Combined density functional and Brazovskii theories for systems with spontaneous inhomogeneities

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Abstract

The low-T part of the phase diagram in self-assembling systems is correctly predicted by the known versions of the density functional theory (DFT). The high-T part obtained in DFT, however, does not agree with simulations even on the qualitative level. In this work, a new version of the DFT for systems with spontaneous inhomogeneities on a mesoscopic length scale is developed. The contribution to the grand thermodynamic potential associated with mesoscopic fluctuations is explicitly taken into account. The expression for this contribution is obtained by the methods known from the Brazovskii field theory.

Apart from developing the approximate expression for the grand thermodynamic potential that contains the fluctuation contribution and is ready for numerical minimization, we develop a simplified version of the theory valid for weakly ordered phases, i.e. for the high-T part of the phase diagram. The simplified theory is verified by a comparison with the results of simulations for a particular version of the short-range attraction long-range repulsion (SALR) interaction potential. Except from the fact that in our theory the ordered phases are stable at lower T than in simulations, a good agreement for the high-T part of the phase diagram is obtained for the range of density that was considered in simulations. In addition, the equation of state and compressibility isotherms are presented. Finally, the physical interpretation of the fluctuation-contribution to the grand potential is discussed in detail.
I. INTRODUCTION

Spontaneously appearing aggregates such as clusters, networks or layers of particles, as well as a distribution in space of these objects, pose a real challenge for experiment, theory and simulation [1–5]. Recently a generic model of self-assembly, where the particles immersed in a solvent interact with effective short-range attraction and long-range repulsion (SALR), has been studied intensely by various methods [1–3, 5–22]. As a result, general features of the phase diagram in the SALR system are already known [1–3, 16–20]. For sufficiently low temperatures, the sequence of structures for increasing volume fraction of the particles is: disordered (D phase), cluster crystal with a cubic symmetry (C phase), hexagonally ordered cylindrical clusters (H phase), parallel layers (L phase), hexagonally ordered cylindrical voids (IH phase), cubic crystal of spherical voids (IC phase), and again the disordered phase. In addition, a gyroid G phase is stable between the H and L phases, and the IG phase is stable between the L and IH phases for some temperature range [1, 3, 13, 20]. Theories of mean-field nature predict the above sequence of phases for the whole range of $T < T_L$, where above $T_L$ only the disordered phase (no periodic structure) is stable for the whole range of the volume fractions [1, 3, 11]. Simulations, however, show that the C phase loses stability at $T = T_C$, and for $T_C < T < T_H$ the disordered phase coexists with the hexagonal phase. For $T > T_H$ the hexagonal phase disappears, and for $T_H < T < T_L$ the disordered phase coexists with the lamellar phase [3, 20]. Moreover, in simulations the ordered phases are stable at higher densities and lower temperatures than predicted by the mean-field (MF) theories. The phase diagram obtained in MF and in simulations, and the structure of the ordered phases are shown in Fig. 1.

The periodic structure is destroyed by long-wavelength fluctuations (displacements or reshaping of the aggregates) that play increasingly important role for increasing $T$, but are neglected in the MF theories. For this reason the MF theories cannot predict the phase diagram that agrees with simulations for relatively high temperature. The fluctuations are taken into account in the Landau-Brazovskii (LB) theory [23], and indeed, the coexistence of the disordered and lamellar phases is obtained in this theory when the fluctuations are taken into account within the field-theoretic (FT) framework [24]. Unfortunately, the LB theory is of phenomenological nature and the functional of the order parameter (OP) depends on phenomenological parameters. A relation of these parameters with the measurable quantities
FIG. 1: The phase diagram in the SALR system. Panel (a): MC simulation results for a particular form of the SALR potential, reprinted from Ref.[5]. Panel (b): phase diagram in the MF version of the mesoscopic theory that is further developed in this work, reprinted from Ref. [17]. Structure of the ordered phases is visualized in the cartoons surrounding the diagram. At the shown surfaces, the local volume fraction of the particles is \( \zeta(r) = \bar{\zeta} \), where \( \bar{\zeta} \) is the space-averaged volume fraction of the particles. In the lamellar L phase the surfaces separate the alternating regions rich and poor in the particles. In the H and C phases stable for \( \rho^* < 0.25 \), the volume fraction inside the cylinders and spheres is larger than \( \bar{\zeta} \), while in the inverted IH and IC phases stable for \( \rho^* > 0.25 \), \( \zeta(r) > \bar{\zeta} \) outside the cylinders and spheres. The dimensionless density \( N\sigma^3/V \) is denoted by \( \rho \) and \( \rho^* \) in panels (a) and (b) respectively. Temperature \( T \) is in different reduced units in the two panels. \( T^* \) in panel (b) should be multiplied by about 22 for comparison with panel (a). Note that at high \( T \) the phase diagrams are qualitatively different; the L phase in panel (a) coexists with the disordered phase, while in panel (b) it coexists with the H and IH phases. Moreover, at high \( T \) the L phase in simulations is stable at significantly higher density (\( \rho \approx 0.39 \)) than in MF (\( \rho \approx 0.25 \)). In a more accurate DFT, a phase diagram qualitatively similar to the one shown in panel (b) was obtained [2, 3]. In particular, at high \( T \) the sequence of phases is D,C,H,L,IH,IC,D, instead of D,L,D obtained in simulations.

An attempt to combine the density functional theory (DFT) with the LB theory has been undertaken in Ref.[1, 25–28]. In this approach, the short- and long-wavelength fluctuations of the local volume fraction are included in two separate contributions to the grand potential. The first contribution has the standard DFT form in the local density approximation. The
second contribution is associated with the long-wavelength fluctuations and has the form known from the statistical field theory. In this approach, the grand potential functional, $\Omega[\zeta]$, depends on the mesoscopic volume fraction $\zeta(r)$ that represents the microscopic volume fraction averaged over the mesoscopic region (somewhat larger than the size of the particles, and smaller than the size of the aggregates) around $r$. The equilibrium structure corresponds to the minimum of the grand-potential functional. The equations obtained in Ref.\,[1, 25], however, are rather difficult, and so far the phase diagram has been obtained in this theory only on the MF level \,[1, 13]. The effects of fluctuations have been taken into account in determination of the equation of state (EOS) for the disordered phase \,[26–28]. It is worth mentioning that the presence of aggregates leads to a significant change of the shape of the lines $\mu(\bar{\zeta})$ and $p(\bar{\zeta})$, where $\mu$ and $p$ are the chemical potential and pressure respectively, and $\bar{\zeta}$ is the space-averaged volume fraction of the particles. In particular, for $\bar{\zeta}$ optimal for a periodic structure, the compressibility is quite small, despite rather small value of $\bar{\zeta}$, and is large for $\bar{\zeta}$ that does not fit any ordered pattern. The predictions of our theory were compared with the exact results obtained in a one-dimensional model \,[14], and a semiquantitative agreement was obtained \,[28]. In particular, at low $T$, i.e. close to the stability of the periodic structure at $T = 0$, a step-like shape of $\mu(\bar{\zeta})$ was obtained, in agreement with the exact results. Thus, the theory is promising and is worth further development.

In this work we make additional assumptions concerning the dominant fluctuation-contribution to the grand potential. With these assumptions, we obtain in sec.II an expression for $\Omega[\zeta]$ that can be directly minimized numerically. In sec.III we limit ourselves to relatively high $T$, where the average volume fraction $\zeta(r)$ has a nearly sinusoidal shape \,[3] in the direction of oscillations. In this case, the average volume fraction $\zeta(r)$ can be characterized by its space-averaged value $\bar{\zeta}$, the period of oscillations $2\pi/k_0$, the amplitude of the oscillations $\Phi$ and by the symmetry of the ordered structure. From minimization of $\Omega$ we obtain equations for $\Phi$, $\mu(\bar{\zeta})$ and $p(\bar{\zeta})$, and from the latter two we get $p(\mu)$ for the stable or metastable structures. These results allow for a construction of the high-$T$ portion of the phase diagram. In sec.IV we consider the SALR systems studied before by simulations in Ref.\,[5, 20]. We obtain the high-$T$ part of the phase diagram and compare our results with simulations. In addition, we obtain and discuss the EOS and compressibility isotherms. Finally, we present $\Phi(\bar{\zeta})$ in the ordered phases and compare it with the fluctuation (standard deviation of the local volume fraction from $\bar{\zeta}$) in the metastable D phase for
the corresponding thermodynamic state. In sec. V, we discuss the effects of spontaneously formed mesoscopic inhomogeneities in the D phase on the internal energy and entropy, and argue that in our theory the fluctuation contributions to the grand potential have a clear physical interpretation. We summarize our results in the same section.

II. DERIVATION OF THE GRAND-POTENTIAL FUNCTIONAL OF THE MESOSCOPIC VOLUME FRACTION OF PARTICLES

The mesoscopic volume fraction has been introduced in Ref. 25. Here we briefly summarize its key properties. Consider first the microscopic volume fraction for $N$ spherical particles with the diameter $\sigma$ and the centers at $\mathbf{r}_\alpha$, $\tilde{\zeta}(\mathbf{r}) = \sum_{\alpha=1}^{N} \theta(\sigma/2 - |\mathbf{r} - \mathbf{r}_\alpha|)$, where $\theta$ is the Heaviside step function (Fig. 2a). In the case of the macroscopic volume $V$, $\frac{1}{V} \int \mathrm{d}\mathbf{r} \tilde{\zeta}(\mathbf{r}) = \frac{4}{3}\pi \sigma^3 N/V = \bar{\zeta}$, where $\bar{\zeta}$ is the macroscopic volume fraction of the particles. We can define the local mesoscopic volume fraction at $\mathbf{r}$ in a similar way as in the formula above, by averaging over the sphere with the center at $\mathbf{r}$ and the diameter $\sigma \leq D \ll \lambda$, where $\lambda$ is the scale of the inhomogeneities in the system (Fig. 2b). The precise value of $D$ has no significant effect on the results, as long as we are interested in the structure formation on the larger length scale $\lambda$. Note that by construction, $\zeta(\mathbf{r})$ is a continuous function and $0 \leq \zeta(\mathbf{r}) \leq \zeta_{cp}$, where $\zeta_{cp}$ is the close-packing volume fraction. In this mesoscopic theory, we can describe the distribution of the clusters or layers, but cannot describe the structure inside the aggregates.

$\zeta(\mathbf{r})$ can be considered as a constraint imposed on the microscopic volume fractions 1, 25. The constraint $\zeta(\mathbf{r})$ means that in the allowed microstates the particles occupy the fraction $\zeta(\mathbf{r})$ of the mesoscopic volume around $\mathbf{r}$. In the presence of the constraint $\zeta(\mathbf{r})$, the grand potential has the form 1, 25

$$\Omega_{co}[\zeta] = U[\zeta] - TS[\zeta] - \mu \int \mathrm{d}\mathbf{r} \zeta(\mathbf{r}),$$

where $U[\zeta], S[\zeta]$ and $\mu$ are the internal energy, the entropy and the chemical potential respectively in the system with the constraint $\zeta(\mathbf{r})$ imposed on the microscopic volume fractions.

When fluctuations $\phi(\mathbf{r})$ around $\zeta(\mathbf{r})$ can occur, they lead to an extra contribution to the
FIG. 2: Panel (a): the microscopic volume fraction in the one-dimensional case for the microscopic state represented by the red circles. Panel (b): Construction of the mesoscopic volume fraction in a two dimensional system with the particles self-assembling into small clusters separated by a distance larger than the range of the repulsion. The mesoscopic regions are shown as the circles with the diameter $D$ and the centers at $r_1$ and $r_2$. $\zeta(r_i)$ is the fraction of the area of the circle that is covered by the particles. The coarse-graining procedure leads to a continuous function $\zeta(r)$, at the cost of smearing of the clusters.

The grand potential, and

$$\beta \Omega[\zeta] = \beta \Omega_{\text{co}}[\zeta] - \ln \left[ \int D\phi e^{-\beta H_f[\zeta, \phi]} \right]$$

(2)

where

$$\beta H_f[\zeta, \phi] = \beta \Omega_{\text{co}}[\zeta + \phi] - \beta \Omega_{\text{co}}[\zeta],$$

(3)

$\beta = 1/k_B T$ and $k_B$ is the Boltzmann constant. $\zeta$ represents the average mesoscopic volume fraction when $\langle \phi \rangle = 0$, and $\Omega[\zeta]$ takes the minimum, i.e.

$$\frac{\delta \beta \Omega[\zeta]}{\delta \zeta(r)} = \frac{\delta \beta \Omega_{\text{co}}[\zeta]}{\delta \zeta(r)} + \langle \frac{\delta \beta H_f[\zeta, \phi]}{\delta \zeta(r)} \rangle = 0.$$ 

(4)

In Eq.(4), $\langle X \rangle$ means $X$ averaged over the fluctuations $\phi$ with the probability $\propto \exp(-\beta H_f)$.

As shown in Ref. [1, 25], $\langle \zeta(r) \rangle$ is equal to the ensemble average of $\zeta(r')$ for $|r' - r| < D/2$, further averaged over the mesoscopic region around $r$ (see Fig.2b). Likewise, the correlation function for $\zeta$ at the points $r_1$ and $r_2$ is equal to the microscopic correlation function between
the points $r'$ and $r''$ belonging to the mesoscopic regions around $r_1$ and $r_2$ respectively, averaged over these regions.

We assume that $U[\zeta]$ is given by the standard expression

$$U[\zeta] = \frac{1}{2} \int dr_1 \int dr_2 V_{co}(r_1 - r_2)\zeta(r_1)\zeta(r_2),$$

(5)

where for the interaction potential $V(r_{12})$ depending only on the distance $r_{12} = |r_1 - r_2|$, $V_{co}(r_{12}) = V(r_{12})g(r_{12})$.

(6)

We assume that the microscopic pair distribution function for the volume fraction, $g$, depends on $r_{12}$, and vanishes for $r_{12} < \sigma$, where $\sigma$ is the particle diameter. In practice, to determine the structure on the mesoscopic length scale, one may use the approximation $g(r) = 0$ or $g(r) = 1$ for $r < \sigma$ or $r > \sigma$, respectively.

We further assume that the entropy $S$ satisfies the relation

$$-TS = F_h = \int dr f_h(\zeta(r)),$$

(7)

where $F_h$ is the free-energy of the reference hard-sphere system in the local-density approximation. The local density approximation is justified in the studies of the structure on the mesoscopic length scale. Indeed, the portion of the phase diagram obtained in Ref. [2] in the much more accurate White Bear version of the DFT [29] agrees quite well with the results obtained in the local density approximation in Ref. [3]. For the free-energy density of the hard-sphere reference system, we assume the Percus-Yevick approximation,

$$\beta f_h(\zeta) = \rho^* \ln(\rho^*) - \rho^* \left[ \frac{3(2 - \zeta)}{2(1 - \zeta)^2} - \ln(1 - \zeta) \right],$$

(8)

where $\rho^* = 6 \zeta/\pi$. Different approximations, such as the Carnahan-Starling approximation, are also possible.

In order to calculate the second term in (2), we need to make approximations. The magnitude of the relevant fluctuations is small ($0 \leq \zeta(r) + \phi(r) \leq \zeta_{cp}$), and [4] can be approximated by a truncated Taylor expansion,

$$\beta H_f[\zeta, \phi] = \int dr \sum_{n=1}^{\infty} \frac{a_n(\zeta(r))}{n!} \phi(r)^n$$

$$+ \int dr_1 \int dr_2 \left[ \frac{1}{2}\beta V_{co}(r_{12})\phi(r_1)\phi(r_2) + \beta V_{co}(r_{12})\zeta(r_1)\phi(r_2) \right] - \beta \mu \int dr \phi(r),$$

(9)
\[ a_n(\zeta(r)) = \frac{\partial^n \beta f_h(\zeta(r))}{\partial \zeta(r)^n}. \]  

(10)

We further assume that the periodic order can be destroyed by the fluctuations that vary slowly on the length scale of the size of the unit cell of the ordered pattern. For slowly varying fluctuations we can assume that within a single unit cell \( \phi \) is nearly constant, and we replace \( H_f \) (Eq.(9)) by

\[ \tilde{H}_f[\zeta, \phi] = \frac{1}{2} \int \frac{dk}{(2\pi)^3} \tilde{\phi}(k)\beta \tilde{V}_{co}(k)\tilde{\phi}(-k) + \int dr \left[ \sum_{n=2} A_n[\zeta] \phi(r)^n + C_1[\zeta] \phi(r) \right], \]  

(11)

where \( C_1[\zeta] = A_1[\zeta] + \beta \tilde{V}_{co}(0)\zeta - \beta \mu \), we have introduced the functionals

\[ A_n[\zeta] = \frac{1}{V_u} \int_{V_u} d\zeta r a_n(\zeta(r)), \]  

(12)

by \( \bar{\zeta} \) we denote the space-averaged volume fraction,

\[ \bar{\zeta} = \frac{1}{V_u} \int_{V_u} d\zeta(\zeta(r)), \]  

(13)

\( V_u \) is the volume of the unit cell, and \( \tilde{f}(k) \) denotes the function \( f \) in the Fourier representation. We use the mixed real-space and Fourier representation for convenience.

Let us compare the correlation functions obtained with the effective Hamiltonian (9) and (11). In the case of ordered structures, the correlation function \( \langle \phi(r_1)\phi(r_2) \rangle \) obtained with the probability distribution \( \propto \exp(-\beta H_f) \), depends on both, \( r_1 \) and \( r_1 - r_2 \). However, when the effective Hamiltonian is approximated by (11), then the correlation function depends only on the distance between the considered points. It is instructive to consider the Gaussian correlations, with the expansions in (9) and (11) truncated at \( n = 2 \). For simplicity let us assume that the term linear in \( \phi \) vanishes. In the Gaussian approximation the inverse correlation functions are given by the second functional derivatives of \( \beta H_f[\zeta, \phi] \) and \( \beta \tilde{H}_f[\zeta, \phi] \) with respect to \( \phi, \)

\[ C_0(r_1, r_1 - r_2) := \frac{\delta^2 \beta H_f}{\delta \phi(r_1)\delta \phi(r_2)} = \beta V_{co}(r_{12}) + a_2(\zeta(r_1))\delta(r_1 - r_2) \]  

(14)

and

\[ C_0(r_1 - r_2) := \frac{\delta^2 \beta \tilde{H}_f}{\delta \phi(r_1)\delta \phi(r_2)} = \beta V_{co}(r_{12}) + A_2[\zeta] \delta(r_1 - r_2), \]  

(15)
From the above expressions for $C_0$ and $C_0$ and from Eq.\(^{12}\) with \(n = 2\), it follows that $C_0$ can be obtained from $C_0$ by averaging over the unit cell of the periodic structure. From now on we consider the approximate theory with the effective Hamiltonian $\bar{H}_f$ (Eq.\(^{11}\)).

As already noted in the introduction, the standard DFT describes very well the structure of simple fluids on the microscopic length scale, but fails to predict the correct topology of the phase diagram in the inhomogeneous, self-assembling systems. We restrict our attention to the latter systems, where the theory needs to be improved. The inhomogeneous distribution of particles occurs when $\tilde{V}_{co}(k)$ takes the global minimum at $k = k_0 > 0$, $\tilde{V}_{co}(k_0) < 0$ and the minimum is deep. For such potentials, we make the approximation

$$\beta \tilde{V}_{co}(k) = \beta^* (-1 + v_2 (k - k_0)^2) + \ldots \approx \beta^* (-1 + \frac{v_2}{4k_0^2}(k^2 - k_0^2)^2) + \ldots$$

(16)

where

$$v_2 = \frac{\tilde{V}_{co}''(k_0)}{2|\tilde{V}_{co}(k_0)|},$$

(17)

and the second equality holds for $k \approx k_0$, i.e. for the relevant fluctuations. The density waves with the wavenumber $k_0$ appear with the highest probability, because $\tilde{V}_{co}(k)$ takes the minimum for $k = k_0$; fluctuations with $k$ significantly different from $k_0$ occur with much smaller probability. We have introduced the dimensionless temperature

$$T^* = 1/\beta^* = \frac{k_B T}{|\tilde{V}_{co}(k_0)|}.$$  

(18)

$T^*$ represents the ratio between the thermal energy, and the energy decrease per unit volume associated with the excitation of the volume-fraction wave $\sqrt{2} \cos(k_0 z)$ in the homogeneous state (see the first term in \(^{11}\)).

Note that Eq.\(^{16}\) is not valid in simple systems with purely attractive interactions. The attractive potential in Fourier representation takes the minimum at $k = k_0 = 0$, and its expansion about the minimum is proportional to $k^2 - |const.|$. The wavelength of the most probable density wave in simple systems is $2\pi/k_0 \to \infty$, while in the self-assembling systems $2\pi/k_0$ is finite. In physical terms, the simple systems tend to a macroscopic separation into the gas and liquid phases, because large aggregates of the particles are favoured by the attractive potential. In contrast, the systems considered in this work tend to a microseparation into aggregates formed on the mesoscopic length scale, because the repulsion suppresses further growth of the clusters. In the rest of this work we assume that the interaction potential
can be approximated by Eq.(16), and only for such systems the considerations in the rest of this work are valid.

Since for each fixed $\zeta(r)$, the coefficients $A_n[\zeta]$ are just numbers, Eq.(11) with (16) has the form similar to the LB functional [23]. When the series in (11) is truncated at the term $\propto \phi^4$, we obtain the LB functional. Thus, we can directly apply the results obtained in the LB theory by the FT methods [23, 26] for determination of the explicit form of the second term in (2). In order to calculate this term, we need to know the correlation function

$$G(r_1 - r_2) := \langle \phi(r_1)\phi(r_2) \rangle. \quad (19)$$

In the Brazovskii $\varphi^4$ theory, inverse correlation function $\tilde{C}(k) = 1/\tilde{G}(k)$ satisfies the self-consistent equation (self-consistent Hartree approximation) [1, 23–26]

$$\tilde{C}(k) = \tilde{C}_0(k) + \frac{A_4[\zeta]}{2} G \quad (20)$$

where $C_0$ is given in (15), and

$$G := \langle \phi(r)\phi(r) \rangle = \int \frac{dk}{(2\pi)^3} \tilde{G}(k). \quad (21)$$

By construction of the mesoscopic theory, the cutoff $2\pi/D$ is present in the integral in (21). When $\tilde{V}_{co}$ is approximated by (16) and $0 \ll k_0 \ll 2\pi/D$, then the main contribution to $G$ is cutoff-independent, and is given by [23, 24, 26]

$$G \approx \frac{2a}{Z[\zeta]} \sqrt{T^*} \quad (22)$$

where

$$a = \frac{k_0^2}{4\pi \sqrt{v_2}}, \quad (23)$$

$$Z[\zeta] := \sqrt{\tilde{C}(k_0)}, \quad (24)$$

and $v_2$ is defined in (17). Note that $a$ characterizes the interaction potential. We should stress that in this mesoscopic theory, $\langle \phi(r)\phi(r) \rangle$ does not represent the microscopic correlation function calculated at zero distance. It is rather the microscopic correlation function between two points belonging to the same mesoscopic region around $r$, and averaged over this mesoscopic region [1, 25]. Thus, $G$ can be considered as a measure of local deviations from the space-averaged volume fraction $\tilde{\zeta}$. 

Eqs. (20), (22) and (24) can be easily solved for $k = k_0$, and $Z[\zeta]$ in the $\varphi^4$ theory is given by the expression \[ Z[\zeta] = \frac{W[\zeta]}{6} + \frac{2(A_2[\zeta] - \beta^*)}{W[\zeta]}, \] (25)

where

\[ W[\zeta] = \left[ 108A_4[\zeta]a\sqrt{T^*} + 12\sqrt{(9aA_4[\zeta])^2T^* - 12(A_2[\zeta] - \beta^*)^3} \right]^{1/3}. \] (26)

In order to evaluate the fluctuation contribution to $\Omega[\zeta]$, we decompose $H_f[\zeta, \phi]$ into two parts \[ H_f[\zeta, \phi] = H_G[\zeta, \phi] + \Delta H[\zeta, \phi], \] (27)

where

\[ H_G[\zeta, \phi] = \frac{1}{2} \int \frac{d\mathbf{k}}{(2\pi)^3} \tilde{\phi}(\mathbf{k}) \tilde{C}(\mathbf{k}) \tilde{\phi}(-\mathbf{k}). \] (28)

Assuming $\Delta H \ll H_G$, we obtain \[ \beta \Omega[\zeta] \approx \beta \Omega_{co}[\zeta] - \log \int D\phi e^{-\beta H_G} + \langle \beta \Delta \mathcal{H} \rangle_G + O((\beta \Delta \mathcal{H})^2_G), \] (29)

where $\langle ... \rangle_G$ denotes averaging with the Gaussian Boltzmann factor $\propto e^{-\beta H_G}$. The fluctuation contribution in Eq. (29) for the approximations (20), (25) was calculated in Ref. [1, 23, 24, 26], and the final expression for $\beta \Omega[\zeta]$ in the $\varphi^4$ theory is

\[ \frac{\beta \Omega[\zeta]}{\mathcal{V}} \approx \frac{\beta \Omega_{co}[\zeta]}{\mathcal{V}} + 2a\sqrt{T^*}Z[\zeta] - \frac{A_4[\zeta]a^2T^*}{2Z[\zeta]^2}, \] (30)

where by $\mathcal{V}$ we denote the volume of the system, $\beta \Omega_{co}[\zeta]$ is given in (11)-(17), and $T^*$, $a$, $A_n[\zeta]$ and $Z[\zeta]$ are given in (18), (23), (12), and (25)-(26). The expression (30) for the grand potential can be minimized numerically to yield the equilibrium structure in the presence of mesoscopic fluctuations for any value of the chemical potential $\mu$ and temperature $T$.

In Eq. (30), the fluctuation contribution has been obtained under many assumptions and approximations. In particular, the expansion in (11) has been truncated at $n = 4$. This is justified when the higher-order terms are negligible for the dominant fluctuations. When the expansion in (11) is truncated at $n = 6$, then on the same level of the self-consistent one-loop approximation in the $\varphi^6$ theory we obtain \[ \tilde{C}(k_0) = A_2[\zeta] - \beta^* + \frac{A_4[\zeta]}{2}C + \frac{A_6[\zeta]}{8}g^2. \] (31)
Using (31), (22) and (24), we obtain the equation for $Z[\zeta]$ in the $\varphi^6$-theory,

$$Z[\zeta]^4 - (A_2[\zeta] - \beta^*) Z[\zeta]^2 - a\sqrt{T^*} A_4[\zeta] Z[\zeta] - \frac{a^2 T^* A_6[\zeta]}{2} = 0$$

(32)

and the expression for the grand potential (see (27)-(29)),

$$\beta \Omega[\zeta]/V \approx \beta \Omega_{\text{co}}[\zeta]/V + 2 a \sqrt{T^*} Z[\zeta] - \frac{A_4[\zeta] a^2 T^*}{2 Z[\zeta]^2} - \frac{A_6[\zeta] a^3 T^*^{3/2}}{3 Z[\zeta]^3}.$$ 

(33)

Eqs. (33) and (32) with (1), (5)-(8), (18), (23) and (12) are the main result of this section. Minimization of $\beta \Omega[\zeta]/V$ gives $\zeta(r)$ corresponding to a stable or a metastable phase.

III. THE CASE OF WEAK ORDER

The average volume fraction in the ordered phase can be written in the form

$$\zeta(r) = \bar{\zeta} + \Phi(r),$$

(34)

where by definition of $\bar{\zeta}$, $\Phi$ must satisfy $\int d\mathbf{r} \Phi(r) = 0$. In the ordered periodic phases

$$\Phi(r) = \sum_{n \geq 1} \Phi_n g_n(r),$$

(35)

where $g_n(r)$ represent orthonormal basis functions for the $n$-th shell that have the symmetry of the considered phase, and satisfy the normalization condition

$$\frac{1}{V_u} \int_{V_u} d\mathbf{r} g_n(r)^2 = 1.$$ 

(36)

By weak order we mean the structure with $\Phi(r)$ that can be approximated by the first shell in (35), and has a small magnitude. The functions $g_1(r)$ are given by a superposition of plane waves with the wavevectors $\mathbf{k}_0^j$ such that $|\mathbf{k}_0^j| = k_0$. In Fourier representation

$$\tilde{g}_1(\mathbf{k}) = \frac{(2\pi)^d}{\sqrt{2n}} \sum_{j=1}^n \left( w \delta(\mathbf{k} - \mathbf{k}_0^j) + w^* \delta(\mathbf{k} + \mathbf{k}_0^j) \right),$$

(37)

where $ww^* = 1$ and $2n$ is the number of the vectors $\mathbf{k}_0^j$ in the first shell. In the case of the lamellar phase with the oscillations in direction $\hat{z}$, $g_1(z) = \sqrt{2} \cos(k_0 z)$. The expressions for $g_1(r)$ for the remaining phases can be found in Appendix. In the one-shell approximation we denote the amplitude by $\Phi$ (we omit the subscript 1). By definition of $\bar{\zeta}$, $\int_{V_u} d\mathbf{r} g_1(r) = 0$. 

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We can Taylor expand \( a_n(\zeta(r)) \) defined in (10),
\[
a_n(\zeta(r)) = a_n(\bar{\zeta}) + \sum_{m \geq 1} \frac{a_{n+m}(\bar{\zeta})}{m!} \Phi(r)^m,
\]
(38)
and the expansion can be truncated in the case of \( \Phi \ll 1 \). Eq.(38) with \( n = 0 \), and Eq.(37) lead to an approximate form of \( \Omega_{co} \) that at this level of approximation becomes a function of \( \bar{\zeta} \) and \( \Phi \) of the form
\[
\beta \Omega_{co}(\bar{\zeta}, \Phi)/\mathcal{V} = \beta \Omega_{co}(\bar{\zeta})/\mathcal{V} - \frac{\beta^*}{2} \Phi^2 + \sum_{n \geq 2} \frac{a_n(\bar{\zeta})}{n!} \kappa_n \Phi^n
\]
(39)
where \( M \geq 4 \),
\[
\beta \Omega_{co}(\bar{\zeta})/\mathcal{V} = \frac{1}{2} \beta^* v_0 \bar{\zeta}^2 + \beta f_b(\bar{\zeta}) - \beta \mu \bar{\zeta},
\]
(40)
\[
v_0 = \frac{V_{co}(0) / |V_{co}(k_0)|},
\]
(41)
and \( \beta^* \) and \( a_n(\bar{\zeta}) \) are defined in (18) and (10), respectively. We have introduced the geometric factors
\[
\kappa_n = \frac{1}{V_u} \int_V d\mathbf{r} g^a_n(r)
\]
(42)
that except from \( \kappa_2 = 1 \) take different values for different phases, and are given in Appendix. Here we limit ourselves to the \( \varphi^M \) theory with \( M = 4 \) and \( M = 6 \).

For \( n \geq 1 \) the expansion (38) leads to approximate forms of \( A_n[\zeta] \) defined in (12) that also become functions of \( \bar{\zeta} \) and \( \Phi \), and inserted in (11) lead to \( \bar{H}_f \) that is a function of \( \bar{\zeta} \) and \( \Phi \), and a functional of the fluctuation \( \phi \). In the case of weak order, where fluctuations play an important role, we may expect that \( \Phi \) and the dominant fluctuations are of the same order of magnitude. Thus, in the \( \varphi^M \)-theory we keep in \( \bar{H}_f \) only terms \( \Phi^n \phi^m \) with \( n + m \leq M \). In this case, \( A_n[\zeta] \) in Eq.(11) is approximated by
\[
A_n(\bar{\zeta}, \Phi) = a_n(\bar{\zeta}) + \sum_{m = 2}^{M-n} \frac{a_{n+m}(\bar{\zeta}) \kappa_n \Phi^m}{m!},
\]
(43)
and the series in Eq.(11) is truncated at \( n = M \).

An important consequence of the reduction of the functionals \( \Omega_{co}[\zeta] \), \( A_n[\zeta] \) to the functions of the two variables, \( \bar{\zeta} \) and \( \Phi \), is the reduction of the equilibrium condition (4) to just two equations,
\[
\left( \frac{\partial \beta \Omega_{co}(\bar{\zeta}, \Phi)}{\partial \Phi} + \frac{\partial \beta \bar{H}_f}{\partial \Phi} \right) = 0
\]
(44)
The explicit forms of Eqs. (44) and (45), and the explicit expression for the thermodynamic pressure \( p = -\Omega/V \) (Eq. (30) or (33)) are given in Appendix. From these equations, we can obtain \( \Phi, \mu^* = \mu/|\tilde{V}_\text{co}(k_0)| \) and \( p^* = p/|\tilde{V}_\text{co}(k_0)| \) for the stable or metastable phase for each value of \( \tilde{\zeta} \), and for each set of the geometric factors \( \kappa_n \) characterizing the considered phases. From \( \mu^*(\tilde{\zeta}) \) and \( p^*(\tilde{\zeta}) \), we obtain \( p^*(\mu^*) \) isotherms by eliminating \( \tilde{\zeta} \). The phase coexistence occurs when the lines \( p^*(\mu^*) \) for two phases intersect. In addition, we obtain the EOS isotherms \( p^*(\tilde{\zeta}) \).

Solving the algebraic equations (see Appendix) is an easier task than finding the minimum of the functional in Eq. (30) or (33). Unfortunately, because of the one-shell approximation, these equations are valid only for nearly sinusoidal shapes of the volume-fraction profiles. Such shapes were found in the MF-type DFT theory [3] only at the high-\( T \) part of the phase diagram. The volume-fraction profiles deviate significantly from sinusoidal shapes in a substantial part of the phase diagram [3], therefore the one-shell approximation developed in this section is certainly an oversimplification, except at relatively high \( T \), where the order is weak and the fluctuations are strong.

**IV. EXAMPLES**

In this section we consider hard spheres that for distances larger than \( \sigma \) interact with the SALR potential of the form of a square well followed by a repulsive ramp, since for this potential the phase diagram has been obtained in MC simulations [3, 20]. In Ref. [3, 20], the potential between the particles has the form

\[
u(r) = \begin{cases} 
\infty & \text{if } r < 1, \\
-\epsilon & \text{if } 1 < r < 3/2, \\
\epsilon\xi(\kappa - r) & \text{if } 3/2 < r < \kappa, \\
0 & \text{if } r > \kappa,
\end{cases}
\]  

(46)

where the length unit is the particle diameter \( \sigma \). The depth of the square well, \( \epsilon \), sets the unit of energy (\( \epsilon = 1 \) is assumed), and the dimensionless temperature is defined by \( \tilde{T} = k_B T/\epsilon \).
We shall focus on two systems, System 1 with $\xi = 0.05$ and $\kappa = 4$, and System 2, with $\xi = 6$ and $\kappa = 2$. In System 1, the slope of the ramp is small, and the weak repulsion has a relatively large range, while in System 2, the strong repulsion is of a short range. In Ref.[5], no stable periodic structures were found for System 2. In System 1, the simulations were restricted to $\rho^* < 0.45$ ($\zeta < 0.236$). For this range of dimensionless densities, the D, C, H and L phases (see Fig[1]) are stable for increasing density for $\bar{T} < \bar{T}_C \approx 0.41$. There is also a narrow window of stability of the double-gyroid phase between the H and L phases at low $\bar{T}$. For $0.41 \approx \bar{T}_C < \bar{T} < \bar{T}_H \approx 0.49$, the sequence of phases is D, H and L. The H phase disappears for $\bar{T} > \bar{T}_H \approx 0.49$. For $0.49 \approx \bar{T}_H < \bar{T} < \bar{T}_L \approx 0.535$ and $\rho^* < 0.45$, L is the only stable ordered phase. For a small range of temperature below $\bar{T}_L \approx 0.535$, a reentrant melting of the L phase was observed, i.e. as long as $\rho^* < 0.43$, the sequence of phases for increasing density is D, L, D.

Note that in the expression for the internal energy (Eq.(5)) we use volume fractions instead of densities, therefore the potential $u$ should be rescaled, i.e. in Eq.(5), $V(r) = (6/\pi)^2 u(r)$. Moreover, we consider the product $V_{co}(r) = V(r)g(r)$, where $g(r) = 0$ for $r < 1$ and $g(r) = 1$ for $r > 1$ (in $\sigma$-units). The function $V_{co}$ for the two considered systems is shown in Fig[3] in Fourier representation.

FIG. 3: $V_{co}$ defined in Eq.(6) in Fourier representation. The solid line corresponds to System 1 (the interaction potential (46) with $\kappa = 4$ and $\xi = 0.05$), and the dashed line corresponds to System 2 (the interaction potential (46) with $\kappa = 2$ and $\xi = 6$). The wavenumber $k$ is in $\sigma^{-1}$ units, and $\tilde{V}_{co}(k)$ is in $\epsilon$-units, with $\sigma$ and $\epsilon$ denoting the particle diameter and the depth of the square-well (Eq.(46)).
The period of the most probable density wave is $2\pi/k_0$, where $\tilde{V}_{co}(k)$ takes the minimum at $k_0$. Fig. 3 shows that the excitation of the most probable density wave leads to a similar energy gain per unit volume in the two systems. From the energy point of view, the two systems should show similar tendency for periodic ordering. Simulations, however, show periodic ordering only in System 1.

Apart from $\tilde{V}_{co}(k_0)$ and $k_0$, the relevant parameters characterizing the potential in our theory are $v_0$ and $a$ defined in Eq. (41) and in Eq. (23), respectively. For the considered potentials we have:

System 1: $\kappa = 4$, $\xi = 0.05$, $k_0 \approx 1.3$, $v_0 \approx 0.2345$, $a \approx 0.116$, (47)

System 2: $\kappa = 2$, $\xi = 6$, $k_0 \approx 2.435$, $v_0 \approx 3.18$, $a \approx 0.566$, (48)

The larger value of $k_0$ in System 2 leads to a value of $a$ almost 5 times larger than in System 1. Note that the fluctuation contributions to the grand potential are proportional to $(a^2T^*)^{n/2}$ with $n = 1 - 3$ (see (33)). Thus, at given $T^*$ the fluctuation contribution in System 2 is expected to be larger than in System 1. However, the increase of $a$ can be compensated by a decrease of $T^*$ to obtain in System 2 the same value of the parameter $(a^2T^*)^{n/2}$ as in System 1. This simple analysis indicates that the ordered phases should occur in System 2, but at much lower temperature than in System 1. Physically, the larger period means a smaller number of aggregates per unit volume, and smaller entropy associated with distribution of these aggregates in space. For this reason the disordering effect of entropy in System 1 is weaker than in System 2, and in the former the ordered phases can be stable at higher temperature than in the latter.

In order to obtain the phase diagrams in the two systems, we perform the analysis described in sec. III. For the reference-system free-energy density we assume the PY approximation (8). The derivatives $a_n(\zeta)$ of $\beta f_h(\zeta)$ can be easily calculated. We solve (56)-(58) (with $Z(\zeta, \Phi)$ given by (25) and (26) in the $\varphi^4$-, or by (32) in the $\varphi^6$-theory, with $A_n[\zeta]$ approximated by (43)). In some cases there is more than one solution for $\Phi$. We have verified that the larger value of $\Phi$ leads to larger $p^*$ for given $\mu^*$; we have selected this solution, and obtained $\mu^*(\zeta)$ and $p^*(\zeta)$ for each set of the geometric factors $\kappa_n$ and for fixed $T^*$. Finally, from the intersections of the isotherms $p^*(\mu^*)$, we have obtained the phase diagrams. The results for the high-temperature part of the phase diagram in System 1 in the $\varphi^4$- and $\varphi^6$-theory are shown in Fig. 4.
FIG. 4: The high-$T^*$ part of the phase diagram in System 1 (the interaction potential (16) with $\kappa = 4$ and $\xi = 0.05$) in the $\varphi^4$-theory (a) and in the $\varphi^6$-theory (b). The reduced temperature $T^*$ is defined in Eq. (18), and the volume fraction $\zeta$ is dimensionless. To compare with the phase diagram obtained in simulations, note that dimensionless temperature and density in Ref. 20 are $\bar{T} = T^*|\tilde{V}_{co}(k_0)| \approx 22.14T^*$ and $\rho^* = 6\zeta/\pi$. D, L, IH, IC denote the disordered, lamellar, inverted hexagonal and inverted cubic (bcc) phases (Fig. 1). The two-phase coexistence regions are gray-shaded. The symbols indicate the values of $T^*$ for which the phase coexistence was calculated according to Eqs. (56)-(58).

The main features of the phase diagram in the $\varphi^4$- and $\varphi^6$-theory are similar, but the details are different. In the $\varphi^6$-theory the IC phase is stable, whereas in the $\varphi^4$-theory it is only metastable for the volume fraction inside the IH-D two-phase region. However, the difference between the grand potentials in the stable IH, D and metastable IC phases is very small, therefore the accuracy of the approximation plays a significant role in determining the stability of the IC phase. In the $\varphi^6$-theory the ordered phases are stable for lower temperature and larger volume fraction than in the $\varphi^4$-theory. The L phase is stable for the volume fractions that in the $\varphi^6$-theory agree pretty well with simulations. Another difference between the two approximations is the reentrant melting of the L phase at high temperature, present only in the $\varphi^6$-theory. Recall that in simulations, the sequence of phases D,L,D was found close to $\bar{T} = \bar{T}_L$, therefore we conclude that the shape of the high-T part of the phase diagram is correctly reproduced by our $\varphi^6$-theory, at least for $\zeta < 0.236$.

Our temperature scale is different than in simulations (see Eq. (18)), and the relation is $T^* = \bar{T}/|\tilde{V}_{co}(k_0)|$, i.e. $T^* \approx \bar{T}/22.14$ in System 1. While the range of volume fraction corresponding to the stability of the L phase in theory and simulations is in rather good
agreement, the temperature range of stability of the L phase in our theory is smaller than in simulations; the L phase loses stability in System 1 at $T^*_L \approx 0.0154$, that corresponds to $\bar{T}_L \approx 0.34$, whereas simulations give $\bar{T}_L \approx 0.535$. On the one hand, the fluctuation contribution in our approximation may be overestimated. On the other hand, in simulations the finite size of the system and periodic boundary conditions suppress the mesoscopic fluctuations of large wavelengths that destroy the periodic order in the bulk. For this reason, in simulations the temperature range corresponding to stability of the periodic structures may be overestimated.

Note that in MF (Fig.1), all the ordered phases are stable up to $\bar{T}_L \approx 2$ (to get $k_BT$ in the $\epsilon$ units, $T^*$ in Fig.1 should be multiplied by 22.14), and at this maximum temperature the density region of all the ordered phases shrinks to $\rho \approx 0.25$. This is in a sharp contrast to both, our theory and simulation results, where at high temperature the H and C phases are not stable, and the low-density D phase coexists with the L rather than with the C phase. For a better comparison between our theory and simulations, we show in Fig.5 the high-T part of the phase diagram obtained in simulations [20] and in this theory.

The large stability region of the IH phase is rather surprising, but since the simulations in Ref.[5] were restricted to $\zeta < 0.236$, we cannot verify if our predictions are correct for large volume fractions. We can only note that the inverse phases, with periodically distributed voids, have been investigated in simulations in Ref.[33, 34]. Unfortunately, in Ref.[33, 34] the phase diagram was not determined.

For the temperature range shown in Fig.4, the phases C and H are not stable. The C phase is not even metastable for $T^* > 0.011$, and the H-phase is not metastable for $T^* > 0.0133$. Unfortunately, for $T^* < 0.013$ the one-shell approximation leads to unphysical results for the lamellar phase. We obtain the amplitude leading to local volume fractions $\zeta(r)$ that in some regions are negative, and in some other regions much greater than one. As shown in Ref.[3], $\zeta(r)$ deviates strongly from the sinusoidal shape at low $T^*$. Our results indicate that for $T^* < 0.013$ the approximation developed in sec.III is a significant oversimplification, and for such temperatures one has to go beyond the one-shell approximation. The H phase becomes metastable for $T^* < 0.864T^*_L$, and the C phase becomes metastable for $T^* < 0.714T^*_L$. In simulations, the H and C phases become stable for $\bar{T} < 0.916\bar{T}_L$ and $\bar{T} < 0.766\bar{T}_L$ respectively. These temperature ratios in the theory and in simulations are similar. Since by decreasing $T^*$ we obtain the metastable H phase and next the metastable C phase (both
FIG. 5: The high-T part of the phase diagram in dimensionless density $\rho$ and temperature in $\epsilon$ units for System 1. Panel (a): the part of the phase diagram obtained in simulations, Ref. [20]. Panel (b): this theory. Since the density range where the IH and IC phases are stable was not studied in simulations, we do not show the part of the phase diagram corresponding to stability of these phases. Note that in the $\varphi^6$ theory the stability region of the ordered phases is shifted to higher densities compared to the $\varphi^4$ theory (see Fig. 4). We may expect that in the $\varphi^8$ or higher order theory this trend will lead to a still better agreement with simulations. Note the coexistence of the L phase with the D phase and the reentrant melting close to $T_L$ in both cases, in contrast to the coexistence of the L phase with the H and IH phases up to $T_L$ in MF (Fig. 1). The different temperature range of the stability of the ordered phases is discussed in the main text.

more stable than the D phase for some temperature interval), we may expect that with the proper shape of the volume-fraction profile of the L phase, i.e. beyond the one-shell approximation, the correct low-T part of the phase diagram can be obtained by a numerical minimization of the functional (33).

The phase diagram in System 2 has been obtained in the $\varphi^6$-theory, and is shown in Fig. 6. The shape of the phase diagram in both systems is similar, except that the IC phase in System 2 is only metastable. Note, however, that the ordered phases in System 2 are stable at much lower temperatures than in System 1, in agreement with the simple arguments discussed above. The relation between the temperature scales in our theory and in simulations in System 2 is $T^* = \bar{T}/|V_{co}(k_0)| \approx \bar{T}/18.76$ (see Fig. 3).

The ratio between the temperature $T^*_L$ in System 2 and in System 1 in our theory is 0.52.
FIG. 6: The high-$T^*$ part of the phase diagram in System 2 (the interaction potential (46) with $\kappa = 2$ and $\xi = 6$) in $\varphi^6$-theory. The reduced temperature $T^*$ is defined in Eq. (18), and the volume fraction $\zeta$ is dimensionless. Note that temperature in Ref. [20] is $\bar{T} \approx 18.76T^*$. Assuming that in simulations of Ref. [20], this ratio is similar, we estimate the boundary of stability of the L phase in simulations of System 2 for $\bar{T}_L \sim 0.27$. In Ref. [20], the simulations were performed for $\bar{T} > 0.25$ and $\rho^* < 0.55$ [35], therefore if the ordered phases are present in System 2 for $\bar{T} < 0.25$, they could not be detected in these simulations. Thus, there is no contradiction between our predictions and simulations in Ref. [20].

Another interesting question concerning the SALR systems is the effect of self-assembly and periodic ordering of clusters or voids on the EOS and mechanical properties such as the compressibility $\chi_T^* = \bar{\zeta}^{-2} \partial \bar{\zeta}/\partial \mu^*$. This question has been much less studied than the phase diagram [26, 28]. We have calculated $p^*(\bar{\zeta})$ and $\chi_T^*(\bar{\zeta})$ for weakly ordered systems in the framework of the theory developed in Sec. III. The $T^* = 0.015$ and $T^* = 0.014$ isotherms for System 1 are shown in Fig. 7 and in Fig. 8 in the $\varphi^4$- and $\varphi^6$-theory, respectively. Note the characteristic shape of the $p^*(\bar{\zeta})$ lines that consist of segments with a large slope separated by the narrow two-phase regions. In the periodic phases the slopes of $p^*(\bar{\zeta})$ are larger than in the metastable D phase for the same volume-fraction interval (Fig. 8). As a result, the compressibility in the ordered phases is very low, despite relatively low density. In particular, at the D-L phase-coexistence the compressibility of the L phase is about 4 times smaller than the compressibility of the D phase, even though the volume fraction in the L phase is not much larger than in the D phase. Even more surprising is the larger compressibility in the D phase than in the coexisting IH phase, despite larger density in the former. Our results show that it is the periodic structure that makes the system quite stiff, despite relatively
large volume available for the particles.

FIG. 7: The $T^* = 0.015$ isotherm for the pressure (a) and compressibility $\chi_T^*$ (b) in the $\varphi^4$-theory, as functions of the particle volume fraction for System 1 (model (46) with $\kappa = 4$ and $\xi = 0.05$). The segments from left to right correspond to the D, L, IH and again D phases, and are separated by two-phase regions. $p^*$ and $1/\chi_T^*$ are in $|\tilde{V}_{\text{co}}(k_0)|/\sigma^3$ units.

FIG. 8: The $T^* = 0.014$ isotherm for the pressure as a function of the particle volume fraction in the $\varphi^6$-theory for System 1 (model (46) with $\kappa = 4$ and $\xi = 0.05$). The thick segments from left to right correspond to the stable D, L, IH, IC and again the D phases, and the thin continuations of the thick lines represent the corresponding metastable phase.

In derivation of the approximate form of $\bar{H}_f$ in sec. III (see Eqs. (9), (43)), we have assumed that in the case of weak order the amplitude $\Phi$ of the oscillation of the average volume fraction, and the dominant fluctuation $\phi$ are of the same order of magnitude. To verify this assumption, we plot $|\Phi|$ and $\sqrt{\langle \phi(r)^2 \rangle}$ in Fig. 9 for $T^* = 0.015$ and a range of $\tilde{\zeta}$. We can see that in the L, IH and IC phases, $\sqrt{\langle \phi(r)^2 \rangle}$ is smaller than $\Phi$ by a factor $\approx 1/2$. 

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Thus, for the high-$T^*$ part of the phase diagram, this assumption is valid. In addition, in Fig. 9 we plot $\sqrt{\langle \phi(r)^2 \rangle}$ in the stable and metastable D phase. Interestingly, $|\Phi|$ in the ordered phase is very similar to $\sqrt{\langle \phi(r)^2 \rangle}$ in the metastable D phase for the same volume fractions. Note that in the D phase, $\sqrt{\langle \phi(r)^2 \rangle}$ can be interpreted as the standard deviation of the local volume fraction in a mesoscopic region from the space-averaged value $\bar{\zeta}$. It is a measure of the excess number of particles in the dense regions, or of depletion of the particles in the dilute regions. Our results show that the local structure in the metastable D and in the stable ordered phases is very similar. Rather large fluctuations in the ordered phases mean a large number of defects in the periodic structure. In experiment, it may be difficult to distinguish the ordered and the disordered phases in the case of weak order.

![Figure 9: Amplitude of density oscillations and mesoscopic fluctuations.](image)

**V. DISCUSSION AND SUMMARY**

The main result of this work is the “user-friendly” expression for the grand-potential functional of the volume fraction of particles, Eqs. (30) with (25), or (33) with (32) that can be directly minimized numerically. In contrast to standard DFT functionals, our formula contains a contribution from mesoscopic fluctuations. This contribution has been obtained within the well-known field-theoretic formalism on the level of the Brazovskii approxima-
Unlike in the earlier phenomenological Landau-Brazovskii theories \[23, 24\], all parameters in our theory have precise relation with measurable quantities. For this reason our density-functional theory allows for predicting phase diagrams and EOS in standard thermodynamic variables for given interactions between the particles.

In the case of simple fluids, with dominant attractive interactions between the particles, the MF theories predict correct topology of the phase diagram. Only details concerning the shape of the coexistence curve close to the critical point are incorrect. In contrast, in the self-assembling systems the topology of the MF phase diagram is incorrect. Only at low temperature the sequence of ordered phases in MF and in simulations agree. When temperature increases, the periodic structures lose stability one by one, whereas in MF they all are stable up to the same temperature; only the range of density corresponding to the stability of the ordered phases decreases for increasing \( T \).

Let us discuss the physical reason for the qualitatively incorrect predictions of the MF theories at relatively high \( T \), and the physical meaning of the fluctuation-contributions in our theory. In the case of the disordered phase, the average volume fraction is position-independent, and the MF internal energy is \( \frac{1}{2} \bar{\zeta}^2 \int dr V_{co}(r) \). In a homogeneous structure, i.e. when the particles are more or less homogeneously distributed in space in majority of microstates, this is a fair approximation. However, in the case of competing interactions, the homogeneous distribution of particles occurs only at very high temperature or at very low density. At moderate temperature, the particles are not homogeneously distributed in the D phase, and aggregates are formed in majority of the microstates, as can be seen in simulation snapshots, cluster analysis [5, 19, 20, 36], and in the cartoon in Fig.2b. Thus, in the most probable microstates the distribution of the particles is significantly different from the position-independent average volume fraction. In a typical microstate, there are much more particle pairs at distances close to the minimum of the interaction potential, and much less particle pairs at distances corresponding to the repulsion, than for a homogeneous distribution of the particles (see Fig.2b.) For this reason, the internal energy in the D phase is much lower than predicted in MF. On the other hand, the entropy decreases when the aggregates are formed.

The decrease of both, the internal energy and the entropy that is associated with a presence of delocalized aggregates should be taken into account in a correction to the MF expression for the grand potential. To see that it is in fact what we do by adding our
fluctuation corrections obtained by formal considerations, let us focus on the $\varphi^4$ theory, and Eq. (30). Using Eqs. (22), (24), (15) and (20), we rewrite the first fluctuation-contribution in Eq. (30) in the form

$$2a\sqrt{T^*}Z[\zeta] = \frac{2a\sqrt{T^*}}{Z[\zeta]}Z[\zeta] = G\left(\beta\tilde{V}_{co}(k_0) + A_2[\tilde{\zeta}] + \frac{A_4[\tilde{\zeta}]}{2}G\right),$$

(49)

and for the D phase we obtain

$$\beta\Omega(\tilde{\zeta})/\mathcal{V} \approx \beta\Omega_{co}(\tilde{\zeta})/\mathcal{V} + \beta\tilde{V}_{co}(k_0)\mathcal{G} + a_2(\tilde{\zeta})\mathcal{G} + \frac{3a_4(\tilde{\zeta})}{8}\mathcal{G}^2.$$

(50)

Note that Eq. (50) is similar to the MF grand potential for a weakly ordered phase in the $\varphi^4$ theory (Eq. (39) with $M = 4$), except that in (50) $\mathcal{G}$ plays a role analogous to $\Phi^2/2$ in (39) (recall that $\beta\tilde{V}_{co}(k_0) = -\beta^*$). In this mesoscopic theory, $\sqrt{\mathcal{G}}$ represents a standard deviation of the local volume fraction from the space-averaged value $\bar{\zeta}$ (see (21)). Note also that the main difference between the D phase and the weakly ordered phase is the fact that the aggregates in the latter phase fluctuate around their average positions, while in the D phase they move freely. In both cases, the effect on the internal energy depends on the increase of the local density in the aggregates and the decrease of the density between them, i.e. on $\sqrt{\mathcal{G}}$ or $\Phi$. In this approximation, only the most probable density waves, with the period $2\pi/k_0$, and the energy decrease proportional to $\tilde{V}_{co}(k_0)$ are taken into account. In Eq. (39), the energy gain in the weakly ordered phases is associated with the MF average deviation from $\tilde{\zeta}$. In our fluctuation-contribution to the internal energy of the D phase, the energy gain is associated with the standard deviation of the local density from $\tilde{\zeta}$. The remaining terms in (39) and (50) represent the decrease of entropy in the presence of inhomogeneities - MF average profiles in (39), and delocalized aggregates in (50). One can see that in our theory the fluctuation contribution leads to the decrease of the internal energy and entropy, as expected on physical grounds. In the ordered phases the average volume fraction profile is smeared because of the fluctuations about the average positions, and the fluctuation contributions play a similar role as in the D phase.

One could consider better approximations for the direct correlation function in (20) or (31). However, since the present approximation captures the main physical effect of spontaneously appearing inhomogeneities, the high-temperature part of the phase diagram is correctly reproduced, and the functional (33) is relatively simple, we think that the present approximation is a good compromise between the accuracy and feasibility.
In the second part of this work we have developed a simplified theory valid for weakly-ordered phases, i.e. for the high-temperature part of the phase diagram. Predictions of this version of the theory agree quite well with simulation results, except that we predict lower temperature range of the stability of the lamellar phase, and the density range in simulations is too small to verify the stability of the IH and IC phases. We therefore could not verify if the IH phase, stable up to higher temperatures than the L phase in our theory, has the same property in reality.

The stability of the inverse phases with periodically distributed voids to higher temperatures than in the case of phases with periodically distributed clusters is an unexpected result. In MF, there is no such difference between the stability ranges of the H and IH phases. Our results show that fluctuations are more destructive for the periodic order of clusters than for the periodic order of voids.

We finally note that the functional (33) can be applied not only for determination of the phase diagram and EOS, but also to studies of interfaces between different phases and effects of confinement.

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VII. APPENDIX

A. The ordered structures in the one-shell approximation

The expressions for the first shells of the phases H, IH and C, IC (with the bcc symmetry), Eq. (37), in the real-space representation are [13]

\[ g_{\text{hex}}^1(r) = \sqrt{2} \left[ \cos(k_b r_1) + 2 \cos \left( \frac{k_b r_1}{2} \right) \cos \left( \frac{\sqrt{3} k_b r_2}{2} \right) \right] \] (51)

\[ g_{\text{bcc}}^1(r) = \frac{1}{\sqrt{3}} \sum_{i<j} \left( \cos \left( \frac{k_b (r_i + r_j)}{\sqrt{2}} \right) + \cos \left( \frac{k_b (r_i - r_j)}{\sqrt{2}} \right) \right), \] (52)

where \( r = (r_1, r_2, r_3) \). The geometric factors (42) for the considered phases are the following:

\[ \kappa_2 = 1 \text{ for all the structures, and} \]

\[ L : \quad \kappa_3 = 0, \kappa_4 = \frac{3}{2}, \kappa_5 = 0, \kappa_6 = \frac{5}{2} \] (53)

\[ \text{H, IH : } \kappa_3 = \sqrt{\frac{2}{3}}, \kappa_4 = \frac{5}{2}, \kappa_5 = 5 \sqrt{\frac{2}{3}}, \kappa_6 = \frac{85}{9} \] (54)

\[ \text{C, IC : } \kappa_3 = \frac{2}{\sqrt{3}}, \kappa_4 = \frac{15}{4}, \kappa_5 = 5 \sqrt{3}, \kappa_6 = \frac{220}{9} \] (55)

B. Explicit expressions for Eqs.(44), (45) and for pressure in the case of weak order

In the \( \varphi^M \) theory, Eqs.(44) and (45) take the explicit forms

\[ a_2(\tilde{\zeta}) - \beta^* + \sum_{n=3}^{M} \frac{a_n(\tilde{\zeta}) \kappa_n \Phi^{n-2}}{(n-1)!} \]

\[ + \frac{a_\sqrt{T^*}}{Z(\tilde{\zeta}, \Phi)} \sum_{n=4}^{M} \frac{a_n(\tilde{\zeta}) \kappa_{n-2} \Phi^{n-4}}{(n-3)!} + \frac{a_6(\tilde{\zeta}) a^2 T^*}{2Z(\tilde{\zeta}, \Phi)^2} = 0, \] (56)

and

\[ \mu^* = \mu / |\bar{V}(k_0)| = v_0 \tilde{\zeta} + T^* \left[ a_1(\tilde{\zeta}) + \sum_{n=2}^{M} \frac{a_{n+1}(\tilde{\zeta}) \kappa_n \Phi^n}{n!} \right] \]

\[ + T^* \left[ a_3(\tilde{\zeta}) + \sum_{n=2}^{M-2} \frac{a_{n+3}(\tilde{\zeta}) \kappa_n \Phi^n}{n!} \right] + \frac{a_7(\tilde{\zeta}) \Phi^2}{2Z(\tilde{\zeta}, \Phi)^2} \] (57)
where in the $\varphi^4$-theory, the terms proportional to $a_n(\bar{\zeta})$ with $n > 4$ in (56), and $n > 5$ in (57) must be disregarded. In obtaining (56) and (57), we have used Eqs. (39), (10), (21) and (22). $Z(\bar{\zeta}, \Phi)$ is given by (25) and (26), or by (32) in the $\varphi^4$ or $\varphi^6$ theory respectively, with $A_n[\zeta]$ approximated by (43). The thermodynamic pressure $p = -\Omega/V$ is given by the equation (see (30) or (33), and (39))

$$p^* = p/|\tilde{V}(k_0)| = -\frac{v_0\bar{\zeta}^2}{2} + \mu^*\bar{\zeta} - T^*\left[\beta f_h(\bar{\zeta}) + \frac{a_2(\bar{\zeta}) - \beta^*}{2}\Phi^2 + \sum_{n=3}^{M} \frac{a_n(\bar{\zeta})}{n!}\kappa_n\Phi^n\right] \tag{58}$$

$$+2a\sqrt{T^*}Z(\bar{\zeta}, \Phi) - \frac{a^2T^*}{2Z(\bar{\zeta}, \Phi)^2}\left[a_4(\bar{\zeta}) + \frac{a_6(\bar{\zeta})\Phi^2}{2} - \frac{a_6(\bar{\zeta})a^3T^{3/2}}{3Z(\bar{\zeta}, \Phi)^3}\right],$$

where $\Phi$ satisfies (50) and $\mu^*$ is given in (57). In the $\varphi^4$-theory, the terms proportional to $a_n(\bar{\zeta})$ with $n > 4$ must be disregarded in (58).
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