Fluctuation theory for the wavevector expansion of the excess grand potential of a liquid–vapour interface and the theory of interfacial fluctuations

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Abstract. We develop a theory for the wavevector expansion of the excess grand potential of a liquid–vapour interface emphasizing the need to minimize the grand potential density functional for a given collective coordinate $l(y)$ denoting the position of a surface of fixed density ρ^X (magnetization m^X). We rederive the Triezenberg–Zwanzig formula for the surface tension γ which has a unique value independent of ρ^X. Our analysis yields a new expression for a rigidity $\kappa(\rho^X)$ which is strongly dependent on the particular value of ρ^X used to define $l(y)$. We show that the expressions derived for $\kappa(\rho^X)$ (and γ) are precisely those that need to be adopted when using the recently developed Fisher–Jin method of deriving an effective interfacial Hamiltonian appropriate to an asymptotically free interface. From the set of effective Hamiltonians describing the fluctuations of surfaces of all possible fixed density/magnetization we derive the correct analytic mean-field expression for the position dependence of the spin–spin correlation function for a free interface modelled by a Landau–Ginzburg–Wilson Hamiltonian. We emphasize that allowing for the m^X-dependence of the rigidity is essential in this study of interfacial correlations to achieve true thermodynamic consistency.

In developing a microscopic theory of inhomogeneous fluids a central concern is the derivation of exact expressions relating the surface tension (or excess grand potential) to integrals involving one-point and two-point (correlation) functions [1]. Analysis of such exact sum rules has been shown to provide a great deal of information about fluctuations and correlations at fluid interfaces [2]. Complementing this approach are studies of effective interfacial Hamiltonians which model the fluctuations of a collective coordinate rather than a microscopic order parameter [3]. Whilst these models are not truly microscopic their analysis has been largely responsible for the recent upsurge in interest and understanding of fluid interfacial phenomena. In the present paper we shall make connection between a formal density-functional (DF) approach to inhomogeneous fluids and the recent seminal work of Fisher and Jin (FJ) [4] who have carefully derived an effective interfacial Hamiltonian from a more microscopic Landau–Ginzburg–Wilson Hamiltonian. We consider how the surface tension γ and a rigidity κ for an asymptotically free interface may be formally defined from DF theory emphasizing the need to impose a minimization principle on the grand potential density functional $\Omega[\rho(r)]$. We rederive the well-known Triezenberg–Zwanzig formula [1] for the surface tension and give a new expression for an appropriately defined rigidity in terms of integrals over one-point and two-point functions [5]. Our expresion for κ properly accounts for the effect of the curvature of a collective coordinate on the density distribution which minimizes the grand potential density functional. The main conclusions of our study are as follows.

(i) The rigidity $\kappa = \kappa(\rho^X)$ is strongly dependent on the choice of crossing-criterion density ρ^X. That is, surfaces of different fixed densities have very different rigidities. In contrast the surface tension γ is unique.

(ii) The expression for $\kappa(\rho^X)$ derived is precisely that which needs to be used when following the FJ method of deriving effective interfacial Hamiltonians.

(iii) The detailed position dependence of the density–density correlation function at mean-field level is correctly described by a continuous set of effective interfacial Hamiltonians each of which models the fluctuations of surfaces of different fixed densities with different rigidities. Allowing for the ρ^X-dependence of κ is essential for true thermodynamic consistency.

To begin consider an equilibrium planar liquid–gas interface separating coexisting bulk liquid and gas phases. We suppose that the interface is localized near the plane $z = 0$ by, say, an extremely weak gravitational field modelled by an external potential $V(r) = mgz$. The grand potential $\Omega \equiv \Omega_{\text{planar}}$ may be written as the sum of the bulk and surface contributions (ignoring the negligible gravitational field):

$$\Omega_{\text{planar}} = -pV + \gamma A \tag{1}$$

where p is the bulk pressure, V is the total (infinite) volume and A is the planar area. According to DF theory the grand potential Ω corresponds to the minimum value of the grand potential density functional $\Omega[\rho(r)]$ in the presence of the external field $V(r)$. It is convenient to write this in the following way. Suppose that the planar equilibrium profile $\rho_0(z)$ has the specific value $\rho_0(z^X) = \rho^X$ at position z^X. Now consider the space of all distributions $\rho_X(r)$ which satisfy $\rho_X(r = (z^X, y)) = \rho^X$ for all values of the transverse position vector y. Then we can write

$$\Omega[\rho_0(r)] < \Omega[\rho_X(r)] \qquad \rho_X \neq \rho_0 \tag{2}$$

and identify

$$\Omega[\rho_0(r)] = \Omega_{\text{planar}}. \tag{3}$$

We wish to generalize the thermodynamic expression (1) and minimization condition (2) by considering non-planar distributions characterized by a collective coordinate $l(y)$. Following FJ we note that there are various possible definitions of $l(y)$. We will adopt a crossing-criterion approach although the formalism is trivially adapted to other definitions. Consider now a space Γ of distributions $\rho_\gamma(r)$ which satisfy the crossing criterion

$$\rho_\gamma(r = (z = l(y), y)) = \rho^X \qquad \forall y. \tag{4}$$

That is the collective coordinate $l(y)$ denotes a surface of fixed density ρ^X. The value of $\rho^X \in (\rho_g, \rho_l)$ but need not be further specified in the formalism. Now we suppose that $\exists \, \rho_\Xi \in \Gamma$ for which

$$\Omega[\rho_\Xi(r)] < \Omega[\rho_\gamma(r)] \qquad \rho_\gamma \neq \rho_\Xi \tag{5}$$

and define a collective coordinate functional

$$\Omega_l[l(y)] = \Omega[\rho_\Xi(r)]. \tag{6}$$

Minimization of $\Omega_l[l(y)]$ with respect to $l(y)$ recovers the unconstrained minimum (3). From the constrained minimum potential (6) we can proceed to define new fluid properties by supposing that $\Omega_l[l(y)]$ has an appropriate representation generalizing (1). First let us suppose that the fluctuations are very small such that $|l(y) - z^X| \ll 1$. Also we assume that the transverse Fourier transform

$$\tilde{\delta l}(Q) = \int \mathrm{d}y \, e^{iQ \cdot y}(l(y) - z^X) \tag{7}$$

is non-zero only for very small values of the wavevector Q. With these provisos we postulate that $\Omega_I[l(y)]$ has an expansion which defines the rigidity κ by

$$\Omega_I[l(y)] = -pV + A\gamma + \frac{1}{2(2\pi)^{d-1}} \int dQ \, (\gamma Q^2 + \kappa Q^4 + \cdots)|\tilde{\delta l}(Q)|^2 + \cdots \quad (8)$$

where the ellipsis denotes terms of higher power in Q or $|\tilde{\delta l}(Q)|$. Before we continue we make the following remarks with regard to the expansion (8).

(a) For consistency the coefficient of Q^2 appearing in parentheses must be associated with the exact equilibrium tension of the planar interface.

(b) We have assumed that there are no terms of order Q^3 as might arise due to the presence of long-ranged dispersion forces. Our subsequent analysis will concentrate on systems with short-ranged forces.

(c) In the case $g \to 0^+$ the expansion is only strictly valid provided γ and κ exist in this limit. Whilst physically γ must be positive finite the behaviour of κ as $g \to 0^+$ is not known *a priori*. As we shall see, however, in the most important application of our formalism the value of κ is well–behaved when the external field is made infinitesimally small.

Having carefully defined $\Omega_I[l(y)]$ it is now straightforward to derive the desired expressions for γ and κ. We suppose that the constrained profile $\rho_\Xi(r)$ may be calculated perturbatively by writing

$$\rho_\Xi(r) = \rho_0(z) + \delta\rho_\Xi(r) \quad (9)$$

and recall that $\rho_0(z^X) = \rho^X$. The value of the grand potential functional is then calculated using a standard functional Taylor series. We find

$$\Omega[\rho_\Xi(r)] = \Omega[\rho_0(z)] + \frac{k_B T}{2} \int \int dr_1 \, dr_2 \, \delta\rho_\Xi(r_1) \, C^{(2)}(r_1, r_2) \delta\rho_\Xi(r_2) + \cdots \quad (10)$$

where $C^{(2)}(r_1, r_2)$ is the equilibrium planar interface direct correlation function [1]. This strategy of expanding about a planar profile is of course not new. However the above analysis is novel because the density fluctuation $\delta\rho_\Xi(r)$ is itself determined by a minimization principle. To proceed we suppose that $\delta\rho_\Xi(r)$ may be expressed as a convolution:

$$\delta\rho_\Xi(r) = \int \Lambda(z; |y - y'|) \, \delta l(y') \, dy'. \quad (11)$$

The function $\Lambda(z; |y - y'|)$ will play a crucial role in the subsequent analysis. Physically, it describes the influence of a local fluctuation in the position of a surface of fixed magnetization on a distant point. Next we introduce further Fourier transforms

$$\tilde{C}^{(2)}(z_1, z_2; Q) \equiv \int dy_{12} \, e^{iQ \cdot y_{12}} C^{(2)}(r_1, r_2) \quad (12)$$

and

$$\tilde{\delta\rho}_\Xi(z_i; Q) \equiv \int dy_i \, e^{iQ \cdot y_i} \delta\rho_\Xi(r_i) \qquad i = 1, 2. \quad (13)$$

From (11) we see that

$$\tilde{\delta\rho}_\Xi(z_i; Q) = \tilde{\Lambda}(z_i; Q) \, \tilde{\delta l}(Q). \quad (14)$$

If we define the moments of a Fourier transform $\tilde{F}(z_1, \ldots; Q)$ by

$$\tilde{F}(z_1, \ldots; Q) = \tilde{F}_0(z_1, \ldots) + \tilde{F}_2(z_1, \ldots)Q^2 + \cdots \quad (15)$$

we can expand (11) about the point $y' = y$ to find

$$\delta\rho_{\Xi}(r) = \tilde{\Lambda}_0(z)\,\delta l(y) - \tilde{\Lambda}_2(z)\nabla^2 l(y) + \cdots. \qquad (16)$$

Thus, the zeroth and second moments of $\tilde{\Lambda}(z; Q)$ are related to the local translations and curvature of the collective coordinate $l(y)$ respectively. The crossing criterion (4) generates the boundary condition

$$\tilde{\Lambda}(z^X; Q) = -\rho_0'(z^X) + \mathcal{O}(\delta l(Q)) \qquad (17)$$

which adds to the bulk condition

$$\tilde{\Lambda}(\pm\infty; Q) = 0. \qquad (18)$$

From these considerations we conclude that to order $\nabla^2 l(y)$ the fluctuation $\delta\rho_{\Xi}(r)$ corresponds to a rigid shift of the equilibrium interface, i.e.

$$\rho_{\Xi}(r) = \rho_0(z - \delta l(y)) + \mathcal{O}(\nabla^2 l(y), \delta l(y)) \qquad (19)$$

and so $\tilde{\Lambda}_0(z) = -\rho_0'(z)$. When calculating the rigidity κ, however, it is essential that the full solution (16) is used. Substituting equations (12), (13), (14) and (15) into (10) and making use of the Yvon equation

$$\int \mathrm{d}z_2\, \rho_0'(z_2)\tilde{C}_0(z_1, z_2) = -V'(z_1) \qquad (20)$$

we find, in the limit $g \to 0^+$,

$$\gamma = k_{\mathrm{B}}T \int\int \mathrm{d}z_1\,\mathrm{d}z_2\, \rho_0'(z_1)\tilde{C}_2(z_1, z_2)\rho_0'(z_2) \qquad (21)$$

and

$$\kappa(\rho^X) = k_{\mathrm{B}}T \int\int \mathrm{d}z_1\,\mathrm{d}z_2\, [\rho_0'(z_1)\tilde{C}_4(z_1, z_2)\rho_0'(z_2) \\ -2\rho_0'(z_1)\tilde{C}_2(z_1, z_2)\tilde{\Lambda}_2(z_2) + \tilde{\Lambda}_2(z_1)\tilde{C}_0(z_1, z_2)\tilde{\Lambda}_2(z_2)]. \qquad (22)$$

Equation (21) is the usual Triezenberg–Zwanzig result for the surface tension, while (22) is a formal equation for the rigidity of the surface of fixed density ρ^X and may be regarded as the main result of the paper. At this point we make the following remarks.

(a) The direct correlation function $\tilde{C}(z_1, z_2; Q)$ and equilibrium profile $\rho_0(z)$ are independent of the choice of ρ^X, so the surface tension γ is *unique*.

(b) The rigidity κ depends on the function $\tilde{\Lambda}_2(z)$. From the boundary condition (17) we have $\tilde{\Lambda}_2(z^X) = 0$, so different choices of ρ^X will result in different locations for the zeros of this function. Consequently the rigidity κ must be regarded as being specific to the surface of fixed density ρ^X. This observation should not be regarded as being a defect of the present formalism. We shall argue that the dependence of κ on the choice of ρ^X is related to the detailed structure of the density–density correlation function $G(r_1, r_2)$.

(c) In some previous fluctuation theories of the rigidity [5] a minimization principle has not been used to define $\rho_{\Xi}(r)$. Consequently the form of the fluctuation $\delta\rho_{\Xi}(r)$ has not been rigorously defined and has been assumed to be the rigid shift (19) neglecting terms of order $\nabla^2 l(y)$. The resulting expression for κ is of the form (22) but with $\tilde{\Lambda}_2(z)$ set to zero. Within the present theory such an *ansatz* for $\delta\rho_{\Xi}(r)$ generates a unique (independent of ρ^X) upper bound on κ

$$\kappa \leqslant k_{\mathrm{B}}T \int\int \mathrm{d}z_1\,\mathrm{d}z_2\, \rho_0'(z_1)\tilde{C}_4(z_1, z_2)\rho_0'(z_2). \qquad (23)$$

The next step in our argument is to show that the expressions (21) and (22) are precisely those that need to be adopted when one uses the method of FJ to construct the effective interfacial Hamiltonian $H_I[l(y)]$ for an asymptotically free interface. For this purpose we shall follow the notation of FJ and use a spin density $m(r)$ as our microscopic order parameter. First FJ carefully define $l(y)$ via, say, a crossing criterion (see equation (4)) then define $H_I[l(y)]$ via a partial trace over configurations $m(r)$ in the space Γ (which, recall, respect the crossing criterion):

$$e^{-H_I[l(y)]/k_B T} = \int_{m(r)\in\Gamma} \mathcal{D}m(r)\, e^{-H[m(r)]/k_B T} \tag{24}$$

where $H[m(r)]$ is the underlying continuum microscopic Hamiltonian. FJ make the (systematic) assumption that the trace may be evaluated using a saddle-point approximation because the fluctuations in $m_\chi(r) \in \Gamma$ are controlled by a small bulk correlation length ξ_b. Hence they first calculate the profile $m_\Xi(r) \in \Gamma$ such that

$$H[m_\Xi(r)] < H[m_\chi(r)] \qquad m_\Xi \neq m_\chi \tag{25}$$

and identify

$$H_I[l(y)] = H[m_\Xi(r)]. \tag{26}$$

Equations (25) and (26) are clearly analogous to equations (5) and (6) in our DF theory. It should be noted however that the minimization condition is exact in the DF formalism whilst it arises from a saddle-point approximation in the FJ theory. From the above it follows that when adopting the FJ method for calculating the effective Hamiltonian for a free interface to order Q^4

$$H_I[l(y)] = \frac{1}{2(2\pi)^{d-1}} \int \mathrm{d}Q\, (\gamma_I Q^2 + \kappa_I Q^4)|\tilde{\delta l}(Q)|^2 \tag{27}$$

the tension and rigidity parameters γ_I and κ_I must be evaluated using the expressions (21) and (22) using the Hamiltonian functional $H[m(r)]$ as a microscopic grand potential density function.

To illustrate our analysis we calculate a rigidity κ_I appropriate to the Landau–Ginzburg–Wilson (LGW) Hamiltonian defined by

$$H_{\text{LGW}}[m(r)] = \int \mathrm{d}r \left(\frac{(\nabla m)^2}{2} + \Phi(m) \right) \tag{28}$$

where $\Phi(m)$ is an appropriate double-well potential function which we assume has the Ising symmetry $\Phi(m) = \Phi(-m)$. Because we are considering the properties of an asymptotically free interface there is no need to introduce a surface term and the boundary conditions used in minimizing (28) are $m(r) \to \pm m_{\text{bulk}}$ for $z \to \pm\infty$. In our calculation we have initially chosen $m^X = 0$ and set $z^X = 0$. Using methods directly related to the calculation of correlation functions in mean-field DF theories [6] we find for the moments of $\tilde{\Lambda}(z; Q)$

$$\tilde{\Lambda}_0(z) = -m'(z) \tag{29}$$

$$\tilde{\Lambda}_2(z) = m'(z) \int_0^{|z|} \mathrm{d}z'\, m'(z')^{-2} \int_{z'}^{\infty} \mathrm{d}z''\, m'(z'')^2 \tag{30}$$

where the derivative of the 'intrinsic' profile satisfies the usual Euler–Lagrange equation

$$\frac{(m'(z))^2}{2} = \Phi(m) - \Phi(m_{\text{bulk}}). \tag{31}$$

For large values of $|z|$ analysis shows that $\tilde{\Lambda}_2(z)$ has the asymptotic behaviour

$$\tilde{\Lambda}_2(z) \sim m'(z)\frac{|z|\xi_b}{2} \quad - \quad \frac{|z|}{\xi_b} \gg 1. \tag{32}$$

This result has important consequences for the local perturbation $\delta m_\Xi(r)$ given by (16). Suppose that $l(y)$ contains a dominant contribution in its Fourier transform at wavevector q. Then we may write $\nabla^2 l(y) \sim q^2 \, \delta l(y)$ from which it follows that the fluctuation $\delta m_\Xi(r)$ is characterized by two different spacial regimes:

(i) if $\xi_b|z| \ll 1/q^2$ the fluctuation is dominated by the 'rigid' shift (19) related to the local translation of the interface— in this region the surface tension largely determines the associated change in (free) energy due to a distortion;

(ii) if $\xi_b|z| \gg 1/q^2$ the fluctuation is dominated by the local curvature of the collective coordinate— in this regime the rigidity of the surface of fixed magnetization m^X $(= 0)$ must be taken into account.

Whilst the solution for $\tilde{\Lambda}_2(z)$ clearly indicates the presence of these two regimes it is not particularly illuminating as regards the function $\Lambda(z; |y - y'|)$. To this end we envoke a simple double-parabola model $\Phi(m) = \xi_b^{-2}(m \pm m_{\text{bulk}})^2$ for the regimes $m < 0$ and $m > 0$ respectively. In this approximation it is possible to solve for $\tilde{\Lambda}(z; Q)$ and invert the function to obtain

$$\delta m_\Xi(r) = -m'(z) \int dy' \frac{\partial}{\partial z} G_b(r) \, \delta l(y') \Big/ \int dy' \frac{\partial}{\partial z} G_b(r) \qquad d = 3 \tag{33}$$

where $G_b(r) \propto e^{-r/\xi_b}/r$ is the (three-dimensional) mean-field bulk correlation function. Here the displacement $r = \sqrt{(z^2 + (y - y')^2)}$. We believe that equation (33) is asymptotically correct for distances $|z|/\xi_b \gg 1$ within the full LGW model (i.e. beyond the double parabola) since it correctly identifies $\tilde{\Lambda}_0(z)$ and $\tilde{\Lambda}_2(z)$ at these length scales. Moreover, we suspect that the relationship between $\delta m_\Xi(r)$ and the bulk correlation function $G_b(r)$ is true beyond the LGW Hamiltonian and is generic to model DF theories at least for systems with short-ranged forces. Hence we believe that the approximation (32) may be used beyond the present LGW theory.

From the explicit results (29) and (30) it is straightforward to calculate the rigidity. For the LGW Hamiltonian the expression for $\kappa_1(0)$ corresponding to the rigidity of the surface of fixed magnetization $m^X = 0$ is

$$\kappa_1(0) = -2k_B T \int_0^\infty dz \, m'(z)^2 \int_0^z dz' \, m'(z')^{-2} \int_{z'}^\infty dz'' \, m'(z'')^2 \tag{34}$$

where, recall, we have set $z^X = 0$. We note that the expression for κ is negative as is required by the inequality (23). Recall that within square-gradient theory $\tilde{C}_4(z_1, z_2) = 0$, so the rigidity vanishes unless proper care is taken of the minimization principle (see the remarks preceding equation (23) above). This is consistent with previous work which in effect has $\tilde{\Lambda}_2(z) = 0$ [5]. The temperature dependence of $\kappa_1(0)$ can be easily calculated from (34). As $t \equiv (T_c - T)/T_c \to 0$ we find $\kappa_1(0) \sim t^{\tilde{\mu}-2\nu}$ where $\tilde{\mu}$ and ν are the surface tension and correlation length critical exponents respectively. This result suggests that the intrinsic rigidity obeys the intriguing hyperscaling relation $\kappa_1(0) \sim t^{(d-3)\nu}$ for $d < 4$.

It is possible to calculate $\kappa_1(m^X)$ within the LGW model for arbitrary m^X. We omit the details and simply quote the result for the case $m^X > 0$:

$$\kappa_1(m^X) = \kappa_1(0) - \gamma \int_0^{|z^X|} dz \, m'(z)^{-2} \int_z^\infty dz' \, m'(z')^2 \tag{35}$$

where z^X satisfies $m(z^X) = m^X$ and $\kappa_1(m^X) = \kappa_1(-m^X)$. For large values of $|z^X|$ we find $\kappa_1(m^X) \sim \kappa_1(0) - \gamma |z^X| \xi_b/2$, so the density dependence of the rigidity is pronounced. This result is rather important as we show below. Furthermore, it follows from equation (35) that the rigidity is maximal for the *normal* choice of collective coordinate corresponding to the surface at $z^X = 0$.

To complete our analysis we show that the predicted m^X-dependence of κ is required in order that we fully describe the singular behaviour of density–density correlations at a liquid–vapour interface. From (34) and (35) it is clear that the FJ method of systematically integrating out degrees of freedom generates a continuous set of Hamiltonians $\{H_I[l(y); m^X]\}$ each of which describes a surface of fixed magnetization m^X. This observation has already been made for the case of wetting transitions [7] where the Hamiltonians $H_I[l(y); m^X]$ have position- ($l(y)$-) dependent parameters [4]. For the case of the free interface there is no position dependence of γ and $\kappa(m^X)$ (because there is no wall) but the set of Hamiltonians is still important. To see this we follow the method introduced in [7] and calculate the mean-field spin–spin correlation function $G(r_1, r_2)$ for the free interface from the set of Hamiltonians. Each of the Hamiltonians $H_I[l(y); m^X]$ can be used to calculate expectation values denoted $\langle \cdot \rangle_{m^X}$. In particular the connected spin–spin correlation function is given by

$$G(r_1, r_2; m^X) = \langle \delta m_{\mathrm{E}}(r_1)\, \delta m_{\mathrm{E}}(r_2) \rangle_{m^X} \tag{36}$$

for each Hamiltonian. From (11) and (16) we see that the relationship between δm_{E} and $\delta l(y)$ is, in general, rather complicated. Consequently the set of all generated correlation functions $\{G(r_1, r_2; m^X)\}$ is difficult to calculate. Following Parry [7], however, we make the *ansatz* that the mean-field (MF) correlation function $G^{\mathrm{MF}}(r, r')$ for $z = z'$ corresponds to the the value of G in the set of all correlation functions $\{G\}$ for which $m^X = m(z)$ with $r = (z, y)$. For the choice of m^X at this particular position the relationship between δm_{E} and $\delta l(y)$ is simple (see (17)). Hence it is easy to calculate

$$G^{\mathrm{MF}}(r, r') \equiv G(r, r'; m(z)) \qquad \text{for } z = z'. \tag{37}$$

The result is most elegantly written in Fourier space:

$$\tilde{G}(z_1, z_2; Q) = \int G(r_1, r_2) e^{iQ \cdot y_{12}}\, dy_{12} \tag{38}$$

and yields the prediction

$$\tilde{G}^{\mathrm{MF}}(z, z; Q) = \frac{k_{\mathrm{B}} T m'(z)^2}{\gamma Q^2} - \frac{k_{\mathrm{B}} T m'(z)^2 \kappa(m(z))}{\gamma^2} + \mathcal{O}(Q^2) \tag{39}$$

where $\kappa(m(z))$ is given by (35). A full discussion of this method will appear in a future paper [8]. Equation (39) is a prediction for the MF form of G from the set of interfacial Hamiltonians using the identification (37). To check this we have calculated the MF correlation function $\tilde{G}^{\mathrm{MF}}(z, z; Q)$ by explicitly solving the appropriate Ornstein–Zernike equation, and find that the result (39) with the identification (35) is indeed the analytic solution. Consequently unless the rigidity is allowed to have the predicted density/magnetization dependence the correct position dependence of the MF correlation function will not be generated. It is important to note that the derivation of the correct MF correlation function is required for true thermodynamic consistency. To see this recall that the MF limit corresponds to the saddle-point approximation to the partition function, so the FJ identification (26) (for every possible m^X) should be capable of exactly reproducing MF theory expressions for correlation functions. This has been shown to be the case using the identification (37).

Acknowledgments

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