

Local Mean Field Models of Uniform to Nonuniform Density Fluid–Crystal Transitions[†]Paolo Buttà[‡] and Joel L. Lebowitz^{*,§}

Dipartimento di Matematica, Università di Roma “La Sapienza”, P.le Aldo Moro 2, 00185 Roma, Italy, and Departments of Mathematics and Physics, Rutgers, the State University of New Jersey, 110 Frelinghuysen Road, Piscataway, New Jersey 08854-8019.

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We investigate the existence of nontranslation invariant (periodic) density profiles, for systems interacting via translation invariant long-range potentials, as minimizers of local mean field free energy functionals. The existence of a second-order transition from a uniform to a nonuniform density at a specified temperature β_0^{-1} is proven for a class of model systems.

1. Introduction

Equilibrium systems at low temperatures and high densities are commonly observed in the form of periodic solids. There is, however, no proof at the present time of the existence of crystalline (periodic) states of matter for particles (atoms) in \mathbb{R}^d , $d > 1$, interacting via translation invariant potentials at any nonzero temperature or nonclose packing density.^{1–3} This implies, ipso facto, that there are no solvable continuum model systems having a fluid–solid transition. Surprisingly, this is true even at the level of local mean field (LMF) theory, the version of mean field theory that includes spatial variation of the density.⁴ Systems whose macroscopic equilibrium properties are described by LMF theory can be derived rigorously from microscopic systems interacting with translation invariant Kac potentials in the limit when the range of the potential goes to infinity.^{4,5} Such systems can be readily proven to exhibit liquid–vapor and mixing–unmixing transitions.^{5,6} One can even go further and prove the existence of such transitions for long but finite ranges of the potential, i.e., without letting the range of the potential become infinite.^{7–9}

The interaction potentials in the LMF theory responsible for these liquid–vapor transitions are, as expected, predominantly attractive.^{5,10,11} In contrast, the interactions responsible for fluid–crystalline-type transition are expected to be predominantly repulsive; for example, hard spheres^{1,3} and one-component plasmas (positively charged particles in a uniform neutralizing negatively charged background) are examples of microscopic models expected to be crystals at high densities and/or low temperatures.^{12–14} It is therefore natural to try proving crystallization in LMF theories for systems with primarily repulsive potentials. There have, in fact, been some partially successful attempts to do this.^{15–17}

Here, we first give a brief review of what is known mathematically about the solution of relevant LMF variational problems and then present some new results. These establish the existence of a second-order transition from a spatially uniform to a spatially nonuniform (presumably periodic) state at a specified critical temperature for a one-component system described by a LMF free energy functional.

The outline of the rest of the paper is as follows. In section 2, we describe the LMF Helmholtz free energy functional $G(n)$, depending on the temperature β^{-1} and on the density profile $n(x)$, with x a vector in d dimensions. The equilibrium density is the one that minimizes $G(n)$ for a given average density ρ . In section 3, we show that for small β and ρ the minimizing density is the uniform one. In section 4, we show, following Gates,¹⁵ that for some models there is, at large β and ρ , a periodic profile that has a lower free energy than that of the uniform one.

Unfortunately, this does not prove that the periodic state has the lowest free energy, nor does it say at what temperature and density the uniform state stops being the free energy minimizer and whether the transition is first- or second-order. The latter question is settled in section 5 for a class of models; we prove the existence of a second-order phase transition from the uniform to the nonuniform (presumably periodic) density profile at a specified critical β_0 .

In section 6, we discuss the Euler–Lagrange equations associated to the minimization problem. These are in general nonlinear integral–differential equations that correspond, in some cases, to the well-known Kirkwood–Monroe equation for the fluid–solid transition. In section 7, we present a toy model for which the explicit solution of the Euler–Lagrange equation is periodic at high densities. Finally, in section 8, we discuss the LMF models studied here in the general context of the density-functional theories of freezing. A rigorous proof of crystallization for realistic interactions remains an open problem.

2. Formulation of the Problem

Let $\rho_c > 0$ be the close packing density for systems with hard cores. Let $a_0(\rho)$ be a strictly convex smooth function of ρ , $0 < \rho < \rho_c$. Denote by $\mathcal{A}(\rho)$, $\rho > 0$, the class of functions $n(x)$, $x \in \mathbb{R}^d$, such that $0 \leq n(x) \leq \rho_c$, $n(x)$ can be constant, $n(x) = \rho$, or periodic with spatial average

$$\frac{1}{|\Gamma|} \int_{\Gamma} dx n(x) = \rho \quad (1)$$

where Γ is (any multiple of) the unit cell of periodicity of n ; see also eqs 4–6 below.

We are interested in the equilibrium Helmholtz free energy $a(\rho)$, given by the minimization over all permissible density

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* Author to whom correspondence should be addressed. E-mail: lebowitz@math.rutgers.edu.

[‡] Università di Roma “La Sapienza”.

[§] Rutgers, the State University of New Jersey.

profiles

$$a(\rho) = \inf_{n \in \mathcal{G}(\rho)} G(n) \quad (2)$$

where

$$G(n) = \frac{1}{|\Gamma|} \int_{\Gamma} dx \left[a_0(n(x)) + \frac{1}{2} n(x) \int dy J(x-y)n(y) \right] \quad (3)$$

is the LMF free energy for a specified $n(x)$ and the integration with respect to y is over all space. We take the function $J(x)$, $x \in \mathbb{R}^d$, to be nonnegative, with $J(x) = J(-x)$, and rapidly decreasing. $G(n)$ is the LMF free energy density for a system with some (short-range) interactions and also long-range pair interactions of the Kac type $\gamma^d J(\gamma r)$, in the limit $\gamma \rightarrow 0$.^{4,5} The function $a_0(\rho)$ is the Helmholtz free energy of the reference system having only short-range interaction.

Simple examples of the kind of $a_0(\rho)$ that we will consider are

$$a_0(\rho) = \beta^{-1} \rho (\log \rho - 1) \quad (i)$$

$$a_0(\rho) = \beta^{-1} [\rho \log \rho + (1 - \rho) \log(1 - \rho)], \text{ so that } \rho_c = 1 \quad (ii)$$

where $\beta > 0$ is the inverse temperature of the system. We have suppressed the dependence of a_0 on β , which in general will be more complicated than that given in eqs i and ii, but we will always assume that $a_0(\rho)$ has no first-order phase transitions.

It is proven⁴ (at least in cases with $\rho_c < \infty$) that the infimum of $a(\rho)$ in eq 2 is also given by

$$a(\rho) = \lim_{|D| \rightarrow \infty} \inf_{n \in \mathcal{G}^{(D)}(\rho)} G(n, D) \quad (4)$$

where $\{D\}$ is an increasing sequence of cubes and $\mathcal{G}^{(D)}(\rho)$ is the class of measurable functions taking values in $(0, \rho_c)$ such that

$$\lim_{|D| \rightarrow \infty} \frac{1}{|D|} \int_D dx n(x) = \rho \quad (5)$$

and

$$G(n, D) \doteq \frac{1}{|D|} \int_D dx \left[a_0(n(x)) + \frac{1}{2} n(x) \int_D dy J(x-y)n(y) \right] \quad (6)$$

Conditions on J . We would like to prove that for some choice of a_0 and J the infimum in eq 2 is reached at some periodic nonconstant function $n^*(x)$ for large β and ρ . For this to be possible, a necessary condition on $J(x)$ is that its Fourier transform

$$\hat{J}(p) = \int dx e^{2\pi i p x} J(x) \quad (7)$$

has a strictly negative minimum \hat{J}_{\min} . To see this, let V_{Γ} be the reciprocal lattice of Γ ; we then have

$$\mathcal{A}(n) \doteq \frac{1}{|\Gamma|} \int_{\Gamma} dx n(x) \int dy J(x-y)n(y) = \sum_{p \in V_{\Gamma}} \hat{J}(p) |\hat{n}(p)|^2 \quad (8)$$

where

$$\hat{n}(p) \doteq \frac{1}{|\Gamma|} \int_{\Gamma} dx e^{2\pi i p x} n(x) \quad (9)$$

Then, if $\hat{J}(p) \geq 0$ for all p , $\mathcal{A}(n) \geq \hat{J}(0) |\hat{n}(0)|^2 = \hat{J}(0) \rho^2$ so that, using the convexity of a_0 ,^{5,15}

$$G(n) = \frac{1}{|\Gamma|} \int_{\Gamma} dx a_0(n(x)) + \frac{1}{2} \mathcal{A}(n) \geq a_0(\rho) + \frac{1}{2} \hat{J}(0) \rho^2 \quad (10)$$

On the contrary, by definition of $a(\rho)$, one has for all J

$$a(\rho) \leq a_0(\rho) + \frac{1}{2} \hat{J}(0) \rho^2 \quad (11)$$

Thus, for $\hat{J}(p) \geq 0$

$$a(\rho) = a_0(\rho) + \frac{1}{2} \hat{J}(0) \rho^2 \quad (12)$$

i.e., the absolute minimum is reached at the constant function $n(x) \equiv \rho$.¹⁵

Following Gates and Penrose¹⁸ and Gates,¹⁵ we now assume $\hat{J}_{\min} < 0$. By means of lower and upper bounds on the functional $G(n)$, one can show that for some choice of a_0 (and β) the constant solution is still the absolute minimum, while for other choices this is no longer true.

3. Lower Bounds on $a(\rho)$

The following lower bounds hold:

(1) For a_0 with $\rho_c < \infty$ ⁵

$$a(\rho) \geq \text{CE} \left\{ a_0(\rho) + \frac{1}{2} \hat{J}_{\min} \rho^2 \right\} + \frac{1}{2} (\hat{J}(0) - \hat{J}_{\min}) \rho^2 \quad (13)$$

(2) For any a_0 ¹⁵

$$a(\rho) \geq \text{CE} \left\{ \text{ME} \left\{ a_0(\rho) - \frac{1}{2} \hat{J}(0) \rho^2 \right\} + \hat{J}(0) \rho^2 \right\} \quad (14)$$

In eqs 13 and 14, $\text{CE}\{f\}$ denotes the convex envelope of the function f (Gibbs double tangent construction) while $\text{ME}\{f\}$ is the midpoint envelope of f , i.e.,

$$\text{ME}\{f\} \doteq \inf_{h \in D_{\rho}} \frac{f(\rho+h) + f(\rho-h)}{2} \quad (15)$$

where D_{ρ} is the set of values of h such that $\rho \pm h$ are in $(0, \rho_c)$.

A consequence of the above bounds is that eq 12 holds if

$$\frac{\partial^2 a_0}{\partial \rho^2}(\rho) \geq |\hat{J}_{\min}| \text{ for } 0 < \rho < \rho_c < \infty \quad (16)$$

For example, in the case where $a_0(\rho) = \beta^{-1} \rho (\log \rho - \log(1 - \rho/\rho_c) - 1)$, the free energy density (approximate for $d > 1$) of a hard sphere system,¹¹ the above condition becomes

$$\frac{1}{\beta \rho (1 - \rho/\rho_c)^2} \geq |\hat{J}_{\min}| \quad (17)$$

In particular, if $\beta \rho_c |\hat{J}_{\min}| \leq 2^{7/4}$, we get eq 12 for any $\rho \in [0, \rho_c)$.

For the case in eq i, the bounds show that eq 12 holds if

$$\beta \rho \leq \frac{1}{\hat{J}(0)} \quad (18)$$

Hence, in these cases, the uniform density gives the minimum free energy.

4. Upper Bounds on $a(\rho)$

To obtain an upper bound, we follow Gates.¹⁵ Let $a_0(\rho)$, $\rho \in [0, \rho_c)$, be given, and let p_0 be such that $\hat{J}(p_0) = \hat{J}_{\min}$. Consider

the function $\bar{n} \in \mathcal{C}(\rho)$ defined by

$$\bar{n}(y) = \rho + h \sin(2\pi p_0 y) \quad (19)$$

where $h > 0$ is chosen in such a way that $[\rho - h, \rho + h] \subset (0, \rho_c)$. By an explicit computation,¹⁸ one obtains

$$\mathcal{A}(\bar{n}) = \hat{J}(0)\rho^2 + \frac{1}{2}\hat{J}_{\min}h^2 \quad (20)$$

where \mathcal{A} was defined in eq 8. Using Taylor's theorem, we can bound, for any $\rho' \in [\rho - h, \rho + h]$,

$$a_0(\rho') \leq a_0(\rho) + \frac{\partial a_0}{\partial \rho}(\rho - \rho') + \frac{1}{2}\phi(\rho, h)(\rho - \rho')^2 \quad (21)$$

where

$$\phi(\rho, h) \doteq \max_{\xi \in [\rho - h, \rho + h]} \frac{\partial^2 a_0}{\partial \xi^2}(\xi)$$

Setting $\rho' = \bar{n}(x)$ in eq 21 and integrating, we get

$$\frac{1}{|\Gamma|} \int_{\Gamma} dx a_0(\bar{n}(x)) \leq a_0(\rho) + \frac{1}{4}\phi(\rho, h)h^2 \quad (22)$$

From eqs 20 and 22, recalling eqs 2 and 3, we finally obtain

$$a(\rho) \leq a_0(\rho) + \frac{1}{4}[\phi(\rho, h) + \hat{J}_{\min}]h^2 + \frac{1}{2}\hat{J}(0)\rho^2 \quad (23)$$

The last inequality shows that there are cases when for some values of the parameters of the constant function cannot be the minimizer of $G(n)$. In fact, assume that

$$\frac{\partial^2 a_0}{\partial \rho^2} < |\hat{J}_{\min}| \quad (24)$$

for ρ in some interval $[\rho_1, \rho_2]$. Then, for any $\rho \in (\rho_1, \rho_2)$, we have $\phi(\rho, h) < |\hat{J}_{\min}|$ for any h small enough. Thus, $a(\rho)$ is strictly less than the value it would have for $h = 0$ in eq 23, i.e.,

$$a(\rho) < a_0(\rho) + \frac{1}{2}\hat{J}(0)\rho^2, \quad \forall \rho \in (\rho_1, \rho_2) \quad (25)$$

When $a_0(\rho) = \beta^{-1}\rho(\log \rho - 1)$, eq 25 reads

$$a(\rho) < a_0(\rho) + \frac{1}{2}\hat{J}(0)\rho^2 \quad \forall \beta\rho > \frac{1}{|\hat{J}_{\min}|} \quad (26)$$

Comparing eqs 18 and 26, we have for this $a_0(\rho)$ a uniform density for $\beta\rho \leq \hat{J}(0)^{-1}$ and a nonuniform one (possibly periodic) for $\beta\rho > |\hat{J}_{\min}|^{-1} > \hat{J}(0)^{-1}$. The question then is at what density and in what form does the change occur? We answer this question for a particular class of $a_0(\rho)$ values in the next section.

5. On the Location of the Transition

Given a free energy $a_0(\rho)$, write $n_h(x) = \rho(1 + h\psi(x))$ with $\psi(x)$ a (nonidentically zero) periodic function with unit cell Γ such that $\int_{\Gamma} dx \psi(x) = 0$ and $\max_x |\psi(x)| = 1$. Choose h in an interval around zero such that $n_h(x) \in (0, \rho_c)$. We next introduce the notation

$$\langle f \rangle = \frac{1}{|\Gamma|} \int_{\Gamma} dx f(x) \quad (27)$$

Then

$$G(n_h) = G(\rho) + F(h) \quad F(h) \doteq g(h) - \frac{1}{2}b(\psi)h^2 \quad (28)$$

with

$$g(h) \doteq \langle a_0(n_h) \rangle - a_0(\rho) \quad (29)$$

and

$$b(\psi) \doteq -\frac{\rho^2}{|\Gamma|} \int_{\Gamma} dx \psi(x) \int dy J(x-y)\psi(y) \quad (30)$$

The stationary homogeneous solution $n_0(x) = \rho$ is a local minimizer whenever the second derivative of G with respect to h is positive at $h = 0$, i.e.,

$$F''(0) = g''(0) - b(\psi) = \rho^2 \langle \psi^2 \rangle \frac{\partial^2 a_0}{\partial \rho^2}(\rho) - b(\psi) \geq 0 \quad (31)$$

We next consider a particular class of $a_0(\rho)$ for which we prove that a second-order transition from uniform to nonuniform density occurs at a value of β where the uniform solution loses its linear stability.

Let $a_0(\rho)$ have the form of the free energy density of a lattice gas interacting with a two-body, nonpositive interaction. This system is isomorphic to the Ising model with ferromagnetic pair interactions with $\rho = (1 + m)/2$, m the magnetization.^{19,20} We assume the temperature large enough so that $a_0(\rho)$ is strictly convex²⁰ and set $\rho = 1/2$. We have in this case

$$g'''(h) = \langle \psi^3 f'''(h\psi) \rangle \quad (32)$$

where $f(m) = a_0((1 + m)/2)$, the free energy density of the ferromagnetic Ising system, is an even (strictly convex) function of $m \in (-1, 1)$.

Calling $H = H(m) = f'(m)$ the magnetic field associated to the magnetization m , we have

$$f'''(m) = H''(m) = -\frac{m''(H)}{m'(H)^3} \quad (33)$$

We now observe that it follows from the GHS inequality²¹ that $m''(H)$ has the opposite sign of H , while $m'(H)$ is positive and $m(H)$ has the same sign as H . From eq 33, we conclude that $f'''(h\psi(x))$ has the same sign as $\psi(x)$ for any $h \in (0, 1]$. By eq 32, this implies $g'''(h) > 0$ for any $h \in (0, 1]$. By Taylor expansion, recalling $F'(0) = 0$, $F''(0) \geq 0$, and $F'''(h) = g'''(h)$, we finally obtain

$$F'(1) \geq \int_0^1 dh (1-h)g'''(h) > 0 \quad (34)$$

This means that there are no stationary points of $G(n_h)$ other than the uniform density, corresponding to $h = 0$ for $\beta < \beta_0$, the value of β where the constant density becomes unstable, i.e., where eq 31 is violated. We then conclude that the transition cannot be of the first order, i.e., the new minimum is generated by the bifurcation of the constant solution at $\beta = \beta_0$. Note that $\beta_0 < \beta_c$, the inverse of the Ising model critical temperature for spontaneous magnetization when $(\partial^2 a_0 / \partial \rho^2)(\rho)$ becomes zero at $\rho = 1/2$.

In the absence of short-range interactions, case in eq ii where $a_0(\rho) = \beta^{-1}[\rho \log \rho + (1 - \rho)\log(1 - \rho)]$, we find, by an explicit computation

$$g'''(h) = \frac{2h}{\beta|\Gamma|} \int_{\Gamma} dx \frac{\psi(x)^4}{(1 - h^2\psi(x)^2)^2} \quad (35)$$

In this case, $\beta_c = \infty$, but β_0 is finite.

6. Euler–Lagrange Equations

Ignoring questions of rigor, the stationary points of the functional $G(n)$ under constraint 1 have to solve the following equation

$$\frac{\partial a_0}{\partial \rho}(n(x)) + \int dy J(x-y)n(y) = \mu \quad (36)$$

where the parameter $\mu \in \mathbb{R}$ is fixed by imposing condition 1 on the solution. In writing eq 36, we assumed that stationarity can occur only at turning points, which is true when $\partial a_0/\partial \rho = \pm \infty$ at the boundary of $(0, \rho_c)$. Observe that eq 36 is the Euler–Lagrange equation for the functional

$$\Omega(n, \mu) \doteq G(n) - \frac{1}{|\Gamma|} \int_{\Gamma} dx \mu n(x) \quad n \in \mathcal{R} \doteq \bigcup_{0 < \rho < \rho_c} \mathcal{G}(\rho) \quad (37)$$

The relation between the Euler–Lagrange equation (eq 36) and the minimization problem is partially known in the cases when $a_0(\rho)$ is defined on a finite interval $[0, \rho_c)$. It can be proven⁴ that if

$$p(\mu) \doteq \sup_{n \in \mathcal{R}} [-\Omega(n, \mu)] \quad (38)$$

then

$$a(\rho) = \max_{\mu} \{\mu\rho - p(\mu)\} \quad (39)$$

This means that if $n^*(x)$ solves $p(\mu) = -\Omega(n^*, \mu)$, then $a(\rho) = G(n^*)$ with $\rho = p'(\mu)$. Moreover, under the continuity condition on J

$$\int dy |J(y - y_1) - J(y - y_2)| \rightarrow 0 \text{ uniformly as } |y_1 - y_2| \rightarrow 0 \quad (40)$$

the following holds.¹⁵ Let \mathcal{R}_{Γ} be the set of functions in \mathcal{R} that have unit cell Γ . For any Γ , there exists $n^* \in \mathcal{R}_{\Gamma}$ that solves eq 36 and such that

$$-\Omega(n^*, \mu) = \sup_{n \in \mathcal{R}_{\Gamma}} [-\Omega(n, \mu)] \quad (41)$$

This means that, if there is a periodic absolute minimizer of $G(n)$, its period is not determined by the stationarity condition; there are solutions of eq 36 for any unit cell Γ . It is not even certain that the absolute minimizer is periodic; it may only be almost periodic.

Kirkwood–Monroe Equation. As already noted, in the case $a_0(\rho) = \beta^{-1}\rho(\log \rho - 1)$ we know that for some $\beta\rho$ in the range

$$\frac{1}{\hat{J}(0)} \leq \beta\rho \leq \frac{1}{|\hat{J}_{\min}|} \quad (42)$$

the constant density ρ ceases to be the minimizer of $G(n)$. In this case, the Euler–Lagrange equation corresponds to the well-known Kirkwood–Monroe equation²²

$$n(x) = \exp[\beta\mu - \beta \int dy J(x-y)n(y)] \quad (43)$$

Grewe and Klein¹⁶ have studied the bifurcation properties of the constant solution. From their analysis, the bifurcation point is located exactly at $\beta\rho = |\hat{J}_{\min}|^{-1}$. We point out however that for these values of the parameters the derivation of eq 43 from the variational problem is not proven (this is actually proven by Grewe and Klein for smaller values of the density ρ). The argument of Grewe and Klein¹⁶ can be sketched in the following way. Let p_0 be the value where the minimum of $\hat{J}(\rho)$ is reached, and denote by Γ_0 the cell of reciprocal lattice vector p_0 . Let \mathcal{H} be the Hilbert space of functions, which are periodic with unit cell Γ_0 and symmetric under reflection about the origin. In this space, the operator defined by the right-hand side of eq 43 is compact, and we can apply the bifurcation theorem of Krasnoselskii.^{16,23} Writing $n(x) = \rho(1 + \psi(x))$ with $\psi(x)$ having zero average, we get a bifurcation point in \mathcal{H} when the linear equation

$$\psi(x) + \beta\rho \int dy J(x-y)\psi(y) = 0 \quad (44)$$

has a nonzero solution in this Hilbert space. It can be seen that this happens exactly at $\beta\rho = |\hat{J}_{\min}|^{-1}$. At this point, the constant solution bifurcates, and from the argument of Gates given before, one could verify that the lowest values of the free energy functional $G(n)$ correspond to the nonconstant branches.

7. Solutions for the Linear Case: An Example

Consider the (nonphysical) case when $a_0(\rho) = 1/2 \beta^{-1}\rho^2$ so that the Euler–Lagrange equation becomes linear. Since $\partial a_0/\partial \rho(0^+) = 0$ and $\partial^2 a_0/\partial \rho^2(0^+) = \beta^{-1}$, it is possible to have stationary points that assume the value 0 somewhere (for some choices of J and β). In fact, this is what happens in the following $d = 1$ example due to Penrose. Let

$$J(x) = J(|x|) = \begin{cases} 1 & \text{if } 1 < |x| < 2 \\ 0 & \text{otherwise} \end{cases} \quad (45)$$

The Euler–Lagrange equations then take the form

$$\beta^{-1}n(x) + \int dy J(x-y)n(y) \begin{cases} = \lambda & \text{if } n(x) > 0 \\ \geq \lambda & \text{if } n(x) = 0 \end{cases} \quad (46)$$

We exhibit a periodic solution of period 3, which is zero in some intervals. By differentiating eq 46, we get, for $n(x) > 0$,

$$\beta^{-1}n'(x) + \int dy J'(x-y)n(y) = 0 \quad (47)$$

But $J'(x) = \delta(x-1) - \delta(x-2) - \delta(x+1) + \delta(x+2)$ so that, if we look for a solution of period 3, eq 47 gives

$$\beta^{-1}n'(x) + 2n(x-1) - 2n(x+1) = 0 \quad (48)$$

We require $n(x) = 0$ for $1/2 + \epsilon < |x| \leq 3/2$, then eq 48 implies that $n'(x) = 0$ (i.e., $n(x) = \beta\lambda$) for $|x| < 1/2 - \epsilon$. We have to determine $n(x)$ for $1/2 - \epsilon \leq |x| \leq 1/2 + \epsilon$. Since $n(x) = 0$ for $1/2 + \epsilon < |x| \leq 3/2$, from eq 48

$$\begin{cases} \beta^{-1}n'(x) + 2n(x-1) = 0 & \text{if } \frac{1}{2} - \epsilon \leq x \leq \frac{1}{2} + \epsilon, \\ \beta^{-1}n'(x) + 2n(x+1) = 0 & \text{if } -\frac{1}{2} - \epsilon \leq x \leq -\frac{1}{2} + \epsilon \end{cases} \quad (49)$$

that is

$$\beta^{-2}n''(x) + 4n(x) = 0 \text{ for } 1/2 - \epsilon \leq |x| \leq 1/2 + \epsilon$$

and then $n(x) = A \cos(2\beta x) + B \sin(2\beta x)$ for any $1/2 - \epsilon \leq |x| \leq 1/2 + \epsilon$. We fix the constants A and B by imposing that $n'(\pm$

$(1/2 - \epsilon) = 0$ and $n(\pm(1/2 + \epsilon)) = 0$. This requires $\epsilon = \pi/8\beta$ (thus β has to be greater than $\pi/4$); hence

$$n^*(x) = \begin{cases} \beta\lambda & \text{if } |x| < \frac{1}{2} - \frac{\pi}{8\beta}, \\ \beta\lambda\cos(2\beta|x| - \beta + \pi/4) & \text{if } \frac{1}{2} - \frac{\pi}{8\beta} \leq |x| \leq \frac{1}{2} + \frac{\pi}{8\beta} \\ 0 & \text{if } \frac{1}{2} + \frac{\pi}{8\beta} < |x| \leq \frac{3}{2} \end{cases} \quad (50)$$

Clearly, when $n^*(x) = 0$, also the inequality in eq 46 is satisfied. The parameter λ is determined by fixing the average density ρ , i.e., $\frac{1}{3} \int_{-3/2}^{3/2} dx n^*(x) = \rho$, getting $\lambda = 3\rho(1 + \beta - \pi/4)^{-1}$.

We now easily compute

$$G(n^*) = \frac{\lambda^2}{6} \left(1 + \beta - \frac{\pi}{4}\right) = \frac{3}{2\left(1 + \beta - \frac{\pi}{4}\right)} \rho^2 \quad (51)$$

while for uniform density ρ

$$G(\rho) = \left(1 + \frac{1}{2\beta}\right) \rho^2 \quad (52)$$

Thus, $G(n^*) < G(\rho)$ for $\beta \geq \pi/4$, i.e., as long as $n^*(x)$ is defined.

On the contrary, the uniform solution to eq 47 bifurcates at $\beta_0 = |\hat{J}_{\min}|^{-1} \approx 0.60$, $\hat{J}_{\min} \approx -1.66$ being the minimum of

$$\hat{J}(p) = \int_{1 < |x| < 2} dx e^{2\pi i p x} = \frac{\sin(4\pi p)}{\pi p} - \frac{\sin(2\pi p)}{\pi p}$$

Moreover, for any periodic profile n

$$G(n) = \frac{1}{2} \sum_{p \in V_{\Gamma}} \left(\frac{1}{\beta} + \hat{J}(p)\right) |\hat{n}(p)|^2$$

so that the phase transition that actually occurs at β_0 (for $\beta \leq \beta_0$ the uniform density is the absolute minimum).

The solution $n^*(x)$ is thus not defined up to β_0 , but only for $\beta \geq \pi/4 > \beta_0$. Since $G(n^*) \rightarrow 0$ as $\beta \rightarrow +\infty$, $n^*(x)$ could be the absolute minimizer of G for β large enough. Actually, it might be the absolute minimizer even for any $\beta \geq \pi/4$. For example, if $\bar{n}(x) \doteq \rho[1 + \sin(2\pi p_0 x)]$ with p_0 the minimizer of \hat{J} , i.e., $\hat{J}(p_0) = \hat{J}_{\min}$, then

$$G(\bar{n}) = \left(\frac{3}{4\beta} + 1 + \frac{\hat{J}_{\min}}{4}\right) \rho^2$$

and it can be easily checked that $G(\bar{n}) > G(n^*)$ for any $\beta \geq \pi/4$.

8. Connection to Density-Functional Theory

There is a direct connection between the LMF models treated here and the usual density-functional (DF) approach to the theory of freezing.^{24–28} The starting point of DF theory is a functional $\Omega(n)$, depending on the one-particle density $n(r)$, at a given temperature β^{-1} and chemical potential μ , defined by

$$\Omega(n) = F(n) - \mu \int dx n(x)$$

where $F(n)$ is the Helmholtz free energy of an equilibrium system with density profile $n(x)$. When evaluated at the equilibrium density $n_0(x)$, $\Omega(\cdot)$ equals the grand canonical equilibrium potential $-PV$.

The inclusion or exclusion of the term $-\mu \int dx n(x)$ to $F(n)$ represents the usual difference between working in the canonical ensemble with a fixed total average density as defined in eq 1 or in the grand canonical ensemble with a fixed chemical potential. They are equivalent for macroscopic systems, and their variation leads to the same Euler–Lagrange equations, as those in section 6. Of course for specific calculations, especially those involving approximations, one formalism may be preferable to another.²⁸

Splitting $F(n)$ into an ideal and excess (i.e., interaction) parts one gets

$$F(n) = F^{\text{id}}(n) + F^{\text{ex}}(n) = \beta^{-1} \int dx n(x) [\log n(x) - 1] + F^{\text{ex}}(n) \quad (53)$$

Setting the functional derivative of $\Omega(n)$ equal to zero at $n(r) = n_0(r)$, we get the Euler–Lagrange equation

$$\mu = \frac{\delta F(n)}{\delta n(x)} \Big|_{n=n_0}$$

or

$$n_0(x) = e^{\beta\mu} \exp[c_0(r)] \quad (54)$$

where

$$c_0(r) = -\beta \frac{\delta F^{\text{ex}}(n)}{\delta n(x)} \Big|_{n=n_0} \quad (55)$$

is the one-particle direct correlation function²⁴ evaluated at $n(x) = n_0(x)$.

To proceed, $F(n)$ is approximated by means of known structure or thermodynamic quantities of a corresponding uniform system. Thus, the DF theory of Ramakrishnan and Yussouff,²⁵ usually adopted in the reformulated form of Haymet and Oxtoby,²⁶ is based on the original idea of Kirkwood and Monroe,¹⁷ in which the properties of a crystalline system are calculated by perturbing about the coexisting liquid phase. Denoting by c_L the constant one-particle direct correlation function in the coexisting fluid phase at density ρ_L , eq 54 becomes

$$\rho_L = e^{\beta\mu} \exp[c_L] \quad (56)$$

so that, taking the ratio of eqs 54 and 56, we obtain

$$n_0(x) = \rho_L \exp[c_0(x) - c_L] \quad (57)$$

Expanding the difference $c_0(r) - c_L$ and keeping only terms up to the first order in $n_0(r) - \rho_L$, we get the approximate equation²⁴

$$n_0(x) = \rho_L \exp \int dy C(x-y) [n_0(y) - \rho_L] \quad (58)$$

where $C(x-y)$ is the Ornstein–Zernike direct correlation function, whose Fourier transform is related to the structure factor $S(k)$ of the liquid by the relation $\rho_L \hat{C}(k) = 1 - 1/S(k)$.

The approximate eq 58 can have, for ρ_L larger than some threshold density ρ_L^* , also a nonuniform solution $n_0(x) = n_S(x)$. This solution, representing a solid phase when $\Omega(n_S) \leq \Omega(\rho_L)$, is found (theoretically and/or numerically) by assuming some crystalline structure, with the hope that the simplest lattice that gives the lowest free energy will be the stable one. The validity of the approximation (eq 58) is hard to evaluate a priori, but the results are reasonable even if not very accurate. Improve-

ments based on using weighted densities in $F(n)$ are more accurate²⁸ but also involve uncontrolled approximations.

The LMF discussed in this paper corresponds to the case where the interaction between the particles can be meaningfully split into a short-range part and a long-range part.⁵ In that case, $F^{\text{ex}}(n)$ also splits into a short-range part and a weak long-range part. The short-range part then gives rise to a local free energy density that, when added to $F^{\text{id}}(n)$, is just what we called $a_0(n)$ while the long-range part gives rise to the quadratic term in $G(n)$, the free energy finite volume defined in eq 3. This separation becomes exact in the Kac limit,⁵ when the long-range part of the interaction is of the form $\gamma^d J(\gamma x)$ with $\gamma \rightarrow 0$. $G(n)$ then involves a rescaling of space by γ , which accounts for the locality of the short-range contribution. When there are no short-range interaction then $a_0(n) = F^{\text{id}}(n)$, as in the example in eq 1 in section 2.

In any case, forgetting about the derivation, the Euler–Lagrange equation (eq 36) obtained from the minimization of $G(n)$ coincides with those given in eqs 54 and 55 when we set $F^{\text{ex}}(n) = G(n) - F^{\text{id}}(n)$, with $G(n)$ taking the form of eq 6. We can therefore think of our results about spontaneous symmetry breaking as applying directly to the DF theory with this kind of an $F^{\text{ex}}(n)$. We hope that our methods will be developed further to apply to more realistic interactions between the atoms, such as those being currently treated approximately by DF theories.

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