Density functional theory for systems with mesoscopic inhomogeneities

A Ciach and W T Gozdz

Institute of Physical Chemistry, Polish Academy of Sciences, 01-224 Warszawa, Poland

E-mail: aciach@ichf.edu.pl

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Abstract
We study the effects of fluctuations on the mesoscopic length scale on systems with mesoscopic inhomogeneities. Equations for the correlation function and for the average volume fraction are derived in the self-consistent Gaussian approximation. The equations are further simplified by postulating the expression for the structure factor consistent with scattering experiments for self-assembling systems. Predictions of the approximate theory are verified by a comparison with the exact results obtained earlier for the one-dimensional lattice model with first-neighbor attraction and third-neighbor repulsion. We find qualitative agreement for the correlation function, the equation of state and the dependence of the chemical potential $\mu$ on the volume fraction $\zeta$. Our results confirm also that strong inhomogeneities in the disordered phase are found only in the case of strong repulsion. The inhomogeneities are reflected in an oscillatory decay of the correlation function with a very large correlation length, three inflection points in the $\mu(\zeta)$ curve and a compressibility that for increasing $\zeta$ takes very large, very small and again very large values.

Keywords: inhomogeneous systems, effects of fluctuations, competing interactions, mesoscopic density functional theory

(Some figures may appear in colour only in the online journal)
regions of two different ordered phases [23, 24], in contrast to the MF results [11, 18, 21]. In the case of a triangular lattice model with competing first-neighbor attraction and third-neighbor repulsion [20], at low temperature $T$ a molten lamella phase occupies some phase-space region between the stability regions of the phase with periodically distributed clusters and the phase with periodically distributed stripes [23]. At higher $T$ the disordered fluid is stable between the ordered cluster phase and the molten lamella. The transition between the fluid and the molten lamella is continuous at high $T$ and becomes first order at the tricritical point. In the molten lamella discovered in [23] the orientational order of stripes is present but the translational order is absent. A similar phase called a ‘nematic phase’ was recently detected in magnetic films with competing interactions [25] in a continuous Brazovskii-type model [26]. According to these new discoveries, instead of the fluctuation-induced first-order phase transition between the disordered and the periodically ordered phases predicted earlier by Brazovskii [26], a continuous or a first-order transition between the fluid and the molten-lamella phases occurs.

In addition to the presence of new phases and significant modifications of the phase-coexistence, the fluctuations at the mesoscopic length scale lead to significantly different properties of the disordered inhomogeneous phase. In simulation snapshots of the disordered phase clusters or layers are clearly visible, indicating that this phase can be very inhomogeneous [8, 9, 23, 24]. Even though the distribution of these objects is not periodic, they can be correlated over large distances. The disordered inhomogeneous phase may thus be considered as a molten periodic phase, with the long-range order destroyed by the mesoscopic fluctuations.

In one-dimensional (1D) systems the fluctuations destroy ordering, and there are no phase transitions for $T > 0$, in contrast to the MF predictions. Thus, it is interesting to apply theories with included fluctuations to 1D systems, where the MF fails. Moreover, the structural, mechanical and thermal properties of the disordered inhomogeneous phase in 1D can shed light on the corresponding properties of the inhomogeneous phase for $d > 1$. An important advantage of the 1D systems is the possibility of verifying various approximate theories by comparison with exact results. The effects of fluctuations on the disordered phase were determined in a 1D lattice model with competing first-neighbor attraction and third-neighbor repulsion by the exact transfer matrix method [19]. In the ground state ($T = 0$) of this model a dilute phase (vacuum) is stable for small values of the chemical potential $\mu$ and a dense phase (fully occupied lattice) is stable for large values of $\mu$. When the repulsion is sufficiently strong, an ordered phase with periodic distribution of clusters and density $\rho = 1/2$ is stable for intermediate values of $\mu$. At $T > 0$ only a disordered phase is stable, but the presence of clusters at low $T$ is reflected in a very large correlation length, and in a specific shape of the $\rho(\mu)$ curve. It contains three inflection points at low $T$—the central one at $\rho = 1/2$ and the other two at $\mu$ corresponding to the $T = 0$ phase transitions. For $T \to 0$ a step-like $\rho(\mu)$ curve was obtained. The very small compressibility of the system for $\rho \approx 1/2$ indicates formation of clusters that repel each other at short separations. The very large compressibility at the other two inflection points signals an approach to the phase transitions that occur at $T = 0$. Only at high $T$ a single inflection point at $\rho = 1/2$ is present. In contrast, in MF the $\rho(\mu)$ curve has a single inflection point for the whole range of stability of the disordered phase. Thus, MF fails to predict the qualitative features of the disordered inhomogeneous phase. Only for high $T$, where strong inhomogeneities are no longer present, qualitative properties of the disordered phase are correctly described by MF. MF predicts stability of a periodically ordered phase instead of strongly inhomogeneous disordered phase.

From the comparison of the MF and simulation or exact results it evidently follows that an inclusion of the most relevant mesoscopic fluctuations is necessary not only for the quantitative, but also for the qualitative description of systems with mesoscopic inhomogeneities. A tractable theory that would accurately predict properties of systems with inhomogeneities on the mesoscopic length scale is still missing, however. A theory correctly incorporating mesoscopic fluctuations should predict at least a correct topology of the phase diagram and correct properties of the disordered phase. Effects of periodic fluctuations of the order parameter (OP) $\phi$ are described by the Brazovskii field theory [26]. However, the Brazovskii functional $L_\phi[\phi]$ depends on free parameters, and quantities such as compressibility for a particular volume fraction $\zeta$ and $T$ cannot be determined, unless a relation between the free parameters and measurable quantities is known. An attempt to express the free parameters in $L_\phi[\phi]$ in terms of $T$ and $\zeta$ was made in [15, 18, 27]. The theory developed in [15, 18, 27] is rather complex, however, and additional approximations are necessary to solve the obtained equations.

The purpose of this work is to develop further the mesoscopic description of inhomogeneous systems that combines DFT and field-theoretic approaches [18, 27, 28]. We introduce a tractable approximation for the disordered phase. In section II we present a derivation of a self-consistent equation for the correlation function, and the equation for the average volume fraction in terms of $T$ and $\mu$. The equations are obtained using DFT methods, and the contributions associated with the mesoscopic fluctuations can be calculated by the methods of field theory. We show that the term $\propto \phi^3$, usually neglected in Brazovskii-type theories, plays a very important role in fluids and soft-matter systems. In section III we derive the equations in the self-consistent Gaussian approximation. In section IV we limit ourselves to the disordered phase, make further assumptions and obtain much simpler equations that can be solved easily. In section V our equations are solved for a 1D model with the SALR potential. The results of our theory are compared with the exact solutions obtained in [19] for a 1D lattice model. We discuss the accuracy of our approximations in section VI.

II. Derivation of the mesoscopic density functional theory

We consider systems with competing interactions, where mesoscopic inhomogeneities occur on a length scale $\lambda$ significantly larger than the size of molecules $\sigma$. Following [18, 27]
we collect all the microscopic states into disjoint sets; each set represents one mesostate described by a smooth function \( \zeta(\mathbf{r}) \). \( \zeta(\mathbf{r}) \) is equal to the fraction of the volume of a sphere with a center at \( \mathbf{r} \) and a radius \( \lambda \gg R \gg r \) that is covered by the particles in each microstate belonging to the set represented by \( \zeta(\mathbf{r}) \). In other words, the mesoscopic state represents all of the microscopic states that are obtained by changing the positions of the particles without changing the volume occupied by the particles in each mesoscopic region. By fixing the mesostate \( \zeta(\mathbf{r}) \) we impose a constraint on the available microstates. The grand thermodynamic potential in the presence of this constraint is denoted by \( \Omega_{co}[\zeta(\mathbf{r})] \). \( \exp(-\beta \Omega_{co}[\zeta(\mathbf{r})]) \) is equal to the sum of the Boltzmann factor \( e^{-\beta H} \) over all microscopic states with frozen mesoscopic fluctuations. In the above \( \beta = 1/(k_B T) \), \( k_B \), \( T \) and \( H \) are the Boltzmann factor, temperature and the Hamiltonian respectively. The grand potential in the presence of mesoscopic fluctuations is given by

\[
\Omega = -k_B T \ln \Xi
\]

where

\[
\Xi = \int D\zeta e^{-\beta \Omega_{co}[\zeta]}
\]

and the functional integral is over all mesoscopic states that by definition are \( \zeta < 1 \). Since the summation of \( e^{-\beta H} \) over all microstates \( \zeta(\mathbf{r}) \) is included in \( e^{-\beta \Omega_{co}[\zeta]} \), and in (2) we perform the summation over all mesostates \( \zeta(\mathbf{r}), \Omega \) contains contributions from both, microscale and mesoscale fluctuations.

We introduce mesoscopic fluctuation by

\[
\phi := \zeta - \bar{\zeta}
\]

where \( \bar{\zeta} \) denotes the average volume fraction, and rewrite (1) in the equivalent form

\[
\Omega = \Omega_{co}[\bar{\zeta}] - k_B T \ln \left( \int D\phi e^{-\beta H_{\phi}} \right)
\]

with

\[
H_{\phi}[\bar{\zeta}, \phi] = \Omega_{co}[\bar{\zeta} + \phi] - \Omega_{co}[\bar{\zeta}].
\]

Equation (4) contains two contributions, and each of them is associated with the fluctuations on a different length scale. In the first term the mesoscopic volume fraction has its equilibrium form. This term contains the contribution from the fluctuations on the microscopic length scale. The second term contains the contributions from the fluctuations on the mesoscopic length scale, i.e. from different mesoscopic inhomogeneities that are thermally excited with the probability \( e^{-\beta H_{\phi}/\Xi} \). When \( \bar{\zeta} \) is the average volume fraction, then it follows that \( \langle \phi \rangle = 0 \), where

\[
\langle X \rangle := \frac{\int D\phi X e^{-\beta H_{\phi}}}{\int D\phi e^{-\beta H_{\phi}}}.
\]

In the following \( \langle \phi \rangle = 0 \) is always assumed.

Our purpose here is the development of an approximate theory that allows for a determination of \( \bar{\zeta} \) for given temperature and chemical potential with the fluctuation contribution in (4) taken into account. We shall also find approximations for the equation of state (EOS), the pair distribution function and the boundary of stability of the disordered phase. Note that both terms on the rhs of equation (4) are functionals of \( \bar{\zeta} \). The equilibrium volume fraction \( \bar{\zeta} \) corresponds to the minimum of the grand potential i.e. in equilibrium the first functional derivative of \( \Omega[\bar{\zeta}] \) w.r.t. \( \bar{\zeta} \) must vanish, and the second functional derivative must be positive definite. We introduce the functional derivatives

\[
C_n(\mathbf{r}_1, ..., \mathbf{r}_n) := \frac{\delta^n \beta \Omega}{\delta \zeta(\mathbf{r}_1) ... \delta \zeta(\mathbf{r}_n)} = C_n^{(0)}(\mathbf{r}_1, ..., \mathbf{r}_n) - \frac{\delta^n \beta H}{\delta \zeta(\mathbf{r}_1) ... \delta \zeta(\mathbf{r}_n)} \ln \left( \int D\phi e^{-\beta H(\zeta, \phi)} \right)
\]

where (4) was used,

\[
C_n^{(0)}(\mathbf{r}_1, ..., \mathbf{r}_n) := \frac{\delta^n \beta \Omega_{co}}{\delta \zeta(\mathbf{r}_1) ... \delta \zeta(\mathbf{r}_n)}
\]

and we do not indicate the functional dependence of \( C_n \) on \( \zeta \).

For \( n = 1, 2 \) we obtain from (7)

\[
C_1(\mathbf{r}) = C_1^{(0)}(\mathbf{r}) + \frac{\delta \beta H}{\delta \zeta(\mathbf{r})} f_{\phi^2} \tag{9}
\]

and

\[
C_2(\mathbf{r}_1, \mathbf{r}_2) = C_2^{(0)}(\mathbf{r}_1, \mathbf{r}_2) + \left( \frac{\delta^2 \beta H}{\delta \zeta(\mathbf{r}_1) \delta \zeta(\mathbf{r}_2)} f_{\phi^2} - \left( \frac{\delta \beta H}{\delta \zeta(\mathbf{r}_1)} \frac{\delta \beta H}{\delta \zeta(\mathbf{r}_2)} \right) f_{\phi^2} \right) f_{\phi^2} \tag{10}
\]

where

\[
\langle XY \rangle^c := \langle XY \rangle_f - \langle X \rangle_f \langle Y \rangle_f \tag{11}
\]

We neglect the fluctuation contribution to \( C_n \) for \( n \geq 3 \), i.e. we make the approximation

\[
C_n = C_n^{(0)} \quad \text{for} \quad n \geq 3. \tag{12}
\]

From (9) and the requirement \( C(\mathbf{r}) = 0 \) we can obtain \( \bar{\zeta} \) for given \( T \) and the chemical potential \( \mu \), if we know the form of \( \Omega_{co} \) and we can perform the functional integrals in the second term on the rhs of (9).

We assume the standard local mean-field approximation for the grand potential with suppressed mesoscopic fluctuations,

\[
\Omega_{co}[\zeta] = U[\zeta] - TS[\zeta] - \mu N[\zeta]. \tag{13}
\]

Equation (13) is the well known thermodynamic relation between the internal energy \( U \), entropy \( S \) and the number of particles \( N \) in the system with the mesoscopic volume fraction constrained to have the form \( \zeta \). The entropy \( S \) in the local density approximation for fixed mesoscopic volume fraction is given by

\[
-S[\zeta] = \int d\mathbf{r} f_{\phi^2}(\zeta(\mathbf{r})). \tag{14}
\]

Different approximations for the free-energy density of the reference (hard sphere) system, \( f_{\phi^2}(\zeta) \), can be chosen. The internal energy for fixed mesoscopic volume fraction is given by
\[
U[\zeta] = \frac{1}{2} \int \! \! d\mathbf{r}_1 \int \! \! d\mathbf{r}_2 \zeta(\mathbf{r}_1) V(\mathbf{r}_1 - \mathbf{r}_2) \zeta(\mathbf{r}_2),
\]

where \(V(\mathbf{r}_1 - \mathbf{r}_2) = u(\mathbf{r}_1 - \mathbf{r}_2)g(\mathbf{r}_1 - \mathbf{r}_2)\), with \(u\) and \(g\) denoting the interaction potential and the pair distribution function respectively. In the standard statistical-mechanical expression for the internal energy \(g\) is the pair correlation function in the system with the interaction potential \(u(\mathbf{r}_1 - \mathbf{r}_2)\) and depends on the mesoscopic volume fraction \(\zeta\). Different forms of \(g\) are expected for clusters with different internal structure (liquid or solid). We expect that the internal structure of clusters plays a subdominant role for the properties at the mesoscopic length scale and the detailed shape of \(g\) is irrelevant. Since we are interested not in the internal structure of clusters, but in their distribution in space, in practice we shall assume \(g(r) = \theta(r - 1)\) (\(r\) is in \(\sigma\)-units). This approximation for \(g\) ensures that the contribution to the internal energy from overlapping hard cores of the particles is not included, and for large separations \(g = 1\) as required. Note that we use volume fraction rather than density in (15), therefore we should re-scale the chemical potential, \(\mu\), so that

\[
\mu N[\zeta] = \bar{\mu} \int \! \! d\mathbf{r} \zeta(\mathbf{r}),
\]

where \(N[\zeta]\) is the number of particles for given \(\zeta\). In this local density approximation we have

\[
C_1^{(0)}(\mathbf{r}) = \int \! \! d\mathbf{r}' \zeta(\mathbf{r}') V(\mathbf{r}' - \mathbf{r}) + A_1(\zeta(\mathbf{r})) - \beta \bar{\mu}
\]

(17)

\[
C_2^{(0)}(\mathbf{r}_1, \mathbf{r}_2) = \beta V(\mathbf{r}_1 - \mathbf{r}_2) + A_2(\zeta(\mathbf{r}_1)) \delta(\mathbf{r}_1 - \mathbf{r}_2)
\]

(18)

and for \(n \geq 3\)

\[
C_3^{(0)}(\mathbf{r}_1, ..., \mathbf{r}_n) = A_d(\zeta(\mathbf{r}_1)) \delta(\mathbf{r}_1 - \mathbf{r}_2) ... \delta(\mathbf{r}_{n-1} - \mathbf{r}_n).
\]

(19)

where

\[
A_d(\zeta) = \frac{d^\nu \beta f_\nu(\zeta)}{d\zeta^n}.
\]

In order to perform the functional integrals in (4), (9) and (10) we approximate \(H[\zeta, \phi]\) in a functional Taylor series w.r.t. \(\phi\),

\[
\beta H[\zeta, \phi] = \beta H_0 + \beta \Delta H
\]

(21)

with

\[
\beta H_0[\zeta, \phi] = \frac{1}{2} \int \! \! d\mathbf{r}_1 \int \! \! d\mathbf{r}_2 \phi(\mathbf{r}_1) C_2^{(0)}(\mathbf{r}_1, \mathbf{r}_2) \phi(\mathbf{r}_2)
\]

(22)

and

\[
\beta \Delta H[\zeta, \phi] = \int \! \! d\mathbf{r} C_1^{(0)}(\mathbf{r}) \phi(\mathbf{r}) + \sum_{n \geq 3} \frac{1}{n!} \int \! \! d\mathbf{r} A_d(\zeta(\mathbf{r})) \phi(\mathbf{r})^n.
\]

(23)

We truncate the expansion in (23) at the fourth order term. For small fluctuations, \(\phi \ll 1\), this truncation is justified, because the higher order terms in (23) are irrelevant. Recall that by definition the volume fraction is less than 1. The functional integral in (4) can be extended to arbitrarily large functions \(\phi\), because the large fluctuations are strongly damped in (4) by the Boltzmann factor \(e^{-\beta H}\) for \(H\) given in (21)–(23), and do not influence the results in a significant way.

Note that when \(H\) is given by (21)–(23), the fluctuation contributions in (9) and (10) can be expressed in terms of \(\langle \phi^m(\mathbf{r}) \rangle\) and \(\langle \phi^m(\mathbf{r}) \phi^m(\mathbf{r}') \rangle\). Thus, it is necessary to calculate the correlation functions for the mesoscopic fluctuations of the volume fraction in order to obtain the expressions for \(C_1\) and \(C_2\). In order to calculate these functions field-theoretic methods could be used. In the next section we present an approximation that allows determination of \(C_2\) and \(\langle \phi(\mathbf{r}_1) \phi(\mathbf{r}_2) \rangle\) in a relatively simple way.

### III. Self-consistent Gaussian approximation

In practice we can calculate the Gaussian functional integrals only. We approximate \(H[\zeta, \phi]\) by an effective functional that is quadratic in the fluctuation \(\phi\),

\[
\beta H_{G} \approx \beta H_G = \frac{1}{2} \int \! \! d\mathbf{r}_1 \int \! \! d\mathbf{r}_2 \phi(\mathbf{r}_1) C(\mathbf{r}_1, \mathbf{r}_2) \phi(\mathbf{r}_2).
\]

(24)

In this approximation the form of \(C\) differs from \(C^{(0)}\), so that the effect of \(\Delta H\) (see (21)–(23)) is indirectly included in the average quantities (see (6)). Note that when \(H\) is approximated by \(H_G\), then the correlation function \(G(\mathbf{r}_1, \mathbf{r}_2) := \langle \phi(\mathbf{r}_1) \phi(\mathbf{r}_2) \rangle\) is given by

\[
\int \! \! d\mathbf{r}_2 G(\mathbf{r}_1, \mathbf{r}_2) C(\mathbf{r}_1, \mathbf{r}_2) = \delta(\mathbf{r}_1, \mathbf{r}_2).
\]

(25)

The best approximation for \(C(\mathbf{r}_1, \mathbf{r}_2)\) is such that \(G\) in (25) is as close as possible to the exact correlation function. This means that \(C\) should be as close as possible to the exact inverse correlation function [1]. Here, we assume that \(C = C_2\).

Let us stress the difference between the microscopic and the mesoscopic theories. In the microscopic theory the Boltzmann factor is given in terms of the microscopic Hamiltonian that depends on the interaction potential, and measures the probability of a single microscopic state. In our coarse-grained or mesoscopic theory we consider mesoscopic fluctuations rather than microscopic states. Each such fluctuation \(\phi\) corresponds to a set of microstates, and its probability is given by the Boltzmann factor with the Hamiltonian replaced by the excess grand potential associated with the fluctuation \(\phi\) (see (2) and (5)). For this reason the direct correlation function rather than the interaction potential appears in equation (24) in our mesoscopic field theory in contrast to the microscopic theories.

Note that in the Gaussian approximation the 2n-point correlation functions can be expressed in terms of products of the two-point correlation functions. Thus, because the fluctuation contribution in equation (10) consists of terms proportional to \(\langle \phi^m(\mathbf{r}_1) \phi^m(\mathbf{r}_2) \rangle\), it relates \(C_2 = C\) with \(G\), and equation (25) relates \(G\) with \(C\). In this self-consistent Gaussian approximation \(X_i\), in equation (10) is replaced by

\[
\langle X \rangle = \int D\phi \mathcal{X} \exp(-\beta H_G) \int D\phi \exp(-\beta H_G), \text{ with } H_G \text{ given in (24)}.
\]

In order to calculate the functional integrals in equations (9) and (10) in the above Gaussian approximation, we note that from (7), (12), (19) and (24) it follows that
\[
\frac{\delta^2 H_G}{\delta \zeta(r)} = \frac{1}{2} A_3(\zeta(r)) \phi(r)^2 \tag{26}
\]

and
\[
\frac{\delta^3 H_G}{\delta \zeta(r_1) \delta \zeta(r_2)} = \frac{1}{2} A_4(\zeta(r_1)) \phi(r_1) \delta(r_1 - r_2). \tag{27}
\]

After inserting the above equations in (9) and (10), using (17)–(20) and performing the Gaussian integrals, we obtain the main results of the self-consistent Gaussian approximation

\[
\beta \tilde{\mu} = \int \! d\zeta \beta V(\zeta) + A_1(\zeta) + \frac{A_3(\zeta)}{2} \bar{G}(r, r) \tag{28}
\]

and
\[
C(r_1, r_2) = C_2^0(r_1, r_2) + \frac{A_4(\zeta(r_1))}{2} G(r_1, r_2) \delta(r_1 - r_2)
- \frac{A_3(\zeta(r_1)) A_3(\zeta(r_2))}{2} G^2(r_1, r_2). \tag{29}
\]

Equations (25) and (29) have to be solved self-consistently. The last term in (28) and the last two terms in (29) represent the contributions from the mesoscopic fluctuations. We should stress that because of the coarse graining, the correlation function for the mesoscopic volume fraction, \(G(r_1, r_2)\), differs from the correlation function for the microscopic density. In [18, 27] it was shown that \(G(r_1, r_2)\) represents the microscopic correlations averaged over mesoscopic regions (smaller than the scale of inhomogeneities) around the points \(r_1\) and \(r_2\). As a consequence, \(G(r_1, r_2) \neq 0\) for \(r_1 = r_2\), because it contains contributions from the microscopic correlations between the particles with the centers belonging to the sphere of the radius \(R\) larger than \(\sigma/2\), i.e. between the particles which do not overlap. Note also that the fluctuation contribution leads to a shift of the average volume fraction for given \(T\) and \(\bar{\mu}\) compared to the MF prediction.

Our result (29) agrees with the well known expression in the field theory [26] at the self-consistent one-loop approximation. The corresponding Feynman diagrams are shown in figure 1. In the standard field-theoretic approaches, however, \(A_4\) are free model parameters, and the last term in (29) is usually neglected. In our theory \(A_3\) is a function of \(\zeta\) and vanishes only at a single value of the volume fraction, corresponding to the critical point in a system with attractive interactions. In our theory \(A_3\) plays a very important role for the relation between the average volume fraction and the chemical potential.

**IV. Self-consistent Gaussian approximation for the disordered phase**

In this section we restrict our considerations to a disordered isotropic phase with the mesoscopic volume fraction independent of the position, and to isotropic interactions, i.e. \(V(r_1 - r_2)\) depending only on \(r = |r_1 - r_2|\). In this phase \(G\) and \(C\) depend only on \(r = |r_1 - r_2|\), and we simplify the notation, introducing \(G(r) \equiv G(r_1, r_2)\) and \(C(r) \equiv C(r_1, r_2)\). Due to the translational invariance, equation (28) takes the form

\[
\beta \tilde{\mu} = \zeta \int \! d\zeta \beta V(\zeta) + A_1(\zeta) + \frac{A_3(\zeta)}{2} \bar{G}, \tag{30}
\]

and we can write equation (29) in Fourier representation

\[
\tilde{C}(k) = \tilde{C}^0(k) + \frac{A_4(\zeta)}{2} \bar{G} - \frac{A_3^2(\zeta)}{2} \tilde{D}(k), \tag{31}
\]

where \(\tilde{F}\) denotes the Fourier transform of \(F\), and we have introduced

\[
\bar{G} = G(r, r) \tag{32}
\]

and

\[
\tilde{D}(k) = \int \! d\zeta \bar{G}(\zeta) \exp(ik \cdot r). \tag{33}
\]

In the disordered isotropic phase equation (25) takes the form

\[
\tilde{C}(k) \bar{G}(k) = 1. \tag{34}
\]

In the context of fluids with competing interactions, \(A_3 \neq 0\) except from the critical value of the volume fraction, \(\zeta_c\). \(A_3(\zeta) > 0\) for \(\zeta < \zeta_c\) and \(A_3(\zeta) < 0\) for \(\zeta > \zeta_c\). Thus, the fluctuation contribution in (30) leads to decreased and increased value of the chemical potential for \(\zeta < \zeta_c\) and \(\zeta > \zeta_c\), respectively compared to the MF prediction, provided that \(\bar{G} > 0\). This effect of mesoscopic fluctuations is independent of the details of the interaction potential. Note that the value of \(\bar{G}\) is the larger the stronger are the inhomogeneities on the mesoscopic length scale.

In order to solve equation (31) for a particular system, we need to know the form of the interaction potential. However, we can make general qualitative or semi-quantitative predictions for a class of systems with interactions such that \(\tilde{V}(k)\) has a pronounced minimum at \(k = k_0 \neq 0\). The wavenumbers of the dominant mesoscopic fluctuations correspond to the maximum of the Boltzmann factor \(\exp(-\beta \tilde{V}(k))\). We assume that only \(k \approx k_0\) are relevant when the peak in \(\exp(-\beta \tilde{V}(k))\) is pronounced and narrow [18, 27]. We focus on such systems, and make the approximation

\[
\tilde{C}^0_2(k) \approx c_0 + v_0(k^2 - k_0^2)^2 \tag{35}
\]

where

\[
c_0 = A_2 + \beta \tilde{V}(k_0) \tag{36}
\]
We have used (18) and have made the approximation \( k + k_0 \approx 2k_0 \), valid in the neighborhood of \( k_0 \). The above assumption is justified for an even function of \( k \) in the neighborhood of \( k_0 > 0 \), where the first derivative w.r.t. \( k \) is \( \tilde{V}'(k_0) = 0 \), and the second derivative is \( \tilde{V}''(k_0) > 0 \). The results obtained with this assumption concern any system with inhomogeneities on the mesoscopic length scale \( \sim 2\pi/k_0 \) strongly favoured energetically compared to inhomogeneities on different length scales. Thus, the results presented below concern systems with a deep minimum of \( \tilde{V}(k) \) for potentials with a shallow minimum the approximation (35) can be an oversimplification.

The equations (31)–(34) are still rather difficult. It is thus reasonable to make further approximations in order to verify if the predictions of this theory are correct at least on a qualitative level. Instead of solving numerically equations (31)–(34), we postulate a particular form of \( \tilde{C}(k) \), and determine the parameters in the postulated expression. Experimental results for the structure factor in systems with mesoscopic inhomogeneities are reasonably well described by a function inversely proportional to \( \tilde{C}_2^{00}(k) \) given in equation (35), with \( c_0, k_0 \) and \( v_0 \) treated as fitting parameters. Based on this observation we assume for \( \tilde{C}(k) \) the same form as in equation (35), but with renormalized parameters, i.e. we postulate

\[
\tilde{C}(k) \approx c_r + v_r(k^2 - k_0^2)^2. \tag{38}
\]

In order to determine the renormalized parameters we need three equations for the three unknowns. We require that the first derivative of the function given by equation (31) vanishes at \( k = k_r \). The value of this function at its minimum is \( c_r \). Finally, we require that the second derivatives at \( k_r \) of both expressions, equations (31) and (38), are the same. The three requirements guarantee that the shape of \( \tilde{C}(k) \), equation (31), is reproduced by equation (38) at least near the minimum. From these requirements we obtain the set of equations

\[
c_r = c_0 + v_0(k_r^2 - k_0^2)^2 + \frac{A_4}{2}G - \frac{A_2}{2}D(k_r), \tag{39}
\]

\[
4v_0(k_r^2 - k_0^2)k_r = \frac{A_2}{2}D'(k_r), \tag{40}
\]

\[
8v_0k_r^2 = 4v_0(3k_r^2 - k_0^2) - \frac{A_2}{2}D''(k_r). \tag{41}
\]

Note that in the standard Brazovskii approximation, i.e. with \( A_3 = 0 \), from (40) and (41) we obtain \( k_r = k_0 \), \( v_r = v_0 \), and equation (39) can be easily solved analytically [28].

The pressure \( p = -\Omega/\mathcal{V} \), where \( \mathcal{V} \) is the system volume, in this theory is given by (see (1), (13)–(16))

\[
p = \frac{1}{2} \tilde{V}(0)\xi^2 - f_0(\xi) + \bar{\mu} \ln \left( \int D\phi e^{-\beta \bar{\mu}_k} \right). \tag{42}
\]

We express \( \bar{\mu} \) in terms of \( \zeta \) according to equation (30), evaluate the functional integral and obtain from (42) the EOS of the form

\[
p = \frac{1}{2} \tilde{V}(0)\xi^2 - f_0(\xi) + k_BT A_0(\xi) \zeta
\]

\[
+ k_BT \int \frac{dk}{2(2\pi)^2} \ln \left( \frac{\tilde{C}(k)}{2\pi} \right). \tag{43}
\]

The integral in (43) is over the spectrum of mesoscopic fluctuations, and is cutoff-dependent for \( \tilde{C}(k) \) given in equation (38). In the mesoscopic theory the cutoff is naturally provided by the scale \( R \) of coarse-graining. However, the pressure should be independent of the coarse-graining procedure and the cutoff-dependent part should cancel against the neglected cutoff-dependent contribution to \( \Omega_{\text{co}} \). We find that the cutoff-independent contribution to the integral in (43) is proportional to \( \sqrt{c_r h_0} \) for the 3D and 1D systems. Note that the approximations (35) and (38) are valid for strong inhomogeneities at a well-defined length scale, i.e. for \( c_r h_0 \ll 1 \). Since \( G \approx 1/\sqrt{c_r} \) \[26\] (see also the next section), in the range of validity of the approximations, the last term in (43) is negligible compared to the fluctuation contribution proportional to \( G \), and will be disregarded.

V. Results for the SALR potential in 1D

In this section we test the accuracy of the self-consistent Gaussian approximation with the further approximations described in section IV by comparing our results with the exact solutions obtained in [19] for a 1D lattice model with competing attractive and repulsive interactions between the first and the third neighbors respectively. In the lattice model solved exactly in 1D the ratio between the third-neighbor repulsion \( J_2 \) and the first-neighbor attraction \( J_1 \) is denoted by \( J \), and the interaction potential in Fourier representation takes the form

\[
\beta \tilde{V}(k) = 2\beta^* (J \cos(3k) - \cos(k)) \tag{44}
\]

where \( \beta^* = 1/\beta^* \), and \( T^* = k_BT/J_1 \) is temperature in units of the first-neighbor attraction. \( \tilde{V}(k) \) in equation (44) assumes a negative minimum for \( k_0 > 0 \) if \( J > 1/9 \). By \( \tilde{V}''(k) \), \( \mu^* \) and \( p^* \) we shall denote the corresponding quantity in units of \( J_1 \).

From the form of \( \tilde{C}_2^{00} \) (equations (35)–(37)) it immediately follows that in MF the disordered phase is unstable for \( T^* < -\tilde{V}''(k_0)/A_0(\zeta) \). The explicit form of \( A_0(\zeta) \) follows from (20) and the reference-system free energy of the lattice-gas form (note that in 1D the volume fraction and the dimensionless number density are identical),

\[
\beta f_0(\zeta) = \zeta \ln \zeta + (1 - \zeta) \ln(1 - \zeta). \tag{45}
\]

This well known MF result [11, 18, 21] is incorrect, since in 1D models with short-range interactions there are no phase transitions for \( T > 0 \) [29]. Exact results [19] indicate, however that the disordered phase is strongly inhomogeneous in the phase-space region where MF predicts its instability. Thus, it is interesting to verify predictions of our theory for


\[ T^* < -\tilde{\Psi}^*(k_0)/A_3(\zeta). \]

We shall focus on \( T^* < -\tilde{\Psi}^*(k_0)/A_3(\zeta) \) for \( J = 3 \) and \( J = 1/4 \), because most of the exact results of [19] concern \( J = 3 \) and \( J = 1/4 \). The phase-space region of interest is enclosed by the solid and dashed lines in figure 2 respectively.

The two chosen values of \( J \) correspond to systems with qualitatively different properties. In the case of \( J = 1/4 \) only the empty or the fully occupied lattice is present in the ground state (GS) for small or large values of \( \mu^a \) respectively. In a system with the short-range attraction stronger than the long-range repulsion, exact results [19] show stability of the disordered phase with oscillatory and monotonic decay of correlations at large and at very small \( T^* \) respectively. The compressibility at \( \zeta \approx 1/2 \) is very large at low \( T^* \), signaling the approach to the phase separation at \( T^* = 0 \).

For strong repulsion (\( J > 1 \)) clusters composed of three particles separated by three empty sites are favoured energetically, since there are as many attractions (occupied nearest-neighbour sites) as possible in the absence of repulsion. Such a periodic phase is stable for intermediate values of \( \mu^a \) in the GS. Exact results [19] show that for \( J = 3 \) the correlation function exhibits oscillatory decay with the wavelength \( \sim 6 \). The correlation length is several orders of magnitude larger than the particle size for \( \zeta \approx 1/2 \) and \( T^* \ll -\tilde{\Psi}(k_0)/A_3(\zeta) \).

Both the correlation length and the amplitude of \( G(r) \) decay to much smaller values when the line of MF instability is approached. The compressibility at low \( T^* \) is very small for \( \zeta \approx 1/2 \) and very large otherwise. The small compressibility signals formation of regularly distributed clusters that repel each other upon compression of the system (when their separation becomes shorter than the range of repulsion). The large compressibility signals the approach to the phase transitions between the periodic phase and the dilute gas or dense liquid phases at \( T = 0 \).

Figure 2. The lines of instability of the disordered phase in the 1D lattice model of [19] in the MF approximation for the repulsion to attraction ratio \( J = 3 \) (solid line) and \( J = 1/4 \) (dashed line). Temperature is in units of the nearest-neighbor attraction \( (T^* = k_B T/L) \). The volume fraction of particles \( \zeta \) is dimensionless. We study properties of the disordered phase inside the region where this phase is unstable in MF, i.e. below the shown lines.

Figure 3. \( \tilde{\Psi}^*(k) \) (equation (44)) for \( J = 3 \) and \( J = 1/4 \) (solid lines) and the Taylor expansion leading to the approximate form of \( C_2^{(0)} \) (dashed lines). The deeper minimum corresponds to \( J = 3 \). \( \tilde{\Psi}^*(k) \) is in units of the nearest-neighbor attraction \( J_0 \) and \( k \) is in units of \( 1/\sigma \), with \( \sigma \) the particle diameter.

Our purpose is the verification if the mesoscopic theory in the self-consistent Gaussian approximation and with the further assumptions made in section IV is able to reproduce the above exact results. In order to calculate the correlation function and the \( \mu^a(\zeta) \) and \( \rho^a(\zeta) \) lines, we have to solve equations (39)–(41). To solve these equations we need the form of \( D(k) \), which depends on \( G(r) \) (see (33)). In real space representation the correlation function \( G^{(0)}(k) = 1/C_2^{(0)}(k) \) for \( C_2^{(0)}(k) \) approximated by equation (35) takes the form

\[ G^{(0)}(r) = A_0 e^{-r/\xi_0} (\alpha_0 \cos(\alpha_0 r) + \xi_0^{-1} \sin(\alpha_0 r)), \]

where the correlation length is

\[ \xi_0 = 2\alpha_0 \sqrt{\zeta_0} / c_0, \]

and the wavenumber of the damped oscillations \( \alpha_0 \) and the amplitude \( A_0 \) are given by

\[ \alpha_0^2 = k_0^2 + k_0^4 + c_0 v_0 / 2, \]

and

\[ A_0^2 = \frac{1}{4 \nu_0 c_0 (k_0^4 + c_0 v_0)} \]

Equation (46) was obtained for continuum space. Our goal is to verify if our approximate theory reproduces the qualitative features of the exact results, therefore we assume the same form for the lattice model because of its simplicity. According to the ansatz (38), \( G(r) \) has the form given in equation (46), but with the parameters \( A_0, \xi_0, \alpha_0 \) replaced by the renormalized ones, \( A_1, \xi_1, \alpha_1 \). The relation of the parameters \( A_0, \xi_0, \alpha_0 \), with \( c_0, k_0, v_0 \) is analogous to the relation between \( A_0, \xi_0, \alpha_0 \) and \( c_0, k_0, v_0 \) given above. The explicit form of \( D(k) \) can be easily obtained, and reads...
Figure 4. Comparison of the inverse correlation function $C$ in MF (dash–dotted line), and as given by equations (31) and (38), (dashed and solid line respectively). Left panel: $J = 3$, $\zeta = 0.24$ and $T^* = 0.1$. Right panel: $J = 1/4$, $\zeta = 0.41$ and $T^* = 0.1$. The parameters in (38) satisfy equations (39)–(41). Note the negative values in MF, indicating the instability of the disordered phase, and the very small positive values in our theory. Note also that in the case of $J = 1/4$ the assumption (38) is not satisfactory for $k < k_c$. $C$ is dimensionless and $k$ is in units of $1/\sigma$, with $\sigma$ the particle diameter.

$\mathcal{D}(k) = \frac{A^2_r}{2\zeta_r} \left[ \frac{\alpha^2 - \zeta_r^2 - 2\alpha_r(k - 2\alpha_r)}{(k - 2\alpha_r)^2 + 4\zeta_r^{-2}} + \frac{\alpha^2_r - \zeta_r^2 + 2\alpha_r(k + 2\alpha_r)}{(k + 2\alpha_r)^2 + 4\zeta_r^{-2}} + \frac{4(\alpha^2_r + \zeta_r^2)}{k^2 + 4\zeta_r^{-2}} \right]$ \hspace{1cm} (50)

The above and equations (20), (36), (37) and (45) allow us to solve equations (39)–(41) numerically.

Before presenting the results we first verify if the assumption that $\tilde{C}(k)$ can be approximated by equation (35) is valid for this model. We Taylor expand $\tilde{V}(k)$ given by equation (44) in terms of $k^2$ about its minimum at $k^2 = k_0^2$. The form of $\tilde{V}(k)$ (equation (44)) and the Taylor expansion truncated as in equation (35) are shown in figure 3 for $J = 3$ and $J = 1/4$.

We can see that our approximation is good for $k \approx k_0$. However, the approximate formula overestimates and underestimates the effects of fluctuations with the wavelengths $k < k_0$ and $k > k_0$ respectively. Contrary to the assumption of a deep minimum (section IV), in the case of $J = 1/4$ the minimum of $\tilde{V}(k)$ is very shallow.

In the second step we verify the ansatz (38). In our self-consistent Gaussian approximation the inverse correlation function $\tilde{C}(k)$ should satisfy both, equations (31) and (38). We compare equations (31) and (38) with each other, and with the MF version (35). In figure 4(a) we show equations (31), (35) and (38) for $\zeta = 0.24$, $T^* = 0.1$ and $J = 3$, and in figure 4(b) for $\zeta = 0.41$, $T^* = 0.1$ and $J = 1/4$. Since $-\mathcal{D}(k)$ has minima at $k = 0, 2\alpha_r$ (see (50)) and in the ansatz (38) there is a single minimum at $k = k_0$, the agreement between equations (31) and (38) becomes worse for increasing $|\zeta|$, i.e. for increasing $|\zeta - 1/2|$. Hence, the ansatz can be acceptable only for a limited range of $\zeta$.

For $J = 1/4$ it turns out that solutions of (39)–(41) exist only in the central region of the MF instability of the disordered phase. For $T^* \approx 0.1$ the solutions exist only for $0.4 < \zeta < 0.6$. As shown in figure 4(b), however, the agreement between (38) and (31) is still not satisfactory for $k < k_c$, except in the vicinity of $\zeta = 1/2$. Thus, the ansatz (38) is incorrect and either a different form of $\tilde{C}(k)$ should be assumed, or numerical solution of (31) is necessary.

For $J = 3$ the agreement between the ansatz (38) and the equation (31) is fair for a broader range of $k$. We shall consider $0.1 < \zeta < 0.9$, since our approximation (38) becomes increasingly oversimplified when small and large volume fractions are approached. We have verified that the set of equations (39)–(41) has solutions with $c_r > 0$ below the line of MF instability shown in figure 2. This indicates the lack of instability of the disordered phase, in agreement with exact results (see (38)).

Let us focus on the structure of the disordered phase. In figure 5 we show the correlation length $\zeta$ and the amplitude $A_r$ of the correlation function as functions of $\zeta$ for three different temperatures. The correlation function (see equation (46) with renormalized parameters) is shown for $\zeta = 0.24$ and two values of temperature, $T^* = 0.1$ and $T^* = 0.7$ in figure 6. For low $T^*$ the correlation length is very large for $\zeta \approx 1/2$, and rapidly decreases when $|\zeta - 1/2|$ increases, in agreement with the results of [19]. On the quantitative level, however, the accuracy of the approximation decreases for decreasing $T^*$. For $T^* \sim 0.5$ we obtain semi-quantitative agreement between the approximate and exact results, but for $T^* \sim 0.1$ the correlation length is significantly smaller and the amplitude is significantly larger than obtained in [19]. $A_r > 1$ (figure 6) is an artifact of our approximations. Note, however that in MF $A_0 \rightarrow \infty$ for $T^* \rightarrow -\tilde{V}(k_0)/A_2(\zeta)$ from above, so the improvement in our theory is significant.

In figure 7 the wavenumber $k_c$ at the minimum of $\tilde{C}(k)$ (maximum of the structure factor) is shown for $J = 3$ and $T^* = 0.4$. It decreases slightly for increasing $|\zeta - 0.5|$, indicating increasing wavelength of inhomogeneities, in agreement with exact results [19]. However, the magnitude of $k_c$ obtained in [19] is slightly smaller.
Let us focus on the effect of mesoscopic fluctuations on thermodynamic and mechanical properties in the 1D model. The explicit expressions for the chemical potential and the EOS for $f_h$ given in equation (45) have the form (see (30) and (43))

$$\mu = V^*(0) \zeta + T^* \ln \left( \frac{\zeta}{1-\zeta} \right) + T^* \frac{G(2\zeta-1)}{2\zeta^2(1-\zeta)^2} \quad (51)$$

and

$$p = \frac{1}{2} V^*(0) \zeta^2 - T^* \ln(1-\zeta) + T^* \frac{G(2\zeta-1)}{2(1-\zeta)^2} \quad (52)$$

As discussed at the end of section IV, we have neglected the last term in equation (43).

When the fluctuation contribution (the last term in equation (51)) is neglected, the slope of the line $\mu^*(\zeta)$ at low $T^*$ is determined by $V^*(0)$. The system energy for $\zeta = \text{const}$, $V(0)$, is positive for the strong repulsion to attraction ratio $J = 3$, and negative for $J = 1/4$ (see figure 3), therefore in MF the slopes of the $\mu^*(\zeta)$ line are positive and negative for $J = 3$ and $J = 1/4$ respectively. In the former case three-particle clusters separated by three empty sites are energetically favourable and no phase separation occurs at $T^* = 0$, whereas in the latter case a separation into dilute and dense phases occurs at $T^* = 0$ for

**Figure 5.** The correlation length $\xi$ (left panel) and the amplitude $A_r$ (right panel) as functions of the volume fraction $\zeta$ (dimensionless) for $J = 3$. From the top to the bottom line $T^* = 0.1, 0.4, 0.7$. $\xi$ is in units of $1/\sigma$, with $\sigma$ the particle diameter, and $A_r$ is dimensionless.

**Figure 6.** Correlation function for $\zeta = 0.24$ in the case of $J = 3$. $T^* = 0.1$ (left) and $T^* = 0.7$ (right). $G(r)$ is dimensionless and $r$ is in units of the particle diameter $\sigma$.

**Figure 7.** The wavenumber $k_r$ corresponding to the maximum of the structure factor (minimum of $C(k)$) as a function of the average volume fraction $\zeta$ (dimensionless) for $J = 3$ and $T^* = 0.4$. $k_r$ is in units of $1/\sigma$, with $\sigma$ the particle diameter.
The MF instability for $J = 1/4$ (negative slope of the $\mu^\ast(\zeta)$ line) is associated with the MF phase separation that in exact results is absent for $T^\ast > 0$. For $T^\ast > 0$ exact results [19] show positive slopes of $\mu^\ast(\zeta)$ in both cases, in agreement with the results of our theory (solid lines in figure 8). From the exact results it follows that for $J = 3$ the slope at $\zeta \approx 1/2$ is very large and increases for decreasing $T^\ast$, whereas for $J = 1/4$ the slope at $\zeta \approx 1/2$ is very small and decreases for decreasing $T^\ast$. In figure 8 we show the effects of mesoscopic fluctuations on $\mu^\ast(\zeta)$ for $J = 3$ and $J = 1/4$ at $T^\ast = 0.1$. The very large difference between the slopes of the $\mu^\ast(\zeta)$ lines at $\zeta = 1/2$ for $J = 3$ and $J = 1/4$ agrees with exact results. The compressibility at $\zeta = 1/2$ is very small for $J = 3$ and very large for $J = 1/4$; the ratio between the compressibility is $\sim 40$.

Let us describe the case of $J = 3$ in more detail. The slope of the $\mu^\ast(\zeta)$ lines for $0.4 \leq \zeta \leq 0.6$ is almost independent of $T^\ast$. Thus, our approximate theory does not reproduce the decreasing compressibility for decreasing temperature for $\zeta \approx 1/2$. On the other hand, when $\zeta \lesssim 0.3$ and $\zeta \gtrsim 0.7$ the decreasing slopes of the $\mu^\ast(\zeta)$ lines with decreasing temperature are correctly predicted (see figure 9). This behavior indicates that the compressibility increases to very large values at very small $T^\ast$ for small and large volume fractions. The increasing compressibility for decreasing $T^\ast$ signals the approach to the phase transitions that occur at $T^\ast = 0$. The effect of the last term in equation (30) is clearly seen in figure 8(a). For $J = 3$ this term leads to a much smaller slope of the $\mu^\ast(\zeta)$ line for large- and small-volume-fractions, and to a much larger slope for the volume fractions $\sim 1/2$, than in the absence of mesoscopic fluctuations. Note also that since $\mu^\ast \to -\infty$ and $\mu^\ast \to \infty$ for $\zeta \to 0$ and $\zeta \to 1$ respectively, three inflection points at the line $p^\ast(\zeta)$ must be present at low $T^\ast$. This is a characteristic feature of the systems with strong mesoscopic inhomogeneities.

Most of the above results agree qualitatively with the exact results in the 1D lattice model. On the quantitative level, however, the accuracy of our predictions decreases for decreasing $T^\ast$. The exact results for $J = 3$ show much smaller compressibility at $\zeta = 1/2$ for low $T^\ast$ than obtained in our approximation. Moreover, the very small compressibility at $\zeta \approx 1/2$ increases to a very large value in a range of $\zeta$ that is much more narrow than shown in figure 8. Finally, the isotherms $\mu^\ast(\zeta)$ intersect at three points: $\mu^\ast = -2/3, 2, 14/3$ [19], whereas in our approximation they are tangent to one another at $\mu^\ast = 2$.

In figure 10 we present the EOS for $J = 3$. As in the case of the chemical potential, we obtain qualitative agreement with the exact results. In particular, at low $T^\ast$ the slope of the $p^\ast(\zeta)$ line in the neighborhood of $\zeta = 1/2$ is much larger than for $\zeta < 0.4$ or $\zeta > 0.6$. When $T^\ast$ increases, the $p^\ast(\zeta)$ line becomes smoother, in agreement with [19]. However, the changes of the slope of the $p^\ast(\zeta)$ line found in [19] are much more pronounced at low $T^\ast$ than our theory predicts. Our isotherms do not intersect, in contrast to the isotherms obtained in [19], where they intersect in two points.
and EOS isotherms also have the characteristic curves respectively. A very large compressibility for the volume fraction $\zeta \approx 0.3$ becomes small for $\zeta \approx 0.5$, and very large again for $\zeta \approx 0.7$, in agreement with [19]. The very small compressibility results from the repulsion between the clusters when the separation between them decreases upon compression. The very large compressibility accompanies the approach to the phase transitions that occur at $T = 0$. The characteristic shape of the osmotic pressure can be used as an indication of inhomogeneities in experimental studies, when scattering experiments are not possible. We should note that in the case of weak repulsion, when the phase separation between dilute and dense phases occurs at $T = 0$, the compressibility at $\zeta \approx 0.5$ is very large when $T \to 0$, in a striking contrast to the system with the strong repulsion between the particles, $J = 3$ (figure 8). The only qualitative feature that is not correctly reproduced by our theory is the decrease of the compressibility at $\zeta \approx 1/2$ upon a decrease of temperature for $J = 3$.

On the quantitative level the accuracy of our results decreases for decreasing $T$. At very low $T$ we obtain significantly smaller $\xi$, and larger amplitude than in [19]. We should stress that the correlation function averaged over mesoscopic regions is not expected to be equal to the standard microscopic correlation function. Moreover, our numerous approximations applied to simplify the calculations influence the results on the quantitative level. Another source of discrepancy between the self-consistent Gaussian approximation and the exact results is the neglected effect of mesoscopic fluctuations on the higher-order correlation functions. Finally, the results could be systematically improved within the field-theoretic perturbation expansion beyond the self-consistent one-loop approximation. Still, the self-consistent Gaussian approximation gives results that agree qualitatively with the exact solutions, in contrast to MF, where a non existing phase transition and a divergent amplitude of the correlation function are obtained.

VI. Discussion

We have combined DFT and field-theoretic methods in a coarse-grained theory for systems with mesoscopic inhomogeneities [18, 27, 28]. Equations for the average volume fraction and the correlation function, (28) and (29) with (25) have been obtained in the self-consistent Gaussian approximation equivalent to the self-consistent 1-loop approximation in the field theory. Predictions of the theory for the disordered phase, (30)–(34), have been verified by the comparison with the exact results obtained in [19] for a 1D lattice model with first-neighbor attraction and third-neighbor repulsion. In order to simplify the calculations, we have made further approximations concerning the inverse correlation function in MF, equation (35), and beyond, equation (38), and adopted for the correlation function in the lattice model the expression (46) obtained for a continuous system. Thus, we have in fact compared a continuous system with the lattice-gas form of the entropy, (45), with the exact results obtained for a lattice model.

Despite all the simplifying assumptions, we have obtained a qualitative agreement for all the key features of the system with mesoscopic inhomogeneities, for the phase-space region where the ansatz (38) is a reasonable approximation. First of all, we predict stability of the disordered phase for $T > 0$. However, when the repulsion-to-attraction ratio is large, $J > 1$, the disordered phase is strongly inhomogeneous in this part of the phase-space region where MF predicts stability of the ordered periodic phase. In the ordered phase regularly distributed clusters are separated by voids. In the presence of mesoscopic fluctuations the long-range order is absent, but the inhomogeneity is reflected in the oscillatory decay of the correlation function. The correlation length $\xi$, is very large and increases for decreasing $T$. Both the correlation length and the amplitude of the correlation function decay rapidly when the MF transition from the periodic to the homogeneous phase is approached (figure 5 for $J = 3$). All these features agree with exact results.

The $\mu(\zeta)$ and EOS isotherms also have the characteristic features observed in [19] in the case of strong repulsion ($J = 3$). For low $T$ there are 3 and 2 inflection points in the $\mu(\zeta)$ and $p(\zeta)$ curves respectively. A very large compressibility for the volume fraction $\zeta \approx 0.3$ becomes small for $\zeta \approx 0.5$, and very large again for $\zeta \approx 0.7$, in agreement with [19].

**Figure 10.** Pressure $p^*$ (in units of the short-range attraction $J_1$ per particle volume) as a function of the volume fraction $\zeta$ (dimensionless) for $J = 3$. In the left panel equation (32) is shown for $T^* = 0.1$ (solid) $T^* = 0.4$ (dash) and $T^* = 0.7$ (dash-dotted line). In the right panel the effect of fluctuations is highlighted by comparison of the pressure with the MF result (dashed line) for $T^* = 0.1$. 
We conclude that the disordering effect of mesoscopic fluctuations, neglected in MF, is overestimated in our theory, especially at low $T$. We expect significantly better results without the simplifying assumptions, (35), (38) and (46), but rather involved numerical computations are necessary to solve equations (30)–(34).

Our results show that most of the qualitative features of the disordered phase with strong inhomogeneities are correctly predicted even when very incomplete information about the interaction potential is taken into account (see the assumption (35)). Thus, the same properties are obtained at this level of approximation for all interaction potentials which in Fourier representation have the same shape near the minimum. More generally, from our theory it follows that for $\zeta < \zeta_c$ ($\zeta > \zeta_c$), where $\zeta_c$ is the critical volume fraction, the chemical potential and pressure (see (30) and (42)) are smaller (larger) than predicted by MF. The fluctuation correction is the larger the stronger are the inhomogeneities, as measured by $G(r,r)$.

We hope that in future studies our self-consistent Gaussian approximation can be applied to systems with $d > 1$, where the exact results are not feasible. The present comparison with the exact results can help to interpret and critically analyze the results.

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References

[1] Evans R 1979 Adv. Phys. 28 143
[2] Goldenfeld N 1992 Lectures on Phase Transition and the Renormalization Group (Oxford: Westview Press)
[3] Evans R 1990 Liquids and Interfaces: Les Houches, Session XLVIII 1988 ed J Charvolin et al (Amsterdam: North Holland)
[4] Seul M and Andelman D 1995 Science 267 476
[5] Sear R P and Gelbart W M 1999 J. Chem. Phys. 110 4582
[6] Pini D, Jialin G, Parola A and Reatto L 2000 Chem. Phys. Lett. 327 209
[7] Pini D, Parola A and Reatto L 2006 J. Phys.: Condens. Matter 18 S2305
[8] Imperio A and Reatto L 2004 J. Phys.: Condens. Matter 18 S2319
[9] Barci D G and Stariolo D A 2007 Phys. Rev. E 76 031501
[10] Stradner A, Sedgwick H, Cardinaux F, Poon W C K, Egelhaaf S U and Schurtenberger P 2004 Nature 432 492
[11] Ciach A and Góźdź W T 2010 Condens. Matter Phys. 13 23603
[12] de Candia A, Del Gado E, Fierro A, Sator N, Tarzia M and Coniglio A 2006 Phys. Rev. E 74 010403
[13] Zhuang Y, Zhang K and Charbonneau P 2015 arXiv:1509.08872v1
[14] Ciach A and Góźdź W T 2001 Annu. Rep. Prog. Chem. Sect. C: Phys. Chem. 97 269
[15] Ciach A, Pękalski J and Góźdź W T 2013 Soft Matter 9 6301
[16] Barci D G and Stariolo D A 2007 Phys. Rev. Lett. 98 200604
[17] Barci D G and Stariolo D A 2009 Phys. Rev. B 79 075437
[18] Ciach A 2008 Phys. Rev. E 78 061505
[19] Pękalski J, Ciach A and Almarza N G 2013 J. Chem. Phys. 138 144903
[20] Pękalski J, Ciach A and Almarza N G 2014 J. Chem. Phys. 140 114701
[21] Archer A J 2008 Phys. Rev. E 78 031402
[22] Ciach A, Góźdź W T and Evans R 2003 J. Chem. Phys. 118 3702
[23] Almarza N G, Pękalski J and Ciach A 2014 J. Chem. Phys. 140 164708
[24] Imperio A and Reatto L 2006 J. Chem. Phys. 124 164712
[25] Barci D G, Mendoza-Coto A and Stariolo D A 2013 Phys. Rev. E 88 062140
[26] Brazovskii S A 1975 Sov. Phys.—JETP 41 85
[27] Ciach A 2011 Mol. Phys. 109 1101
[28] Ciach A and Patsahan O 2012 Condens. Matter Phys. 15 23604
[29] Landau L D and Lifshitz E M 1980 Statistical Physics 3 edn (London: Pergamon)