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Fundamental measure theory for lattice fluids with hard-core interactions

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Abstract

We present the extension of Rosenfeld's fundamental measure theory to lattice models by constructing a density functional for d -dimensional mixtures of parallel hard hypercubes on a simple hypercubic lattice. The one-dimensional case is exactly solvable and two cases must be distinguished: all the species with the same length parity (additive mixture), and arbitrary length parity (nonadditive mixture). To the best of our knowledge, this is the first time that the latter case has been considered. Based on the one-dimensional exact functional form, we propose the extension to higher dimensions by generalizing the zero-dimensional cavity method to lattice models. This assures the functional will have correct dimensional crossovers to any lower dimension, including the exact zero-dimensional limit. Some applications of the functional to particular systems are also shown.

1. Introduction

The spirit that has traditionally guided the construction of approximate density functionals has been to collect as much information as possible about the fluid and cook up a functional out of it under reasonable simple assumptions. This is the idea behind widely used approximations such as the weighted density or the effective liquid approximations, which produce a functional from the Helmholtz free energy and direct correlation function of the fluid (see Evans (1992) for a review), or even more recent approaches (Zhou 2001a, 2001b) which in addition incorporate the pair correlation function. As an alternative to this there stands Rosenfeld's fundamental measure (FM) theory, whose aim is to construct the density functional upon geometrical grounds, and to obtain as output all the ingredients that classical approaches need as input. Since Rosenfeld's pioneering work for hard spheres (Rosenfeld 1989), later extended approximately to nonspherical objects (Rosenfeld 1994), this theory has developed far from its roots, giving rise to functionals for hard spheres that reproduce extraordinarily well the structure of the crystal

phase (Tarazona 2000), functionals for the fluid mixture of parallel hard cubes (Cuesta and Martínez-Ratón 1997a, 1997b) which have been applied to study entropic demixing (Martínez-Ratón and Cuesta 1998, 1999) and even functionals for soft interactions (Schmidt 1999) as well as for nonadditive mixtures (Schmidt 2000a, 2000b).

Rosenfeld's original approach (Rosenfeld 1989), applied to hard spheres, consisted of three steps:

- (i) decomposing the Mayer function into a sum of convolutions of one-particle measures;
- (ii) using these measures to define a set of weighted densities and assuming that the density functional depends on the density profile only through them and
- (iii) determining the functional form by resorting to scaled-particle theory.

The functional so obtained had an interesting functional structure and worked well when applied to problems such as the adsorption profiles at hard walls. However it dramatically failed the test of freezing because of some built-in singularities, which could be repaired by imposing exact dimensional reduction of the functional to *zero-dimensional* cavities, i.e. cavities which do not hold more than one particle (Rosenfeld *et al* 1996, 1997). This idea was later exploited by Tarazona and Rosenfeld (1997) and Tarazona (2000) as a more fundamental idea to construct a functional free from divergences. The method amounts to extending to higher dimensions the exact form of the one-dimensional hard-rod functional (Percus 1976) and then adding the appropriate extra terms (with a form dictated by the original FM functional structure) so as to cancel whatever exceeds the exact result when the functional is reduced to properly tailored zero-dimensional cavities. This method avoids the use of scaled-particle theory while at the same time imposing a first-principles constraint (the zero-dimensional reduction) to the functional. It is then not surprising that the resulting functional performs much better than the original one, for instance in describing the crystal phase (Tarazona 2000).

The FM functional for the fluid of parallel hard cubes was first obtained using Rosenfeld's original method (Cuesta 1996) supplemented with the exact zero-dimensional reduction requirement (Cuesta and Martínez-Ratón 1997a, 1997b). However, this system seems to be more suitable for FM theory than the hard-sphere one, for at least two reasons: first, because the functional turns out to be derivable through an extraordinarily simple recipe, and second, because, as we shall show for its lattice counterpart, the method of cavities leads precisely to this functional. Moreover, this remains true not only for the monocomponent system but also for a mixture, where the FM functional for hard spheres shows its more prominent weaknesses (Cuesta *et al* 2002).

In principle nothing precludes us from extending this theory to lattice systems. However, when one naively tries to do this one immediately runs into difficulties. To illustrate these let us suppose we want to follow Rosenfeld's method. To begin with, there is no equivalent to scaled-particle theory for lattice fluids (Soto-Campos *et al* 1999) and it is not clear how to devise it, so this makes step (iii) of the derivation infeasible, but there is even more: the decomposition of the Mayer function is ambiguous in the sense that there is no unique way to define the FMs. Take, for instance, the one-dimensional fluid of hard rods in the continuum. The Fourier transform of its Mayer function is

$$-\hat{f}_{ij}(q) = 2 \frac{\sin(a_i + a_j)q}{q} = 2 \cos a_i q \frac{\sin a_j q}{q} + 2 \cos a_j q \frac{\sin a_i q}{q},$$

where the indices i, j are introduced to distinguish particles and $2a_i$ is the rod length of particle i . As is clear from this expression, the decomposition suggests itself. For the lattice counterpart of this model we have, however,

$$-\hat{f}_{ij}(q) = \frac{\sin(a_i + a_j - \frac{1}{2})q}{\sin(q/2)};$$

without being too imaginative, there are several ways of decomposing $\hat{f}_{ij}(q)$, all equally plausible:

$$\begin{aligned} -\hat{f}_{ij}(q) &= \frac{\sin(a_i - \frac{1}{2})q}{\sin(q/2)} \cos a_j q + \frac{\sin a_j q}{\sin(q/2)} \cos\left(a_i - \frac{1}{2}\right)q = \frac{\sin(a_i - \frac{1}{2})q}{\sin(q/2)} \cos a_j q \\ &\quad + \frac{\sin(a_j - \frac{1}{2})q}{\sin(q/2)} \cos a_i q + \cos a_i q \cos a_j q + \sin a_i q \sin a_j q \\ &= \frac{\sin(a_i - \frac{1}{4})q}{\sin(q/2)} \cos\left(a_j - \frac{1}{4}\right)q + \frac{\sin(a_j - \frac{1}{4})q}{\sin(q/2)} \cos\left(a_i - \frac{1}{4}\right)q, \end{aligned}$$

and many other possibilities. In contrast to the continuum case, this gives no clue as to how to define the weighted densities.

An alternative to this approach is to use the method of cavities, but there is also a problem here. The exact one-dimensional functional (Robledo 1980, Robledo and Varea 1981, Buschle *et al* 2000a) is very different in its structure from the continuum one, so there is no equivalent to defining convolutions of delta-shells with appropriate kernels (we shall see later that this has no counterpart in a lattice system). So here again we do not have a guide to follow.

The method we have employed to achieve the extension and to provide the correct way to define what could be referred to as *lattice FM theory* (LFMT), rests on two pillars: first, an appropriate analysis of the extension to mixtures of the exact one-dimensional functional of hard rods (which, to our knowledge, we present for the first time in this article), and second, a similarity, in the case of cubic lattices, to the fluid of parallel hard cubes. After devising the correct way to define LFMT we shall show how to make sense of the theory of cavities for lattice fluids. A further byproduct of this theory is that it would allow for an alternative way to define a scaled-particle theory for lattice fluids were we able to fill in step (iii) of Rosenfeld's method in such a way as to obtain the same functional. We are currently working along this line.

The structure of the article goes as follows. In section 2 we analyse the mixture of hard rods on a lattice. This means considering two cases: (i) all rod diameters having the same parity and (ii) some having odd and some even diameter. The former corresponds to an additive mixture, while the latter is nonadditive. The functional for case (i) is derived first, following the derivation by Vanderlick *et al* (1989) for the continuum; this method cannot be applied to case (ii), which is then obtained through an appropriate mapping to an additive mixture in a particular external field. The way in which these exact functionals are finally written suggests, by analogy with the fluid of parallel hard cubes, the extension to higher dimensions (only in cubic lattices). This is carried out in section 3, where it is also proven that this extension has a correct dimensional reduction to any lower dimension. It is then shown how to extend the method of cavities for these lattice models. Finally, in section 4, we present some results from applying the obtained functional to some particular two- and three-dimensional systems.

2. Hard-rod lattice fluid revisited

The exact density functional for the continuum fluid of hard rods was first obtained by Percus (1976) and extended to multicomponent mixtures by Vanderlick *et al* (1989). Robledo (1980) and Robledo and Varea (1981) derived the exact functional for the lattice fluid of hard rods by means of potential-distribution theory (Widom 1978), but they focused on the continuum limit. Buschle *et al* (2000b) have recently dealt with the general problem of the derivation of exact density functionals for one-dimensional lattice gases with finite-range pairwise interaction. They made use of a generalized Markov property satisfied by the

conditional particle distribution probabilities. In this way, they rederived (Buschle *et al* 2000a) the functional for the monocomponent hard-rod lattice fluid.

In this section, we are going to derive the exact density functional of a multicomponent lattice fluid of hard rods. The starting point will be the adaptation to lattice models of the derivation by Vanderlick *et al* (1989) for the continuum.

Let us consider a system of hard rods with different sizes, such that the interaction between α -type and α' -type rods at positions s and s' respectively on a one-dimensional lattice (i.e. $s, s' \in \mathbb{Z}$) is given by

$$\phi_{\alpha\alpha'}(s, s') = \begin{cases} 0 & \text{if } |s - s'| \geq \sigma_{\alpha\alpha'}, \\ \infty & \text{if } |s - s'| < \sigma_{\alpha\alpha'}, \end{cases} \quad (2.1)$$

where $\sigma_{\alpha\alpha'} = \frac{1}{2}(\sigma_\alpha + \sigma_{\alpha'})$, $\sigma_\alpha \in \mathbb{N}$ being the diameter of an α -type rod. Because of the particle ordering in one-dimensional systems, the pairwise interaction will appear in the grand canonical partition function Ξ via the modified Boltzmann factor, defined by

$$e_{\alpha\alpha'}(s, s') \equiv e^{-\beta\phi_{\alpha\alpha'}(s, s')} \Theta(s - s') = \Theta(s - s' - \sigma_{\alpha\alpha'}), \quad (2.2)$$

where $\Theta(s) = 1$ if $s \geq 0$ and 0 otherwise, and $\beta = 1/kT$ with T the temperature and k the Boltzmann constant. Note that this eliminates the combinatorial factor $1/N!$ of the partition function. Let us also suppose that every species α is in chemical equilibrium with a particle reservoir of fixed chemical potential μ_α and that over an α -type particle at position $s \in \mathbb{Z}$ is acting the external potential $u_\alpha(s)$. In the same way, the external and chemical potentials will only appear in Ξ via

$$w_{\alpha\alpha'}(s, s') \equiv e^{\beta[\mu_\alpha - u_\alpha(s)]} \delta_{\alpha\alpha'} \delta_{ss'} \equiv w_\alpha(s) \delta_{\alpha\alpha'} \delta_{ss'}, \quad (2.3)$$

where $\delta_{\alpha\alpha'}$ is the Kronecker delta. With the above definitions we can write the grand canonical partition function as

$$\Xi = 1 + \sum_{N=1}^{\infty} \text{Tr} \left[w_{\alpha_1}(s_1) \prod_{i=1}^{N-1} e_{\alpha_i \alpha_{i+1}}(s_i, s_{i+1}) w_{\alpha_{i+1}}(s_{i+1}) \right], \quad (2.4)$$

where $\text{Tr} \equiv \sum_{\{(\alpha_i, s_i)\}}$ sums over all indices (α, s) appearing in the expression, α_i denotes the species of the i th particle and $s_i \in \mathbb{Z}$ its position. Considering e and w as operators defined over the (α, s) -space, the term under the sum over N is just $\text{Tr}\{[w(ew)^{N-1}]_{\alpha\alpha'}(s, s')\}$; thus we can perform the sum and rewrite (2.4) as

$$\Xi = 1 + \text{Tr}\{[w(I - ew)^{-1}]_{\alpha\alpha'}(s, s')\}, \quad (2.5)$$

I denoting the identity operator in the (α, s) -space.

The density profile of species α , $\rho_\alpha(s)$, can be expressed as the functional derivative (Hansen and McDonald 1990)

$$\rho_\alpha(s) = \frac{w_\alpha(s)}{\Xi} \frac{\partial \Xi}{\partial w_\alpha(s)}, \quad (2.6)$$

which in this case, given the discrete nature of s , is a partial derivative. Using (2.5) for Ξ in (2.6), we can write $\rho_\alpha(s)$ as

$$\rho_\alpha(s) = \frac{\Xi_\alpha^-(s) w_\alpha(s) \Xi_\alpha^+(s)}{\Xi}, \quad (2.7)$$

where we have introduced the *truncated partition functions* defined as

$$\Xi_\alpha^-(s) \equiv \sum_{(\alpha', s')} (I - ew)_{\alpha\alpha'}^{-1}(s, s'), \quad (2.8)$$

$$\Xi_\alpha^+(s) \equiv \sum_{(\alpha', s')} (I - we)_{\alpha'\alpha}^{-1}(s', s). \quad (2.9)$$

From the above definitions and multiplying by $(I - ew)$ to the left of $\Xi_{\alpha}^{-}(s)$ and by $(I - we)$ to the right of $\Xi_{\alpha}^{+}(s)$, it is straightforward to obtain the following recursive relations satisfied by the truncated partition functions:

$$\begin{aligned}\Xi_{\alpha}^{-}(s) &= 1 + \sum_{(\alpha', s')} (ew)_{\alpha\alpha'}(s, s') \Xi_{\alpha'}^{-}(s'), \\ \Xi_{\alpha}^{+}(s) &= 1 + \sum_{(\alpha', s')} \Xi_{\alpha'}^{+}(s') (we)_{\alpha'\alpha}(s', s).\end{aligned}\quad (2.10)$$

At this point, our original problem may be posed as to solve (2.7) and (2.10) in such a way that $w_{\alpha}(s)$ could be expressed as a functional depending only upon the densities $\rho_{\alpha}(s)$.

As noted by Vanderlick *et al* (1989) and Percus (1997), the solvability of (2.7) and (2.10) depends on the rank of the Boltzmann factor (2.2) regarded as an operator in the (α, s) -space. For the additive continuum system it can be shown that this is of rank one, and then it is possible to solve these equations. In contrast, for the lattice system we are dealing with this is not always true. In this case, due to the discrete nature of the system, we should distinguish between a mixture of rods all of them with even (odd) diameters (*additive mixture*) and one of rods some of which have even diameter and some odd (*nonadditive mixture*). Indeed, for the former case, $\sigma_{\alpha\alpha'}$ is always an integer and, consequently, from (2.1) it follows that the corresponding mixture is additive. The solution in this case is just a rephrasing of the resolution of (2.7) and (2.10) reported for the continuum system (we shall sketch it in section 2.1). For the mixed even–odd case, however, $\sigma_{\alpha\alpha'}$ may take half-integer values. If $\sigma_{\alpha\alpha'}$ is a half-integer then $|s - s'| \geq \sigma_{\alpha\alpha'}$ in (2.1) is also $|s - s'| \geq \sigma_{\alpha\alpha'} + 1/2$, so effectively the interaction is nonadditive. In spite of this, it should be noticed that this nonadditivity is peculiar to the lattice system and disappears in the continuum limit. For nonadditive mixtures the Boltzmann factor (2.2) is not a rank-one operator; nevertheless, we shall show (in section 2.2) how to obtain the exact density functional for that system as a particular case of the additive mixture.

2.1. Additive mixture

Let us consider a mixture of hard rods such that $\sigma_{\alpha} = 2a_{\alpha} + \epsilon$ with $a_{\alpha} \in \mathbb{N}$ and $\epsilon = 0, 1$ depending on whether all the rods have even or odd diameters, respectively. In this case, the Boltzmann factor (2.2) is a rank-one operator. If we define the vectors $e_{\alpha}^{+}(s) \equiv \delta_{s, a_{\alpha}}$ and $e_{\alpha}^{-}(s) \equiv \Theta(s - a_{\alpha} - \epsilon)$ and the convolution $*$ as $f * g(s) \equiv \sum_r f(s - r)g(r)$, (2.2) can be written as

$$e_{\alpha\alpha'}(s, s') = e_{\alpha}^{-} * e_{\alpha'}^{+}(s - s') = e_{\alpha'}^{+} * e_{\alpha}^{-}(s - s'). \quad (2.11)$$

Inserting (2.11) in (2.10) we obtain

$$\begin{aligned}\Xi_{\alpha}^{-}(s) &= 1 + \sum_r e_{\alpha}^{-}(s - r) \left[\sum_{(\alpha', s')} e_{\alpha'}^{+}(r - s') w_{\alpha'}(s') \Xi_{\alpha'}^{-}(s') \right], \\ \Xi_{\alpha}^{+}(s) &= 1 + \sum_r \left[\sum_{(\alpha', s')} \Xi_{\alpha'}^{+}(s') w_{\alpha'}(s') e_{\alpha'}^{+}(s' - r) \right] e_{\alpha}^{-}(r - s).\end{aligned}\quad (2.12)$$

We can now use (2.7) to eliminate $w_{\alpha'}(s')$ from (2.12); besides, as $e_{\alpha}^{-}(s + a_{\alpha}) = \Theta(s - \epsilon)$, hence independent of α , it is handy to define

$$\Xi_{\alpha}^{\pm}(s) \equiv \Xi_{\alpha}^{\pm}(s \mp a_{\alpha}), \quad (2.13)$$

$$\rho_{\alpha}^{\pm}(s) \equiv \sum_{\alpha} \rho_{\alpha}(s \pm a_{\alpha}), \quad (2.14)$$

which allow us to rewrite equations (2.12) in the more suitable form

$$\begin{aligned}\Xi^-(s) &= 1 + \Xi \sum_{r=-\infty}^{s-\epsilon} \frac{\rho^-(r)}{\Xi^+(r)}, \\ \Xi^+(s) &= 1 + \Xi \sum_{r=s+\epsilon}^{\infty} \frac{\rho^+(r)}{\Xi^-(r)}.\end{aligned}\quad (2.15)$$

From the above expressions it is straightforward to obtain the following system of finite difference equations:

$$\begin{aligned}\Delta \Xi^-(s) &= \Xi \frac{\rho^-(s+1-\epsilon)}{\Xi^+(s+1-\epsilon)}, \\ \Delta \Xi^+(s) &= -\Xi \frac{\rho^+(s+\epsilon)}{\Xi^-(s+\epsilon)},\end{aligned}\quad (2.16)$$

with boundary conditions

$$\begin{aligned}\Xi^\pm(\mp\infty) &= \Xi, \\ \Xi^\pm(\pm\infty) &= 1,\end{aligned}\quad (2.17)$$

where we have introduced the difference operator Δ , defined by $\Delta f(s) \equiv f(s+1) - f(s)$. This system is exactly solvable and is equivalent to the original recursion relations (2.10). In order to solve (2.16) we have to combine the two equations of the system, taking into account the discrete Leibnitz rule $\Delta(fg)(s) = f(s+1)\Delta g(s) + g(s)\Delta f(s) = g(s+1)\Delta f(s) + f(s)\Delta g(s)$. This yields

$$\Delta(\Xi^- \Xi^+)(s) = \Xi[\rho^-(s+1-\epsilon) - \rho^+(s+\epsilon)], \quad (2.18)$$

whose solution, taking into account the boundary conditions (2.17), is

$$\Xi^-(s)\Xi^+(s) = \Xi \left\{ 1 + \sum_{r=-\infty}^{s-1} [\rho^-(r+1-\epsilon) - \rho^+(r+\epsilon)] \right\}, \quad (2.19)$$

or, using the definitions (2.14),

$$\Xi^-(s)\Xi^+(s) = \Xi \left(1 - \sum_{\alpha} \sum_{r=s-a_{\alpha}+1-\epsilon}^{s+a_{\alpha}-1+\epsilon} \rho_{\alpha}(r) \right). \quad (2.20)$$

This equation permits us to decouple the system (2.16) and solve it for $\Xi^\pm(s)$. After a little algebra and index manipulation, the solution has the form

$$\begin{aligned}\frac{\Xi^-(s)}{\Xi} &= [1 - n^{(0)}(s - \epsilon)] \prod_{r=s-\epsilon}^{\infty} \frac{1 - n^{(1)}(r)}{1 - n^{(0)}(r)}, \\ \Xi^+(s) &= \prod_{r=s}^{\infty} \frac{1 - n^{(0)}(r)}{1 - n^{(1)}(r)},\end{aligned}\quad (2.21)$$

where we have introduced the *weighted densities*, $n^{(k)}(s)$ ($k = 0, 1$), defined as

$$n^{(k)}(s) = \sum_{\alpha} \omega_{\alpha}^{(k)} * \rho_{\alpha}(s), \quad \omega_{\alpha}^{(k)}(s) = \begin{cases} 1 & \text{if } -a_{\alpha} - k - \epsilon < s < a_{\alpha}, \\ 0 & \text{otherwise.} \end{cases} \quad (2.22)$$

With (2.21) we have basically solved our problem, since from (2.21) and (2.17) we can write the grand potential, $\beta\Omega \equiv -\ln \Xi$, as

$$\beta\Omega = \sum_{s \in \mathbb{Z}} \ln \left(\frac{1 - n^{(1)}(s)}{1 - n^{(0)}(s)} \right). \quad (2.23)$$

Finally, the free-energy density functional, $\beta\mathcal{F}$, defined as (Evans 1979)

$$\beta\mathcal{F}[\rho_\alpha] = \beta\Omega[\rho_\alpha] + \sum_\alpha \sum_{s \in \mathbb{Z}} \rho_\alpha(s) \ln w_\alpha(s), \quad (2.24)$$

takes, from (2.7), (2.13) and (2.21), the form

$$\begin{aligned} \beta\mathcal{F}[\rho_\alpha] = & \sum_\alpha \sum_{s \in \mathbb{Z}} \rho_\alpha(s) \ln \rho_\alpha(s) + \beta\Omega[\rho_\alpha] - \sum_\alpha \sum_{s \in \mathbb{Z}} \rho_\alpha(s) \\ & \times \left[\sum_{r=s-a_\alpha-\epsilon}^{s+a_\alpha-1} \ln(1-n^{(1)}(r)) - \sum_{r=s-a_\alpha-\epsilon+1}^{s+a_\alpha-1} \ln(1-n^{(0)}(r)) \right]. \end{aligned} \quad (2.25)$$

For reasons that will be made clear later, we prefer to write this functional in the equivalent, but more convenient, form

$$\beta\mathcal{F}[\rho_\alpha] = \beta\mathcal{F}^{\text{id}}[\rho_\alpha] + \sum_{s \in \mathbb{Z}} [\Phi_0(n^{(1)}(s)) - \Phi_0(n^{(0)}(s))], \quad (2.26)$$

where $\beta\mathcal{F}^{\text{id}} = \sum_\alpha \sum_{s \in \mathbb{Z}} \rho_\alpha(s) [\ln \rho_\alpha(s) - 1]$ refers to the ideal part of the free energy and $\Phi_0(\eta) \equiv \eta + (1-\eta) \ln(1-\eta)$ is the zero-dimensional excess free energy for a zero-dimensional cavity with mean occupancy η (Rosenfeld *et al* 1996).

2.2. Nonadditive mixture

As we have mentioned above, the exact density functional for this special system can be derived as a particular case of the additive functional (2.26). Let us suppose that we want to study a system of hard rods whose diameters are $\sigma_\alpha = 2a_\alpha + \epsilon_\alpha$, where $a_\alpha \in \mathbb{N}$ and $\epsilon_\alpha = 0, 1$. Because of the α -dependence in ϵ_α , the factorization (2.11) cannot be applied to (2.2). This difficulty can be overcome if we notice (see figure 1) that this nonadditive mixture can be mapped to an additive mixture of hard rods whose diameters are $\tilde{\sigma}_\alpha = 2\sigma_\alpha$, while their positions are restricted to lie on the even sites of the lattice (i.e. $\tilde{\rho}_\alpha(s) = 0$ if $s = 2r + 1$ with $r \in \mathbb{Z}$; this amounts to setting an infinite external potential on the odd sites, while keeping it arbitrary on the even sites). Therefore, the density functional for the nonadditive system will arise by introducing in (2.26) the density profile

$$\tilde{\rho}_\alpha(s) = \sum_{r \in \mathbb{Z}} \rho_\alpha(r) \delta_{s, 2r}, \quad (2.27)$$

where $\rho_\alpha(s)$ is the density profile corresponding to the original nonadditive system. This yields for the weighted densities (2.22)

$$\begin{aligned} n_0^{(k)}(s) & \equiv \tilde{n}^{(k)}(2s) = n_e^{(k)}(s) + n_o^{(1)}(s-1), \\ n_1^{(k)}(s) & \equiv \tilde{n}^{(k)}(2s+1) = n_e^{(1)}(s) + n_o^{(k)}(s), \end{aligned} \quad (2.28)$$

where $s \in \mathbb{Z}$, $k = 0, 1$ and the subindex $\{e, o\}$ states that the sum over species in the definition (2.22) is restricted to those with even or odd diameter, respectively. There are thus four instead of two weighted densities for this special case. An alternative way of expressing these weighted densities is $n_j^{(k)}(s) = \sum_\alpha \omega_{j,\alpha}^{(k)} * \rho_\alpha(s)$ ($k, j = 0, 1$), if the following nonadditive weights are introduced:

$$\omega_{j,\alpha}^{(k)}(s) \equiv \begin{cases} \omega_\alpha^{(j+k(1-j))}(s) & \text{if } \sigma_\alpha \text{ is even,} \\ \omega_\alpha^{(1-j+kj)}(s-1+j) & \text{if } \sigma_\alpha \text{ is odd.} \end{cases} \quad (2.29)$$

With these definitions, the excess free-energy density functional for the nonadditive mixture (the ideal part remains the same) adopts the form

$$\beta\mathcal{F}^{\text{ex}}[\rho_\alpha] = \sum_{s \in \mathbb{Z}} [\Phi_0(n_1^{(1)}(s)) + \Phi_0(n_0^{(1)}(s)) - \Phi_0(n_1^{(0)}(s)) - \Phi_0(n_0^{(0)}(s))]. \quad (2.30)$$

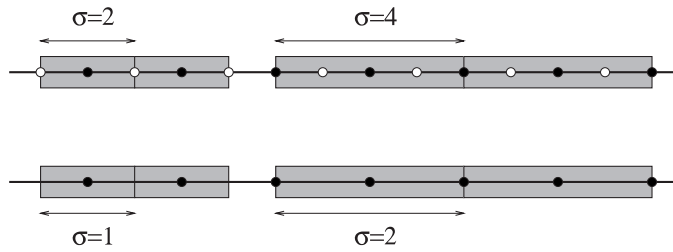


Figure 1. This figure shows how an additive mixture of hard rods of diameters 2 and 4 can be made to have the same configurations as a nonadditive mixture of rods with diameters 1 and 2. The positions of the upper system are restricted to be on the black sites, while the white sites are forbidden.

As far as we know, functionals (2.26) and (2.30) have never been reported in the literature. The additive case is just an exercise of rewriting the original derivation by Vanderlick *et al* (1989) for the continuum, but this nonadditive case cannot be directly obtained with their method. Besides, even the functional (2.26) (which for the monocomponent case reduces to that obtained several times in the literature) has been written in a form that will make of the obtention of an approximate functional in higher dimensions an easy task.

3. From zero-dimensional cavities to higher dimensions

Cuesta and Martínez-Ratón (1997a) proved that the one-dimensional excess free energy functional in the continuum model can be generated from the zero-dimensional one by just applying a differential operator with respect to the particle sizes. The form in which the functionals (2.26) and (2.30) have been written proves that this is also true for the discrete case, but now, due to the discrete nature of the system, the differential operator becomes a difference operator. This suggests rewriting (2.26) and (2.30) as

$$\beta\mathcal{F}^{\text{ex}}[\rho_\alpha] = \sum_{s \in \mathbb{Z}} \mathcal{D}_k \Phi_0(n^{(k)}(s)), \quad \beta\mathcal{F}^{\text{ex}}[\rho_\alpha] = \sum_{s \in \mathbb{Z}} \mathcal{D}_k \left[\sum_{j=0,1} \Phi_0(n_j^{(k)}(s)) \right], \quad (3.1)$$

respectively. Here \mathcal{D}_k is the difference operator $\mathcal{D}_k f(k) \equiv f(1) - f(0)$. Cuesta and Martínez-Ratón (1997a) also proved that the FM functional for the d -dimensional system of parallel hard cubes followed the same simple recipe, i.e. it can be generated from the zero-dimensional functional by successive applications of a differential operator with respect to the particle size along every coordinate axis. The functional so obtained satisfies the zero-dimensional reduction requirement. For the equivalent lattice model it seems natural to propose a similar recipe. Then, taking into account the continuum analogue and (3.1), our proposal for the FM functional of the d -dimensional discrete parallel hard-cube model is

$$\beta\mathcal{F}^{\text{ex}}[\rho_\alpha] = \sum_{s \in \mathbb{Z}^d} \mathcal{D}_k \Phi_0(n^{(k)}(s)) \quad (3.2)$$

for the additive case, and

$$\beta\mathcal{F}^{\text{ex}}[\rho_\alpha] = \sum_{s \in \mathbb{Z}^d} \mathcal{D}_k \left[\sum_{j \in \{0,1\}^d} \Phi_0(n_j^{(k)}(s)) \right] \quad (3.3)$$

for the nonadditive one, where $\mathbf{k} \equiv (k_1, \dots, k_d)$, $\mathbf{j} \equiv (j_1, \dots, j_d)$ are vector indices, $\mathcal{D}_{\mathbf{k}} \equiv \prod_{i=1}^d \mathcal{D}_{k_i}$ is the difference operator and the weighted densities are defined as $n^{(\mathbf{k})}(\mathbf{s}) \equiv \sum_{\alpha} \omega_{\alpha}^{(\mathbf{k})} * \rho_{\alpha}(\mathbf{s})$ with $\omega_{\alpha}^{(\mathbf{k})}(\mathbf{s}) \equiv \prod_{i=1}^d \omega_{\alpha}^{(k_i)}(s_i)$ for the additive system, and as $n_{\mathbf{j}}^{(\mathbf{k})}(\mathbf{s}) \equiv \sum_{\alpha} \omega_{\mathbf{j},\alpha}^{(\mathbf{k})} * \rho_{\alpha}(\mathbf{s})$ with $\omega_{\mathbf{j},\alpha}^{(\mathbf{k})}(\mathbf{s}) \equiv \prod_{i=1}^d \omega_{j_i,\alpha}^{(k_i)}(s_i)$ for the nonadditive one.

Functionals (3.2) and (3.3) are the main results of this work since they constitute, to the best of our knowledge, the first FM functionals for a lattice model. In this sense, it can be checked that they depend on the density profile through a set of weighted densities defined from one-particle measures which are compatible with the decomposition of the Mayer function into a sum of their convolutions, the virial expansion of the direct correlation function is exact up to first order in the density and they consistently reduce to any lower dimension down to $d = 0$. Also, it must be noticed that their continuum counterpart is recovered in the continuum limit of vanishing lattice spacing $\delta \rightarrow 0$ and infinite size $\sigma_{\alpha} \rightarrow \infty$ with $\sigma_{\alpha}\delta = \text{const.}$ (notice that the additive–nonadditive differentiation becomes immaterial in this limit). Points (i) and (ii) are easy to check, so we shall focus in what follows in the crucial point (iii) and its connection with an alternative way of obtaining functionals (3.2) and (3.3).

As mentioned in the introduction, there is an alternative method to Rosenfeld’s original one to construct a FM functional. This method will be referred to as the *zero-dimensional cavity method* (Rosenfeld *et al* 1996, Tarazona and Rosenfeld 1997, Tarazona 2000) because it is based on the exact dimensional reduction of the functional to $d = 0$. Pursuing the same idea but having in mind the form of functionals (2.26) and (2.30), we have devised a similar method suitable for lattice models. The method amounts to (i) directly extending the exact zero-dimensional functional to higher dimensions (note here a difference from the continuum case (Tarazona and Rosenfeld 1997), where it is the one-dimensional functional that is extended to higher dimensions) and then (ii) adding the appropriate extra terms (in the way suggested by (2.26) and (2.30)) in order for the functional to recover the exact form when applied to zero-dimensional cavities.

To illustrate this procedure we must first recall that we are dealing with a mixture, sometimes nonadditive, and, in contrast to the monocomponent case, it is not very clear what a zero-dimensional cavity means for a mixture. Let us therefore start by defining what we shall understand by this. In the monocomponent case, a zero-dimensional cavity is simply a set of connected points in the d -dimensional lattice such that if a particle (its centre of mass) is placed at one of them no other particle can be placed at any other point of this set. For one-dimensional hard rods of length $2a$, the largest zero-dimensional cavity (‘maximal’ cavity) is the interval $[-a + 1, a]$, whereas for hard rods of length $2a + 1$ it is $[-a + 1, a + 1]$. In d dimensions the maximal cavity is the set $[-a + 1, a]^d$ or $[-a + 1, a + 1]^d$, depending on the length parity.

For a mixture, a zero-dimensional cavity can be defined as a collection of sets, one for each species, such that if a particle of any species occupies one of the points of its corresponding set, no other particle of the same or different species can be placed at any point of its corresponding set (figure 2 will help to clarify this concept). In $d = 1$ and in the additive case, this means the collection of sets $\{[-a_{\alpha} + 1, a_{\alpha}]\}_{\alpha}$, if $2a_{\alpha}$ is the rod length of species α (figure 2(a)), or $\{[-a_{\alpha} + 1, a_{\alpha} + 1]\}_{\alpha}$, if this rod length is $2a_{\alpha} + 1$ (figure 2(b)); in the nonadditive case, however, indexing by α the species of even length and by α' those of odd length, there are two maximal cavities: $\{[-a_{\alpha} + 1, a_{\alpha}], [-a_{\alpha'}, a_{\alpha'}]\}_{\alpha,\alpha'}$ (figure 2(c)) and $\{[-a_{\alpha} + 1, a_{\alpha}], [-a_{\alpha'} + 1, a_{\alpha'} + 1]\}_{\alpha,\alpha'}$ (figure 2(d)). In d dimensions the cavities for the additive case generalize as in the monocomponent case, while in the nonadditive case there will appear 2^d different cavities, depending on which of the two choices above we select for each dimension. Because of this proliferation of maximal cavities in the nonadditive case, it is convenient to discuss the two types of mixture separately.

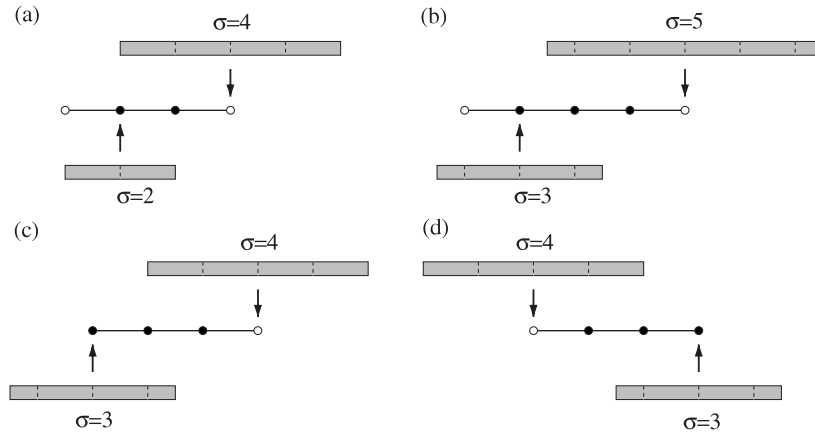


Figure 2. Maximal cavities for binary mixtures in $d = 1$. Large particles can be placed at any point, black or white, but small ones can only be placed at black sites. The figure shows the additive even (a) and odd (b) cases, as well as the two equivalent cavities for one nonadditive case (c) and (d).

3.1. Additive mixture

For density profiles constrained to be zero outside the points of a maximal zero-dimensional cavity it is easy to check (by applying the definition) that the weighted densities (2.22) satisfy the relationships

$$\begin{aligned} n^{(1)}(s) &= n^{(0)}(s+1) & (s < 0), \\ n^{(1)}(s) &= n^{(0)}(s) & (s > 0). \end{aligned} \quad (3.4)$$

These are the keystone of the method. As explained, the method starts off from the straightforward extension of the zero-dimensional excess functional to $d = 1$, $\Phi_0^{(1d)}$. As $n^{(1)}(0) = \eta$, the occupancy probability of the cavity,

$$\Phi_0^{(1d)}[\rho] = \sum_{s \in \mathbb{Z}} \Phi_0(n^{(1)}(s)). \quad (3.5)$$

Now we apply this functional to a zero-dimensional cavity and, by means of (3.4), rewrite it as

$$\begin{aligned} \Phi_0^{(1d)}[\rho] &= \Phi_0(n^{(1)}(0)) + \sum_{s < 0} \Phi_0(n^{(0)}(s+1)) + \sum_{s > 0} \Phi_0(n^{(0)}(s)) \\ &= \Phi_0(n^{(1)}(0)) + \sum_{s \in \mathbb{Z}} \Phi_0(n^{(0)}(s)). \end{aligned} \quad (3.6)$$

However, $\Phi_0(n^{(1)}(0))$ on the rhs of (3.6) is the exact zero-dimensional excess free energy for the cavity, so the method dictates that in order to obtain the excess functional for the one-dimensional system we must subtract from the form we started with all the spurious terms. This leads to

$$\beta \mathcal{F}^{\text{ex}}[\rho] = \sum_{s \in \mathbb{Z}} \Phi_0(n^{(1)}(s)) - \sum_{s \in \mathbb{Z}} \Phi_0(n^{(0)}(s)), \quad (3.7)$$

which coincides with (2.26).

Let us now illustrate how the method works for higher dimensions as well. For the sake of simplicity we shall restrict ourselves to $d = 2$. The corresponding relationships between

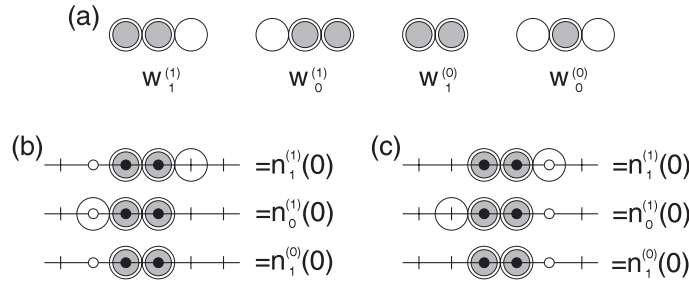


Figure 3. (a) Diagrammatic representation of the weights corresponding to a binary mixture of rods of lengths $\sigma_1 = 3$ and $\sigma_2 = 2$. Circles window points whose density contribute to the weighted density: empty circles for the large rods and shaded circles for the small rods. (b), (c) Result of convoluting the weights with the density profiles of zero-dimensional maximal cavities.

the weighted densities of density profiles vanishing outside a zero-dimensional cavity are

$$\begin{aligned} n^{(k,1)}(s_1, s_2) &= n^{(k,0)}(s_1, s_2 + 1) & (s_2 < 0), \\ n^{(k,1)}(s_1, s_2) &= n^{(k,0)}(s_1, s_2) & (s_2 > 0), \end{aligned} \quad (3.8)$$

with $k = 0, 1$, and similar ones if the coordinate axes are interchanged. Using the same notation as for the one-dimensional case and repeating the steps in (3.6) for s_2 we obtain

$$\Phi_0^{(2d)}[\rho] = \sum_{s \in \mathbb{Z}^2} \Phi_0(n^{(1,1)}(s)) = \sum_{s_1 \in \mathbb{Z}} \Phi_0(n^{(1,1)}(s_1, 0)) + \sum_{s \in \mathbb{Z}^2} \Phi_0(n^{(1,0)}(s)). \quad (3.9)$$

Repeating the trick with $\sum_{s \in \mathbb{Z}^2} \Phi_0(n^{(0,1)}(s))$ we obtain

$$0 = \sum_{s \in \mathbb{Z}^2} \Phi_0(n^{(0,1)}(s)) - \sum_{s_1 \in \mathbb{Z}} \Phi_0(n^{(0,1)}(s_1, 0)) - \sum_{s \in \mathbb{Z}^2} \Phi_0(n^{(0,0)}(s)). \quad (3.10)$$

Adding (3.10) to (3.9) and noticing that

$$\sum_{s_1 \in \mathbb{Z}} \Phi_0(n^{(1,1)}(s_1, 0)) - \sum_{s_1 \in \mathbb{Z}} \Phi_0(n^{(0,1)}(s_1, 0)) = \Phi_0(n^{(1,1)}(\mathbf{0})) \quad (3.11)$$

yields

$$\Phi_0^{(2d)}[\rho] = \Phi_0(n^{(1,1)}(\mathbf{0})) + \sum_{s \in \mathbb{Z}^2} [\Phi_0(n^{(1,0)}(s)) + \Phi_0(n^{(0,1)}(s)) - \Phi_0(n^{(0,0)}(s))]. \quad (3.12)$$

Again, $\Phi_0(n^{(1,1)}(\mathbf{0}))$ is the exact zero-dimensional excess functional, therefore

$$\beta \mathcal{F}^{\text{ex}}[\rho] = \sum_{s \in \mathbb{Z}^2} [\Phi_0(n^{(1,1)}(s)) - \Phi_0(n^{(1,0)}(s)) - \Phi_0(n^{(0,1)}(s)) + \Phi_0(n^{(0,0)}(s))], \quad (3.13)$$

which coincides with (3.2) for $d = 2$. This provides the rationale for (3.2) for arbitrary dimension, and proves in passing that functional (3.2) has a consistent dimensional reduction to any lower dimension.

3.2. Nonadditive mixture

In the additive case it is always the weighted density $n^{(1)}(0)$ that gives the occupancy probability, η , of the (unique) maximal zero-dimensional cavity, so extending the zero-dimensional excess functional is straightforward as equation (3.5) shows. In the nonadditive case, however, this is not as simple. Due to the degeneracy of maximal cavities, which weighted density yields the occupancy probability depends on which cavity we choose. Before proceeding with the

construction of the functional we therefore need a unique expression in terms of the one-dimensional weighted densities that provides the excess free energy of *any* maximal cavity. One such expression is

$$\Phi_0^{(0d)}[\rho] = \Phi_0(n_1^{(1)}(0)) + \Phi_0(n_0^{(1)}(0)) - \Phi_0(n_1^{(0)}(0)). \quad (3.14)$$

In order to make it easy to understand why this is so and the discussions to come, we have introduced a diagrammatic notation for a particular case in figure 3. We shall consider a binary mixture of rods of lengths $\sigma_1 = 3$ and $\sigma_2 = 2$, which is prototypical of this case. For this mixture we represent the weights as a chain of empty and shaded circles (see figure 3(a)). The effect of convoluting a weight with a density profile is to select the density at those sites overlapped by the empty circles for the large rods and by the shaded circles for the small rods, and add them up. The result of this operation is the corresponding weighted density. The application of these weights to each maximal cavity is depicted in figures 3(b) and (c), respectively. Figure 3(b) illustrates that $n_0^{(1)}(0) = \eta$ and $n_1^{(1)}(0) = n_1^{(0)}(0)$, so (3.14) reduces to $\Phi_0(\eta)$, as expected. On the other hand, figure 3(c) illustrates that $n_1^{(1)}(0) = \eta$ and $n_0^{(1)}(0) = n_1^{(0)}(0)$, so again (3.14) reduces to $\Phi_0(\eta)$.

We can now carry on with the method as in the additive case and propose

$$\Phi_0^{(1d)}[\rho] = \sum_{s \in \mathbb{Z}} [\Phi_0(n_1^{(1)}(s)) + \Phi_0(n_0^{(1)}(s)) - \Phi_0(n_1^{(0)}(s))]. \quad (3.15)$$

Whichever the maximal cavity we choose, from definitions (2.28) and the relationships (3.4) the following analogous relationships between the nonadditive weighted densities hold:

$$\begin{aligned} n_0^{(1)}(s) &= n_1^{(0)}(s), & n_1^{(1)}(s) &= n_0^{(0)}(s+1) & (s < 0), \\ n_0^{(1)}(s) &= n_0^{(0)}(s), & n_1^{(1)}(s) &= n_1^{(0)}(s) & (s > 0). \end{aligned} \quad (3.16)$$

Proceeding as we did for the additive case, we use the above relationships to rewrite (3.15) as

$$\Phi_0^{(1d)}[\rho] = \Phi_0^{(0d)}[\rho] + \sum_{s < 0} \Phi_0(n_0^{(0)}(s+1)) + \sum_{s > 0} \Phi_0(n_0^{(0)}(s)) = \Phi_0^{(0d)}[\rho] + \sum_{s \in \mathbb{Z}} \Phi_0(n_0^{(0)}(s)), \quad (3.17)$$

where we have made use of (3.14), which gives the zero-dimensional excess functional; so the method gives

$$\beta \mathcal{F}^{\text{ex}}[\rho_\alpha] = \sum_{s \in \mathbb{Z}} [\Phi_0(n_1^{(1)}(s)) + \Phi_0(n_0^{(1)}(s)) - \Phi_0(n_1^{(0)}(s)) - \Phi_0(n_0^{(0)}(s))], \quad (3.18)$$

which coincides with (2.30).

In order to extend the cavity method to dimensions higher than one, we have to generalize expression (3.14). Due to the cubic symmetry of our system this can be done just by applying the same rule on each coordinate axis. For the sake of simplicity, we can define the operator \mathcal{T}_k^j as $\mathcal{T}_k^j f(k, j) \equiv f(1, 1) + f(1, 0) - f(0, 1)$ and its d -dimensional version as $\mathcal{T}_k^j \equiv \prod_{i=1}^d \mathcal{T}_{k_i}^{j_i}$. Then the natural generalization of (3.14) is simply

$$\Phi_0^{(0d)}[\rho] = \mathcal{T}_k^j \Phi_0(n_j^{(k)}(\mathbf{0})), \quad (3.19)$$

and the extension of the zero-dimensional excess functional to d dimensions

$$\Phi_0^{(d)}[\rho] = \sum_{s \in \mathbb{Z}^d} \mathcal{T}_k^j \Phi_0(n_j^{(k)}(s)). \quad (3.20)$$

Again, as a representative of a higher dimension, we shall apply the cavity method for $d = 2$. In figure 4 is shown the diagrammatic representation of the weights for a binary mixture of squares of edge lengths $\sigma_1 = 3$ and $\sigma_2 = 2$, as well as all maximal cavities for this system.

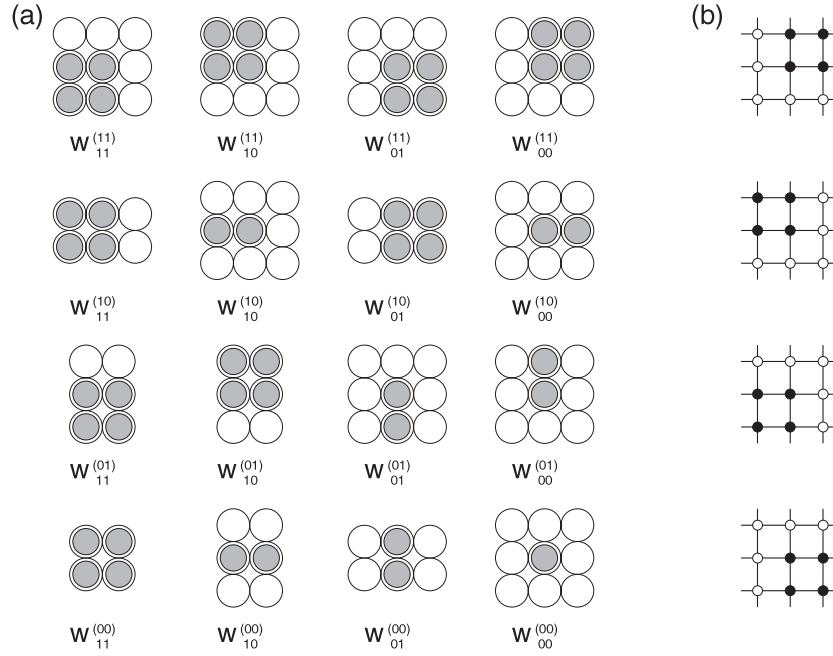


Figure 4. (a) Diagrammatic representation of the weights corresponding to a binary mixture of squares of edge lengths $\sigma_1 = 3$ and $\sigma_2 = 2$ (see caption of figure 3(a) to understand the circle notation). (b) Maximal cavities for this system. Note that the result of convoluting the weights in (a) with the density profiles of (b), $n_j^{(k)}(\mathbf{0})$, is obtained by superposing the lower leftmost shadow circle of the weight with the lower leftmost black point of the cavity.

Expression (3.19) for $d = 2$ accounts for all cavities in figure 4(b). For example, if we take the cavity at the top the application of the weights in figure 4(a) gives $n_{0,0}^{(1,1)}(\mathbf{0}) = \eta$, $n_{1,1}^{(1,1)}(\mathbf{0}) = n_{1,1}^{(0,0)}(\mathbf{0})$, $n_{1,0}^{(1,1)}(\mathbf{0}) = n_{1,0}^{(0,1)}(\mathbf{0})$, $n_{0,1}^{(1,1)}(\mathbf{0}) = n_{0,1}^{(1,0)}(\mathbf{0})$ and $n_{1,1}^{(1,0)}(\mathbf{0}) = n_{1,1}^{(0,1)}(\mathbf{0})$, so (3.19) reduces to $\Phi_0(\eta)$. By symmetry the same happens for any of the cavities.

Proceeding with the method, from (3.20) we shall start with

$$\begin{aligned} \Phi_0^{(2d)}[\rho] = \sum_{s \in \mathbb{Z}^2} [\Phi_0(n_{1,1}^{(1,1)}(s)) + \Phi_0(n_{1,0}^{(1,1)}(s)) - \Phi_0(n_{1,1}^{(1,0)}(s)) + \Phi_0(n_{0,1}^{(1,1)}(s)) + \Phi_0(n_{0,0}^{(1,1)}(s)) \\ - \Phi_0(n_{0,1}^{(1,0)}(s)) - \Phi_0(n_{1,1}^{(0,1)}(s)) - \Phi_0(n_{1,0}^{(0,1)}(s)) + \Phi_0(n_{1,1}^{(0,0)}(s))]. \end{aligned} \quad (3.21)$$

Now, the relationships (3.16) become

$$\begin{aligned} n_{j,0}^{(k,1)}(s_1, s_2) = n_{j,1}^{(k,0)}(s_1, s_2), \quad n_{j,1}^{(k,1)}(s_1, s_2) = n_{j,0}^{(k,0)}(s_1, s_2 + 1) \quad (s_2 < 0), \\ n_{j,0}^{(k,1)}(s_1, s_2) = n_{j,0}^{(k,0)}(s_1, s_2), \quad n_{j,1}^{(k,1)}(s_1, s_2) = n_{j,1}^{(k,0)}(s_1, s_2) \quad (s_2 > 0), \end{aligned} \quad (3.22)$$

and those obtained by interchanging the coordinate axes. As before, by making use of these relationships in (3.21) we obtain

$$\Phi_0^{(2d)}[\rho] = \sum_{s_1 \in \mathbb{Z}} \mathcal{T}_k^j \Phi_0(n_j^{(k)}(s_1, 0)) + \sum_{s \in \mathbb{Z}^2} [\Phi_0(n_{1,0}^{(1,0)}(s)) + \Phi_0(n_{0,0}^{(1,0)}(s)) - \Phi_0(n_{1,0}^{(0,0)}(s))], \quad (3.23)$$

where it must be noticed that the second term in the rhs of (3.23) is just $\sum_{s \in \mathbb{Z}^2} \mathcal{T}_k^j \Phi_0(n_{j,0}^{(k,0)}(s))$. By the same argument, we have

$$0 = \sum_{s \in \mathbb{Z}^2} \mathcal{T}_k^j \Phi_0(n_{0,j}^{(0,k)}(s)) - \sum_{s_1 \in \mathbb{Z}} \mathcal{T}_k^j \Phi_0(n_{0,j}^{(0,k)}(s_1, 0)) - \sum_{s \in \mathbb{Z}} \Phi_0(n_{0,0}^{(0,0)}(s)). \quad (3.24)$$

Adding (3.24) to (3.23) and noticing that because of the zero-dimensional reduction of the one-dimensional case proved above

$$\sum_{s_1 \in \mathbb{Z}} [\mathcal{T}_k^j \Phi_0(n_j^{(k)}(s_1, 0)) - \mathcal{T}_k^j \Phi_0(n_{0,j}^{(0,k)}(s_1, 0))] = \Phi_0^{(0d)}[\rho], \quad (3.25)$$

we obtain

$$\begin{aligned} \Phi_0^{(2d)}[\rho] &= \Phi_0^{(0d)}[\rho] + \sum_{s \in \mathbb{Z}^2} [\Phi_0(n_{1,0}^{(1,0)}(s)) + \Phi_0(n_{0,0}^{(1,0)}(s))] \\ &\quad + \sum_{s \in \mathbb{Z}^2} [\Phi_0(n_{0,1}^{(0,1)}(s)) + \Phi_0(n_{0,0}^{(0,1)}(s))] \\ &\quad - \sum_{s \in \mathbb{Z}^2} [\Phi_0(n_{1,0}^{(0,0)}(s)) + \Phi_0(n_{0,1}^{(0,0)}(s)) + \Phi_0(n_{0,0}^{(0,0)}(s))]. \end{aligned} \quad (3.26)$$

Thus, the cavity method produces

$$\begin{aligned} \beta \mathcal{F}^{\text{ex}}[\rho] &= \Phi_0^{(2d)}[\rho] - \sum_{s \in \mathbb{Z}^2} [\Phi_0(n_{1,0}^{(1,0)}(s)) + \Phi_0(n_{0,0}^{(1,0)}(s))] \\ &\quad - \sum_{s \in \mathbb{Z}^2} [\Phi_0(n_{0,1}^{(0,1)}(s)) + \Phi_0(n_{0,0}^{(0,1)}(s))] \\ &\quad + \sum_{s \in \mathbb{Z}^2} [\Phi_0(n_{1,0}^{(0,0)}(s)) + \Phi_0(n_{0,1}^{(0,0)}(s)) + \Phi_0(n_{0,0}^{(0,0)}(s))], \end{aligned} \quad (3.27)$$

which is (3.3) for $d = 2$.

The extension of this argument to arbitrary dimension proves that (3.3) is the functional produced by the cavity method. In addition, its consistent dimensional reduction to any lower dimension is also proved.

4. Some applications

In order to show the applicability of the theory exposed in the previous sections, we present the results obtained for some particular two- and three-dimensional systems.

4.1. Hard-square-lattice gas

The hard-square-lattice gas is just the lattice gas with first- and second-nearest-neighbour exclusion in the simple square lattice. This system has been widely studied (Bellemans and Nigam 1967, Ree and Chesnut 1967, Nisbet and Farquhar 1974, Slotte 1983, Baram 1983, Baram and Luban 1987) but no definitive conclusion has been reached about its phase behaviour. The results reported cover the whole spectrum, depending on which theory has been used to study it. Some authors have claimed it to have a second-order transition (Bellemans and Nigam 1967, Slotte 1983), others a weaker (third-order) transition (Bellemans and Nigam 1967, Ree and Chesnut 1967, Baram 1983, Baram and Luban 1987) and others even no transition at all (Bellemans and Nigam 1967, Nisbet and Farquhar 1974, Slotte 1983). Nowadays, the only thing that seems clear is the structure of the ordered phase: periodic along one coordinate axis while uniform along the other (i.e. columnar). However, no simulations have ever been performed in order to clarify the disputed order of the transition.

The result of FM theory is shown in figure 5. The system is found to have a second-order transition from a fluid phase to a columnar phase. The value of the packing fraction at the transition is $\eta_c = 3 - \sqrt{5} = 0.764$ and the chemical potential at this point $(\beta\mu)_c = 2.41$. This result is compatible with that obtained by Bellemans and Nigam (1967) using the method of

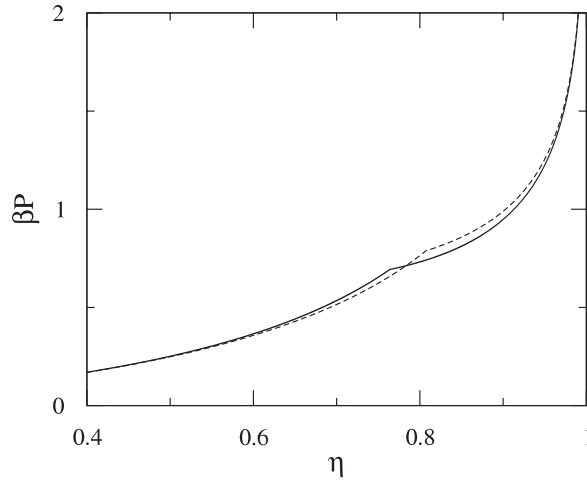


Figure 5. Equation of state (reduced pressure, βP , versus packing fraction, η) from FM theory (solid curve) and from the method of Rushbrooke and Scoins (dashed curve).

Rushbrooke and Scoins (1955). They also found a second-order transition, but at $\eta_c = 0.807$ and $(\beta\mu)_c = 2.85$. The equation of state they obtained with this method is compared with the FM result in figure 5. There is good agreement between the two theories; only in the critical region do the two curves deviate from each other.

It is worth mentioning that within the FM approximation this system is analytically solvable. Omitting the calculations and denoting $L(x) \equiv x \ln x$, we have obtained for the Helmholtz free-energy density of the fluid branch

$$\beta\Phi(\eta) = L(\eta/4) + L(1 - \eta/4) - 2L(1 - \eta/2) + L(1 - \eta), \quad (4.1)$$

and for the columnar branch

$$\beta\Phi(\eta) = \frac{1}{2}[L(\eta_1/2) + L(1 - \eta_1/2) + L(\eta/2 - \eta_1/2) + L(1 - \eta/2 + \eta_1/2) - 2L(1 - \eta/2) - L(1 - \eta + \eta_1) + 2L(1 - \eta)], \quad (4.2)$$

where the occupancy probability of a sublattice is given by

$$\eta_1(\eta) = \frac{\eta}{2} + \sqrt{\frac{\eta^3 - 8\eta^2 + 16\eta - 8}{4\eta}}. \quad (4.3)$$

Clearly more work, either by means of simulations or by other methods, is needed in order to resolve the nature of the transition. This notwithstanding, we do not expect good agreement except at low or high pressures; critical points are difficult (sometimes impossible) to capture, even approximately, with mean-field-like theories such as this one. Nevertheless, we believe the FM approach to be valuable in the sense that it is possible to obtain an analytic approximation, the result obtained is compatible with one previously reported using a different theory and it correctly predicts the structure of the ordered phase.

4.2. Monocomponent and bicomponent hard-cube-lattice gas

We have also applied the theory to three-dimensional systems. In this section we present the results obtained for the monocomponent systems of parallel hard cubes of edge lengths $\sigma = 2$ and 6, as well as for their binary mixture. These being three-dimensional systems,

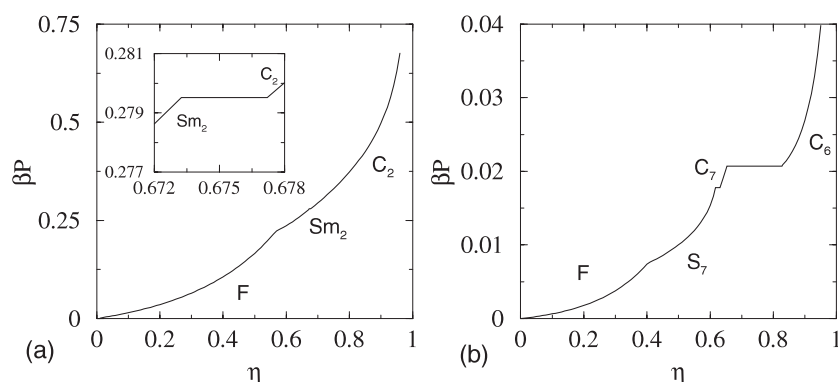


Figure 6. Equation of state obtained from FM theory for the monocomponent hard-cube-lattice gas with edge lengths $\sigma = 2$ (a) and $\sigma = 6$ (b). Phases are labelled F (fluid), Sm_α (smectic) and C_α (columnar), where $\alpha = 2, 6, 7$ represents the ordering period. The inset in (a) shows a very narrow first-order Sm_2 – C_2 transition.

there are three ordered phases that compete in the phase diagrams: smectic (one-dimensional order), columnar (two-dimensional order) and solid (three-dimensional order). The period of the ordering is determined from the wavevector at which the first divergence of the structure factor occurs. In the first case this is π , hence the period is two. As this is also the period of the closest-packed phase it is the only one that is found in stable phases. In the second case the wavevector is $2\pi/7$, implying a period of seven; however, in this case the closest-packed phase has period six, so both period-six and period-seven phases must be considered. The same holds for the binary mixture.

The results for the monocomponent systems are shown in figures 6(a) ($\sigma = 2$) and 6(b) ($\sigma = 6$). The first system undergoes, at $\eta_c = 0.568$, a second-order transition from a fluid phase (F) to a period-two smectic one (Sm_2). At a higher value of the packing fraction the system is found to have a very narrow first-order phase transition, where the smectic phase at $\eta_{\text{Sm}} = 0.673$ coexists with a period-two columnar phase (C_2) at $\eta_c = 0.677$ (see the inset in figure 6(a)). For the $\sigma = 6$ system we find a more complex scenario with several ordered phases, due to the proximity of their free energies. There are six ordered phases in competition: smectic, columnar and solid with periods both six and seven. Only three of them, the two columnar and the period-seven solid, are stable in some region. The other three are just metastable. Again, the columnar phase is the most stable at high density (notice the difference of the high-density ordered phase of these lattice systems with respect to that of the continuum model (Groh and Mulder 2001)). Upon increasing density, the sequence of transitions is as follows: first, a second-order one at $\eta_c = 0.402$ from a fluid phase (F) to a period-seven solid phase (S_7); then a first-order transition in which the S_7 solid coexists, at $\eta_{\text{S}_7} = 0.617$, with a period-seven columnar phase (C_7), at $\eta_{\text{C}_7} = 0.631$; finally, another first-order transition with the C_7 columnar at $\eta_{\text{C}_7} = 0.656$ coexisting with a period-six columnar phase (C_6) at $\eta_{\text{C}_6} = 0.827$. This latter phase extends up to the closest packing.

The competition of different ordered phases in the latter system is remarkable, but it produces a real mess when the two kinds of cube are mixed. The phase diagram for this binary mixture (pressure versus composition) is shown in figure 7. All possible phases are present there. A few particularly complex regions are shown in more detail. Remarkable features of this phase diagram are the very wide F– C_6 phase separation dominating the lower part of the diagram, and the extraordinarily narrow S_6 – C_6 coexistence, extremely close to the

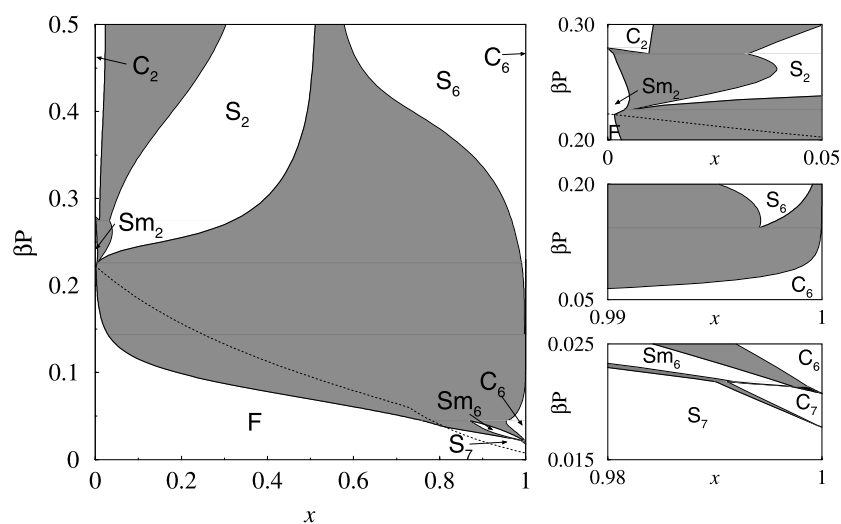


Figure 7. Phase diagram (reduced pressure, βP , versus composition, x) of the lattice binary mixture of hard cubes (size ratio 6:2). Composition is defined by $x = \eta_L/\eta$, where $\eta = \eta_L + \eta_S$ is the total packing fraction of the large (L) and small (S) cubes. Phases are labelled as in figure 6. The dotted curve corresponds to the spinodal of the uniform fluid. For $0.81 \lesssim x$ it marks a stable continuous F– S_7 phase transition.

monocomponent fluid of large cubes. The latter tells us about the proximity of the free energy of the solid phase to that of the columnar in this monocomponent system (a small amount of ‘impurities’ breaks the translational symmetry along the columns of the columnar phase, transforming it into a solid). The former has a very important consequence concerning the demixing scenario for this system.

This binary mixture has been reported, from simulations (Dijkstra and Frenkel 1994), to demix into two fluid phases. As a matter of fact, this is, as far as we know, the only existing evidence of an entropy-driven fluid–fluid demixing in an additive binary mixture. In all other systems of the same kind, e.g. hard spheres (Dijkstra *et al* 1999) or parallel hard cubes in the continuum (Martínez-Ratón and Cuesta 1998, 1999), fluid–fluid demixing is preempted by freezing of (at least) the largest component. Our results contradict this simulations and fit in what seems to be the standard scenario of demixing for additive binary mixtures, namely fluid-ordered phase demixing (the fact that the ordered phase is a columnar is just a peculiarity of the model). A more detailed analysis of this result can be found in Lafuente and Cuesta (2002).

5. Conclusions

In this article we have proposed a formulation of FM theory for lattice models. As mentioned in the introduction, it is not possible just to carry on with Rosenfeld’s original formulation but in discrete space. This is so because of the lack of a scaled-particle theory for lattice models. In fact, FM theory in the continuum can be regarded as a generalization of scaled-particle theory to inhomogeneous phases. For this reason, we believe that the knowledge of a LFMT could guide the derivation of a lattice scaled-particle theory. We are currently working in this direction.

In the recent reformulations of FM theory the scaled-particle equation of state is no longer an input but an output of the theory. Two fundamental ideas appear as the keystone of these formulations: the exact density functional must have a consistent dimensional reduction to any lower dimension and the exact zero-dimensional limit is necessary for the correct description of the freezing transition. The latter turns out to be a very stringent constraint for the functional and seems to contain most of the information needed for the construction of a higher-dimensional functional. In this context, the zero-dimensional cavity method appears as a scheme for the construction of FM functionals. The LFMT we have proposed is the generalization of this method suggested by the exact form of the functional of the one-dimensional mixture of hard rods on a lattice. Although this system has been previously studied in the literature, the originality of our derivation is that this is the first time that the distinction between additive and nonadditive mixtures have been noticed and resolved and the exact functional is written in a form in which the zero-dimensional functional arises naturally. The cavity method can be extended to other particle shapes and other lattice structures. This will be the content of a future work.

We have applied the functional to two- and three-dimensional models and found very reasonable results. In two dimensions these are comparable to those previously obtained by other means, and in three dimensions they agree with previous simulation data, in the case of the mixture (Lafuente and Cuesta 2002), although with an utterly different interpretation, which has yet to be confirmed. One remarkable feature of all three-dimensional models is the very rich and complex phase diagrams they possess (specially the mixture), a complexity which the present theory has nevertheless allowed us to tackle without problems.

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