Self-consistent theory for systems with mesoscopic fluctuations

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Abstract

We have developed a theory for inhomogeneous systems that allows for the incorporation of the effects of mesoscopic fluctuations. A hierarchy of equations relating the correlation and direct correlation functions for the local excess $\phi(r)$ of the volume fraction of particles $\zeta$ has been obtained, and an approximation leading to a closed set of equations for the two-point functions has been introduced for the disordered inhomogeneous phase. We have numerically solved the self-consistent equations for one-dimensional (1D) and three-dimensional (3D) models with short-range attraction and long-range repulsion. Predictions for all of the qualitative properties of the 1D model agree with the exact results, but only semi-quantitative agreement is obtained in the simplest version of the theory. The effects of fluctuations in the two 3D models considered are significantly different, despite the very similar properties of these models in the mean-field approximation. In both cases we obtain the sequence of large–small–large compressibility for increasing $\zeta$. The very small compressibility is accompanied by the oscillatory decay of correlations with correlation lengths that are orders of magnitude larger than the size of particles. In one of the two models considered, the small compressibility becomes very small and the large compressibility becomes very large with decreasing temperature, and eventually van der Waals loops appear. Further studies are necessary in order to determine the nature of the strongly inhomogeneous phase present for intermediate volume fractions in 3D.

Keywords: inhomogeneous systems, fluctuations, charged particles, short-range attraction and long-range repulsion

(Some figures may appear in colour only in the online journal)
spatial inhomogeneities at lengths greater than the size of ions or charged particles. One of the first theoretical observations of the instability of the homogeneous phase with respect to periodic charge- or number-density distribution was made by Stell and co-workers [9–12]. Inhomogeneities, in particular clusters, networks or layers, or exotic crystals, have also been observed in experiments and simulations [13–26]. Instability with respect to the periodic distribution of the particles in space competes with the phase separation and may lead to quite complex phase behavior [4, 10–12, 27].

Despite the progress in studies of ionic systems and charged particles, many important questions remain open as accurate description of systems with mesoscopic inhomogeneities remains a challenge. Liquid matter theories, such as the generalized mean-spherical approximation or the self-consistent Ornstein–Zernike approximation (SCOZA) [28], work very well for simple liquids. In particular, SCOZA yields globally accurate phase diagrams [29]. Theories like SCOZA and hierarchical reference theory (HRT) include fluctuations over all length scales; the limitation of SCOZA and HRT is that no solutions are found when a uniform state becomes unstable with respect to a modulated phase [30, 31]. It is not easy to obtain solutions for inhomogeneous systems with competing interactions, such as the short-range attraction and long-range repulsion (SALR) potential, in liquid-matter theories. Nevertheless, some features due to the SALR potential can and have been studied [30–32]. In particular, enhanced density fluctuations, a tendency towards cluster formation, and the growth of the compressibility in a large density and temperature interval close to the liquid–vapour transition was observed by Pini et al in the case of weak repulsion [31, 32].

The inhomogeneities that occur at the microscopic length scale near external surfaces are successfully described by density functional theory (DFT) [33]. However, in spontaneously occurring mesoscopic inhomogeneities the predictions of DFT deviate from the results of simulations more significantly than they do in simple fluids [34, 35]. This is because fluctuations, such as displacements, reshaping, merging or splitting of the aggregates, play an important role in these systems.

Fluctuations can be taken into account in Brazovskii field theory (BFT) [36] relatively easily but, since this theory is phenomenological in nature, neither the equation of state (EOS) nor the phase diagram in terms of real thermodynamic variables can be determined. Note that the displacement, reshaping, merging or splitting of the aggregates can appear either spontaneously or as a result of external stimuli, and one can expect that thermodynamic susceptibilities, in particular the compressibility and specific heat, are very different to those in homogeneous systems. Since the complexity of these systems leads to serious technical difficulties, their structural, mechanical and thermal properties are not yet fully understood.

The aggregates are periodically distributed in space in ordered phases analogous to lyotropic liquid crystals, but in the disordered phase, analogous to microemulsion, the aggregates are only locally ordered. The SALR and amphiphilic systems have similar properties since, as shown in [37], both can be described by the Brazovskii functional. (We should mention here that Stell studied amphiphilic systems as well, in particular in [38].) However, while lyotropic liquid crystals in amphiphilic systems are quite common [39], only the disordered distribution of spherical or elongated clusters was observed in the SALR system by confocal microscopy [19, 20]. It is unclear if the observations concerned the disordered inhomogeneous phase, or just one state of the ordered phase and after averaging the distribution of the aggregates would be periodic. The ordered hexagonal and lamellar phases were obtained by molecular dynamics simulation, but the spherical clusters were
not ordered periodically in this simulation [24]. In figure 1 we show a schematic representation of a typical distribution of particles in the periodically ordered inhomogeneous phase, and in the disordered phase that is either inhomogeneous (figure 1(b)) or homogeneous (figure 1(c)) on the mesoscopic length scale. The ‘disordered phase’ and ‘homogeneous phase’ are often treated as synonyms for the phase with position-independent average density. However, position-independent average density does not necessarily mean that the structure is homogeneous at the mesoscopic length scale in the majority of states (see figure 1(b)). Here we call the phase with position-independent average density the ‘disordered phase’.

The ordered periodic phases in the SALR and amphiphilic systems are quite well described by mean-field (MF) theories [34, 40, 41]. In the disordered inhomogeneous phase, however, mesoscopic fluctuations play a key role and its properties are not correctly predicted on the MF level. The aggregates can be clearly seen in a confocal microscope and in simulation snapshots, but due to fluctuations the average volume fraction of the particles, $\bar{\zeta}(r)$, is position-independent, $\bar{\zeta}(r) = \text{const.}$. For this reason one cannot distinguish the inhomogeneous and homogeneous structures of the disordered phase solely through the one-particle distribution function. In this work we propose a theoretical method of investigation of the disordered inhomogeneous phase and apply the formalism to a one-dimensional (1D) and a three-dimensional (3D) SALR model with strong repulsion, in order to calculate the EOS.

Some information about properties of the disordered inhomogeneous phase was obtained in [42], where a 1D lattice model with nearest-neighbor attraction and third-nearest repulsion was solved exactly. When the repulsion is strong enough, clusters consisting of three particles separated by three empty sites (i.e., ...,ooo...ooo...ooo...ooo... where ‘.’ and ‘o’ denote the empty and occupied sites, respectively) are energetically favorable. The volume fraction of particles in this ordered structure, stable only at temperature $T = 0$, is $\zeta = 1/2$. There are no phase transitions in 1D models with short-range interaction, but at low $T$ and $\zeta \approx 1/2$ the disordered phase turns out to be strongly inhomogeneous. In [42] it was found that for $T > 0$ the correlation function exhibits an oscillatory decay with a period $\approx 6$. For $\zeta \approx 1/2$, the correlation length increases to very large values and the compressibility decreases to very small values for decreasing $T$. The compressibility is small for $\zeta \approx 1/2$, because the increase of $\zeta$ leads to shorter separation between clusters and to repulsion between them. Large compressibility was obtained for $\zeta$ that is either too small or too large for the formation of the periodic structure that is favorable energetically. The chemical potential $\mu(\zeta)$ and pressure $p(\zeta)$ isotherms at low $T$ are very different to those in simple fluids. When $T$ decreases, the slope of $\mu(\zeta)$ becomes very small for both small and large $\zeta$, and very large for $\zeta \approx 1/2$. The very small slope of $\mu(\zeta)$ was interpreted as a pseudo phase transition between the homogeneous very dilute or very dense phase and the inhomogeneous phase present for $\zeta \sim 1/2$. Interestingly, for $\zeta \sim 0.6$ the pressure decreases for increasing $T$, in contrast to simple fluids.

Properties of the 2D and 3D systems cannot be easily determined by either exact calculation or simulation, due to large finite size effects and the collective motion of the aggregates. For this reason, it is important to develop an approximate predictive theory and test its accuracy by comparison with the exact results obtained in the 1D model.

Development of a tractable theory that could allow for quantitative or at least semi-quantitative description of structural, mechanical and thermal properties of systems with mesoscopic inhomogeneities is our long-term goal. In [37, 43–45] we took the first steps in this direction. The general formalism allows for the investigation of disordered and periodically ordered phases, but the equations obtained are very difficult and in practice approximations are necessary. In order to verify the quality of the various approximations, one should compare the results with exact solutions that so far exist only for the disordered phase [42]. Before considering the modulated phases, we limit ourselves to the disordered phase in order to verify the various approximate schemes.

In this work we further develop our theory, which combines liquid-matter theory, DFT and BFT methods. The present version of the approximate theory is based to a large extent on the derivation described in [45], and summarized briefly in section 2. We focus on a one-component system. In the context of charged particles this means that we integrate out the degrees of freedom of the counterions, and consider screened electrostatic potential between the charged particles. The explicit counterions can be considered within our formalism at a later stage.

The self-consistent Gaussian approximation developed in [45] is rather simple and yields results that agree qualitatively with the majority of the exact results obtained for the 1D lattice model [42]. Unfortunately, in the case of the 3D SALR model in continuum space our equation for the direct correlation function has no solutions for the phase space region where inhomogeneities are expected. This resembles the lack of solution in the SCOZA mentioned above. In order to overcome this problem, in this work we develop a theory beyond the Gaussian approximation. In section 3 a hierarchy of equations relating the many-point correlation and the direct correlation functions for mesoscopic volume fraction is constructed. We make an approximation for the direct four-point correlations, and obtain an equation relating the two-point correlation and direct correlation functions that together with the Ornstein–Zernike (OZ) equation form a closed set of equations. Finally, we obtain expressions for $\mu(\zeta)$ and $p(\zeta)$ which contain contributions resulting from the mesoscopic fluctuations. In section 4 the results obtained in the approximate theory for the 1D lattice model are compared with the exact results of [42]. The agreement is much better than in the Gaussian approximation. In section 5 we present the results of our theory for the 3D SALR model with both the attractive and repulsive parts of the interaction potential having the Yukawa form. We choose two sets of parameters, both favoring the periodic distribution of particles over the homogeneous state. In the first model the attraction range is very short and the repulsion barrier is small. For this potential, small clusters are formed and the gas–liquid separation is energetically unfavorable when compared to the homogeneous state. In the second model the attraction
range and the repulsion barrier are both larger. Larger clusters are formed and the gas–liquid separation is energetically favorable when compared to the homogeneous state. In MF approximation the phase diagrams of the two models are very similar [40]. Here, we ask if the effects of the fluctuations on the shape of the $\mu(\zeta)$ and $p(\zeta)$ curves depend on the range and amplitude of the attractive and the repulsive parts of the interaction potential. Section 6 contains the summary and discussion.

2. Brief summary of the theory for systems with mesoscopic inhomogeneities

We consider systems with inhomogeneities on a length scale significantly larger than the size of molecules $\sigma \equiv 1$ (see figure 1(b)). In our theory [43–45] a mesoscopic volume fraction is described by a smooth function $\zeta(r)$ equal to the fraction of the volume of the mesoscopic region with a center at $r$ that is covered by the particles. The grand thermodynamic potential in the presence of the constraint, mesoscopic fluctuations may appear and the grand potential is given by [43, 45]

$$\Omega = \Omega_{co}[\zeta] - k_B T \ln \left( \int D\phi e^{-\beta H_{\phi}} \right)$$  \hspace{1cm} (1)

with $\beta^{-1} = k_B T$, $k_B$ the Boltzmann constant, and

$$H_{\phi}[\zeta, \phi] = \Omega_{co}[\zeta + \phi] - \Omega_{co}[\zeta],$$  \hspace{1cm} (2)

where $\bar{\zeta}$ denotes the average volume fraction, and

$$\phi := \zeta - \bar{\zeta}$$  \hspace{1cm} (3)

is the mesoscopic fluctuation. The first term in (1) contains contributions from the fluctuations on a microscopic length scale in the absence of mesoscopic fluctuations. 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 $\zeta$ is the average volume fraction, it follows that $\langle \phi \rangle = 0$, where

$$\langle X \rangle := \Xi^{-1} \int D\phi X e^{-\beta H_{\phi}}$$  \hspace{1cm} (4)

and

$$\Xi = \int D\phi e^{-\beta H_{\phi}}.$$  \hspace{1cm} (5)

In the following, $\langle \phi \rangle = 0$ is always assumed.

We introduce the functional derivatives

$$C_n(r_1, ..., r_n) := \frac{\delta^n \beta \Omega}{\delta \zeta(r_1) ... \delta \zeta(r_n)}$$

$$= \frac{C_n^0(r_1, ..., r_n)}{\delta \zeta(r_1) ... \delta \zeta(r_n)} \ln \left( \int D\phi e^{-\beta H_{\phi}[\zeta, \phi]} \right)$$  \hspace{1cm} (6)

where

$$C_n^0(r_1, ..., r_n) = \frac{\delta^n \beta \Omega_{co}}{\delta \zeta(r_1) ... \delta \zeta(r_n)}.$$  \hspace{1cm} (7)

$C_n$ and $C_n^0$ are functionals of $\zeta$.

For $n = 1, 2$ we obtain from (6)

$$C_1(r) = C_1^0(r) + \left( \frac{\delta \beta H_{\phi}}{\delta \zeta(r)} \right),$$  \hspace{1cm} (8)

and

$$C_2(r_1, r_2) = C_2^0(r_1, r_2) + \left( \frac{\delta^2 \beta H_{\phi}}{\delta \zeta(r_1) \delta \zeta(r_2)} - \frac{\delta \beta H_{\phi}}{\delta \zeta(r_1)} \frac{\delta \beta H_{\phi}}{\delta \zeta(r_2)} \right) \text{e}^{\text{con}},$$  \hspace{1cm} (9)

where

$$\langle X(r_1) Y(r_2) \rangle^{\text{con}} := \langle X(r_1) Y(r_2) \rangle - \langle X(r_1) \rangle \langle Y(r_2) \rangle.$$  \hspace{1cm} (10)

The explicit expressions for $C_1$ and $C_2$ are given in appendix A.

We make the standard local MF approximation for the grand potential with suppressed mesoscopic fluctuations,

$$\Omega_{co}[\zeta] = U[\zeta] - TS[\zeta] - \mu N[\zeta],$$  \hspace{1cm} (11)

where $U[\zeta]$, $S[\zeta]$ and $N[\zeta]$ are the internal energy, entropy and internal energy in the local density approximation are given by

$$-TS[\zeta] = \int dr f_\mu(\zeta(r))$$  \hspace{1cm} (12)

and

$$U[\zeta] = \frac{1}{2} \int dr_1 \int dr_2 \zeta(r_1) V(r_1 - r_2) \zeta(r_2).$$  \hspace{1cm} (13)

So as not to include the contributions to the internal energy from overlapping hard cores of the particles, we assume $V(r_1 - r_2) = u(r_1 - r_2) \theta([r_1 - r_2] - 1)$, with $u$ denoting the interaction potential. We use volume fraction rather than density in (13), and therefore we re-scale the interaction potential $u(r_1 - r_2)$ by a factor $(6/\pi)^\nu$ in order to obtain the same energy as in the standard theory. We also re-scale the chemical potential, $\tilde{\mu} = (6/\pi)\mu$, so that

$$\mu N[\zeta] = \tilde{\mu} \int dr \zeta(r).$$  \hspace{1cm} (14)

For $\Omega_{co}$ defined in (11)–(14) we have

$$C_1^0(r) = \int dr_1 \zeta(r_1) \beta V(r_1 - r) + A_1(\zeta(r)) - \beta \tilde{\mu},$$  \hspace{1cm} (15)

$$C_2^0(r_1, r_2) = \beta V(r_1 - r_2) + A_2(\zeta(r_1)) \delta(r_1 - r_2)$$  \hspace{1cm} (16)

and for $n \geq 3$

$$C_n^0(r_1, ..., r_3) = A_n(\zeta(r_1)) \delta(r_1 - r_2) ... \delta(r_{n-1} - r_n),$$  \hspace{1cm} (17)

where

$$A_n(\zeta) = \frac{\delta^n \beta f_\mu(\zeta)}{\delta \zeta^n}. $$  \hspace{1cm} (18)

With the above form of $\Omega_{co}$ we can obtain $\bar{\zeta}$ for given $T$ and $\tilde{\mu}$ from the requirement that $\Omega$ takes the minimum, i.e. $\zeta(r) = 0$, with $C_1$ given in equation (8). The only difficulty is the calculation of the fluctuation correction to the MF equation $C_1^0 = 0$. In order to calculate this correction, it is
necessary to perform functional integrals (see (4) and (8)). In practice only the Gaussian functional integrals can be calculated. In order to perform the functional integrals in (1), (8) and (9), we have to approximate $H_f$ by an effective functional that is quadratic in the fluctuation $\phi$, or expand $H_f[\zeta, \phi]$ in a functional Taylor series w.r.t. $\phi$.

In [45] we have made the approximation

$$\beta H_f \approx \beta H_0 = \frac{1}{2} \int d\mathbf{r} \int d\mathbf{r}' \phi(\mathbf{r}) C(\mathbf{r}, \mathbf{r}') \phi(\mathbf{r}')$$

(19)

and obtained from (9) the following approximate equation:

$$C(\mathbf{r}, \mathbf{r}) \approx C(\mathbf{r}, \mathbf{r}) + \frac{A_4(\zeta(\mathbf{r}))}{2} G(\mathbf{r}, \mathbf{r}) \delta(\mathbf{r} - \mathbf{r}') - \frac{A_4(\zeta(\mathbf{r}))}{2} A(\zeta(\mathbf{r}')) G^2(\mathbf{r}, \mathbf{r}')$$

(20)

where

$$G(\mathbf{r}, \mathbf{r}') := \langle \phi(\mathbf{r}) \phi(\mathbf{r}') \rangle$$

satisfies the OZ equation

$$\int d\mathbf{r}' C(\mathbf{r}, \mathbf{r}') G(\mathbf{r}, \mathbf{r}') = \delta(\mathbf{r}, \mathbf{r})$$

(21)

and $C \equiv C_2$. From now on we will omit the subscript 2 in the case of the two-point correlation and direct correlation functions in order to simplify the notation. Equations (20) and (21) have to be solved self-consistently. Equation (20) is valid for any $\zeta(\mathbf{r})$, including the modulated phases.

The above Gaussian approximation is relatively simple and correctly predicts the main qualitative features of the 1D lattice model that was solved exactly in [42]. Unfortunately, it has a serious disadvantage. In the case of a 3D SALR model equation (20) has solutions only for a limited range of $T$ and $\zeta$ in the disordered phase. This lack of solutions occurs because $A_1(\zeta)$ is large for small or large values of $\zeta$, and the right-hand side (rhs) of equation (20) becomes negative. On the other hand, in Fourier representation $\tilde{C}(k) > 0$ for high $T$ and never vanishes, since the rhs of equation (20) diverges for $C(k) = 0$. The lack of solutions indicates that the self-consistent Gaussian approximation is oversimplified. Thus, if we want to study a 3D system, we have to abandon the elegant and simple Gaussian approximation.

### 3. Beyond the Gaussian approximation

In the first step beyond the Gaussian approximation we expand $H_f[\zeta, \phi]$ in a functional Taylor series w.r.t. $\phi$.

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

(22)

with

$$\beta H_0[\zeta, \phi] = \frac{1}{2} \int d\mathbf{r} \int d\mathbf{r}' \phi(\mathbf{r}) C_{\zeta}^{(0)}(\mathbf{r}, \mathbf{r}') \phi(\mathbf{r}')$$

(23)

and

$$\beta \Delta H[\zeta, \phi] = \int d\mathbf{r} C^{(0)}(\mathbf{r}) \phi(\mathbf{r}) + \sum_{n>3} \int d\mathbf{r} A_n(\zeta) \phi(\mathbf{r}) n! \phi^2(\mathbf{r})$$

(24)

In practice the Taylor expansion is truncated, and only terms up to $\phi^3$ are kept. For stability reasons $n$ must be an even number. The truncation is justified provided the neglected terms are smaller than the kept terms. Since $A_{2n+1}$ vanishes for some value of $\zeta$, we compare the terms $\propto \phi^3$ and $\propto \phi^{n+2}$, and require that $A_n \phi^{n+2} \ln 1 > A_n + 2 \phi^{n+2}(n+2)!$ for even $n$. The necessary condition above must be satisfied by the fluctuations, $\phi$, that yield the major contribution to the average quantities. If the condition is satisfied for such fluctuations, it should be satisfied by $\langle \phi(\mathbf{r})^3 \rangle$.

In this work we develop a lowest-order theory beyond the Gaussian approximation, and keep terms up to $A_4 \phi^4/4!$ in $H_f$. The $\phi^4$ theory is valid if the Taylor expansion of $H_f[\zeta, \phi]$ can be truncated at the fourth-order term for the dominant fluctuations $\phi$. We therefore introduce the necessary condition for validity of the $\phi^4$ theory,

$$\langle \phi(\mathbf{r})^2 \rangle < \frac{30 A_4(\zeta)}{A_6(\zeta)}$$

(25)

If criterion (25) is violated, the $\phi^4$ theory may be oversimplified. Before discussing the results of our theory for particular models, we will verify whether the results for $G(\mathbf{r}, \mathbf{r}')$ satisfy (25) for $\mathbf{r} = \mathbf{r}'$. Note that the rhs of (25) depends on $\zeta$, therefore the accuracy of the $\phi^4$ theory can be different for different volume fractions.

By construction of the mesoscopic theory, $G(\mathbf{r}, \mathbf{r}')$ is proportional to the correlation function for the microscopic density at the point belonging to a mesoscopic region with the center at $\mathbf{r}$, and at the point belonging to a mesoscopic region with the center at $\mathbf{r}'$. Averaged over these two mesoscopic regions [43, 44]. In [43, 44] it was assumed that these mesoscopic regions are smaller than the size of the aggregates, and significantly larger than $\sigma$.

In this work we limit ourselves to the disordered phase with an average volume fraction independent of the space position, $\tilde{\zeta} = \text{const}$. In the disordered fluid

$$G := G(\mathbf{r}, \mathbf{r})$$

(26)

is a number independent of $\mathbf{r}$. It increases with increasing deviation from the average volume fraction in regions with excess density. It can be considered as a measure of the inhomogeneity of the system, or the compactness of the aggregates.

Let us first consider the relation between $\tilde{\zeta}$ and $\bar{\mu}$. When $H_f$ is truncated at the $\phi^4$ term, then from (8) and (15) we obtain

$$\beta \bar{\mu} \approx \tilde{\zeta} \int d\mathbf{r} V(\mathbf{r}) + \frac{A_4(\zeta)}{2} \langle \phi(\mathbf{r})^2 \rangle + \frac{A_4(\zeta)}{3!} \langle \phi(\mathbf{r})^3 \rangle + \frac{A_6(\zeta)}{4!} \langle \phi(\mathbf{r})^4 \rangle.$$  

(27)

In order to evaluate $\mu$, we need approximations for $\langle \phi(\mathbf{r})^n \rangle$ with $n \leq 4$.

Our approach is a generalization of the method developed in [45]. We calculate the correlation function $G$ using the OZ equation (21) and equation (9) for $C$. Since, in $\phi^4$ theory, $G$ depends only on $A_n$ with $n \leq 4$ (see (4), (22) and (24)), in the consistent approach $C$ should be expressed in terms of $A_n$ with $n \leq 4$ too.

Thus, from (9), for the disordered phase we obtain
The first term is given in equation (17). The shaded loop connecting the vertices at \( \bar{r}_1 \) and \( \bar{r}_2 \) is a solution of the self-consistent equation (32). It represents our approximation for \( \langle \phi(\bar{r})^2 \rangle \phi(\bar{r}^m)^{\text{con}} \), and is shown in the form of Feynman diagrams in the lower panel of figure 3.

\[
C(r_1, r_2) \approx C_{12}^0(r_1, r_2) + \frac{A_1(\tilde{G})}{2} G(r_1, r_2) \delta(r_1 - r_2)
- \frac{A_3(\tilde{G})^2}{4} \langle \phi(r_1)^2 \phi(r_2)^2 \rangle^{\text{con}}. \tag{28}
\]

In order to have a closed set of equations (21) and (28), we need an approximation for \( \langle \phi(r_1)^2 \phi(r_2)^2 \rangle^{\text{con}} \). In [45] we assumed \( \langle \phi(r_1)^2 \phi(r_2)^2 \rangle^{\text{con}} = 2G(r_1, r_2)^2 \), but this approximation turns out to be an oversimplification for 3D systems, as discussed in section 2. Thus, we must take into account the well-known relation of the four-point correlation function with \( G \) and the three- and four-point direct correlation functions [33, 46]. In our theory, the expressions for \( C_3 \) and \( C_4 \) are obtained from equation (6). The approximate forms of \( C_3 \) and \( C_4 \) for \( H \) Taylor-expanded up to \( \delta^4 \) (see (22)–(24)) are given in terms of the correlation functions in appendix A.

In order to obtain a closed set of equations for \( \langle \phi(r_1)^2 \phi(r_2)^2 \rangle^{\text{con}} \), we neglect the contribution proportional to \( C_3 \),

\[
\langle \phi(r_1)^2 \phi(r_2)^2 \rangle^{\text{con}} \approx 2 \langle \phi(r_1) \phi(r_2) \rangle^2
- \int dr' \int dr'' \int dr''' \int dr'''' G(r_1, r') G(r_2, r''') G(r_2, r') G(r_2, r''') C_4(r_1, r', r'', r''', r''''), \tag{29}
\]

and for \( C_4 \) (equation (A.4) in appendix A) we make the approximation

\[
C_4(r_1, r', r'', r''', r''''') \approx A_4 \delta(r' - r'') \delta(r'' - r''') \delta(r''' - r''''')
- \left[ \langle \phi(r')^2 \phi(r'')^2 \rangle^{\text{con}} \right]
\times \langle \phi(r') \phi(r'') \rangle \delta(r'' - r''')
+ \delta(r' - r''') \delta(r'' - r''') \delta(r''' - r''''')
+ \langle \phi(r')^2 \phi(r'''')^2 \rangle^{\text{con}} \delta(r' - r'') \delta(r'' - r''') \delta(r''' - r'''''). \tag{30}
\]

Graphical representation of the above equations is shown in figure 2. We insert (30) in (29), and obtain

\[
\langle \phi(\bar{r})^2 \rangle \phi(\bar{r}'')^2, \langle \phi(\bar{r})^2 \rangle \phi(\bar{r}'')^2
+ \left( \frac{A_1}{2} \right)^2 \int dr' \int dr'' \int dr''' \int dr'''' G(r_1, r') G(r_2, r'') G(r_2, r''') G(r_2, r''''') C_4(r_1, r', r'', r''', r'''''),
\]

and for \( C_4 \) (equation (A.4) in appendix A) we make the approximation

\[
\langle \phi(r)^2 \phi(r')^2 \rangle^{\text{con}} \approx 2 \langle \phi(r) \phi(r') \rangle^2
- A_4 \int dr' \int dr'' \int dr''' \int dr'''' G(r_1, r') G(r_2, r'') G(r_2, r''') G(r_2, r''''') C_4(r_1, r', r'', r''', r'''''),
\]

Figure 2. Upper panel: graphical representation of equation (29). The bullets represent the external points \( r \) and \( r' \). The large shaded square represents \( C_4 \). The open circles represent internal points. The thick line connecting points \( r' \) and \( r'' \) represents \( G(r', r'') \). An integration over \( r \) is associated with each internal point \( r \). The first and second diagrams represent the first and second terms in equation (29), respectively. Lower panel: graphical representation of our approximation (30) for the four-point direct correlation function \( C_4 \). The small shaded squares at the vertices represent \( A_4 \). Thin line emanating from the vertex at \( r \) represents the corresponding argument of \( C_4(r, r, r, r) \). The first term is given in equation (17). The shaded loop connecting the vertices at \( r \) and \( r'' \) is a solution of the self-

consistent equation (32). It represents our approximation for \( \langle \phi(\bar{r})^2 \rangle \phi(\bar{r}'')^2 \), and is shown in the form of Feynman diagrams in the lower panel of figure 3.

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+ \left( \frac{A_1}{2} \right)^2 \int dr' \int dr'' \int dr''' \int dr'''' G(r_1, r') G(r_2, r'') G(r_2, r''') G(r_2, r''''') C_4(r_1, r', r'', r''', r'''''),
\]

and for \( C_4 \) (equation (A.4) in appendix A) we make the approximation

\[
C_4(r_1, r', r'', r''', r''''') \approx A_4 \delta(r' - r') \delta(r'' - r'') \delta(r''' - r''''')
- \left[ \langle \phi(r')^2 \phi(r'')^2 \rangle^{\text{con}} \right]
\times \langle \phi(r') \phi(r'') \rangle \delta(r'' - r''')
+ \delta(r' - r''') \delta(r'' - r''') \delta(r''' - r''''')
+ \langle \phi(r')^2 \phi(r'''')^2 \rangle^{\text{con}} \delta(r' - r'') \delta(r'' - r''') \delta(r''' - r'''''). \tag{30}
\]

Graphical representation of the above equations is shown in figure 2. We insert (30) in (29), and obtain

\[
\langle \phi(r)^2 \rangle \phi(r'^{2}) \phi(r'^{2})^{\text{con}} \approx 2 \langle \phi(r) \phi(r') \rangle^2
- A_4 \int dr' \int dr'' G(r_1, r') G(r_2, r'') \delta(r_1 - r_2)
+ \left( \frac{A_1}{2} \right)^2 \int dr' \int dr'' \int dr''' \int dr'''' G(r_1, r') G(r_2, r'') G(r_2, r''') G(r_2, r''''') C_4(r_1, r', r'', r''', r'''''),
\]

and for \( C_4 \) (equation (A.4) in appendix A) we make the approximation

\[
C_4(r_1, r', r'', r''', r''''') \approx A_4 \delta(r' - r') \delta(r'' - r'') \delta(r''' - r''''')
- \left[ \langle \phi(r')^2 \phi(r'')^2 \rangle^{\text{con}} \right]
\times \langle \phi(r') \phi(r'') \rangle \delta(r'' - r''')
+ \delta(r' - r''') \delta(r'' - r''') \delta(r''' - r''''')
+ \langle \phi(r')^2 \phi(r'''')^2 \rangle^{\text{con}} \delta(r' - r'') \delta(r'' - r''') \delta(r''' - r'''''). \tag{30}
\]

Graphical representation of the above equations is shown in figure 2. We insert (30) in (29), and obtain

\[
\langle \phi(r)^2 \rangle \phi(r'^{2}) \phi(r'^{2})^{\text{con}} \approx 2 \langle \phi(r) \phi(r') \rangle^2
- A_4 \int dr' \int dr'' G(r_1, r') G(r_2, r'') \delta(r_1 - r_2)
+ \left( \frac{A_1}{2} \right)^2 \int dr' \int dr'' \int dr''' \int dr'''' G(r_1, r') G(r_2, r'') G(r_2, r''') G(r_2, r''''') C_4(r_1, r', r'', r''', r'''''),
\]

and for \( C_4 \) (equation (A.4) in appendix A) we make the approximation

\[
C_4(r_1, r', r'', r''', r''''') \approx A_4 \delta(r' - r') \delta(r'' - r'') \delta(r''' - r''''')
- \left[ \langle \phi(r')^2 \phi(r'')^2 \rangle^{\text{con}} \right]
\times \langle \phi(r') \phi(r'') \rangle \delta(r'' - r''')
+ \delta(r' - r''') \delta(r'' - r''') \delta(r''' - r''''')
+ \langle \phi(r')^2 \phi(r'''')^2 \rangle^{\text{con}} \delta(r' - r'') \delta(r'' - r''') \delta(r''' - r'''''). \tag{30}
\]
Equations (21), (33)–(35) form a closed set of equations for \( G \). This result agrees with the results of the perturbation expansion in terms of Feynman diagrams in the self-consistent approximation, where only 1-loop diagrams and diagrams that have the form of chains of loops are included. The diagrams contributing to the direct correlation function \( C \) in the approximation equivalent to our theory are shown in figure 3.

Note that in contrast to the Gaussian approximation, a positive solution of equation (35) exists when \( C_2^{0}(k) < 0 \) even for \( \zeta \to 0 \), since \( \bar{D}_G < \bar{D} \), and the sum of the last two terms on the rhs is positive and large. Recall that we have neglected the term of order \( C_2 \) in equation (29). Since \( C_3 = A_1 \) and \( A_3(\zeta) = 0 \), where \( \zeta \) is the critical density, the accuracy of the solution of equation (35) decreases for increasing \( |\zeta - \zeta_c| \).

Let us return to the chemical potential, equation (27). In the lowest-order approximation we keep the dominant terms only, i.e. we neglect \( \langle \phi(r)^3 \rangle \) and assume \( \langle \phi(r)^4 \rangle \approx 3\langle \phi(r)^2 \rangle^2 \). In this approximation

\[
\beta \tilde{\mu} \approx \tilde{\zeta} \int dr \beta \mathcal{V}(r) + A_1(\tilde{\zeta}) + \frac{A_3(\tilde{\zeta})}{2} G + \frac{A_5(\tilde{\zeta})}{8} G^2. \tag{36}
\]

The fluctuation contribution is given in the last two terms, where \( G \) must be obtained from the solution of equations (21), (33)–(35). Both \( A_3(\zeta) \) and \( A_5(\zeta) \) are negative for small values of \( \zeta \) and positive for large values of \( \zeta \), (see (18)). Thus, the fluctuations lead to decreased and increased \( \tilde{\mu} \) for small and large \( \zeta \), respectively, as already found in the Gaussian approximation in [45]. Note that the leading-order corrections to (36), associated with \( \langle \phi(r)^3 \rangle \) and \( \langle \phi(r)^4 \rangle - 3\langle \phi(r)^2 \rangle^2 \), are of the opposite sign to \( A_{2n+1} \), hence the difference between the exact and the MF result for \( \tilde{\mu} \) should be smaller than predicted by (36).

The EOS is obtained from

\[
p = -\Omega/V = p^\text{MF} + k_B T \ln \Xi/V \tag{37}
\]

where \( V \) denotes the system volume, \( \Xi \) is defined in equation (5), and \( p^\text{MF} = -\Omega_{\text{MF}}/V \). From (11) we have

\[
p^\text{MF} = -\frac{1}{2} \bar{V}(0) \tilde{\zeta}^2 - f_0(\tilde{\zeta}) + \tilde{\mu} \tilde{\zeta}. \tag{38}
\]

Note that the fluctuation contribution to the pressure is included already in \( p^\text{MF} \), if we use our result (36) for \( \tilde{\mu} \) in order to obtain the EOS.

We want to estimate the correction to \( p^\text{MF} \) in the phase-space region where the MF predicts instability of the disordered phase with respect to periodic fluctuations. In this case \( C_2^{0}(k) < 0 \) for some range of \( k > 0 \), and the functional integrals in the standard perturbation expansion diverge. In order to overcome this problem we write \( \ln \Xi \) in the form

\[
\ln \Xi = \ln \int D\phi e^{-\beta H_0} + \ln \left( 1 + \sum_{n=1}^{\infty} \frac{(-\beta \Delta H_G)^n}{n!} \right) \tag{39}
\]

where \( (-\beta)_G \) is the average calculated with the probability proportional to \( \exp(-\beta H_G) \), \( H_f = H_G + \Delta H_G \), \( H_G \) is given in (19), and

\[
\Delta H_G = -\frac{1}{2} \int dr_1 dr_2 \phi(r_1) \phi(r_2) \left( A_1 G + \frac{A_3}{2} \phi(r_1)^2 \phi(r_2)^2 \right) + \int dr \left( C_1^{(0)} \phi(r) + \frac{A_3}{3!} \phi(r)^3 + \frac{A_5}{4!} \phi(r)^4 \right). \tag{40}
\]

In the first term on the rhs of equation (40) the explicit form of \( C_2^{0} - C \) is used (see (35)). We obtain the approximation for pressure using (39) and (40), and keeping only the leading-order contribution,

\[
p \approx p^\text{MF} + \frac{A_4 G^2}{8}. \tag{41}
\]
The procedure developed in this section is just the first step beyond the self-consistent Gaussian approximation. Systematic improvement of the accuracy of the results is possible within the framework described when \( C \) is taken into account. The Gaussian approximation does not take into account the compressibility for \( \zeta \approx 1/2 \) is independent of \( T \) and no anomalous decrease of pressure in a heated system is obtained for \( \zeta \approx 0.6 \).

Note that when \( \zeta = \text{const} \), the only difference between equation (35) and equation (20) (rewritten in Fourier representation) is the replacement of \( D \) by \( \tilde{D} \) (see (33) and (34)). Thus, in order to find \( C \) we can repeat the procedure described in detail in \([45]\). In short, for \( C_{2}^{(0)} \) defined in equation (16) we make the approximation

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

The parameters \( c_0, v_0, k_0 \) are obtained from the form of the interaction potential and from the form of \( f_h \) in the lattice-gas model by fitting (42) to (16) for \( k \) close to \( k_0 \), corresponding to the minimum of \( C_{2}^{(0)} \) \([45]\). For \( \tilde{C} \) we postulate the same form, i.e. equation (42), with the parameters \( c_0, v_0, k_0 \) replaced by the renormalized ones, \( c, v, k \), respectively. The equations for \( c, v, k \) are analogous to equations (39)–(41) in \([45]\), with \( \tilde{D}(k) \) replaced by \( \tilde{D}(k) \). For the form of \( \tilde{D}(k) \) and more details see \([45]\).

We solve the equations for \( c, v, k \) numerically in this part of the phase space, where MF predicts instability of the disordered phase. The MF line of instability, obtained from \( \tilde{C}_{2}^{(0)}(k_0) = 0 \), is \( k_B T = -\tilde{V}(k_0)/A_3(\zeta) \), and the interesting thermodynamic states are \( k_B T < -\tilde{V}(k_0)/A_3(\zeta) \). For such states the inhomogeneous distribution of particles is more probable than the homogeneous one. Following \([42, 45]\) we introduce the dimensionless temperature, \( T^* = k_0 T/J_0 \), and consider \( T^* \leq 1 \), where strong inhomogeneities are predicted by the exact results. We firstly verify if the necessary condition for validity of the \( \phi^4 \) theory, equation (25), is satisfied for \( T^* \leq 1 \). In figure 4 we compare \( G \) (see (26)) with the rhs of equation (25) for several temperatures.

We can see that for all the temperatures the \( \phi^4 \) theory is oversimplified for \( \zeta < 0.1 \) and \( \zeta > 0.9 \). Moreover, for \( T^* \leq 0.5 \) the criterion (25) is violated for \( 0.25 < \zeta < 0.75 \). Thus, we
should limit ourselves to \( T^* > 0.5 \) and \( 0.1 < \xi < 0.9 \). The case \( T^* \lesssim 0.5 \) will be shown in order to see how the oversimplified theory compares with the exact results.

In figure 5 the correlation length \( \xi \) increases with decreasing temperature and/or \( |\xi - \zeta| \). This behavior agrees with the exact results. However, when necessary condition (25) is not satisfied and our \( \phi^4 \) theory is oversimplified, we obtain significantly smaller \( \xi \) than found in [42]. The difference between our predictions and the exact results increases for decreasing \( T^* \) because the accuracy of our theory decreases with decreasing temperature (see figure 4).

In figure 6(a) we present the chemical potential for a few temperatures, and in the inset the exact results are shown for comparison. In figure 6(b) the predictions of our theory are compared with the results of the MF and Gaussian theories for \( T^* = 0.7 \). By MF prediction we mean here equation (36) without the fluctuation contributions (i.e. the last two terms), but in MF the disordered phase is unstable with respect to periodic ordering for the considered temperatures. Figure 6(a) suggests mechanical instabilities for two intervals of \( \zeta \) at \( T^* = 0.5 \). The exact results for very low \( T^* \), however, show only very large compressibility and pseudo phase transitions (i.e. a very large change of \( \zeta \) for very small change of \( \mu \)) at \( \zeta \approx 0.25, 0.75 \). As can be seen in figure 4, for \( T^* = 0.5 \) the \( \phi^4 \) theory is oversimplified. Thus, these instabilities are artefacts resulting from the truncation of the Taylor expansion of \( H_I \) at the \( \phi^4 \) term. Very large compressibility for large volume fractions usually signals an approach to a phase transition. In this model there are no phase transitions for \( T^* > 0 \), but the properties of the disordered phase differ significantly from the properties of the disordered phase in simple fluids. We conclude that peculiar behavior, such as the pseudo phase transitions observed in [42], but not necessarily a real phase transition should be expected when mechanical instabilities are predicted by our approximate theory, especially when criterion (25) is not satisfied.

From figure 6 we can see a significant improvement of our approximation when compared to the Gaussian theory [45] for \( T^* > 0.5 \). Our theory and the exact results both indicate that for increasing \( \xi \) the slope of the \( \mu(\xi) \) line is small (large compressibility) for \( \zeta \sim 0.25 \), then increases to much larger values for \( \zeta \approx \zeta_c \) (the compressibility decreases), and decreases again for \( \zeta \approx 0.75 \). The crossover from large to small to large compressibility occurs more and more rapidly when the temperature decreases, and a sequence of very large—very small—very large compressibility is obtained for \( 0.2 < \zeta < 0.8 \) at low \( T^* \). The slope of the \( \mu(\xi) \) line at \( \zeta = 0.5 \) increases with decreasing \( T^* \), and the lines corresponding to different \( T^* \) intersect in three points, \( \zeta \approx 0.25, 0.5, 0.75 \), in agreement with the exact results. The value of \( \mu \) at the points of intersection, \( \mu \approx -2, 2, 6 \), is only in semi-quantitative agreement with \( \mu = -2/3, 2, 14/3 \) obtained exactly. The accuracy of the present approximation decreases for increasing \( |\zeta - \zeta_c| \) (see figures 6 and 7). This should be expected because, as discussed below equation (35), for increasing \( |\zeta - \zeta_c| \) the neglected contribution associated with \( C_3 \) in equation (29)
increases, therefore the smaller $|\zeta - \zeta_c|$ is, the better the accuracy of the present approximation.

We conclude that the effects of fluctuations in our approximation are overestimated but, as discussed in section 3, we expect that a better approximation for $\langle \phi(r)^2 \phi(r)^2 \rangle_{\text{con}}$ and higher-order corrections to $\mu$ should lead to smaller deviations of $\mu$ from $\mu_{\text{MF}}$, hence to better agreement with the exact results. The consequence of the too-small value of $\mu$ for $\zeta < 0.5$ is the negative pressure value, as can be seen in figure 7. Despite these negative values for small $\zeta$, the shape of the $p(\zeta)$ lines agrees quite well with the exact results [42]. In particular, we obtain the anomalous decrease of pressure for increasing $T$ for $\zeta \approx 0.6$.

5. Results for a 3D SALR model

We consider charged particles with hard cores of diameter $\sigma$ taken as a length unit. The particles repel each other at large distances with screened electrostatic interactions, and attract each other at short distances with solvent-mediated effective potentials. The reference-system free energy is given by the Percus–Yevick approximation

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

(43)

where $\rho^* = 6\zeta/\pi$ is the dimensionless density. For the interaction potential we choose the form studied in [25, 30, 37, 40, 47]

$$
V(r) = \left[ -\frac{A_1}{r} e^{-3r} + \frac{A_2}{r} e^{-3r} \right] \theta(r-1),
$$

(44)

where $r$ is in $\sigma$ units. In Fourier representation $V$ takes the form

$$
\tilde{V}(k) = 4\pi \left[ \frac{A_1 e^{-3z}}{z_1^2 + k^2} \left( \frac{\sin k}{k} + \cos k \right) - \frac{A_2 e^{-3z}}{z_2^2 + k^2} \left( \frac{\sin k}{k} + \cos k \right) \right].
$$

(45)

$\tilde{V}(k)$ represents the increase of the system energy per unit volume when a volume-fraction wave with the wavenumber $k$ and unit amplitude is excited in the initially homogeneous system. We choose two sets of parameters, considered in [40] in the context of the most probable inhomogeneous structures and in [47] in the Gaussian approximation of the Brazovskii type, i.e. in a linear order in the parameters $A_n$.

System 1 : $A_1 = 1$, $A_2 = 0.05$, $z_1 = 3$, $z_2 = 0.5$;
System 2 : $A_1 = 1$, $A_2 = 0.2$, $z_1 = 1$, $z_2 = 0.5$. (46)

$V(r)^2$ for both systems is shown in figure 8(a) and $\tilde{V}(k)$ is shown in figure 8(b). In both systems the global minimum of $V(k)$ is assumed for $k_0 > 0$, with $k_0 \approx 1.8$ in System 1, and $k_0 \approx 0.6$ in System 2, and $\tilde{V}(k_0) < 0$. Thus, the volume-fraction wave with a wavelength $2\pi/k_0$ is more probable than the homogeneous distribution of the particles.

In System 1 the attraction strength and range are small and the repulsion dominates, but it is not very strong either. Separation into dilute and dense homogeneous phases is neither entropically nor energetically favorable when $\tilde{V}(0) > 0$. Because $\tilde{V}(0) > 0$ in System 1, phase separation is less favorable than the homogeneous distribution of particles. The latter is in turn energetically less favorable than the formation of small compact clusters (presumably of tetrahedral shape). Since the minimum of $\tilde{V}(k)$ is shallow, the energy gain associated with density waves with wavelengths somewhat different from $2\pi/k_0$ is comparable. Such waves can be excited with quite high probability. Thus, small clusters at different separations for different $\zeta$, rather than transitions between an ordered phase with the period $2\pi/k_0$ and homogeneous dilute or dense phases, should be expected.

In System 2 the strength and range of attraction are both much larger than in System 1, and clusters larger than those in System 1 are formed. The repulsion is stronger too, and the repulsive and attractive parts of the potential compete. The global minimum of $\tilde{V}(k)$ at $k_0$ is deep, and the density waves with a wavenumber $k_0$ are energetically favored over waves with different wavenumbers more strongly than they are in System 1. Thus, we can expect a stronger tendency for periodic order with the period $2\pi/k_0$. Since $\tilde{V}(0) < 0$, phase separation is energetically favored over the homogeneous state. When the average volume fraction of the particles does not
allow for the preferable periodic structure, phase separation might compete with periodic ordering.

In MF, periodic ordering of clusters or voids into lamellar, hexagonal, gyroid and bcc structures was found for both systems [40]. It is well known, however, that periodic order is destroyed by fluctuations for a large part of the MF stability region of the ordered phases [36, 48]. Thus, we are interested in the phase-space region below the MF boundary of stability – that follow from equations (21), (33) – in appendix B. The expression for $\tilde{D}(k)$ (see (33)) can be easily obtained, and is also given in appendix B. We solve the equations for $c_r, v_r, k_r$ that follow from equations (21), (33)–(35) numerically, using the procedure described in section 3 and in more detail in [45].

In fact $\tilde{C}$ should be determined by directly solving the integral equations (21), (33)–(35), because the assumed functional form of $\tilde{C}$ is appropriate only for systems with strong mesoscopic inhomogeneities and isotropic correlations. As shown in [48, 49], anisotropic correlations may appear in systems with competing interactions. Moreover, as argued in [45], equation (42) can be a fair approximation when $V(k)$ assumes a deep minimum. For System 1 this approximation can be too crude. Since solving the full equations is a very difficult task, we have decided to make all of the above simplifying assumptions in order to obtain preliminary results.

5.1. System 1

Let us firstly verify if the necessary condition (25) for validity of the $\phi^4$ theory is satisfied for the temperature range we are interested in. In figure 9 $G$ is shown along with $30G_0/A_0$ calculated for the Percus–Yevick approximation (43), with $A_0$ defined in (18). We can see that in the absence of the particle–hole symmetry the necessary condition (25) is satisfied for large volume fractions and is not for small volume fractions. The accuracy of the approximation increases with increasing temperature, when the inhomogeneities measured by $G$ decrease. The necessary condition for validity of the $\phi^4$ theory is satisfied for the whole range of $\zeta$ when $T^* > 0.015$.

Correlation length, chemical potential and pressure are shown in figures 10–12. Note the very large correlation length for $T^* \leq 0.003$. At $T^* = 0.0015$ the necessary condition (25) is satisfied for $\zeta > 0.25$, and we can see that $\xi \sim 10^3$ for volume fractions $\zeta \sim 0.3$. The oscillatory decay of the correlations with the mesoscopic period and the very large correlation length is a signature of the mesoscopic inhomogeneity for the corresponding thermodynamic parameters.

The results for $\tilde{\mu}(\zeta)$ and $p(\zeta)$ show large slope (indicating small compressibility) for $\zeta \approx \zeta_c$. The slope of $\tilde{\mu}(\zeta)$ and $p(\zeta)$ increases with decreasing $T^*$ (the compressibility decreases). The slope of $\tilde{\mu}(\zeta)$ and $p(\zeta)$ is small (large compressibility) for $\zeta \approx 0.1$ and decreases with decreasing $T^*$ (the compressibility increases). For $\zeta$ increasing from $\zeta \approx 0.2$ the slope of $\tilde{\mu}(\zeta)$ and $p(\zeta)$ decreases a little, but neither increasing $\zeta$ nor decreasing $T^*$ leads to very large compressibility in this system. Even for very small $T^*$, where our theory is expected to overestimate the effects of mesoscopic fluctuations, the compressibility at $\zeta_c$ is significantly larger, and for $\zeta \sim 0.3$ the compressibility is significantly smaller than in the 1D system with strong repulsion. Note that because the repulsion barrier is small, the
increase in the volume fraction for \( \zeta \approx \zeta_c \) does not require a very large increase in \( \bar{\mu} \) or \( p \), therefore the compressibility is not very small. Our results show no sign of the phase transition or pseudo phase transition between the inhomogeneous and the dense homogeneous phase for \( \zeta > \zeta_c \) for the range of \( T^* \) considered. Recall that in System 1 the attraction range is very small and \( V(0) > 0 \). For this reason, if the volume fraction is too large for the formation of the periodic structure with the wavenumber \( k_0 \), instead of the (pseudo) phase transition to the dense phase, a decrease in the separation between the small clusters takes place. We cannot predict if the phase transition (or a pseudo phase transition) between dilute gas and inhomogeneous fluid found for the 1D model in [42] can occur for \( \zeta < \zeta_c \), because our \( \phi^4 \) theory is oversimplified for \( \zeta < \zeta_c \) and \( T^* < 0.015 \).

5.2. System 2

We firstly verify which thermodynamic states our \( \phi^4 \) theory is not oversimplified for. As shown in figure 13, we obtain very similar behavior of \( G \) to that in System 1, namely the \( \phi^4 \) theory is oversimplified for small \( \zeta \) whose range increases with decreasing temperature. For \( T^* \geq 0.015 \), however, the necessary condition (25) is satisfied for the whole range of \( \zeta \). The correlation length is larger than in System 1 for the same dimensionless temperature, as can be seen by comparison of figures 10 and 14. Thus, the tendency for periodic order is stronger, as expected from the interaction potentials (figure 8).

The shapes of the \( \bar{\mu}(\zeta) \) and \( p(\zeta) \) isotherms in System 2 are much more complex than in System 1 (see figures 15 and 16). For \( T^* = 0.015 \) equation (25) is satisfied for all \( \zeta \). At this temperature we obtain a very small slope of \( \bar{\mu}(\zeta) \) and \( p(\zeta) \) (very large compressibility) for \( \zeta \sim 0.05 \sim 0.1 \), and a significantly larger slope of \( \bar{\mu}(\zeta) \) and \( p(\zeta) \) (smaller compressibility) that weakly depends on \( \zeta \) for \( \zeta > 0.15 \). When \( T^* \) is decreased to 0.009, we obtain a van der Waals loop for \( \zeta < 0.15 \), a very large slope of \( \bar{\mu}(\zeta) \) and \( p(\zeta) \) (very small compressibility) for \( \zeta \approx 0.2 \) and very large compressibility for \( \zeta > 0.3 \). The theory becomes oversimplified for \( \zeta < 0.15 \) for \( T^* = 0.009 \) (see figure 13) and, based on comparison with the 1D model, we can expect that very large compressibility may be present rather than the van der Waals loop obtained in our approximation. We can only conclude that either very...
large compressibility or a phase transition occurs for low volume fractions for \( T^* \lesssim 0.009 \). The very small compressibility for \( \zeta \sim 0.2 \) occurs with the very large correlation length of the correlation function that exhibits oscillatory decay. For decreasing \( T^* \), the compressibility for \( \zeta \sim 0.2 \) significantly decreases, and the correlation length increases. This behavior may indicate that when \( T^* \) decreases the clusters or layers of particles become more and more ordered in space for \( \zeta \sim \zeta_c \), where the inhomogeneous distribution of particles dominates. To compress such a system one has to decrease the separation between the aggregates, and overcome the repulsion between them. For \( T^* \lesssim 0.007 \) the van der Waals loops are present for both small and large volume fractions. It is possible that phase transitions between the disordered gas and liquid phases, and the inhomogeneous phase stable for intermediate \( \zeta \), occur for some range of \( T^* \). What remains unclear is the nature of the phase or phases with very small compressibility. We considered only \( \zeta = \text{const.} \) and isotropic correlations but in reality periodically ordered phases, or phases with \( \zeta = \text{const.} \) and anisotropic correlations, may be stable for some temperature range for intermediate \( \zeta \). Further studies are necessary before drawing definite conclusions concerning the phase behavior in this 3D system. Either pseudo phase transitions between the dilute and dense phases, and the inhomogeneous phase with periodic or quasi-periodic order, or real phase transitions can occur. In either case, when van der Waals loops are obtained in this approximation we can expect a huge change of compressibility with increasing \( \zeta \).

6. Summary and discussion

We have developed a theory for systems with inhomogeneities that form spontaneously on the mesoscopic length scale. In this work we focused on the disordered phase, where the particles self-assemble into aggregates that do not form an ordered periodic pattern. A hierarchy of equations relating the direct correlation functions \( C_n \) with correlation functions for the fluctuations of the local volume fraction of particles, \( \phi(\mathbf{r}) \), has been constructed. In order to obtain a closed set of equations we neglected terms associated with \( C_3 \) in the equation for \( \langle \phi(\mathbf{r}_1)^2\phi(\mathbf{r}_2)^2 \rangle^\text{conf} \). Next, neglecting the higher-order terms in the expression for \( C_n \), we obtained and solved a self-consistent equation for \( \langle \phi(\mathbf{r}_1)^2\phi(\mathbf{r}_2)^2 \rangle^\text{conf} \). This result leads to a closed set of equations for the two-point correlation and direct correlation functions, equations (21), (33)–(35). Solutions of our self-consistent equations for the two-point functions allow us to calculate fluctuation corrections to the chemical potential \( \mu(\zeta) \) and pressure, equations (36) and (41).

The general framework of our theory allows for the systematic improvement of the accuracy of the results. One can improve both the approximation for the Boltzmann factor \( \exp(-\beta H_f) \) that describes the probability of spontaneous appearance of \( \phi(\mathbf{r}) \), and the approximation for \( \langle \phi(\mathbf{r}_1)^2\phi(\mathbf{r}_2)^2 \rangle^\text{conf} \). In our theory \( H_f \) is Taylor expanded in \( \phi \), and the expansion is truncated. We have introduced a necessary condition for validity of a theory with the Taylor expansion truncated at the \( n \)th order (see equation (25) for \( n = 4 \)).

We applied our \( \phi^4 \) theory to the 1D lattice model with competing interactions, and to two variants of the SALR model.
in 3D. Following [45], we postulated a functional form of the correlation function $G$ and have solved the equations for the parameters in the expression for $G$ that follow from our self-consistent equations for the two-point correlation and direct correlation functions numerically. Next, we calculated $\bar{\mu}(\zeta)$ and pressure for these models.

Comparison of the predictions of our approximate theory with the exact results obtained for the 1D model in [42] allows for the verification of the accuracy of our approximations. The shape of the $\bar{\mu}(\zeta)$ and $\rho(\zeta)$ lines agrees with exact results very well when criterion (25) is satisfied. All of the qualitative trends are correctly reproduced. However, we do not obtain quantitative agreement at this level of approximation. When criterion (25) is not satisfied, i.e. for low $T^*$, van der Waals loops in $\bar{\mu}(\zeta)$ are predicted in our theory, although in reality only pseudo phase transitions occur in this model. Thus, when necessary condition (25) is violated, the theory is indeed oversimplified. We have made preliminary calculations for $\mu(\zeta)$ in the $\phi^6$ theory (not presented here) and obtained very similar shapes of the lines, and reasonably good quantitative agreement with the exact results for $0.2 < \zeta < 0.8$. In the $\phi^4$ theory the van der Waals loops appear for lower $T^*$ than in the $\phi^4$ theory. Thus, systematic improvement in the accuracy of the results is indeed possible within the general framework of our theory. In order to obtain better accuracy for $\zeta < 0.2$ and $\zeta > 0.8$, the term associated with $C_3$ should be included in equation (29).

We applied our theory to two versions of the 3D SALR model (equation (44)) described and discussed in section 5. In System 1 the phase separation into homogeneous dilute and dense phases is strongly energetically unfavorable and the periodic structure with the most probable period is only weakly favored as compared to the homogeneous structure. In System 2 the optimal periodic structure is strongly favorable, and the phase separation is weakly energetically favorable as compared to a homogeneous structure with given $\zeta$. The MF phase diagrams for the two versions of the 3D SALR model considered are nearly the same [40]. It is well known, however, that the ordered phases are stable for much lower temperatures than predicted by MF. Our aim was the investigation of the structure and EOS in the high-$T$ part of the MF instability region of the homogeneous phase, where weakly ordered phases are predicted by MF, but in reality a disordered inhomogeneous phase is stable.

Our results show the anomalous decrease of pressure for increasing $T$ for a range of $\zeta > \zeta^*$ in both systems. Apart from this common feature, the effects of fluctuations depend very strongly on the shape of the interaction potential. In the repulsion-dominated System 1 and in System 2 where neither repulsion nor attraction dominates, the EOS is qualitatively different (see figures 12 and 16). The disordering effects of fluctuations are much stronger in System 1. On the other hand, the shape of the $\mu(\zeta)$ and $\rho(\zeta)$ lines is much more complex in System 2.

In System 1 we do not obtain any rapid change of the compressibility for increasing $\zeta$ even for very small $T^*$. Unfortunately, for small $T^*$ the theory is oversimplified, especially for $\zeta < \zeta^*$, and we cannot draw definite conclusions concerning the phase transition between the dilute gas and inhomogeneous phases. For $\zeta > \zeta^*$ we do not obtain the large compressibility that would indicate an approach to a phase transition between the inhomogeneous phase and the dense liquid, even for temperature as low as $T^* = 0.0015$ (in reduced units).

In contrast, in System 2 the compressibility changes rapidly for increasing $\zeta$ even for relatively high $T^*$, and van der Waals loops occur at sufficiently low $T^*$. The van der Waals loops suggest that phase transitions or pseudo phase transitions between the gas and liquid phases, and the \textit{disordered inhomogeneous phase} which is stable for intermediate volume fractions occurs. Based on comparison with the 1D case, however, we expect that pseudo phase transitions, indicating significant structural changes in the disordered phase, occur when $T^*$ is high. For low $T^*$ we may expect stability of the ordered periodic phases for intermediate $\zeta$, and transitions between the disordered and the ordered phases. We cannot rule out the possibility that for intermediate $T^*$ and $\zeta$ the \textit{disordered inhomogeneous phase} is a thermodynamically distinct phase that can coexist with the homogeneous dilute and dense phases, but it is rather unlikely.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure16.png}
\caption{The pressure isotherms in $k_BT/\sigma^3$ units as a function of the volume fraction for System 2 (a) in our theory, equation (41), for $T^* = 0.005, 0.009, 0.015$ from top to bottom on the right and (b) in our theory (solid line) and in MF (dashed line) for $T^* = 0.015$.}
\end{figure}
At present we can only speculate about the phase behavior, because we have considered neither periodic phases nor phases with orientational order (anisotropic correlation functions). We cannot exclude phase transitions between inhomogeneous phases with different degrees of order when $T^*$ decreases. However, such transitions cannot be investigated with the assumptions of $\zeta = \text{const.}$ and isotropic correlations that we made in this work. We will investigate phases with anisotropic correlations and the periodically ordered phases in future studies.

We conclude that the theory developed in this work can offer a convenient tool for studying inhomogeneous systems. Further studies are necessary in order to develop an approximation that would yield more accurate results on the quantitative level within our general framework.

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**Appendix A. Explicit expressions for $C_3$ and $C_4$**

From equation (6) we obtain for $C_3$ and $C_4$

$$C_3(r_1, r_2, r_3) = A_3 \delta(r_1, r_2) \delta(r_2, r_3) + \left( \frac{\delta^3 H_f}{\delta \zeta^3(1) \delta \zeta(2) \delta \zeta(3)} \right)$$

$$- \left[ \frac{\delta^3 H_f}{\delta \zeta^3(1) \delta \zeta(2) \delta \zeta(3)} \right] \zeta(3) \text{permute(2)}$$

$$+ \left( \frac{\delta^3 H_f}{\delta \zeta^3(1) \delta \zeta(2) \delta \zeta(3)} \right) \text{permute(3)}$$

and

$$C_4(r_1, r_2, r_3, r_4) = A_4 \delta(r_1, r_2) \delta(r_2, r_3) \delta(r_3, r_4)$$

$$+ \left( \frac{\delta^4 H_f}{\delta \zeta(1) \delta \zeta(2) \delta \zeta(3) \delta \zeta(4)} \right)$$

$$- \left[ \frac{\delta^4 H_f}{\delta \zeta(1) \delta \zeta(2) \delta \zeta(3) \delta \zeta(4)} \right] \zeta(4) \text{permute(3)}$$

$$- \left[ \frac{\delta^4 H_f}{\delta \zeta(1) \delta \zeta(2) \delta \zeta(3) \delta \zeta(4)} \right] \text{permute(2)}$$

$$+ \left( \frac{\delta^4 H_f}{\delta \zeta(1) \delta \zeta(2) \delta \zeta(3) \delta \zeta(4)} \right) \text{permute(5)}$$

$$- \left( \frac{\delta^4 H_f}{\delta \zeta(1) \delta \zeta(2) \delta \zeta(3) \delta \zeta(4)} \right) \text{permute(4)}$$

(A.2)

where we have simplified the notation introducing $\zeta(i) \equiv \zeta(r_i)$ and ‘permute(n)’ means n different terms obtained by permutations of (1, 2, 3) or (1, 2, 3, 4) in (A.1) or (A.2) respectively. $(X_1(r_1) ... X_n(r_n))^{\text{permute}}$ is the part of $(X_1(r_1) ... X_n(r_n))$ that cannot be represented as a product of the average quantities calculated for disjoint sets of points. When $H_f$ is Taylor expanded and only terms proportional to $A_n$ with $n \leq 4$ are kept, we obtain the approximate expressions

$$C_3(r', r'', r''') = A_3 \delta(r', r'') \delta(r'', r''')$$

$$- \frac{A_1 A_3}{4} \left[ (\delta(r')^2 \delta(r'')^2)^\text{permute(3)} \right.$$

$$\times (\delta(r', r'') + \delta(r'', r'''))$$

$$+ (\delta(r')^2 \delta(r''')^2 \delta(r'', r'''))$$

$$+ \left( \frac{A_3}{2} \right)^3 (\delta(r')^2 \delta(r'')^2 \delta(r''')^2)^\text{permute(3)}$$

(A.3)

and

$$C_4(r', r'', r''', r''''') = A_4 \delta(r', r'') \delta(r'', r''') \delta(r'', r''''')$$

$$- \frac{A_1 A_4}{2} \left[ (\delta(r')^2 \delta(r'')^2)^\text{permute(3)} \right.$$

$$\times (\delta(r', r'') + \delta(r'', r'''))$$

$$+ (\delta(r')^2 \delta(r''')^2 \delta(r'', r'''))$$

$$+ \left( \frac{A_4}{2} \right)^3 (\delta(r')^2 \delta(r'')^2 \delta(r''')^2)^\text{permute(3)}$$

(A.4)

**Appendix B. Parameters $\xi_0, \alpha_0, \theta_0$ in equation (47) and the expression for $\hat{D}$ in 3D**

$$A_0^2 = \frac{1}{(4\pi)^2 v_0 c_0}, \quad \text{(B.1)}$$

$$\xi_0^2 = \alpha_0^2 = \frac{c_0}{4v_0}, \quad \text{B.2)}$$

$$\xi_0^2 = 2 \left[ \frac{v_0 k_0^2 + \sqrt{v_0 k_0^4 + v_0 c_0^2}}{c_0}, \quad \text{B.3)}$$

and for $G$ given in equation (47) $\hat{D}(k)$ defined in equation (33) takes the explicit form

$$\hat{D}(k) = \frac{\pi A_0^2}{k} \left[ \arctan \left( \frac{k \xi_0}{2} \right) - \arctan \left( \frac{(k + 2\alpha_0) \xi_0}{2} \right) - \arctan \left( \frac{(k - 2\alpha_0) \xi_0}{2} \right)\right]$$

(B.4)

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