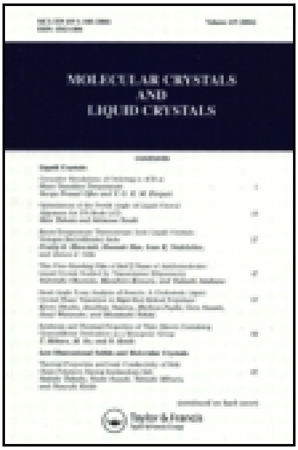

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PHASE DESCRIPTION IN POLAR LIQUID CRYSTALS USING MODIFIED WEIGHTED DENSITY APPROXIMATION (MWDA)

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PHASE DESCRIPTION IN POLAR LIQUID CRYSTALS USING MODIFIED WEIGHTED DENSITY APPROXIMATION (MWDA)

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The compatibility of different approximations to the Helmholtz free energy F is analysed in order to provide the consistent definition of the order parameters for liquid crystalline phases. In particular the diagrammatic expansion theory is compared to the weighted, also modified weighted, density approximations. The weight function w is shown to be proportional to the Mayer function. The explicit form of the weight function for the system of non-uniaxial polar molecules is given and the interaction terms of the polar and orientational order parameters in the free energy expansion are discussed.

Keywords: density functional theory; liquid crystals; phase transitions theory

INTRODUCTION

The density-functional theory (DFT) of a nonuniform system was originally formulated for a quantum-mechanical many body system [1,2]. The classical version of its formalism proved useful for the study of classical inhomogeneous systems using its single-particle density as the basic variable [3–6]. The application of DFT to phase transitions, first given by Ramakrishnan and Youssouf [7] in the theory of freezing of classical fluids, now is used to many systems [8], also for liquid crystals [9–15].

The basic physical assumption of the density-functional theory is the fact that at the most phase transitions in liquids the correlation length is only a few atomic spacings. All phenomena at distances greater than the correlation length can be treated in a mean-field approximation. One can divide the system into cells with a diameter of the order of the correlation

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length, centered at a point with a coarse-grained local number density $\rho(\mathbf{r})$. For the application of DFT to molecular fluids one considers the position $\mathbf{r}$ of the center of a molecule and its orientation $\mathbf{\Omega}$ given by the Euler angles. The single-particle density distribution $\rho(\mathbf{r}, \mathbf{\Omega})$ gives in the coarse grained model, the number of molecules per unit volume centered at position $\mathbf{r}$ and having the orientation $\mathbf{\Omega}$. The important ideas of DFT are: that a knowledge of the equilibrium single-particle density $\rho(\mathbf{r}, \mathbf{\Omega})$ is sufficient in principle to determine all molecular properties of the system; the Helmholtz free energy F of the many particle system can be expressed as a unique functional of its single particle density. That functional reaches its minimum value at the equilibrium density. For a uniform fluid $\rho(\mathbf{r}, \mathbf{\Omega})$ is constant, independent of position and orientation. The calculations of the difference in the Helmholtz free energy F between the uniform phase and the ordered phase with an inhomogeneous density distribution at different values of the external parameters (temperature, the average density) lead to the phase transition descriptions, predicted from the relative stability of those two phases.

Within DFT, the free energy of system F can be expressed by the unique functional of the single-particle density $\rho(x), x \equiv (\mathbf{r}, \mathbf{\Omega})$;

$$F[\rho(x)] = F_{id}[\rho(x)] + F_{ex}[\rho(x)] \tag{1}$$

where F_{id} is the ideal gas part of the free energy F.

The exact form of the free energy functionals is unknown for a general inhomogeneous density distribution. Numerous approximate methods to obtain suitable forms of the free energy functionals were developed [4–6, 10–14]. Here we propose an approach used in diagram expansion method [16–18], which can be useful in discussion of the density functional theories. We try to construct the unified method of finding the free energy for the wide range of non-uniform anisotropic systems. Our particular goal is to discuss the systematic treatment of the problem of the ferroelectric type orderings in systems of uniaxial and non-uniaxial polar molecules.

The ferroelectric liquid crystals are composed of mesogenic chiral molecules possessing a permanent electric dipole moment perpendicular to their long axes. Polar orderings are also observed in systems of uniaxial polar molecules. Consider the system of identical anisotropic rigid molecules. The position and orientation of the i-th molecule is given by a six-dimensional variable $x_i = (\mathbf{r}_i, \mathbf{\Omega}_i)$, where $\mathbf{r}_i$ is the position of the molecule center of mass, and $\mathbf{\Omega}_i$ specifies molecule orientation. The molecules constituting the system are regarded as elongated forms with built-in permanent dipole moments at a given angle $\mathbf{\Phi}$ to the long axis of the molecule. Each molecule can be represented by the set of two unit vectors $\{\mathbf{n}_\mathrm{i}, \mathbf{p}_\mathrm{i}\}$, where $\mathbf{n}_\mathrm{i}$ is parallel to the long axis of the ith molecule and $\mathbf{p}_\mathrm{i}$ points in the direction of its dipole moment. Such model enables us to discuss the interaction of non-uniaxial molecules, $\Phi \neq 0$ and uniaxial ones when $\Phi = 0$. We can also make use of this model to describe the interaction of chiral molecules.

THEORECTICAL MODELS OF THE HELMOHOLTZ FREE ENERGY

In the theoretical descriptions of ordered fluids exhibiting various liquid crystalline phases two kinds of molecular interactions, short range – repulsive and long range – attractive, should be considered. All the physical information of the system is contained in the Helmholtz free energy F expressed as the function of molecules' positions and orientations and interaction potential parameters. The basic theoretical approach to the free energy calculation was developed in terms of diagram expansion method but its application met difficulties in explicit evaluation due to the anisotropic character of both kinds of interactions. Recently the considerable progress in the free energy calculations was achieved within the local density functional theory (LDF) approach [3–6,8–14].

In our previous work the diagrammatic approach was exploited yielding the essential definition of order parameters in terms of the given interaction potential while in the framework of local density approximations the order parameters are rather phenomenologically postulated. In this work we show that the order parameters can be defined by the weight function, crucial factor in the local density theories [4–6,10–14].

In the diagram expansion method the Helmholtz free energy F of the system is calculated as [16,17]

$$\beta F = \int dx dx' \rho(x)\rho(x')\{[1 + c(x,x')] \ln \frac{1 + c(x,x')}{1 + b(x,x')} - c(x,x')\} + \int dx \rho(x)[\lambda_B^3 \ln \rho(x) - 1] + \text{higher order contributions} \qquad (2)$$

where: $x \equiv (\mathbf{r}, \mathbf{\Omega})$ is the set of one particle configuration variables, $\rho(x)$-one particle distribution function, $c(x,x') = \frac{\rho^{(2)}(x,x')}{\rho(x)\rho(x')} - 1$ - correlation function, $b(x,x') = \exp(-\beta U_2(x,x')) - 1$ - Meyer function , $U_2(x_1,x_2)$ is the intermolecular interaction potential between molecule 1 and 2, $\beta = (k_B T)^{-1}$, λ_B is the thermal wavelength.

Introducing the orthonormal basis in the configurational space

$$e_\kappa(x) \equiv \sqrt{\frac{2l+1}{8\pi^2 V}} \exp(i\boldsymbol{qr}) D^l_{mn}(\mathbf{\Omega}) \qquad (3)$$

(where $\kappa = (q,\ l,\ m,\ n)$ denote reciprocal space variables), each one-particle function $A(x)$ can be represented by coefficients $\widetilde{A}(\kappa)$ in the generalized reciprocal space according to

$$A(x) = \sum_{\kappa} \widetilde{A}(\kappa) e_{\kappa}(x) \tag{4}$$

Then the free energy F can be expressed as the polynomial of one particle density coefficients $\widetilde{\rho}(\kappa)$ and in the second order approximation reads

$$F = -\frac{1}{2\beta} \sum_{k} \widetilde{b}(\kappa)\widetilde{\rho}(\kappa)\widetilde{\rho}(\bar{\kappa}) \tag{5}$$

where $\widetilde{b}(\kappa)$ is the transform of the Meyer function and $\bar{\kappa} = (-\boldsymbol{q}, l, -m, n)$.

In the weighted density functional approximation (WDA) the free energy is written in the form [4–6]

$$F = F_{id} + F_{ex} \tag{6}$$

where the excess free energy part F_{ex} is modelled by the hard core free energy density $\boldsymbol{\Psi}_{HC}(\bar{\rho})$

$$F_{ex} = \int dx\ \rho(x) \boldsymbol{\Psi}_{HC}(\bar{\rho}(x)) \tag{7}$$

Here $\bar{\rho}$ is the smoothed one-particle distribution function defined by the convolution integral

$$\bar{\rho}(x) = \int ds\ w(x-s)\rho(s) \tag{8}$$

where $w(x)$ is the appropriate normalized real space weight function. Taking into account the expansions

$$w(x) = \sum_{\kappa} \widetilde{w}(\kappa) e_{\kappa}(x) \text{ and } \bar{\rho}(x) = \sum_{\kappa} \widetilde{\bar{\rho}}(\kappa) e_{\kappa}(x) \tag{9}$$

one gets

$$\widetilde{\bar{\rho}}(\kappa) = \widetilde{w}(\kappa)\widetilde{\rho}(\kappa) \tag{10}$$

Expanding the density $\boldsymbol{\Psi}_{HC}$ in Maclaurin's series

$$\boldsymbol{\Psi}_{HC} = \sum_{n=0}^{\infty} \psi_n \bar{\rho}^n \tag{11}$$

we obtain for the free energy

$$F_{ex} = \sum_{n=0}^{\infty} \int dx \rho(x) \psi_n \left[\int ds\, w(x-s)\rho(s) \right]^n \tag{12}$$

With the accuracy to the first order term in $\bar{\rho}$

$$F_{ex} = \psi_0 \int dx \rho(x) + \psi_1 \int dx \int ds w(x-s) \rho(s) \rho(x) \tag{13}$$

which in the second order approximation gives

$$F = \psi_1 \sum_{\kappa} \widetilde{w}(\kappa) \widetilde{\rho}(\kappa) \widetilde{\rho}(\bar{\kappa}) \tag{14}$$

Those general calculations, when comparing the formulas (5) and (14) yield that in the lowest order of approximation the weight function $w(x)$ is proportional to the Meyer function

$$w(x) \cong \frac{b(x)}{\int dx\, b(x)} \tag{15}$$

In the modified weighted density approximation [5] (MWDA) the excess free energy is given by the free energy density ($F = \Psi_{HC}(\hat{\rho})$) calculated for the averaged one particle function $\hat{\rho}$

$$\hat{\rho} = \int dx \rho(x) \bar{\rho}(x) \tag{16}$$

Since

$$\hat{\rho} = \sum_{\kappa} \widetilde{w}(\kappa) \widetilde{\rho}(\kappa) \widetilde{\rho}(\bar{\kappa}) \tag{17}$$

we get as in the MWDA

$$F^{MWDA} = \psi_1 \sum_{\kappa} \widetilde{w}(\kappa) \widetilde{\rho}(\kappa) \widetilde{\rho}(\bar{\kappa}) \tag{18}$$

The order parameters in the diagrammatic approximation are determined as those amplitudes $\widetilde{\rho}(\kappa)$, for which the free energy reaches its minimum. In density functional theories the order parameters should be defined by the same minimalization condition. This procedure should yield the same order parameters provided the weight function is determined by the Eq. (15).

DISCUSSION

The direct correspondence between the weight function of weighted density approximation and the Mayer function established in Eq. (15) enables performing the calculations of the free energy in the weighted density approximation for almost arbitrary intermolecular potentials with both repulsive and attractive parts. This approach provides also the method for the order parameters definition within the WDA. Note that the formula (15) can explain various approximations used previously [4–6,10–14] for the configurational dependence of the weight function.

The derived formula (15) can be used for the system composed of non uniaxial polar molecules described in the introduction. The intermolecular interaction potential for molecules with non-collinear long and polar axes can be written as

$$U_2(x_1,x_2) = \sum_{\substack{a_1 b_1 \\ a_2 b_2}} \sum_{l=0,1,2} V^l_{ab}(|\mathbf{r}_1 - \mathbf{r}_2|) P_1(\mathbf{a}_1 \cdot \mathbf{b}_2) \tag{19}$$

where $\mathbf{a}_i, \mathbf{b}_j = \mathbf{n}_i, \mathbf{p}_j$.

In that case according to the Eq. (15) the weight function $w(x)$ is explicitly proportional to the Mayer function $b(x)$, which for the assumed interaction potential takes the form

$$w(x_1 - x_2) = C\,b(x_1 - x_2) = C \sum_{\substack{0 \le k_0 \le k_1 \le k_2 \\ k_0 + k_1 + k_2 \ge 1}}^{\infty} \frac{(-\beta)^{k_0+k_1+k_2}(k_0+k_1+k_2)!}{k_0! k_1! k_2!} V_0^{k_0}(r_{12}) V_1^{k_1}(r_{12}) V_2^{k_2}(r_{12}) \times [P_1(\cos\vartheta_{12})]^{k_1} [P_2(\cos\vartheta_{12})]^{k_2} \tag{20}$$

with $x_1 - x_2 = (r_{12}, \mathbf{\Omega}_{12})$ and C the normalisation constant.

Considering the properties of the Legendre polynomials the mixing of polar (odd l) and orientational (even l) order parameters $\widetilde{\rho}(\kappa = \mathbf{q}, l, m, n)$ should occur in the free energy expansion terms with even powers in $\widetilde{\rho}$. These terms may stabilise the polar phases as imposed on the already orientationally ordered phases. The presence of the orientational (long axes) order is then the necessary condition for the emerging polar axes order. Without order parameter mixing terms in the free energy expansion the respective phase orderings would be apparently independent unless their critical temperatures are determined by the single anisotropic interaction potential. In practice the anisotropic repulsive hard core part is treated separately but it can be written in terms of the series expansion in terms of space rotations basis functions [19] producing in effect the usual orientational and polar order.

The Mayer function expansion (20) leads in effect to modification of the critical and phase transition temperatures as well as to presence of higher order orientation parameters like $\langle P_2 \rangle$ coming out of the P_1^2 and $\langle P_4 \rangle$ from the presence of P_2^2 term. Moreover, the same remark concerns also doubling of the density wave induced mainly by the hard core interaction.

One should notice that according to formula (15) this mechanism is present in MWDA as well as in the diagram expansion approaches.

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