Criticality in multicomponent spherical models: Results and cautions

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To enable the study of criticality in multicomponent fluids, the standard spherical model is generalized to describe an $\mathcal{S}$-species hard-core lattice gas. On introducing $\mathcal{S}$ spherical constraints, the free energy may be expressed generally in terms of an $\mathcal{S}\times\mathcal{S}$ matrix describing the species interactions. For binary systems, thermodynamic properties have simple expressions, while all the pair correlation functions are combinations of just two eigenmodes. When only hard-core and short-range overall attractive interactions are present, a choice of variables relates the behavior to that of one-component systems. Criticality occurs on a locus terminating a coexistence surface; however, except at some special points, an unexpected "demagnetization effect" suppresses the normal divergence of susceptibilities at criticality and distorts two-phase coexistence. This effect, unphysical for fluids, arises from a general lack of symmetry and from the vectorial and multicomponent character of the spherical model. Its origin can be understood via a mean-field treatment of an *XY* spin system below criticality.

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I. INTRODUCTION

Criticality in liquid-vapor or fluid-fluid phase separation still warrants study: even after the advent of renormalization group theory, and its successful comparisons with experiment, open questions remain. One example is criticality in charged fluids such as electrolytes, molten salts, ionic solutions, etc. The long range of the Coulomb interactions impedes the application of most established methods and the interplay between electrostatic effects and long-range critical fluctuations is not fully understood theoretically. Indeed, the basic issue of the universality class of ionic fluids has been under debate for many years [1] and some questions still remain open. To gain insight into this and related problems, exactly soluble models can be valuable. Indeed, even if a model needs to be considered with circumspection in light of unavoidable simplifications, it may reveal significant features of criticality beyond those established by scaling and renormalization group analyses.

In the history of models in statistical mechanics, the spherical or, equivalently, the mean spherical model [2,3], has played a special role. This "poor man's" Ising model [4,5] has proved to be a mine of information because of its mathematical tractability: Thus only as regards criticality, one can readily investigate [4–6] the role of dimensionality, scaling relations, finite size effects [7], and the influence of long-range integrable interactions (such as $1/r^{d+\sigma}$, where d is the dimension of the space and $\sigma>0$). Consequently the spherical model has been applied in many physical situations, initially ferromagnets and later spin glasses [8], quantum transitions [9], spin kinetics [10], actively mode-locked lasers [11], critical Casimir forces [12], etc. The model became all the more interesting when it appeared [13] that it belongs as a limiting case, $n\to\infty$, to the important class of spin systems in which n is the dimension of the order parameter (with $n=1,2,3,\ldots$ for Ising, *XY*, Heisenberg, … models).

It is natural, therefore, to consider spherical models with long-range Coulombic coupling. A pioneering investigation of a one-component plasma (OCP) spherical model has been undertaken by Smith [14]; but the limitations of an OCP model are well known and, in particular, a gas-liquid transition and corresponding critical behavior cannot be realized. Conversely, to treat electrolyte solutions a realistic model should first represent the neutral solvent, typically water; then two further species, namely, positive and negative ions, must be accounted for. Even if the solvent is appoximated by a uniform, structureless dielectric medium, a colloidal system, for example, requires not only the macroions and their microscopic counterions but also the representation at some level of an ionic salt; thereby a ternary or quaternary system is called for. Accordingly it is desirable to develop spherical models for *multicomponent systems*. That is the aim of this paper. The investigation of the multicomponent model proves interesting in itself although we will focus on the conclusions that can be drawn for simple binary fluids with short-range attractive interactions; applications to ionic fluids are presented elsewhere [15–17].

Explicitly, we address a lattice gas with $\mathcal{S}$ species of particles, labeled $\sigma=1,2,\ldots,\mathcal{S}$, in the grand canonical ensemble. Particles of a given species may occupy or leave vacant sites of only one sublattice so that the displacements separating the different interlaced sublattices introduce the crucial hard-core effects in a direct and transparent manner: see Fig. 1. We will use the vectors $\boldsymbol{\rho}=\{\rho_\sigma\}$, $\mathbf{m}$, $\boldsymbol{\mu}$, $\mathbf{h}$, etc., to denote the corresponding sets of densities, magnetizations, chemical potentials, magnetic fields, etc., for the $\mathcal{S}$ species. Using the correspondence between lattice-gas and Ising spin models, and enforcing the $\mathcal{S}$ distinct spherical conditions with Lagrange multipliers, we extend to this multicomponent situation, the usual spherical model approach. This yields the free energy in terms of an $\mathcal{S}\times\mathcal{S}$ matrix that describes the

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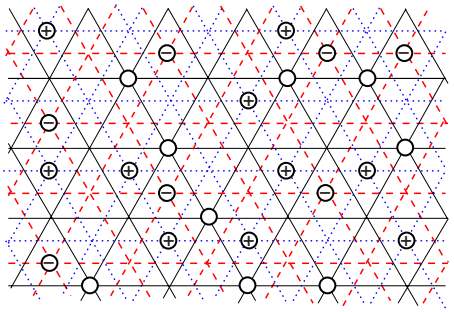

FIG. 1. (Color online) Illustration of a two-dimensional ternary lattice gas with species labeled $\sigma=+,-,0$. Particles of each species occupy only one of the interlacing sublattices shown as dotted, broken, and solid lines, respectively; however, each particle may interact with all others via pairwise potentials $\phi_{\sigma\tau}(\mathbf{R}^{\sigma}-\mathbf{R}^{\tau})$.

pairwise interactions between the different species: see Sec. II below and Eqs. (22)–(28). It transpires that the singular part displays a form similar not only to one-component spherical models but also to Onsager's exact expression for the two-dimensional (2D) Ising model [4,5].

In the case of binary fluids ($\mathcal{S}=2$), considered in Sec. III, major simplifications allow us to obtain explicitly all the thermodynamic and correlation properties in terms of the eigenvalues of the interaction matrix. The density correlations or (for charged fluids) charge correlations for the different species, appear as *combinations* of two eigenmodes. These contributions become uncoupled only in the often considered but usually unrealistic fully symmetric case.

To study critical behavior we go on in Sec. IV to consider systems with only hard cores and sufficiently attractive short-range interactions. With a proper choice of mixing coefficients, one can define $\check{m}$ and $\check{m}^{\dagger}$, two linear combinations of the species mean magnetizations or local densities, so that the usual spherical model critical singularities occur in the $(T,\check{m})$ plane at fixed $\check{m}^{\dagger}$. Thence, a critical locus emerges in the full $(T,\check{m},\check{m}^{\dagger})$ space which, together with a first-order surface, describes the influence of composition on the location of phase separation in the system. Via standard geometric arguments, criticality in the multicomponent model can then be deduced from corresponding one-component systems. Precisely, the same critical universality classes are realized as in short-range (attractive) spherical models.

Nevertheless, a significant difference arises in the *equation of state* where a new, unexpected mixing term appears. This can be understood heuristically as a type of demagnetization effect arising as a consequence of the vectorial character of the model coupled to asymmetry and multispecies features. This term indeed suppresses the normal divergence of susceptibilities at criticality; furthermore, it induces a linear dependence of the chemical potential and pressure as functions of the total density in the two-phase region! These are certainly undesirable and unphysical features of any fluid model. This wayward behavior reinforces the remark [18] that, because of the *de facto* vectorial character of the order parameter in spherical models, their predictions must be handled with perspicacity when modeling fluids.

To gain some further insight into this unanticipated "demagnetization effect" we study in Sec. V an *XY* model beneath T_c using a mean-field approach in which the vectorial character of the order parameter, coupled to an asymmetry of the external fields, leads transparently to a very similar demagnetization effect. Finally, some general conclusions are drawn in Sec. VI and we remind readers that detailed applications to systems with long-range Coulomb potentials have been undertaken [17].

II. MULTICOMPONENT SPHERICAL MODELS

A. Fluid and spin systems

We consider a d-dimensional lattice fluid in the grand-canonical ensemble that consists of $\mathcal{S}$ species labeled $\sigma=1,\ldots,\mathcal{S}$, each being associated explicitly with only one of $\mathcal{S}$ identical interlaced sublattices (see Fig. 1). Every sublattice is taken as the image of a periodic reference sublattice $\mathcal{R}^0$ after translation by a vector $\boldsymbol{\delta}^{\sigma}$ so that every site i on a lattice σ is characterized by a position $\mathbf{R}_i^{\sigma}=\mathbf{R}_i^0+\boldsymbol{\delta}^{\sigma}$. The reference sublattice is generated by the vectors $\mathbf{a}_{\alpha}$ $(\alpha=1,\ldots,d)$, has a unit cell volume v_0 and contains $\mathcal{N}=\Pi_{\alpha}N_{\alpha}$ sites at positions $\mathbf{R}_i^0=\Sigma_{\alpha}\tilde{R}_{i,\alpha}^0\mathbf{a}_{\alpha}$ specified by the integers $\tilde{R}_{i,\alpha}^0=1,2,\ldots,N_{\alpha}$.

It is well known that a grand-canonical lattice fluid is in correspondence with a canonical spin system [19]. Indeed, let us write the grand partition function of a fluid as

$$\Xi(T,\boldsymbol{\mu})=\prod_{\sigma}\left(\sum_{N_{\sigma}}\frac{1}{N_{\sigma}!}\sum_{\mathbf{r}_i^{\sigma}}\right)\exp\left[-\beta\left(\mathcal{H}^{\mathrm{gas}}-\sum_{\tau}\mu_{\tau}N_{\tau}\right)\right], \tag{1}$$

where β is the inverse temperature $1/k_BT$, while N_{σ} and μ_{σ} denote the number of particles and chemical potential of species σ. The Hamiltonian $\mathcal{H}^{\mathrm{gas}}$ is expressed as a sum over particles $k=1,\ldots,n^{\sigma}$ and $l=1,\ldots,n^{\tau}$ as

$$\mathcal{H}^{\mathrm{gas}}=\frac{1}{2}\sum_{(\sigma,k)\neq(\tau,l)}\varphi_{\sigma\tau}(\mathbf{r}_k^{\sigma}-\mathbf{r}_l^{\tau}), \tag{2}$$

where $\varphi_{\sigma\tau}$ is the pair interaction potential while $\mathbf{r}_k^{\sigma}$ is the position of the kth particle of species σ, occupying sites on the lattice σ. Considering a system with hard cores, i.e., $\varphi_{\sigma\sigma}(\mathbf{0})=+\infty$, the sum in (1) refers to configurations where the local lattice density $n_{\sigma}(\mathbf{R}_i^{\sigma})=\Sigma_k\delta(\mathbf{R}_i^{\sigma}-\mathbf{r}_k^{\sigma})$ can be only 0 or 1, so that the local spin variable

$$s_{\sigma}(\mathbf{R}_i^{\sigma})=2n_{\sigma}(\mathbf{R}_i^{\sigma})-1 \tag{3}$$

takes the values ±1 as in the Ising model. A straightforward generalization of the procedure described in [19] then leads to the partition function of a spin system, namely,

$$\Xi(T,\boldsymbol{\mu})=\prod_{\sigma}\sum_{s_{\sigma}(\mathbf{R}_i^{\sigma})=\pm1}\exp(-\beta\mathcal{H}^{\mathrm{spin}}), \tag{4}$$

where the spin Hamiltonian is

$$\mathcal{H}^{\text{spin}} = -\frac{1}{2}\sum_{(\sigma,i),(\tau,j)} J_{\sigma\tau}(\mathbf{R}_i^\sigma - \mathbf{R}_j^\tau) s_\sigma(\mathbf{R}_i^\sigma) s_\tau(\mathbf{R}_j^\tau) - \sum_\sigma h_\sigma \sum_i s_\sigma(\mathbf{R}_i^\sigma) + \mathcal{H}_o(\boldsymbol{\mu}). \quad (5)$$

In this correspondence, the link between the coupling energies and pair interactions is

$$J_{\sigma\tau}(\mathbf{R}_i^\sigma - \mathbf{R}_j^\tau) = -\tfrac{1}{4}\varphi_{\sigma\tau}(\mathbf{R}_i^\sigma - \mathbf{R}_j^\tau) \quad \text{if } \mathbf{R}_i^\sigma \neq \mathbf{R}_j^\tau, \quad (6)$$

with $J_{\sigma\sigma}(\mathbf{0})=\mathbf{0}$, while the external fields are given by

$$h_\sigma = \tfrac{1}{2}\mu_\sigma - \tfrac{1}{4}\phi_\sigma, \quad (7)$$

with reference level

$$\phi_\sigma = \sum_{(\tau,j)\neq(\sigma,i_0)} \varphi_{\sigma\tau}(\mathbf{R}_{i_0}^\sigma - \mathbf{R}_j^\tau), \quad (8)$$

where i_0 is a fixed position. Finally, the background term in (5) is merely

$$\mathcal{H}_o(\boldsymbol{\mu}) = -\frac{1}{2}\mathcal{N}\sum_\sigma \mu_\sigma + \frac{1}{8}\sum_{(\sigma,i)\neq(\tau,j)} \varphi_{\sigma\tau}(\mathbf{R}_i^\sigma - \mathbf{R}_j^\tau). \quad (9)$$

The correspondence between fluid and spin systems follows straightforwardly for the other properties. For instance, the local density $\rho_\sigma(\mathbf{r})=n_\sigma(\mathbf{r})/v_0$ is related to the local spin via

$$v_0\rho_\sigma(\mathbf{R}_i^\sigma) = \tfrac{1}{2}[s_\sigma(\mathbf{R}_i^\sigma)+1], \quad (10)$$

while the species correlation functions

$$G_{\sigma\tau}(\mathbf{R}_i^\sigma - \mathbf{R}_j^\tau; T, \boldsymbol{\mu}) = \langle \rho_\sigma(\mathbf{R}_i^\sigma)\rho_\tau(\mathbf{R}_j^\tau)\rangle - \langle \rho_\sigma(\mathbf{R}_i^\sigma)\rangle\langle \rho_\tau(\mathbf{R}_j^\tau)\rangle \quad (11)$$

are related to spin correlations via

$$v_0^2 G_{\sigma\tau}(\mathbf{R}_i^\sigma - \mathbf{R}_j^\tau; T, \boldsymbol{\mu}) = \tfrac{1}{4}[\langle s_\sigma(\mathbf{R}_i^\sigma)s_\tau(\mathbf{R}_j^\tau)\rangle - \langle s_\sigma(\mathbf{R}_i^\sigma)\rangle\langle s_\tau(\mathbf{R}_j^\tau)\rangle]. \quad (12)$$

As usual, the angular brackets denote grand-canonical expectation values.

In order to define density or charge correlations simply in this lattice geometry, it is convenient to work in Fourier space. We consider periodic boundary conditions and define Fourier series with respect to the reference sublattice $\mathcal{R}^0$ by

$$\hat{s}_\sigma(\mathbf{k}) = \sum_i e^{-i\mathbf{k}\cdot\mathbf{R}_i^\sigma} s_\sigma(\mathbf{R}_i^\sigma). \quad (13)$$

Then, when $J_{\sigma\tau}$ is periodic over the reference sublattice, we may write

$$\hat{J}_{\sigma\tau}(\mathbf{k}) = \sum_i e^{-i\mathbf{k}\cdot(\mathbf{R}_i^\sigma - \mathbf{R}_{j_0}^\tau)} J_{\sigma\tau}(\mathbf{R}_i^\sigma - \mathbf{R}_{j_0}^\tau) = \sum_j e^{-i\mathbf{k}\cdot(\mathbf{R}_{i_0}^\sigma - \mathbf{R}_j^\tau)} J_{\sigma\tau}(\mathbf{R}_{i_0}^\sigma - \mathbf{R}_j^\tau), \quad (14)$$

with any fixed positions i_0 and j_0. The wave vectors should be combinations of the reciprocal vectors $\mathbf{b}_\alpha$ (defined by $\mathbf{a}_\alpha\cdot\mathbf{b}_{\alpha'}=2\pi\delta_{\alpha,\alpha'}$) such as $\mathbf{k}=\Sigma_\alpha \tilde{k}_\alpha \mathbf{b}_\alpha$ with $\tilde{k}_\alpha=0,\ \pm 1/N_\alpha,\ \pm 2/N_\alpha,\ldots$. In the following, the first Brillouin zone is denoted as $\mathcal{B}$. The density correlation function G_{NN}, and, for fluids of particles carrying charges q_σ, charge G_{ZZ} and charge-density G_{NZ} correlations can then be defined via

$$\hat{G}_{XY}(\mathbf{k}; T, \boldsymbol{\rho}) = \sum_{\sigma,\tau} q_\sigma^{\vartheta_X} q_\tau^{\vartheta_Y} \hat{G}_{\sigma\tau}(\mathbf{k}; T, \boldsymbol{\rho}), \quad (15)$$

where X and Y stand for either N or Z, with $\vartheta_{\mathcal{N}}=0$, $\vartheta_{\mathcal{Z}}=1$. We also define structure factors as

$$S_{XY}(\mathbf{k}; T, \boldsymbol{\rho}) = \frac{v_0}{\rho q^{\vartheta_X+\vartheta_Y}} \hat{G}_{XY}(\mathbf{k}; T, \boldsymbol{\rho}), \quad (16)$$

where q is an elementary charge, while the total density is $\rho=\Sigma_\sigma\langle\rho_\sigma\rangle$. The term v_0 compensates here for the homogeneity difference between the discrete and continuum Fourier transforms.

B. Mean spherical model

We are not able to perform the multiple sums in (4) in general. Instead, we adopt the appropriate mean spherical model [3] and compute the multiple integral

$$\Xi'(T,\mathbf{h}) = \int \prod_\sigma ds_\sigma e^{-\beta\mathcal{H}'}, \quad (17)$$

with

$$\mathcal{H}' = \mathcal{H}^{\text{spin}} + \sum_\sigma \tilde{\lambda}_\sigma \sum_i s_\sigma^2(\mathbf{R}_i^\sigma). \quad (18)$$

As usual, the Lagrange multipliers $\tilde{\lambda}_\sigma$ are introduced to allow imposition of the mean spherical conditions which need to be enforced uniformly for every species; specifically, the relations

$$\left\langle \sum_i s_\sigma^2(\mathbf{R}_i^\sigma) \right\rangle = \mathcal{N}, \quad \sigma = 1, \ldots, \mathcal{S}, \quad (19)$$

define the Lagrange multipliers or *spherical fields* $\tilde{\lambda}_\sigma$ as implicit functions of $(T,\mathbf{h})$. Consequently, the free energy per site (of the reference sublattice) is

$$-\beta f[T,\mathbf{h},\boldsymbol{\lambda}(T,\mathbf{h})] = \ln \Xi'(T,\mathbf{h})/\mathcal{N}, \quad (20)$$

in terms of which the spherical conditions (19) can be rewritten as

$$\langle s_\sigma^2\rangle = \left.\frac{\partial f}{\partial \tilde{\lambda}_\sigma}\right|_{T,\mathbf{h},\tilde{\lambda}_{\tau};\tau\neq\sigma} = 1, \quad \sigma = 1, \ldots, \mathcal{S}. \quad (21)$$

As already remarked in Sec. I, the spherical model in this form describes exactly spin models with fixed length or continuous n-component spins in the limit $n\to\infty$ with appropriate scalings [13,20].

As is standard [3], the calculation of Ξ' is performed in Fourier space. For consistency, we will suppose that $J_{\sigma\tau}$ satisfies the symmetry condition $J_{\sigma\tau}(\mathbf{R}_i^\sigma - \mathbf{R}_j^\tau) = J_{\sigma\tau}[-(\mathbf{R}_i^\sigma - \mathbf{R}_j^\tau)]$. The calculation is then a straightforward generalization of the mean spherical techniques used for single-species systems. The free energy per site can be decomposed into a sum of three parts: $f=f_s+f_h+f_o$. The singular part of the free energy is

$$-\beta f_s(T,\mathbf{h}) = -\frac{1}{2\mathcal{N}}\sum_{\mathbf{k}\in\mathcal{B}} \ln\{\beta^{\mathcal{S}}\mathrm{Det}[\mathbf{\Lambda}(\mathbf{k};\boldsymbol{\lambda})]\}, \tag{22}$$

where the sum runs over the reference Brillouin zone $\mathcal{B}$ while $\mathbf{\Lambda}(\mathbf{k};\boldsymbol{\lambda})$ is the $\mathcal{S}\times\mathcal{S}$ interaction matrix with elements

$$\Lambda_{\sigma\tau}(\mathbf{k};\boldsymbol{\lambda}) = \delta_{\sigma,\tau}[\lambda_\sigma + \Delta\hat{J}_{\sigma\sigma}(\mathbf{k})] - \tfrac{1}{2}(1-\delta_{\sigma,\tau})\hat{J}_{\sigma\tau}(\mathbf{k}), \tag{23}$$

in which for any function $\hat{g}(\mathbf{k})$ we employ the notation

$$\Delta\hat{g}(\mathbf{k}) = \tfrac{1}{2}[\hat{g}(\mathbf{0}) - \hat{g}(\mathbf{k})], \tag{24}$$

while, dropping the tildes in (18) and (21), the shifted or net spherical fields are

$$\lambda_\sigma = \tilde{\lambda}_\sigma - \tfrac{1}{2}\hat{J}_{\sigma\sigma}(\mathbf{0}). \tag{25}$$

On the other hand, the h-dependent part of the free energy is given by

$$-\beta f_h(T,\mathbf{h}) = \tfrac{1}{4}\beta\langle\mathbf{h}|\mathbf{\Lambda}^{-1}(\mathbf{0},\boldsymbol{\lambda})|\mathbf{h}\rangle, \tag{26}$$

while the analytic background part, following from (9), is

$$-\beta f_o(T,\mathbf{h}) = \tfrac{1}{2}\mathcal{S}\ln\pi - \beta\mathcal{H}_o/\mathcal{N}, \tag{27}$$

which will be neglected henceforth. Because of the logarithm in (22), these results are valid while the eigenvalues of the matrices $\mathbf{\Lambda}(\mathbf{k};\boldsymbol{\lambda})$ are positive for every $\mathbf{k}$; when one vanishes, the expressions (22) and (26) become singular and phase transitions are implicated.

The last step is taking the thermodynamic limit $\mathcal{N}\to\infty$ (valid provided the Fourier transforms remain well defined), with the result

$$-\beta f_s(T,\mathbf{h}) = -\frac{1}{2}\int_{\mathbf{k}} \ln\{\beta^{\mathcal{S}}\mathrm{Det}[\mathbf{\Lambda}(\mathbf{k};\boldsymbol{\lambda})]\}, \tag{28}$$

where $\int_{\mathbf{k}}$ is a shorthand notation for $\int_{\mathbf{k}\in\mathcal{B}} v_0 d^d\mathbf{k}/(2\pi)^d$, while the $\mathbf{h}$-dependent free energy f_h is still given by [26]. At this point, it is worth noting that the structure of f_s, as an integral over the Brillouin zone of the logarithm of the interactions in Fourier space, is similar to that present in Onsager's exact solution of the 2D Ising model [21]. The consequences for charged systems are dramatic [15–17] since this form determines the coupling or decoupling of correlations in symmetric and asymmetric systems.

With these results in hand, we find that the mean particle densities $\rho_\sigma = \langle\rho_\sigma(\mathbf{R}_i^\sigma)\rangle$ are related to the mean magnetizations via

$$2\rho_\sigma v_0 - 1 = m_\sigma = \langle s_\sigma\rangle = -\left.\frac{\partial f_h}{\partial h_\sigma}\right|_{T,h_\tau\boldsymbol{\lambda};\tau\neq\sigma}, \tag{29}$$

which, in turn, enter the free energy in standard manner as

$$f_h = -\frac{1}{2}\sum_\sigma m_\sigma h_\sigma. \tag{30}$$

As a result of (26) and (29), the link between $\mathbf{h}$ and $\mathbf{m}$ is then merely

$$\mathbf{h} = \tfrac{1}{2}\boldsymbol{\mu} - \tfrac{1}{4}\boldsymbol{\phi} = 2\mathbf{\Lambda}(\mathbf{0})\mathbf{m}, \tag{31}$$

where $\boldsymbol{\mu}=\{\mu_\sigma\}$ and we have recalled (7) and introduced a fixed vector $\boldsymbol{\phi}=\{\phi_\sigma\}$: see (8). Finally, in the thermodynamic limit, the spin-spin correlation functions are given by

$$\langle s_\sigma(\mathbf{R}_i^\sigma)s_\tau(\mathbf{R}_j^\tau)\rangle = -\frac{1}{2-\delta_{\sigma,\tau}}\left.\frac{\partial(f-f_o)}{\partial J_{\sigma\tau}(\mathbf{R}_i^\sigma-\mathbf{R}_j^\tau)}\right|_{T,\mathbf{h},\boldsymbol{\lambda}}, \tag{32}$$

where $2-\delta_{\sigma,\tau}$ is merely a symmetry factor, while we recall (12) for the density correlation functions $G_{\sigma\tau}$.

III. BINARY SYSTEMS

The previous analysis holds for an arbitrary number of species. From here on, however, we focus on the simplest case, i.e., binary mixtures with species labels 1 and 2. For many properties, it is useful to decompose densities, chemical potentials, etc., in terms of means and differences; so for every function g_σ (or $g_{\sigma\sigma}$) we define

$$\bar{g} = \tfrac{1}{2}(g_1+g_2), \quad g^\dagger = \frac{1}{2}(g_1-g_2). \tag{33}$$

Moreover, for simplicity, we suppose that the translation vectors $\boldsymbol{\delta}^\sigma = \Sigma_\alpha\tilde{\delta}_\alpha\mathbf{a}_\alpha$ satisfy $\tilde{\delta}_\alpha = 0$ or $1/2$ so that the Fourier transforms $\hat{J}_{\sigma\tau}$ are real.

A. Basic features

For the case $\mathcal{S}=2$, simplifications allow more explicit results. First, let us introduce the energy scale

$$j_0 = \tfrac{1}{2}\hat{J}_{12}(\mathbf{0}), \tag{34}$$

and, following (33), write

$$\Delta\bar{J}(\mathbf{k}) = \tfrac{1}{2}(\Delta J_{11} + \Delta J_{22}), \tag{35a}$$

$$\Delta J^\dagger(\mathbf{k}) = \tfrac{1}{2}(\Delta J_{11} - \Delta J_{22}). \tag{35b}$$

Then the eigenvalues of the 2×2 matrix $\mathbf{\Lambda}$ may be written

$$\Lambda_\pm(\mathbf{k};\boldsymbol{\lambda}) = \bar{\lambda} + \Delta\bar{J}(\mathbf{k}) \pm D(\mathbf{k};\boldsymbol{\lambda}), \tag{36}$$

where

$$D(\mathbf{k};\boldsymbol{\lambda}) = \sqrt{[\lambda^\dagger + \Delta J^\dagger(\mathbf{k})]^2 + \tfrac{1}{4}[\hat{J}_{12}(\mathbf{k})]^2} \geqslant 0. \tag{37}$$

As remarked above, these expressions are valid when Λ_- and Λ_+ are nonnegative while singularities arise only when $\Lambda_-(\mathbf{k};\boldsymbol{\lambda})[\leqslant\Lambda_+(\mathbf{k};\boldsymbol{\lambda})]\to 0$.

Now the argument of the free energy integral in (28) is $\ln\{\beta^2\mathrm{Det}[\mathbf{\Lambda}]\}$, where the determinant of the interaction matrix can now be written

$$\Lambda_-\Lambda_+(\mathbf{k};\boldsymbol{\lambda}) = u + 2\bar{\lambda}\Delta\bar{J}(\mathbf{k}) - 2\lambda^\dagger\Delta J^\dagger(\mathbf{k}) + \Delta J^2(\mathbf{k}), \tag{38}$$

where we have introduced the crucial parameter

$$u(\boldsymbol{\lambda}) \equiv \Lambda_-\Lambda_+(\mathbf{0};\boldsymbol{\lambda}) = \bar{\lambda}^2 - \lambda^{\dagger 2} - j_0^2, \tag{39}$$

which vanishes when $\mathrm{Det}[\mathbf{\Lambda}(\mathbf{k})]$ vanishes at $\mathbf{k}=\mathbf{0}$, while the squared interaction term in (38), namely,

$$\Delta J^2(\mathbf{k}) = j_0^2 - \tfrac{1}{4}\hat{J}_{12}^2(\mathbf{k}) + \Delta\hat{J}_{11}(\mathbf{k})\Delta\hat{J}_{22}(\mathbf{k}), \tag{40}$$

vanishes as $|\mathbf{k}^2|$.

In terms of the eigenvalues, the spherical conditions (21) become

$$1 = \frac{1}{2}k_BT\int_{\mathbf{k}} \frac{\lambda_\sigma + \Delta\hat{J}_{\sigma\sigma}(\mathbf{k})}{\Lambda_-\Lambda_+(\mathbf{k};\boldsymbol{\lambda})} + m_\tau^2, \quad \tau \neq \sigma. \tag{41}$$

Finally, the h-dependent part of the free energy entails

$$\boldsymbol{\Lambda}^{-1}(\mathbf{0};\boldsymbol{\lambda}) = \frac{1}{\Lambda_-\Lambda_+(\mathbf{0};\boldsymbol{\lambda})}\begin{pmatrix} \lambda_2 & j_0 \\ j_0 & \lambda_1 \end{pmatrix}, \tag{42}$$

while the magnetization-field or density-chemical potential relation (31) becomes

$$\tfrac{1}{2}h_\sigma = m_\sigma\lambda_\sigma - m_\tau j_0, \quad \tau \neq \sigma. \tag{43}$$

At this point, Eqs. (34)–(43) entirely define the system and the need is to analyze their structure and consequences.

B. Correlation functions

The density pair correlation functions are given generally by (12) and (32) which, when $\mathcal{S}=2$, reduce to

$$\hat{G}_{\sigma\sigma}(\mathbf{k};\boldsymbol{\lambda}) = \frac{k_BT}{8v_0^2}\frac{\lambda_\sigma + \Delta\hat{J}_{\sigma\sigma}(\mathbf{k})}{\Lambda_-\Lambda_+(\mathbf{k};\boldsymbol{\lambda})} \quad (\sigma = 1,2), \tag{44}$$

$$\hat{G}_{12}(\mathbf{k};\boldsymbol{\lambda}) = \frac{k_BT}{16v_0^2}\frac{\hat{J}_{12}(\mathbf{k})}{\Lambda_-\Lambda_+(\mathbf{k};\boldsymbol{\lambda})} = \hat{G}_{21}(\mathbf{k};\boldsymbol{\lambda}). \tag{45}$$

In terms of these, one can use (15) to obtain the overall density-density correlation function $\hat{G}_{NN}$ and the complementary compositional correlations or, for charged systems, the charge-charge correlation function $\hat{G}_{ZZ}$.

From a purely mathematical perspective, it is also instructive to decompose the fluctuations with respect to the eigenvectors of $\boldsymbol{\Lambda}$ which, of course, depend on the wave vector $\mathbf{k}$ and the fields $\boldsymbol{\lambda}$. Thus if we define $\phi(\mathbf{k})$ via

$$\tan\phi(\mathbf{k}) = 2\{D(\mathbf{k};\boldsymbol{\lambda}) - [\lambda^\dagger + \Delta J^\dagger(\mathbf{k})]\}/\hat{J}_{12}(\mathbf{k}), \tag{46}$$

it can be interpreted as the angle determined by the eigenvector associated with $\Lambda_+(\mathbf{k};\boldsymbol{\lambda})$ relative to the $\sigma=1$ axis. Then if we introduce the density fluctuations $\rho^+(\mathbf{k};\boldsymbol{\lambda})$ and $\rho^-(\mathbf{k};\boldsymbol{\lambda})$ via

$$\rho^\pm = [\rho_1\cos\phi(\mathbf{k};\boldsymbol{\lambda}) \mp \rho_2\sin\phi(\mathbf{k};\boldsymbol{\lambda})]/\sqrt{2}, \tag{47}$$

and define the corresponding correlation function $\hat{G}_{\pm\pm}$ in the natural way, we find

$$\hat{G}_{++}(\mathbf{k};\boldsymbol{\lambda}) = \frac{k_BT}{16v_0^2}\frac{1}{\Lambda_+(\mathbf{k};\boldsymbol{\lambda})}, \tag{48a}$$

$$\hat{G}_{--}(\mathbf{k};\boldsymbol{\lambda}) = \frac{k_BT}{16v_0^2}\frac{1}{\Lambda_-(\mathbf{k};\boldsymbol{\lambda})}, \tag{48b}$$

while $\hat{G}_{+-}=\hat{G}_{-+}$ vanishes identically.

However, the eigenmodes (47) will rarely be of direct physical significance. Rather the physically accessible fluctuations, represented in particular by the structure functions introduced in (15) and (16), will typically involve a *mixture* of the underlying eigenmodes. Specifically we find

$$\frac{S_{NN}(\mathbf{k};T,\boldsymbol{\rho})}{k_BT/4\rho v_0} = \frac{B(\mathbf{k};\boldsymbol{\lambda})}{\Lambda_-(\mathbf{k};\boldsymbol{\lambda})} + \frac{1-B(\mathbf{k};\boldsymbol{\lambda})}{\Lambda_+(\mathbf{k};\boldsymbol{\lambda})}, \tag{49a}$$

and, for charged systems with $q_+=-q_-=q$,

$$\frac{S_{ZZ}(\mathbf{k};T,\boldsymbol{\rho})}{k_BT/4\rho v_0} = \frac{B(\mathbf{k};\boldsymbol{\lambda})}{\Lambda_+(\mathbf{k};\boldsymbol{\lambda})} + \frac{1-B(\mathbf{k};\boldsymbol{\lambda})}{\Lambda_-(\mathbf{k};\boldsymbol{\lambda})}, \tag{49b}$$

where the mixing amplitude B is

$$B(\mathbf{k};\boldsymbol{\lambda}) = \tfrac{1}{2} + \tfrac{1}{4}\hat{J}_{12}(\mathbf{k})/D(\mathbf{k};\boldsymbol{\lambda}). \tag{50}$$

Evidently, singular behavior, anticipated at criticality in $\Lambda_-(\mathbf{k};\boldsymbol{\lambda})$, will in general affect *both* S_{NN} and S_{ZZ} as we discuss in detail elsewhere [15–17].

However, a special situation arises when the two species 1 and 2 are symmetrically related so that $\hat{J}_{11}(\mathbf{k})=\hat{J}_{22}(\mathbf{k})$ which implies, via (35b), $\Delta J^\dagger(\mathbf{k})\equiv 0$. For a charged system this corresponds to complete charge symmetry as exemplified most simply in the *restricted primitive model* (RPM) of equisized hard spheres with charges of equal magnitude but opposite sign. But neutral systems where species 1 and 2 differ only in chirality demand a symmetric description quite naturally. Then, on the locus of symmetry where $\rho_1=\rho_2$ (corresponding to electroneutrality in 1:1 ionic fluids) one has $\mu_1=\mu_2$ and, hence, via (31), $\lambda_1=\lambda_2$ and thence, via (33), $\lambda^\dagger\equiv 0$. In this case one sees from (50) that $B(\mathbf{k};\boldsymbol{\lambda})$ vanishes identically so that the eigenmodes precisely specify S_{NN} and S_{ZZ} which, therefore, become totally *decoupled*! This turns out to play a crucial role in the study of charge screening near ionic criticality [15–17] albeit for generally unrealistic charge-symmetric systems.

A small technical detail deserves mention in this fully symmetric case if $\hat{J}_{12}(\mathbf{k})$ should change sign for $\mathbf{k}\neq\mathbf{0}$ (which is not unreasonable); then the ratio $\hat{J}_{12}/D(\mathbf{k};\boldsymbol{\lambda})$ in (50) together with Λ_+ and Λ_- involve nonanalytic absolute values but in such a way that the combinations S_{NN} and S_{ZZ} in (49a) and (49b) remain completely analytic.

Finally, the cross charge-density structure function is also expressible as a combination of the two eigenmodes via

$$\frac{S_{NZ}(\mathbf{k};T,\boldsymbol{\rho})}{k_BT/8v_0\rho} = \frac{\lambda^\dagger + \Delta J^\dagger(\mathbf{k})}{D(\mathbf{k};\boldsymbol{\lambda})}\left[\frac{1}{\Lambda_-(\mathbf{k};\boldsymbol{\lambda})} - \frac{1}{\Lambda_+(\mathbf{k};\boldsymbol{\lambda})}\right]. \tag{51}$$

As is to be anticipated, this vanishes identically on the symmetry locus when (1, 2) symmetry is present.

C. Appropriately mixed thermodynamic variables

Depending on the symmetry of the system, the previous relations may be handled more or less conveniently. In the general asymmetric case ($\hat{J}_{11}\neq\hat{J}_{22}$), the spherical constraints (41) can be rewritten as

$$1 = \frac{1}{2} k_B T \int_{\mathbf{k}} \frac{\bar{\lambda} + \Delta \bar{J}(\mathbf{k})}{\Lambda_- \Lambda_+(\mathbf{k};\boldsymbol{\lambda})} + m^2 + m^{\dagger 2} \tag{52}$$

and

$$2mm^\dagger = \frac{1}{2} k_B T \int_{\mathbf{k}} \frac{\lambda^\dagger + \Delta J^\dagger(\mathbf{k})}{\Lambda_- \Lambda_+(\mathbf{k};\boldsymbol{\lambda})}, \tag{53}$$

while the external fields are given by

$$\bar{h} = 2[m(\bar{\lambda} - j_0) + m^\dagger \lambda^\dagger], \tag{54a}$$

$$h^\dagger = 2[m\lambda^\dagger + m^\dagger(\bar{\lambda} + j_0)]. \tag{54b}$$

Note that, since Λ_- and Λ_+ are nonnegative, the condition (52) is consistent with the expectations $|m| \leqslant 1$ and $|m^\dagger| \leqslant 1$.

For further analysis it is convenient to introduce the basic integral functions

$$\mathcal{G}(\boldsymbol{\lambda}) = \frac{1}{2} \int_{\mathbf{k}} \frac{1}{\Lambda_- \Lambda_+(\mathbf{k};\boldsymbol{\lambda})}, \tag{55}$$

$$\mathcal{L}_\sigma(\boldsymbol{\lambda}) = \frac{1}{2} \int_{\mathbf{k}} \frac{\Delta \hat{J}_{\sigma\sigma}(\mathbf{k})}{\Lambda_- \Lambda_+(\mathbf{k};\boldsymbol{\lambda})}, \tag{56}$$

which are simple generalizations of the typical integrals involved in the analysis of standard spherical models.

Now, in the fully symmetric case, $\Delta J^\dagger$, $\lambda^\dagger$, and $m^\dagger$ vanish identically so that the relations (53) and (54b) have no role to play. Then (52) and (54a) closely resemble the basic expressions for the single-species ($\mathcal{S}=1$) or standard spherical model. These in turn lead to the basic *equation of state* which, in terms of the reduced temperature variable

$$t = (T - T_c)/T_c, \tag{57}$$

can be written most transparently near the critical point ($T = T_c$, $m=0$) as [4–6]

$$p_0 u^{1/\gamma} \approx c_t t + c_m m^2, \tag{58}$$

where, recalling (39), $u = \bar{\lambda}^2 - j_0{}^2$ while $\gamma \geqslant 1$ is the fundamental dimensionality-dependent exponent, and p_0, c_t, and c_m are fixed positive coefficients.

Now physicochemical insight into the behavior of binary fluid mixtures suggests strongly that their critical behavior will, when expressed in terms of suitable density and field variables, be essentially the same as for a single-component fluid. However, the "suitable" or "appropriate" variables will, in leading order, be linear combinations or mixtures of the related binary thermodynamic variables, specifically, the fields and densities. Furthermore, the appropriate mixing coefficients must, in general, be *nontrivial* functions of the state variables.

It follows that our primary task now is to find what the appropriate mixing coefficients are. To that end, we introduce the general linear combinations

$$\check{\lambda} = \tfrac{1}{2}(\theta^{-1}\lambda_1 + \theta\lambda_2), \quad \check{\lambda}^\dagger = \tfrac{1}{2}(\theta^{-1}\lambda_1 - \theta\lambda_2), \tag{59}$$

together with corresponding remixed interactions

$$\Delta\check{J}, \Delta\check{J}^\dagger = \tfrac{1}{2}(\theta^{-1}\Delta J_{11} \pm \theta \Delta J_{22}). \tag{60}$$

The mixing parameter θ is to be determined later. In terms of these new variables and interactions, the basic determinant becomes

$$\mathrm{Det}[\boldsymbol{\Lambda}] = u + 2\check{\lambda}\Delta\check{J}(\mathbf{k}) - 2\check{\lambda}^\dagger \Delta\check{J}^\dagger(\mathbf{k}) + \Delta J^2(\mathbf{k}), \tag{61}$$

where, following (39), the value at $\mathbf{k}=\mathbf{0}$ is now

$$u(\lambda_1, \lambda_2) = \check{\lambda}^2 - \check{\lambda}^{\dagger 2} - j_0^2. \tag{62}$$

Then it proves necessary to introduce a second state-dependent mixing parameter θ_m by writing

$$\check{m}, \check{m}^\dagger = \tfrac{1}{2}(\theta_m^{-1} m_1 \pm \theta_m m_2). \tag{63}$$

In terms of these new variables and the integrals (55) and (56), the original spherical conditions (41) become

$$1 = \theta^{-1} k_B T(\check{\lambda} - \check{\lambda}^\dagger)\mathcal{G}(\boldsymbol{\lambda}) + \mathcal{L}_2(\boldsymbol{\lambda}) k_B T + \theta_m^2(\check{m}^2 + \check{m}^{\dagger 2} + 2\check{m}\check{m}^\dagger), \tag{64a}$$

$$1 = \theta k_B T(\check{\lambda} + \check{\lambda}^\dagger)\mathcal{G}(\boldsymbol{\lambda}) + \mathcal{L}_1(\boldsymbol{\lambda}) k_B T + \theta_m^{-2}(\check{m}^2 + \check{m}^{\dagger 2} - 2\check{m}\check{m}^\dagger). \tag{64b}$$

Finally, it is helpful to define new external fields via

$$\check{h} = \tfrac{1}{2}(\theta_h^{-1} h_1 + \theta_h h_2), \quad \check{h}^\dagger = \tfrac{1}{2}(\theta_h^{-1} h_1 - \theta_h h_2), \tag{65}$$

which are linked to the generalized magnetizations via

$$\begin{aligned} \check{h} = {} & \check{m}[(\check{\lambda} - j_0)\omega_+ + \check{\lambda}^\dagger \omega_- + j_0 \pi_m^+] \\ & + \check{m}^\dagger[(\check{\lambda} - j_0)\omega_- + \check{\lambda}^\dagger \omega_+ + j_0 \pi_{m^\dagger}^+], \end{aligned} \tag{66}$$

and similarly for $\check{h}^\dagger$ in terms of π_m^- and $\pi_{m^\dagger}^-$ with ω_+ and ω_- interchanged while the coefficients $\omega_\pm$, $\pi_m^\pm$, and $\pi_{m^\dagger}^\pm$ are found to be

$$\omega_\pm = \theta\theta_m/\theta_h \pm \theta_h/\theta\theta_m, \tag{67}$$

$$\pi_m^\pm/(\theta_m - 1/\theta\theta_m) = \pi_{m^\dagger}^\pm/(\theta_m + 1/\theta\theta_m) = \theta/\theta_h \mp \theta_h. \tag{68}$$

With these new fields and magnetizations, the free energy per site reduces to

$$\begin{aligned} f_h = {} & -\tfrac{1}{2}(\theta_h\theta_m + 1/\theta_h\theta_m)(\check{m}\check{h} + \check{m}^\dagger \check{h}^\dagger) \\ & + \tfrac{1}{2}(\theta_h\theta_m - 1/\theta_h\theta_m)(\check{m}\check{h}^\dagger + \check{m}^\dagger \check{h}). \end{aligned} \tag{69}$$

As we will show, the choice of the coefficients θ, θ_m, and θ_h will be dictated by physical arguments in order to ensure compact and familiar expressions for the critical behavior.

IV. BINARY LATTICE GASES WITH SHORT-RANGE ATTRACTIVE INTERACTIONS

To obtain explicit results for critical behavior we focus now on binary systems with short-range interactions (in addition to the hard cores already accounted for). Accordingly,

we suppose that the small-$\mathbf{k}$ expansions of the interactions in $\mathbf{k}$ space are

$$\hat{J}_{\sigma\tau}(\mathbf{k}) = \hat{J}_{\sigma\tau}(\mathbf{0})[1 - k^2 R_{\sigma\tau}^2 + \mathcal{O}(k^4)] \quad (\sigma,\tau = 1,2), \quad (70)$$

with fixed range parameters $R_{\sigma\tau}$. Moreover, to ensure simple criticality, we suppose that the interactions are "overall attractive," which we take to mean that j_0, $\Delta\hat{J}_{12}$, and $\Delta\bar{J}$ are real and satisfy

$$j_0 = \tfrac{1}{2}\hat{J}_{12}(\mathbf{0}) > 0 \quad \text{and} \quad \Delta|\hat{J}_{12}(\mathbf{k})| > 0, \quad (71)$$

$$\Delta\bar{J}(\mathbf{k}) > 0 \quad \forall \quad \mathbf{k} \neq \mathbf{0}.$$

These conditions are easily fulfilled, as, for example, when $J_{12}(\mathbf{r}) = J_{12}(-\mathbf{r})$ while $J_{11}(\mathbf{r})$ and $J_{22}(\mathbf{r})$ are positive for all $\mathbf{r}$.

A. Critical loci

To identify the singularities of the binary systems, we recall that they are signaled by the vanishing of one of the eigenvalues of $\mathbf{\Lambda}$, which occurs first when $\Lambda_-(\mathbf{k};\boldsymbol{\lambda})$ vanishes. As shown in Appendix A, these singularities arise only when (i) $\mathbf{k}=\mathbf{0}$, and, thence, (ii) when the spherical fields $\boldsymbol{\lambda}$ satisfy

$$u(\lambda_1,\lambda_2) = 0, \quad (72)$$

provided the *asymmetries* of the interactions are *not too extreme* in the sense that, as we suppose henceforth, $\Delta J^\dagger(\mathbf{k})$ [defined in (35b)] satisfies the conditions (A2) and (A7).

Now, any state of the system is specified *ab initio* by the three thermodynamic fields (T,μ_1,μ_2) which, via (21), give $\boldsymbol{\lambda}(T,\mathbf{h})$, and then the densities $\mathbf{m}$. However, for the location of critical points, it is more convenient to utilize the set of variables $(T,\check{m},\check{m}^\dagger)$ introduced in (63) and then to solve for $(\check{\lambda},\check{\lambda}^\dagger)$ as defined in (59).

Next, let us choose $\theta_m > 0$ in (63) so that $\check{m}_c$ vanishes at criticality or, in other words, take $\theta_m = (-m_{1,c}/m_{2,c})^{1/2}$. This condition will be analyzed below in seeking a critical point, at a given value of $\check{m}^\dagger$. Likewise, we choose $\theta > 0$ in (59) so that $\check{\lambda}_c^\dagger = 0$. This condition then enforces the link between θ and $\check{m}^\dagger$, since it implies $\theta^2 = \lambda_{1,c}/\lambda_{2,c}$. As established in Appendix A, the singularities are characterized by $u=0$, which via (62) means $\lambda_c = j_0$ and thence, $\lambda_{1,c} = \theta j_0$ and $\lambda_{2,c} = j_0/\theta$.

At this point, one must pay attention to the behavior of integral expressions (55) and (56) when $\Lambda_-(\mathbf{0})$ approaches zero. If we accept (70) we find that Λ_- varies as k^2 when $\Lambda_-(\mathbf{0}) = 0$ and then $\mathcal{G}(\boldsymbol{\lambda})$ and $\mathcal{L}_\sigma(\boldsymbol{\lambda})$ remain finite at the singularity provided $d > d_< = 2$ (in this case) as seen in [22]. Accordingly, from here on we suppose the dimensionality exceeds $d=2$ and may then write

$$\mathcal{G}(\boldsymbol{\lambda}_c) = g_0(\theta)/j_0^2,$$

$$\mathcal{L}_\sigma(\boldsymbol{\lambda}_c) = g_0(\theta) l_{\sigma,0}(\theta)/j_0 \quad (\sigma = 1,2). \quad (73)$$

The residual θ dependence arises from $\Delta\tilde{J}$ and $\Delta\check{J}^\dagger$; see (60), (61), (55), and (56).

Putting these considerations together we find that the critical locus, $T_c(\check{m}^\dagger)$ with $\check{m}_c = 0$, may be defined parametrically via

$$k_B T_c(\check{m}^\dagger) = \frac{j_0(1 - \theta_m^2 \check{m}^{\dagger 2})}{g_0(\theta)[1/\theta + l_{2,0}(\theta)]}, \quad (74)$$

$$\check{m}^{\dagger 2} = \frac{(\theta - 1/\theta) + l_{1,0}(\theta) - l_{2,0}(\theta)}{(\theta\theta_m^2 - 1/\theta\theta_m^2) + l_{1,0}(\theta)\theta_m^2 - l_{2,0}(\theta)/\theta_m^2}. \quad (75)$$

In fact, the latter relation must be seen as an implicit equation giving θ as a function of $\check{m}^\dagger$ while, as shown below, θ_m will also be related to θ. Hence, if one realizes that $\check{m}^\dagger$ (i.e., some combination of the densities other than the total density) characterizes the composition of the system, the function $T_c(\check{m}^\dagger)$ describes naturally the composition dependence of criticality in the binary fluids.

B. Critical neighborhood

We seek an expression for the physical properties of the binary system in terms of $(T,\check{m},\check{m}^\dagger)$ near the critical locus $(T_c,0,\check{m}^\dagger)$. For this purpose, we first solve for $\check{\lambda}^\dagger$ in terms of T, $\check{m}$, and $\check{m}^\dagger$: this can be done *implicitly* in the general case by invoking (64), and *explicitly* in the vicinity of a critical point by implementing a perturbation scheme at fixed $\check{m}^\dagger$. To this end, consider the critical point at $T_c(\check{m}^\dagger)$ and $\check{m}_c = 0$ and its vicinity defined by the two small parameters, $t(T - T_c)$, as introduced in (57) and $\check{m}$. By construction, u and $\check{\lambda}^\dagger$ are small parameters near criticality, so that the integral involved in $\mathcal{G}(\boldsymbol{\lambda})$ can be computed as usual in spherical models; see [4,6,22]. However, a significant new feature is that the integral is now a function of *two* vanishing parameters, u and $\check{\lambda}^\dagger$. The appropriate extension of the standard critical expansion [22] yields

$$\mathcal{G}(\boldsymbol{\lambda}) = g_0 j_0^{-2}[1 - p(1 - p^\dagger\check{\lambda}^\dagger)u^{1/\gamma} + q_0 u + g_1\check{\lambda}^\dagger/j_0 + g_2\check{\lambda}^{\dagger 2}/j_0^2 + \mathcal{O}(u^{1/\gamma}\check{\lambda}^{\dagger 2}, \check{\lambda}^{\dagger 3}) + o(u)], \quad (76)$$

with coefficients p, $p^\dagger$, q_0, g_1, and g_2 which in general still depend on θ, and with the critical exponent

$$\gamma = \max[2/(d-2); 1]. \quad (77)$$

The integrals $\mathcal{L}_\sigma(\boldsymbol{\lambda})$ are less singular and one finds

$$\mathcal{L}_\sigma(\boldsymbol{\lambda}) = g_0 j_0^{-1}[l_{\sigma,0} + l_{\sigma,1}\check{\lambda}^\dagger/j_0 + l_{\sigma,2}\check{\lambda}^{\dagger 2}/j_0^2 + \mathcal{O}(u, \check{\lambda}^{\dagger 3})]. \quad (78)$$

We note that g_1 and $l_{\sigma,1}$ vanish in the symmetric case when $\Delta J^\dagger = 0$, while g_1, g_2, $p^\dagger$, $l_{\sigma,0}$, $l_{\sigma,1}$, and $l_{\sigma,2}$ are all of order $\Delta J_{\sigma\sigma'}/j_0$. It is worth remarking, furthermore, that the expression (77) can be generalized by replacing 2 by σ when long-range integrable $1/r^{d+\sigma}$ interactions are present (with $0 < \sigma < 2$).

Using these expansions one can explicitly expand the terms in the spherical constraints (64) about their values at criticality, which then provides the required relation between $u^{1/\gamma}$ and $\lambda^\dagger$ and t and $\check{m}$. To proceed further, we aim to

choose the mixing parameters and, explicitly, θ_m, to ensure that the resulting expansion for $u^{1/\gamma}$ begins at orders t and $\check{m}^2$, as in (58), rather than with $\check{m}$ as (64) naively implies. This can be done by imposing the condition

$$\theta_m^4 = \frac{1 - g_1(\theta) - \theta l_{2,1}(\theta)}{\theta[\theta + \theta g_1(\theta) + l_{1,1}(\theta)]}. \tag{79}$$

To study this, consider first the symmetric case when $g_1 = l_{\sigma,1} = 0$; the condition then reduces simply to $\theta_m^2 = 1/\theta$, which, in combination with (75), leads to the equation

$$(1 + \check{m}^{\dagger 2} l_{\sigma,0})(1 - \theta^2) = 0. \tag{80}$$

The conditions (71) enforce $\Delta\hat{J}_{\sigma\sigma} \geqslant 0$ in symmetric systems, which leads to $l_{1,0} = l_{2,0} > 0$. Consequently, the only positive solution of this equation is $\theta = 1$, independently of $\check{m}^\dagger$. Thus we obtain $\theta = \theta_m = 1$. Finally, we discover, as naturally expected, that symmetric criticality is confined to the manifold $\bar{m}_c = 0$ or $(\rho_1 + \rho_2)_c = \frac{1}{2} v_0^{-1}$, while the critical locus is given explicitly by the simple parabolic form

$$\frac{T_c^{\rm sym}(\rho_1, \rho_2)}{T_{c,\max}^{\rm sym}} = 1 - m^{\dagger 2} = 1 - v_0^2(\rho_1 - \rho_2)^2, \tag{81}$$

where $k_B T_{c,\max}^{\rm sym}/j_0 = 1/g_0(1)[1 + l_{\sigma,0}(1)]$.

In the general, nonsymmetric case the condition (79) is less tractable and might even lead, one could suspect, to multiple solutions. To keep the analysis at the simplest level, we note that the coefficients $g_1(\theta)$ and $l_{\sigma,1}(\theta)$ are actually of order $\hat{J}_{11}(\mathbf{0})/j_0$ and $\hat{J}_{22}(\mathbf{0})/j_0$. For the present work, we will, thus, restrict attention to systems in which the (1, 1) and (2, 2) interactions are sufficiently small relative to the (1, 2) attractions (which, then, predominantly drive phase separation and yield criticality). In these circumstances the right-hand side of (79) remains positive, ensuring solutions for real θ_m and θ: we then select a positive root for θ_m.

Supposing, then, that the condition (79) is satisfied, the spherical constraint in the general case has the expansion

$$p u^{1/\gamma}[1 + \mathcal{O}(u^{1-1/\gamma}, t, \check{m})] = c_t t + c_m \check{m}^2 + \mathcal{O}(t\check{m}, \check{m}^3), \tag{82}$$

where, with the coefficients $p, l_{1,0}, \ldots$ defined via the expansions (76) and (78), we find

$$c_t = 1 + \frac{\theta_m^4 l_{1,0} + l_{2,0}}{\theta\theta_m^4 + 1/\theta} \tag{83}$$

and, with

$$c_0 = j_0/g_0 k_B T_c \quad \text{and} \quad w(\theta) = 1 - g_1(\theta) - \theta l_{2,1}(\theta), \tag{84}$$

$$c_m = \frac{2c_0}{\theta\theta_m^2 + 1/\theta\theta_m^2} + \frac{2\theta^2\theta_m^4 c_0^2}{w^2(\theta)} \check{m}^{\dagger 2} \times \left[1 + 2g_1 \frac{\theta^2\theta_m^4 - 1}{\theta^2\theta_m^4 + 1} + 2g_2 + 2\frac{\theta_m^4 l_{1,2} + l_{2,2}}{\theta\theta_m^4 + 1/\theta}\right]. \tag{85}$$

These expressions are derived only for $\gamma > 1$, but the general expansion (82) remains valid when $\gamma = 1$ with, however, different coefficients. For $\Delta\hat{J}_{\sigma\sigma}$ small enough, c_t and c_m are positive (which we suppose from here on). Thus the structure of (82) leads to the usual form of the critical singularity in the spherical model.

The second spherical field $\check{\lambda}^\dagger$, which, recalling (38) enters into u, is given by

$$\check{\lambda}^\dagger/j_0 = 2\theta\theta_m^2 \check{m}\check{m}^\dagger c_0/w(\theta) + c_t' t + c_m' \check{m}^2 + \mathcal{O}(t^2, \check{m}t, \check{m}^3), \tag{86}$$

where, in similar fashion, the coefficients are found to be

$$c_t' = [\theta l_{2,0} - l_{1,0}/\theta]/w(\theta)(1 + 1/\theta^2\theta_m^4), \tag{87a}$$

$$c_m' = \frac{\theta\theta_m^2 c_0}{w(\theta)(1 + 1/\theta^2\theta_m^4)} \times [1 - 1/\theta^2\theta_m^4 + 4\theta\theta_m^2 c_0(\theta l_{2,2} - l_{1,2}/\theta - 2g_1)\check{m}^{\dagger 2}/w^2(\theta)]. \tag{87b}$$

It should be noted that in the symmetric case, where $\theta = \theta_m = 1$, both these coefficients, c_t' and c_m', vanish. At this stage, having obtained expansions for u and $\check{\lambda}^\dagger$—and thus for λ_1 and λ_2—as functions of T, $\check{m}$, and $\check{m}^\dagger$, we are in a position to derive all the physical properties of the system in terms of the fluid variables T, μ_1, μ_2, and ρ_1 and ρ_2.

C. Equation of state

To calculate the equation of state, we need to rewrite the relation (66) for the field $\check{h}$ using the expansions of u and $\check{\lambda}^\dagger$ in terms of t and $\check{m}$, at fixed $\check{m}^\dagger$, together with the expansion

$$\check{\lambda} - j_0 = (u + \check{\lambda}^{\dagger 2})/2j_0 + \mathcal{O}(\check{\lambda}^{\dagger 4}, u\check{\lambda}^{\dagger 2}, u^2), \tag{88}$$

which follows from (39). At this point, we resolve the freedom to choose θ_h in (65) by requiring that the resulting expression for $\check{h}$ is minimally singular. We achieve this by canceling the $\mathcal{O}(u)$ term introduced by the factor $\check{m}^\dagger(\check{\lambda} - j_0)$ on the right-hand side of (66), by choosing

$$\theta_h = \theta\theta_m, \tag{89}$$

so that ω_- in (67) vanishes identically. With this choice the equation of state can be written

$$\check{h} - [\check{h}_c + j_0 c_h t + \mathfrak{n}\check{m} + \mathcal{O}(\check{m}t, t^2)] = j_0^{-1} p^{-\gamma} \check{m}\{c_t t + c_m \check{m}^2 + \mathcal{O}(\check{m}^3, t\check{m})\}^\gamma [1 + \mathcal{O}(t, \check{m}, u^{1-1/\gamma})], \tag{90}$$

provided the expression in braces, which derives from u, remains nonnegative; otherwise, this expression must be replaced by zero. Recall, indeed, that u must be nonnegative for the free energy to be well defined.

On the left-hand side of (90) the coefficient

$$\check{h}_c(\check{m}^\dagger) = j_0 \check{m}^\dagger(1 - \theta^2\theta_m^4)/\theta\theta_m^2, \tag{91}$$

serves to specify the critical fields $h_{1,c}$ and $h_{2,c}$ [via (65) and (88)] and thence the critical chemical potentials $\mu_{1,c}$ and $\mu_{2,c}$. Note that $\check{h}_c$ vanishes with $\check{m}^\dagger$ so that in a symmetric

system, where $\theta=\theta_m=\theta_h=1$, criticality occurs, as natural, when $\bar{h}_c=0$.

The linear term in t, with mixing coefficient

$$c_h(\check{m}^\dagger)=2\check{m}^\dagger c_t', \tag{92}$$

similarly determines the near-critical T dependence of the chemical potentials, $\mu_{\Sigma,1}(T;\check{m}^\dagger)$ and $\mu_{\Sigma,2}(T;\check{m}^\dagger)$, on the phase boundary, a feature to be anticipated in binary fluid mixtures.

Finally, note the linear term in $\check{m}$ on the left-hand side of the equation of state (90): this is quite unanticipated from the perspective of previously studied spherical models, at least to the authors' knowledge. The corresponding coefficient, which for reasons to be explained below we call the "demagnetization factor," is given by

$$\mathfrak{n}(\check{m},\check{m}^\dagger)/j_0=-\frac{(1-\theta\theta_m^2)^2}{\theta\theta_m^2}+4c_0\frac{\theta\theta_m^2}{w(\theta)}\check{m}^{\dagger 2}+2c_m'\check{m}\check{m}^\dagger+\mathcal{O}(\check{m}^2), \tag{93}$$

in which further powers of $\check{m}$ should be noticed. In a symmetric model, this factor simplifies to the fairly explicit expression

$$\mathfrak{n}(\bar{m},m^\dagger)=4j_0(1+l_{\sigma,0})\frac{m^{\dagger 2}}{1-m^{\dagger 2}}\left[1+\frac{2\bar{m}^2}{(1-m^{\dagger 2})^2}+\mathcal{O}(\bar{m}^4)\right]. \tag{94}$$

Finally, as regards the second external field $\check{h}^\dagger$, or chemical potential, near criticality we have

$$\check{h}^\dagger-[\check{h}_c^\dagger+\mathfrak{n}'\check{m}+\mathcal{O}(t^2,\check{m}t)]=j_0^{-1}p^{-\gamma}\check{m}^\dagger[c_t t+c_m\check{m}^2+\mathcal{O}(t\check{m},\check{m}^3)]^\gamma[1+\mathcal{O}(t,\check{m},u^{1-1/\gamma})], \tag{95}$$

where the right-hand side has the same form and is subject to the same conditions as in (90) while the critical point value is determined by

$$\check{h}_c^\dagger(\check{m}^\dagger)=j_0\check{m}^\dagger(1+\theta\theta_m^2)^2/\theta\theta_m^2, \tag{96}$$

and the modified demagnetization factor is

$$\mathfrak{n}'(\check{m},\check{m}^\dagger)=j_0\frac{\theta^2\theta_m^4-1}{\theta\theta_m^2}+4j_0c_0\frac{\theta\theta_m^2}{w(\theta)}\check{m}\check{m}^\dagger\left(1+c_0\frac{\theta\theta_m^2}{w(\theta)}\check{m}^\dagger\right)+\mathcal{O}(\check{m}^2). \tag{97}$$

For symmetric models, these three relations reduce simply to

$$h^\dagger=4j_0m^\dagger+\mathcal{O}(\bar{m},t^2). \tag{98}$$

D. Phase diagram and critical behavior

Our result (90) and subsequent relations (91)–(93), describe the equation of state, i.e., the relations between the densities, m_1, m_2, or ρ_1 and ρ_2, and the fields, h_1, and h_2, or chemical potentials, μ_1 and μ_2, at temperature T close to criticality. To reveal specific, characteristic features we consider, first, the *phase boundary* in terms of the sum and difference densities $\check{m}$ and $\check{m}^\dagger$. It follows from (90) that the phase boundary below and up to $T_c(\check{m}^\dagger)$ is determined by the relation $u(t,\check{m},\check{m}^\dagger)=0$. Figure 2 depicts the boundary in the space $(T,\bar{m},m^\dagger)$ for a symmetric system, for which the critical locus was already derived in (81). Evidently, at fixed $m^\dagger$ and for $T<T_c(m^\dagger)$ there is a composition gap $\Delta\bar{\rho}(T)=\bar{\rho}_\alpha-\bar{\rho}_\beta$, where α and β label the two phases. This vanishes as $T\to T_c(m^\dagger)$ and from the magnetic perspective is most readily expressed in terms of the spontaneous magnetization which is described by

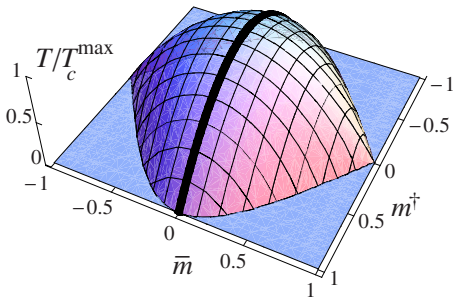

FIG. 2. (Color online) Phase boundary in terms of the magnetization $\bar{m}=\frac{1}{2}(m_1+m_2)$ and $m^\dagger=\frac{1}{2}(m_1-m_2)$ in the symmetric case. Criticality occurs on the bold line. The surface represents the limit of the single-phase region. Below the surface the parameter u sticks at zero.

$$\check{m}_0(T)\approx B|t|^\beta \quad \text{with } \beta=\tfrac{1}{2}, \tag{99}$$

where $B=(c_t/c_m)^{1/2}$. In fact the critical exponent $\beta=\frac{1}{2}$ represents the standard "universal" spherical model result!

As regards the other critical exponents of the general binary fluid model, our choice of the mixing parameters θ, θ_m, and θ_h at fixed $\check{m}^\dagger$ ensures that they basically match those of the corresponding single-component spherical models. This, of course, is in agreement with general considerations of the thermodynamics of multicomponent fluids [23]. Thus regarding the density correlation functions, the decomposition (49a) and (49b) shows that the dominant behavior of the density structure function near criticality is given by

$$S_{NN}(\mathbf{k};T,\boldsymbol{\rho})\approx 1/(u+k^2R_c^2+\cdots), \tag{100}$$

where R_c is a nonzero range parameter, while on the critical isochore, $\check{m}=\check{m}_c=0$, we have $u\sim t^\gamma$ as follows from (82). Hence, we find $S_{NN}(\mathbf{k}=\mathbf{0};T,\boldsymbol{\rho}_c)\sim 1/t^\gamma$, which is consistent with the definition of the critical exponent γ via, say, light scattering experiments. At criticality, this result also implies $S_{NN}(\mathbf{k};T_c,\rho_c)\sim 1/k^2$, which confirms the classical value $\eta=0$ of the critical point decay exponent.

Moreover, in leading order close to but above criticality one can establish the scaling form

$$S_{NN}(\mathbf{k};T,\rho_c)\approx t^{-\gamma}X_{NN}[k\xi_N(T)], \tag{101}$$

where the density correlation length is $\xi_N(T)\approx\xi_0/t^\nu$ with critical exponent $\nu=\frac{1}{2}\gamma$ in accord with the general scaling relation $\gamma=(2-\eta)\nu$. The scaling function $X_{NN}(x)$ has the standard Ornstein-Zernike form varying as $1/(1+x^2)$.

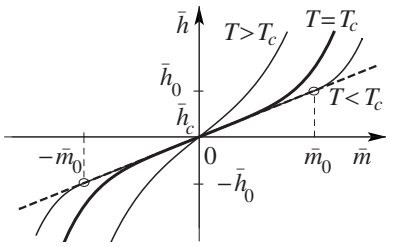

FIG. 3. Schematic depiction of the equation of state at fixed $\check{m}^\dagger$ $(\neq 0)$ in a symmetric system for temperatures above, at, and below criticality. In the latter case, the equation of state reduces to the linear demagnetization form $\bar{h}=\mathfrak{n}\bar{m}$ (dashed line) for $-\bar{m}_0 \leqslant \bar{m} < \bar{m}_0$ (where $\bar{m}_0 \sim t^\beta$) and $\bar{h}$ in the interval $(-\bar{h}_0, \bar{h}_0)$.

However, the equation of state in terms of T, $\check{m}$, and the field $\check{h}$ requires further examination. Thus, while the standard spherical model singularities embodied in (58) are evident, new features arise from the "demagnetization" term $\mathfrak{n}\check{m}$ on the left-hand side of (90). To understand their significance, consider symmetric systems (i.e., with $\hat{J}_{11}=\hat{J}_{22}$), where (90) reduces to

$$\bar{h} \approx \mathfrak{n}\bar{m} + j_0 p^{-\gamma}(c_t t + c_m \bar{m}^2)^\gamma, \tag{102}$$

while the demagnetization factor $\mathfrak{n}(\bar{m}, m^\dagger)$ is then given by (94) and vanishes only if $m^\dagger=0$. More generally, however, we note that $\mathfrak{n}(\check{m}=0, \check{m}^\dagger)$ vanishes in asymmetric systems, *only* on the special two loci $\check{m}^\dagger = \pm \check{m}_s^\dagger$ where one finds

$$\check{m}_s^{\dagger 2} = (1-\theta\theta_m^2)^2 w(\theta)/4\theta^2\theta_m^4 c_0. \tag{103}$$

It now follows from (102) that the inverse thermodynamic susceptibility or partial compressibility, $1/\chi \equiv (\partial\bar{h}/\partial\bar{m})_t$, does *not* vanish at the critical point $t=0$, $\bar{m}_c=0$: see Fig. 3. Consequently, the susceptibility does not diverge near criticality in the general case! The culprit is clearly the demagnetization effect, i.e., the term $\mathfrak{n}\bar{m}$ which arises both from the compositional asymmetry (when $\check{m}^\dagger \neq 0$) reflecting the multicomponent nature of the binary fluid, and from the underlying vectorial character of the order parameter: recall that spherical models correspond to the $n \to \infty$ limit of systems of vector-valued spins. Indeed, as we demonstrate in the next section, the origin of the demagnetization effect in spherical models can be understood directly in terms of vector spin models.

The nondivergence of the susceptibility-compressibility χ means that standard isothermal plots of the chemical potential (or, similarly, the pressure) vs density or of magnetic field vs magnetization near criticality take the form illustrated in Fig. 3 with, in general, a nonzero slope *at* $T=T_c$ fixed by the value, $\mathfrak{n}_c$, of the demagnetization coefficient. Note, in particular, that below T_c what would in a standard fluid system be a constant isotherm of zero slope through the two-phase region—i.e., the interval set by the spontaneous magnetization, $m_0(T)$—is now replaced by a straight line with the same fixed slope $\mathfrak{n}_c$ (at least close to T_c).

It is this fact that leads us to call this anomalous behavior, certainly unphysical in a fluid model, a "demagnetization effect." To be more specific, in a real magnetic system with long-range dipole-dipole interactions, one must distinguish between the externally applied magnetic field H_{ext}, analogous here to $\bar{h}$ (or $\check{h}$), and the *internal field*, H_{int}, which is what is "seen" by individual atomic and molecular spins. The relation between these may be written

$$H_{\text{int}} = H_{\text{ext}} - NM, \tag{104}$$

where M, analogous here to $\bar{m}$ (or $\check{m}$) is the magnetization while N is the demagnetization coefficient [24–26]. More generally the fields $\mathbf{H}_{\text{int}}$ and $\mathbf{H}_{\text{ext}}$ are real-space vectors, as is $\mathbf{M}$, and the relation (104) can be used only when the system is in the form of an ellipsoid and directions parallel to the major axes are considered. (In the case of a sphere one has $N=4\pi/3$ [24–26].)

One might, in light of these considerations, ask if one should not, similarly, be able to introduce an "effective internal field," $\check{h}_{\text{int}} \approx \check{h}_{\text{ext}} - \mathfrak{n}\check{m}$, that would play a natural thermodynamic role. However, on the one hand, given the implicit variation of $\mathfrak{n}(\check{m}, \check{m}^\dagger)$, this seems unlikely to be related to the basic thermodynamic parameters, T, μ_σ, and ρ_σ, sufficiently directly to be of real value, and, on the other hand, the higher-order terms in (90) indicate that the linear slope shown in Fig. 3 for the "two-phase" region will become *nonlinear* outside the critical region.

Two further points need to be made. First, the unphysical nondivergence of the susceptibility (or compressibility) appears only in two-component systems that *lack symmetry*. Indeed, by (94), the demagnetization factor vanishes identically when $\varphi_{11}(\mathbf{R})=\varphi_{22}(\mathbf{R})$ and $m_1=m_2$ (so that $m^\dagger=0$). In general such symmetry is nonphysical; but it would apply, for example, to two species that differ only in being of opposite chirality, i.e., two entiatiomers, present in equal concentrations, so constituting a racemic mixture. Second, since the range of potentials enters only through the integrals $\mathcal{G}(\boldsymbol{\lambda})$ and $\mathcal{L}_\sigma(\boldsymbol{\lambda})$, defined in (55) and (56) and via the second- and higher-order terms in the expansion (71), one sees that the basic anomaly of nondivergence does *not* depend on the short- or long-range character of the interaction potentials. Thus a neutral electron-positron plasma also represents a fully symmetric situation and the corresponding spherical model would be anomaly-free. Less obvious, but as can be shown [15–17], a neutral 1:1 electrolyte also escapes the demagnetization effects *even* if the short-range parts of the $(+,+)$ and $(-,-)$ ionic interactions differ.

Finally, as a further caution, another unphysical feature of the present multicomponent fluid models must be noted. Indeed, it enters even in single-component spherical models [4,5,18]! Specifically, whenever $\gamma>1$ and $\mathfrak{n}_c=0$ so that the susceptibility χ diverges to ∞ on approach to T_c along the critical isochore, it *also* diverges when the phase boundary is approached below T_c. Even for $\mathfrak{n}_c \neq 0$, a corresponding anomalous feature arises and is embodied in Fig. 3 where the *slope* of the isotherm below T_c remains *continuous through* the phase boundaries (marked by open circles); but in realistic fluid models there would be breaks in the slope!

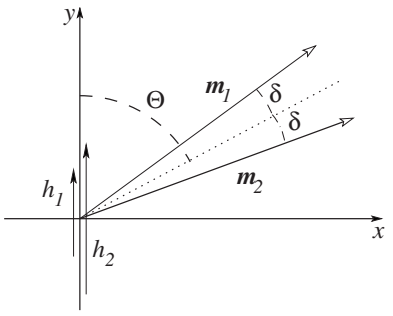

FIG. 4. Vectorial representation of the two-species spherical model within a mean-field picture in which $\mathbf{m}_1$ and $\mathbf{m}_2$ are the two sublattice magnetization vectors that can rotate with respect to the direction, the y axis, set by the parallel external fields, $\mathbf{h}_1$ and $\mathbf{h}_2$.

V. VECTOR SPIN MODEL ANALYSIS

To understand the origin of the demagnetizationlike effects that enter the present multicomponent spherical models, it is helpful to recognize that spherical models correspond precisely to the $n\to\infty$ limit of appropriate systems of n-component spins [13]. The vectorial character of the order parameter is thus a trademark of the model [4,5], coupled here to asymmetry and multicomponent features. The "secret" of the demagnetization effect appearing first in (90) can then be understood by regarding our binary-fluid spherical models as magnetic models with two classes of spins on separate sublattices, just as in (1)–(14), but now as fixed length *vector spins*, $\mathbf{s}_\sigma(\mathbf{R}_i^\sigma)$ $(\sigma=1,2)$, rather than scalar Ising spins as originally contemplated.

To obtain insight into the behavior of the model below T_c, we may use a simple mean-field approach by representing the overall sublattice magnetizations by two mean values, $\mathbf{m}_1$ and $\mathbf{m}_2$. The lengths of these magnetization vectors should ideally be taken as $m_\sigma^0(T)$, the spontaneous magnetizations (at fixed $T<T_c$); but it suffices here to consider the symmetric situation and so accept equal fixed lengths $|\mathbf{m}_1|=|\mathbf{m}_2|=1$.

Then, in contrast to most realistic magnetic systems, it is imperative to allow for the imposition of two distinct external magnetic fields $\mathbf{h}_1$ and $\mathbf{h}_2$, corresponding, as is fundamental for fluid models, to two distinct chemical potentials μ_1 and μ_2. However, for the "chemical interpretation," we must take $\mathbf{h}_1$ parallel to $\mathbf{h}_2$ and may identify the preferred direction as the y axis: see Fig. 4. The components $(\mathbf{m}_1)_y$ and $(\mathbf{m}_2)_y$ then correspond to the densities m_1 and m_2 in our previous analysis, while

$$\bar{h}=\tfrac{1}{2}(h_1+h_2) \quad \text{with } h_\sigma=(\mathbf{h}_\sigma)_y \tag{105}$$

describes the external field or chemical potential. On the other hand, $h^\dagger=\frac{1}{2}(h_1-h_2)$ characterizes the compositional *asymmetry* of the system (even when the two species, here the magnetic sublattices, are symmetrically related): that asymmetry is at the heart of the matter. As regards the vector-spin dimensionality, however, it suffices to allow for only one more dimension and so regard the $\mathbf{m}_\sigma$ as XY or O(2) order parameters.

Finally, beyond the symmetric *intra*sublattice ferromagnetic couplings (that lead to the spontaneous magnetizations), we allow for the *inter*sublattice interactions by a coupling constant $j>0$ (analogous to j_0 above). Thus we take the essential part of the mean-field free energy to be

$$\mathcal{F}(\bar{h};h^\dagger;\mathbf{m}_1,\mathbf{m}_2)=-\mathbf{h}_1\cdot\mathbf{m}_1-\mathbf{h}_2\cdot\mathbf{m}_2-j\mathbf{m}_1\cdot\mathbf{m}_2. \tag{106}$$

Here the external field $\bar{h}$ is the control variable while $h^\dagger$ is fixed and, as usual, $\mathcal{F}$ is to be minimized with respect to $\mathbf{m}_1$ and $\mathbf{m}_2$.

Let us, as in Fig. 4, introduce the mean tilt angle Θ between the y axis and $\bar{\mathbf{m}}=\frac{1}{2}(\mathbf{m}_1+\mathbf{m}_2)$ and the splitting or separation angle δ, between the $\mathbf{m}_\sigma$ and the $\bar{\mathbf{m}}$. For simplicity we suppose that δ is small (which requires $|h^\dagger|\ll j$); then minimization on δ yields

$$\mathcal{F}_{\min}(\Theta)=-j-2\bar{h}\cos\Theta-\frac{2h^{\dagger 2}\sin^2\Theta}{2j+\bar{h}\cos\Theta}+\mathcal{O}(h^{\dagger 2}/j^2). \tag{107}$$

Consider, first, the fully symmetric case in which $h^\dagger=0$ (and $\delta_{\min}=0$). Minimizing this expression on Θ then gives $\Theta_{\min}=0$ for $\bar{h}=0$ but $\Theta_{\min}=\pi$ for $\bar{h}<0$. This evidently corresponds to the usual ferromagnetic situation in which (*neglecting* dipolar interactions and demagnetization effects) the magnetization $\bar{\mathbf{m}}$ switches abruptly from $\bar{m}\equiv(\bar{\mathbf{m}}_\sigma)_y=-1$ to $+1$ as the field $\bar{h}$ passes through zero.

On the other hand when $h^\dagger\neq 0$ the minimizing value of Θ assumes a nontrivial value for $\bar{h}$ between the limits $\pm\bar{h}_0$ given by

$$\bar{h}_0=j(\sqrt{1+h^{\dagger 2}/j^2}-1)\approx\tfrac{1}{2}h^{\dagger 2}/j, \tag{108}$$

up to corrections of relative order $(h^\dagger/j)^2$. As a consequence, the magnetization $\bar{m}(\bar{h})$ no longer jumps discontinuously at $\bar{h}=0$ from $\bar{m}=-1$ to $\bar{m}=+1$ but rather varies continuously and almost linearly over the interval $-\bar{h}_0\leqslant\bar{h}<\bar{h}_0$ according to

$$\bar{m}(\bar{h})\simeq\frac{\bar{h}}{\bar{h}_0}\left[1-\frac{3}{8}(h^\dagger/j)^2\right]\Bigg/\left[1-\frac{3}{8}(h^\dagger/j)^2(\bar{h}/\bar{h}_0)^2\right]. \tag{109}$$

More explicitly to leading order in $(h^\dagger/j)^2$ one finds for $|\bar{h}|<\bar{h}_0$,

$$\bar{m}=\cos\Theta_{\min}=\frac{2j}{\bar{h}}\left[\sqrt{\frac{1-\bar{h}^2/4j^2}{1-2\bar{h}^2/h^{\dagger 2}}}-1\right], \tag{110}$$

while for $|\bar{h}|>\bar{h}_0$ one has $\cos\Theta=\mathrm{sgn}\{\bar{h}\}$.

In words, for an external field $\bar{h}$ not too large compared to the square of the asymmetric field $h^\dagger$, the spins cant themselves in a direction $\Theta_{\min}\neq 0$, with, indeed, $\Theta_{\min}=\pi/2$ when $\bar{h}=0$! This minimizing behavior of vector spins is clearly the origin of the seeming demagnetization effect and explains

our result for the spherical model. Indeed, near the origin, for $\bar{h}/\bar{h}_0 \to 0$, we find $\cos\Theta_{\min} \approx 2\bar{h}j/h^{\dagger 2}$ which leads to a nondivergent susceptibility of magnitude

$$\chi = (\partial\bar{m}/\partial\bar{h})_{T,\bar{h}=0} = 2j/h^{\dagger 2}. \tag{111}$$

Thus, as the spherical model itself, the asymmetry of the spin model, coupled to the vectorial character of the order parameter, leads to a nonvanishing inverse susceptibility near criticality in the general case. Note also that, as in the spherical model, the divergence of χ reemerges in the symmetric case when $h^{\dagger}=0$. Finally, the nonlinear terms in $\bar{h}$ implied by (109) show that one cannot hope to find a simple demagnetization description as in [24–26].

VI. CONCLUSIONS

We have introduced multicomponent generalizations of the standard spherical model that embody lattice-gas hard cores for many-species fluids by using interlaced sublattices. Taking into account a spherical constraint for each distinct species, we have obtained exact expressions for the free energy and pair correlation functions in the general case, in terms of the basic Fourier space interaction matrix. We have then focused on binary fluids where the diagonalization of 2×2 matrices leads to relatively simple results for the physical properties of the system. We find that density and (for ionic fluids) charge correlation functions can be decomposed naturally in terms of two eigenmodes. This formulation, which could well have broader validity, has dramatic consequence for charged fluids as we expound elsewhere [4,5,15–17].

The present analysis addresses fluids where, in addition to hard cores, only short-range overall attractive interactions are present. We show that with an appropriate choice of variables (in the form of linear combinations of the mean magnetizations-densities or external fields-chemical potentials for the two species), the usual critical properties of single-component spherical models can be uncovered in accord with general thermodynamic arguments for multicomponent solutions. Specifically, as the relative composition of the system varies, criticality is realized on a well-defined locus in the full phase diagram.

However, an unexpected and intrinsically unphysical "pseudodemagnetization phenomenon" arises that, except on certain submanifolds, prevents the usual divergence of the thermodynamic susceptibilities-compressibilities at criticality. This feature, undesirable for model fluids, is found to be a consequence of an interplay between species and compositional asymmetry and the multidimensional characteristics represented by the hidden vectorial character of the order parameter in spherical models. The behavior can, indeed, be understood via a simple mean-field description of a corresponding XY spin model. Despite this artificial aspect, requiring caution in interpreting results, further aspects of the multicomponent spherical models seem worth pursuing: on the one hand, ternary fluid models with, say, positive and negative ions in solutions of neutral molecules, could be instructive; on the other hand, magnetic systems with different types of ions could reveal interesting behavior.

ACKNOWLEDGMENTS

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APPENDIX A: LOCATION OF SINGULARITIES

In this appendix, we locate the singularities of the binary spherical model for the generic case of short-range interactions. The singularities derive from the vanishing of $\Lambda_{-}(\mathbf{k};\boldsymbol{\lambda})$ and we obtain sufficient conditions to ensure that they arise only when $\mathbf{k}=\mathbf{0}$.

1. Vicinity of the origin

We first consider the small-$\mathbf{k}$ behavior of $\Lambda_{-}(\mathbf{k};\boldsymbol{\lambda})$. Owing to the second condition (71), the range R_{12} defined in (70) satisfies $R_{12}^2>0$. Note also the relations $\Delta\bar{J}(\mathbf{k}) \approx j_0\bar{R}^2k^2$ and $\Delta J^{\dagger}(\mathbf{k}) \approx j_0 R^{\dagger 2}k^2$, where $\bar{R}$ and $R^{\dagger}$ are characteristic ranges. At leading order in k we then have

$$\frac{\Lambda_{-}(\mathbf{k};\boldsymbol{\lambda}) - \Lambda_{-}(\mathbf{0};\boldsymbol{\lambda})}{j_0k^2} = \bar{R}^2 + \frac{j_0R_{12}^2 - \lambda^{\dagger}R^{\dagger 2}}{\sqrt{\lambda^{\dagger 2}+j_0^2}} + \cdots, \tag{A1}$$

which will be valid in a domain $|\mathbf{k}| \leqslant k_m > 0$. From the third condition (71) we find $\bar{R}^2>0$ and if, recalling the definition (35b) of $\Delta J^{\dagger}$, we accept the further condition

$$|R^{\dagger 2}| = \lim_{k\to 0} \Delta J^{\dagger}(\mathbf{k})/j_0k^2 \leqslant \bar{R}^2, \tag{A2}$$

we are assured that $\mathbf{k}=\mathbf{0}$ is indeed the minimum of $\Lambda_{-}(\mathbf{k};\boldsymbol{\lambda})$ when $k \leqslant k_m$.

2. Remainder of the Brillouin zone

Consider now the subdomain $\mathcal{B}'$ of the Brillouin zone $\mathcal{B}$, consisting of all vectors $\mathbf{k}$ outside the origin domain $|\mathbf{k}| \leqslant k_m$. In the symmetric case when $\Delta J^{\dagger}=0$ (marked by superscripts "sym"), the second condition (71) leads to $|\hat{J}_{12}(\mathbf{k})| < j_0$ so that

$$\Delta\Lambda_{-}^{\mathrm{sym}} \equiv \Lambda_{-}^{\mathrm{sym}}(\mathbf{k};\boldsymbol{\lambda}) - \Lambda_{-}^{\mathrm{sym}}(\mathbf{0};\boldsymbol{\lambda}) > \Delta\bar{J}(\mathbf{k}). \tag{A3}$$

But, according to the last member of (71), there exists a $\delta\Lambda_{-}^{\mathrm{sym}}$ such that

$$\Delta\Lambda_{-}^{\mathrm{sym}}(\mathbf{k};\boldsymbol{\lambda}) \geqslant \delta\Lambda_{-}^{\mathrm{sym}} > 0 \quad \text{for } \mathbf{k} \in \mathcal{B}'. \tag{A4}$$

In the general case where $\Delta J^{\dagger}$ is arbitrary, we may write

$$\Lambda_{-}(\mathbf{k};\boldsymbol{\lambda}) - \Lambda_{-}(\mathbf{0};\boldsymbol{\lambda}) = \Delta\Lambda_{-}^{\mathrm{sym}}(\mathbf{k};\boldsymbol{\lambda}) + \delta\Lambda_{-}[\Delta J^{\dagger}(\mathbf{k})], \tag{A5}$$

where from (36) we define

$$\delta\Lambda_{-}[\Delta J^{\dagger}(\mathbf{k})] = \sqrt{\lambda^{\dagger 2} + \tfrac{1}{4}\hat{J}_{12}^{2}(\mathbf{k})} - \sqrt{[\lambda^{\dagger} + \Delta J^{\dagger}(\mathbf{k})]^{2} + \tfrac{1}{4}\hat{J}_{12}^{2}(\mathbf{k})}. \tag{A6}$$

Then, noting that $|\partial(\delta\Lambda_{-})/\partial\Delta J^{\dagger}(\mathbf{k})| \leqslant 1$ and $\Delta J^{\dagger}(0)=0$, we see that $|\delta\Lambda_{-}[\Delta J^{\dagger}(\mathbf{k})]| \leqslant |\Delta J^{\dagger}(\mathbf{k})|$. Hence, accepting the further condition

$$\max_{\mathbf{k}\in\mathcal{B}'}[|\Delta J^{\dagger}(\mathbf{k})|] < \delta\Lambda_{-}^{\mathrm{sym}}, \tag{A7}$$

which means that the asymmetry is not too strong, one concludes that $\Lambda_{-}(\mathbf{k};\boldsymbol{\lambda}) > \Lambda_{-}(\mathbf{0};\boldsymbol{\lambda})$ for all $\mathbf{k}$ in $\mathcal{B}'$.

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