), (9), (14), (15) one can calculate the nonzero matrix elements of $\alpha_{m_1m_2}^{\mu_1\mu_2}(k)$:

$$\begin{aligned}\alpha_{01}^{00}(k)&=\alpha_{10}^{00}(k)=\gamma i_0(k), &\alpha_{11}^{00}(k)&=\gamma_1 i_0(k)\\ \alpha_{11}^{-1,1}(k)&=\alpha_{11}^{1,-1}(k)=-3\gamma_2 i_2(k), &\alpha_{11}^{11}(k)&=\alpha_{11}^{-1,-1}(k)=-\gamma_2 i_0(k)\end{aligned}\tag{72}$$

where

$$\gamma=4\left(\frac{\pi}{3}\right)^{1/2}\frac{\varepsilon_2}{\varepsilon_1}a,\qquad \gamma_1=\frac{8\pi\varepsilon_2}{3\varepsilon_1}a,\qquad \gamma_2=\frac{4\pi}{3}a,\qquad a=\frac{2\pi d^2\beta_B\rho_0}{(\varepsilon_1+\varepsilon_2)\sigma}$$

$$i_m(k)=\int_1^\infty \mathscr{E}_m(xy)\,x^{-2}\,dx\qquad (m=0,2;\ y=k\sigma)$$

The oscillations of the correlation function $h^{(2)}(R_{ij})$ decreasing as R_{ij}^{-3} according to the character of the potential decrease can be modeled by the function

$$h^{(2)}(R_{ij})=\begin{cases}-1, & \text{if } R_{ij}<\sigma\\[4pt] A\dfrac{\sigma^3}{R_{ij}^3}\cos\left[2\pi\left(\dfrac{R_{ij}}{\sigma}-1\right)\right], & \text{if } R_{ij}>\sigma\\ \qquad A=\text{const}\end{cases}\tag{73}$$

and as the intention of this section is the estimation of the spontaneous polarization due to the pair dipole–dipole interactions in the system, the dependence of the dimensionless constant A on the thermodynamic parameters (temperature and density) is not significant.

Define the dimensionless value of the longitudinal component of the polarization by the expressions$^{(1)}$

$$p=\int_0^{\pi/2}d\vartheta\sin\vartheta\int_0^{2\pi}d\varphi\sin\vartheta\cos\varphi F^{(1)}(\Omega)=p_0+\Delta p\tag{74}$$

$$p_0=\int_0^{\pi/2}d\vartheta\sin\vartheta\int_0^{2\pi}d\varphi\sin\vartheta\cos\varphi F_0^{(1)}(\Omega)\tag{75}$$

$$\Delta p = \int_0^{\pi/2} d\vartheta \sin\vartheta \int_0^{2\pi} d\varphi \sin\vartheta \cos\varphi \left[\frac{1}{N}\frac{\delta\Delta\mathscr{F}}{\delta u_0(\Omega)}\right] \tag{76}$$

$$\begin{aligned} F_0^{(1)}(\Omega) &= \exp(ap_1 \sin\vartheta \sin\varphi)\, G(\vartheta,\varphi) \\ &\quad \times \left[\int_0^{\pi/2} d\vartheta \sin\vartheta \int_0^{2\pi} d\varphi \exp(ap_1 \sin\vartheta\sin\varphi)\, G(\vartheta,\varphi)\right]^{-1} \end{aligned} \tag{77}$$

where

$$\Delta\mathscr{F} = \mathscr{F} - \mathscr{F}_{RP},$$

$$G(\vartheta,\varphi) = \exp\left[(ap_0 + c)\sin\vartheta\cos\varphi - \frac{2a\varepsilon_2}{\varepsilon_1} p_\perp \cos\vartheta - u_0(\vartheta)\right]$$

$$p_1 = \langle \sin\vartheta \sin\varphi\rangle, \qquad p_\perp = \langle\cos\vartheta\rangle, \qquad u_0(\vartheta) = b(1 - \exp(-b_1\vartheta^2))$$

$$c = \beta_B E_0 d, \qquad b = \beta_B u_0$$

and the coefficient b_1 determines the angular dependence of $u_0(\vartheta)$. Here u_0 is the energy of bonding of the adsorbed molecule to the surface, c the dimensionless value of the external electric field directed along the axis $\varphi = 0$. The expression for $u_0(\vartheta)$ determines the angular dependence of the energy of bonding of the adsorbed molecule to the surface.

The vector of polarization is expressed by (74) in the form of two components, the first of them p_0 follows from the SCMF theory [see Eq. (23)] and the second Δp results from the variation of the free energy $\Delta\mathscr{F}$ determined by SPA [Eqs. (43), (49)] and by all connected diagrams considered in Section 4. The expression (77) explicitly represents the singlet correlation function in the SCMF approximation (23).

As it was mentioned above the expression (75) is the multiparametrical transcendental equation for the polarization in the SCMF approximation. This equation was derived and investigated in Ref. 1[3] for the case $p_1 = 0$ and in the first-order iterative approximation for $p_1 = (1 - p_0^2)^{1/2}$. In general case, however, we expect $p_1 \neq 0$ and at sufficiently large polarization (corresponding to the approximate inequality $a\langle\sin^2\vartheta\sin^2\varphi\rangle \gtrsim 1$, see below) the parameters of the singlet orientational function and the value of the polarization vector are to be calculated from the following set of the transcendental equations:

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[3] The Eqs. (11)–(13) of Ref. 1 corresponding to the Eqs. (75) and (77) of the current paper contain an erratum in the definition of the permittivities dependence of the a, and the term $\sin\vartheta$ is to be inserted into the integrands.

$$\begin{aligned} p_0 &= G_0^{-1} \int_0^{\pi/2} d\vartheta \sin\vartheta \int_0^{\pi} d\varphi \sin\vartheta \cos\varphi \cosh(ap_1 \sin\vartheta \sin\varphi)\, G(\vartheta, \varphi) \\ p_\perp &= G_0^{-1} \int_0^{\pi/2} d\vartheta \sin\vartheta \int_0^{\pi} d\varphi \cos\vartheta \cosh(ap_1 \sin\vartheta \sin\varphi)\, G(\vartheta, \varphi) \qquad (78) \\ p_1 &= G_0^{-1} \int_0^{\pi/2} d\vartheta \sin\vartheta \int_0^{\pi} d\varphi \sin\vartheta \sin\varphi \sinh(ap_1 \sin\vartheta \sin\varphi)\, G(\vartheta, \varphi) \end{aligned}$$

where

$$G_0 = \int_0^{\pi/2} d\vartheta \sin\vartheta \int_0^{\pi} d\varphi \cosh(ap_1 \sin\vartheta \sin\varphi)\, G(\vartheta, \varphi)$$

These equations were solved using the computer program involving the iteration procedure and the chord method[18] the results are plotted in Fig. 1 showing the dependence of p_0 on c at $\varepsilon_1 = \varepsilon_2 = 1$ for different values of the parameters a, b, b_1. The calculations show that there are no values $p_1 \neq 0$ at all, i.e., only the longitudinal part (directed along the field) of the surface component of the polarization vector can exist.

We now turn to the more precise calculation of the polarization using Eq. (74) and taking account of the contribution of the free energy variation due to RPA and all connected diagrams into the Δp. We shall consider the case of small polarization ($p \ll 1$) and in the calculation of the free energy we shall restrict ourselves to the evaluation of the first-order term in p.

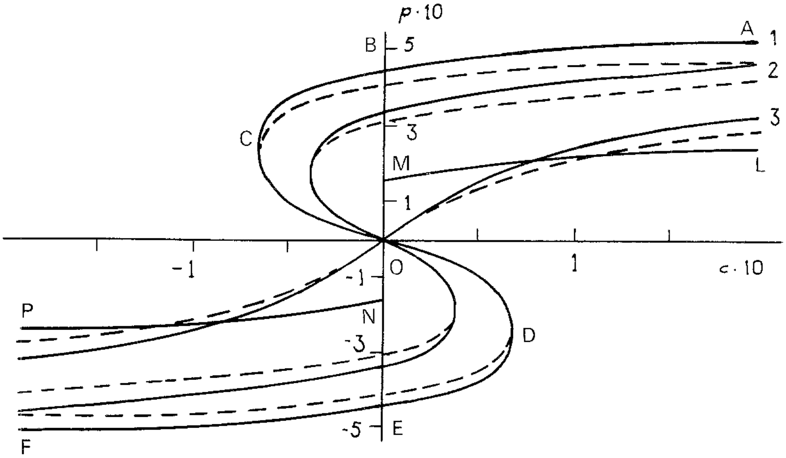

Fig. 1. The dependence of p_0 [Eq. (80), dashed lines] and $p = p_0 + \Delta p$ [Eqs. (79), (80), solid lines] on c at different values of parameters: 1, $a = 4.8$, $b = 8.0$, $b_1 = 1$; 2, $a = 4.6$, $b = 8.0$, $b_1 = 1$; 3, $a = 4.2$, $b = 8.0$, $b_1 = 1$. For curve ABCD see text.

First it can be seen that in this approximation the contribution of the diagram into $\Delta\mathscr{F}$ can be neglected. In fact, the most significant contribution is due to the diagram (69), which contains the least number of the field vertices and bonds entering them. If one realizes that $\langle Y_1^0\rangle \sim p^2$, $(Y_1^{\pm 1}\rangle \sim p$, calculate the order of the correlators of the products of spherical functions, and use Eqs. (55) and (72), the contribution of this diagram will be proved to be $O(p^3)$. Thus only the RPA term [Eqs. (48)–(50)] will contribute into Δp. Taking into account the terms of order p in $\det(\hat{I} + \hat{\mathscr{M}}\hat{\alpha})$ and performing the calculations defined by expressions (48)–(50), (76) one obtains

$$\Delta p = A\gamma \left\langle \frac{\delta\langle Y_1^0\rangle}{\delta\beta_B u_0(\Omega)} \sin\vartheta \cos\varphi \right\rangle \int_1^\infty \cos(2\pi x) x^{-5}\, dx \tag{79}$$

where the Fourier transformations (73), the expressions (72), and the asymptotic formula

$$\lim_{L\to\infty} \int_0^L \mathscr{C}_m(xz)\, \mathscr{C}_m(xz')x\, dx = \frac{\delta(z-z')}{z}$$

were used. For the functional derivative one has to substitute the expression (50); the averaging in (79) is to be performed over the distribution with respect to the SCMF approximation (77) with the constants which can be calculated from the set of the equations that can be obtained from (78) by performing the φ integration at $p_1 = 0$:

$$\begin{aligned}
p_0 &= G^{-1} \int_0^{\pi/2} \sin^2\vartheta\, G_1(\vartheta)\, d\vartheta \\
p_1 &= G^{-1} \int_0^{\pi/2} \sin\vartheta \cos\vartheta\, G_0(\vartheta)\, d\vartheta \\
G_m(\vartheta) &= I_m[(ap_0 + c)\sin\vartheta] \exp\left[-\frac{2a\varepsilon_2}{\varepsilon_1} p_\perp cos\,\vartheta - u_0(\vartheta)\right], \qquad m = 0, 1 \\
G &= \int_0^{x/2} G_0(\vartheta) \sin\vartheta\, d\vartheta
\end{aligned} \tag{80}$$

where $I_m(x)$ is the Bessel function of an imaginary argument. The result of the calculation of p_0 according to the SCMF theory [Eqs. (80)] and the values of the resulting polarization vector $p = p_0 + \Delta p$ [Eq. (79)] are shown in Fig. 1 for $\varepsilon_1 = \varepsilon_2 = 1$.

The curves $p_0(c)$ contain the metastable (BC and DE) and the unstable (CD) sections (of the van der Waals curve); this feature is due to the assumptions involved in the SCMF approximation.$^{(1)}$ The restoration of the stability using Maxwell's rule$^{(19)}$ yielding the straight line BE enables us to calculate the polarization jump at zero external electric field, thus the system undergoes the first-order phase transition.

The van der Waals loop characteristic to the curve of types 1 and 2 vanishes at sufficiently low values of a (or large b and b_1), so that the resulting c dependence of p becomes monotonic and the first-order phase transition does not exist. It is seen from Fig. 1 that the disconsistency between p and p_0 becomes more significant as p increases.

For the typical values of the parameters (characteristic for the water molecule) $\sigma = 4.0$ Å, $d_0 = 1.84$ D, and $T = 300$ K, $\rho_0 = 4/\pi\sigma^2$ one obtains $a = 5.15$. The constant b describes the bonding energy of the molecule with the substrate and for $u_0 = 4$ kcal/mol $b = 6.66$.

Thus the monolayer packed sufficiently dense with the molecules (large a) polarizes, and the arising of the total macroscopic dipole moment corresponds to the first-order phase transition. The polarization of this kind was in fact observed experimentally (see Refs. 20 and 21); this polarization results in the arising of the rigid dipole moment of anisotropic colloid particles in a polar media. One can easily prove that the polarization of the surface of colloid particle leads to the constant dipole moment arising along the anisopy axis.$^{(1)}$

Finally it is interesting to discuss from the viewpoint of the general results obtained in the present paper the behavior of the polarization in the model in which all the molecular dipoles possess the same orientation with respect to the surface. We proposed this model in Ref. 1 as an example of the most simple approach to the calculation of the polarization with the possible variations of the dipole orientations neglected. The solution of the appropriate algebraic equation corresponds to the fractured curve LMNP shown in Fig. 1 for parameter values $a = 10.5$, $b \cdot b_1 = 9.5$ (see Ref. 1). One can show however the assumption of the multiplicative splitting (22) to be exact for this model. It follows from Eq. (50) that the corrections to the singlet correlation function arising from the RPA and from all connected diagrams vanish, thus in the framework of the proposed model the solution for the polarization is exact.

REFERENCES

1. B. V. Derjaguin and Yu. V. Shulepov, *Surf. Sci.* **81**:149 (1979).
2. D. N. Zubarev, *Dokl. Acad. Nauk USSR* **95**:757 (1954).
3. I. R. Yukhnovsky and M. F. Holovko, *Statistical Theory of the Classical Equilibrium Systems* (Naukova Dumka, Kiev, 1980).
4. J. L. Lebowitz, G. Stell, and S. Baer, *J. Math. Phys.* **6**:1282 (1965).
5. G. Stell, in *Phase Transitions and Critical Phenomena*, Vol. 5b, C. Domb and M. S. Green, eds. (Academic Press, New York, 1975), p. 205.

6. P. C. Hemmer and J. L. Lebowitz, in *Phase Transition and Critical Phenomena*, Vol. 5b, C. Domb and M. S. Green, eds. (Academic Press, New York, 1975), p. 107.
7. J. S. Høye and G. Stell, *J. Chem. Phys.* **61**:562 (1974).
8. J. S. Høye, J. L. Lebowitz, and G. Stell, *J. Chem. Phys.* **61**:3253 (1974).
9. J. S. Høye and G. Stell, *J. Chem. Phys.* **72**:1597 (1980).
10. G. Stell, G. N. Patey, and J. S. Høye, *Adv. Chem. Phys.* **48**:183 (1981).
11. T. F. Meister and B. U. Felderhof, *Physica* **102A**:145 (1980).
12. F. P. Buff and N. S. Goel, *J. Chem. Phys.* **56**:2405 (1972).
13. P. C. Das and J. I. Gersten (1982). *J. Chem. Phys.* **76**:3177 (1982).
14. R. Kubo, *J. Phys. Soc. Japan* **17**:1100 (1962).
15. H. C. Andersen and D. Chandler, *J. Chem. Phys.* **55**:1447 (1971).
16. H. C. Andersen and D. Chandler, *J. Chem. Phys.* **57**:1918 (1972).
17. I. S. Gradstein and I. M. Rishik, *Tables of the Integrals, Sums, Series, and Products* (Nauka, Moskow, 1971), p. 120.
18. B. P. Demidovich and I. A. Maron, *The Basis of Computational Mathematics* (Nauka, Moskow, 1970), p. 120.
19. Kerson Huang, *Statistical Mechanics* (Mir, Moskow, 1966).
20. N. A. Tolstoj, A. A. Spartakov, and A. A. Trusov, in *Research in the Field of Surface Forces* (Nauka, Moskow, 1967), p. 67 [Consultants Bureau, New York, 1971), p. 49].
21. V. V. Vojtilov, N. A. Tolstoj, and A. A. Trusov, *Kolloid J.* **42**:1051 (1980).