The Spin-One Ising Model in the Mean-Spherical Approximation

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The spin-one Ising ferromagnet on a simple cubic lattice is treated in the mean-spherical approximation (MSA) for an exchange potential $J(\mathbf{r})$ parametrized by a Kac–Baker inverse-range parameter γ. The mean-field result is recovered when $\gamma \to 0$; in this limit the result is exact. For $\gamma \neq 0$, a detailed analysis is given of the phase separation associated with the tricritical point that occurs. The analysis is made through the relation that gives the internal energy via $\langle J(\mathbf{r}) \rangle$. It shows that the MSA result satisfactorily captures the important thermodynamic features of the tricritical point as long as γ is not too large. The case of Coulombic $J(r)$ is also considered; here $J(\mathbf{r})$ is antiferromagnetic. An argument is given in support of the expectation that on the simple cubic and body-centered cubic lattices the Coulombic $J(\mathbf{r})$ will give rise to a tricritical point at which a λ-line of Néel points meets a paramagnetic-antiferromagnetic coexistence boundary.

1. INTRODUCTION

In this paper we solve the spin-one Ising model in the mean-spherical approximation (MSA) on a simple cubic lattice for an exchange potential parametrized by a Kac–Baker inverse-range parameter [1, 2] γ, $J(\mathbf{r}) = \gamma^3 f(\gamma \mathbf{r})$. We then go on to consider Coulombic $J(\mathbf{r})$.

We first consider the ferromagnetic case in the Kac–Baker limit, $\gamma \to 0$, in which we recover the mean-field result, which is the exact result in this

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limit. The model exhibits tricritical behavior, as expected, and for nonzero γ we find that the MSA treats the coexistence associated with the tricriticality of the model more accurately than mean-field theory as long as γ is sufficiently small. For larger values of γ, the spin-1 MSA shows some of the same spurious features that appear in the spin-1/2 behavior of the MSA (for all $\gamma > 0$) when one evaluates the thermodynamics from the expression for the internal energy in terms of $\langle J(\mathbf{r}) \rangle$, hereafter referred to as the energy relation. From this expression one finds (for both spin-1/2 and spin-1) a critical temperature at which

$$H = Am^5 - Cm^3 + \cdots (A, C > 0) \tag{1}$$

(H is magnetic field and m is magnetization.) The magnitude of A and C is determined by $A \sim O((\gamma^3)^{-2})$ and $C \sim O(1)$. Since $C > 1$, the "double" loops that result from (1) are unavoidable as m^3 will dominate for sufficiently small m. (This behavior of MSA-like theories follows from the analysis made in [3].)

The equation of state can also be found from the correlation function via the susceptibility relation of fluctuation theorem, which yields a critical isotherm that is without the m^3 term,

$$H = Dm^5 + \cdots (D > 0). \tag{2}$$

An earlier study by one of us [4] of the lattice-gas (or equivalently, the spin-1/2 Ising model) indicated that in the MSA the approximation resulting from use of the susceptibility relation is not of a form that yields a coexistence curve from a Maxwell construction in a three-dimensional system—the associated equations have no real solution. This unpromising result has led us to focus exclusively here on the use of the energy relation in obtaining MSA thermodynamics for the spin-1 system. We find that if the Curie point becomes tricritical then the $-Cm^3$ term in (1) and the spurious double loop to which it gives rise vanishes. Moreover, when γ is reduced so that the B of Eq. (83) is below the value 0.22, the λ-line of Curie points and the phase boundary for paramagnetic-ferromagnetic coexistence obtained from the energy relation do not meet at the tricritical point at an angle of $180°$ in the $\rho - T$ plane as they do in a mean-field treatment (ρ = density, T = temperature).

The presence of a tricritical point in the $\rho - T$ plane rather than a simple critical point is to be expected on the basis of earlier theoretical studies [5, 6], as is the way the location of that point and the shape of the associated phase diagram in the $\rho - T$ plane hinges so strongly on the potential range through the single parameter B of Eq. (83). The abrupt loss

of tricriticality at $B = 0.22$ appears to be an artifact of the approximation, however. On the basis of existing theory [7, 8], one would expect tricriticality for short-ranged as well as long-ranged potentials.

In the above analysis, detailed in Section II, we consider only the ferromagnetic case. But for lattices that can be decomposed into two identical interlaced sublattices there is a correspondence between the thermodynamic properties in the spin-1 ferromagnetic case and the properties in the antiferromagnetic case in which $J(\mathbf{r})$ is replaced by a "staggered" $J_s(\mathbf{r})$ which is $-J(\mathbf{r})$ on the sublattice bearing a nearest-neighbor site and $J(\mathbf{r})$ otherwise, e.g., for the cubic lattice of unit spacing, $J_s(\mathbf{r}) = (-1)^{x+y+z} J(\mathbf{r})$ where $\mathbf{r} = (x, y, z)$. In the $\rho - T$ plane the locus of Curie points becomes a locus of Néel points and the coexistence of paramagnetic and ferromagnetic phases becomes coexistence of paramagnetic and antiferromagnetic phases. In general, $J_s(\mathbf{r})$ will have a different range than $J(\mathbf{r})$ and will correspond to a different value of B. Thus in the $\rho - T$ plane one expects the location of the tricritical point and the phase boundaries to shift as one goes from J to J_s, but one does not expect to lose the tricriticality. One of the implications of this observation, developed in Section III, is that on lattices that permit staggering of $J(\mathbf{r})$, one would expect tricriticality in the spin-1 Coulombic antiferromagnetic case, which is the lattice-gas version of the restricted primitive model. This follows from the fact that the spin-1 antiferromagnet with a Coulombic $J(\mathbf{r})$ is isomorphic to the spin-1 ferromagnet with a staggered $J(\mathbf{r})$ that formally is of short range, when its range is characterized by the range parameter γ. And as we have noted, for the spin-1 ferromagnet with short-ranged $J(\mathbf{r})$, one expects the presence of a tricritical point in the $\rho - T$.

II. THE MSA FOR THE SPIN ONE MODEL OF $He^3 - He^4$ MIXTURES

In the lattice-gas version of the $He^3 - He^4$ mixture [5] the continuum fluid of $He^3 - He^4$ is replaced by a lattice gas in which either one He^3 or one He^4 is always present at each lattice site. This is equivalent to a spin-one model where spin $s = 0$ means a He^3 atom while $s = \pm 1$ means a He^4 atom. The difference between the number of spins with $s = 1$ and $s = -1$ measures the superfluid ordering parameter. When this difference is zero, the fluid is in the normal fluid state. Between spins s_i and s_j at sites $\mathbf{r}_i$ and $\mathbf{r}_j$, respectively, there will be an interaction of exchange form ($\beta = 1/k_B T$).

$$\varphi_{s_i s_j}(\mathbf{r}_{ij}) = \frac{-2}{\beta} J(\mathbf{r}_{ij}) \, s_i s_j; \qquad (\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j) \tag{3}$$

Such a spin system can also be used to model a classical lattice-gas mixture in an even more direct way. Spin $s = -1$ can be identified with a particle of one species, spin $s = 1$ with another species, and spin $s = 0$ is an empty cell (vacuum). This identification of $s = 0$ with vacuum is consistent with (3) which gives no interaction with other cells whenever $s_i = 0$. We further consider this interpretation in Section III.

The densities of each species (and thus also the number of empty cells, i.e., number of He^3 atoms), will be determined by their chemical potentials and vice versa. [The chemical potentials are determined by the spin distribution before the interaction is turned on.]

The MSA for a lattice gas is defined by the expression

$$
\begin{aligned}
c_{s_i s_j}(\mathbf{r}_{ij}) &= 2J(\mathbf{r}_{ij})\, s_i s_j && \text{for } \mathbf{r}_{ij} \neq 0 \\
h_{s_i s_j}(\mathbf{r}_{ij}) &= -1 && \text{for } \mathbf{r}_{ij} = 0
\end{aligned}
\tag{4}
$$

for the direct correlation function $c_{s_i s_j}$ and pair correlation function $h_{s_i s_j}$, respectively. To obtain these functions in full, (4) has to be used as a condition in solving the OZ (Ornstein–Zernike) equation which in its Fourier-transformed version reads

$$
\tilde{h}_{s_i s_j}(\mathbf{k}) = \tilde{c}_{s_i s_j}(\mathbf{k}) + \sum_{s_k \neq 0} \rho_{s_k} \tilde{c}_{s_i s_k}(\mathbf{k})\, \tilde{h}_{s_k s_j}(\mathbf{k})
\tag{5}
$$

One will find the solution to be of the form

$$
\begin{aligned}
c_{s_i s_j}(\mathbf{r}) &= c_0(\mathbf{r}) + c(\mathbf{r})\, s_i s_j \\
h_{s_i s_j}(\mathbf{r}) &= h_0(\mathbf{r}) + h(\mathbf{r})(s_i - m)(s_j - m)
\end{aligned}
\tag{6}
$$

where

$$
\begin{aligned}
\tilde{h}_0(\mathbf{k}) &= \tilde{c}_0(\mathbf{k}) + \rho \tilde{c}_0(\mathbf{k})\, \tilde{h}_0(\mathbf{k}) \\
\tilde{h}(\mathbf{k}) &= \tilde{c}(\mathbf{k}) + R \tilde{c}(\mathbf{k})\, \tilde{h}(\mathbf{k})
\end{aligned}
\tag{7}
$$

with boundary conditions

$$
\begin{aligned}
c_0(\mathbf{r}) &= 0 \quad \text{and} \quad c(\mathbf{r}) = 2J(\mathbf{r}) && \text{for } \mathbf{r} > 0; \\
h_0(\mathbf{r}) &= -1 \quad \text{and} \quad h(\mathbf{r}) = 0 && \text{for } \mathbf{r} = 0.
\end{aligned}
\tag{8}
$$

Here the subscript zero refers to the reference system in which $J(r) = 0$, and

$$\rho = \sum_{s \neq 0} \rho_s = \rho_1 + \rho_2$$

$$m = \langle s \rangle = \sum_s s\rho_s = \rho_2 - \rho_1 \qquad (9)$$

$$R = \langle (s - m)^2 \rangle = \sum_s (s^2 - m^2) \rho_s = \rho - m^2$$

($\sum_s \rho_s = 1$ with cell volume 1. Note $\rho_{s=1} = \rho_2$ and $\rho_{s=-1} = \rho_1$). The ρ will be the density or fraction of He^4 while m will become the superfluid order parameter. From (7) and (8) one easily finds

$$h_0(\mathbf{r}) = 0 \quad \text{for} \quad \mathbf{r} \neq 0 \quad \text{and} \quad c_0(0) = -1/(1 - \rho) \qquad (10)$$

which is the exact solution for the lattice gas with no interactions between different sites. Use of (7) and (8) yields

$$\tilde{c}(\mathbf{k}) = 2[-K + \tilde{J}(\mathbf{k})] \qquad (11)$$

where

$$\tilde{J}(\mathbf{k}) = \sum_{\mathbf{r} \neq 0} e^{i\mathbf{k}\mathbf{r}} J(\mathbf{r})$$

and where the constant K will be determined by the core condition $(-\pi \leqslant k_i \leqslant \pi; \; i = x, y, z)$

$$0 = h(0) = \frac{1}{(2\pi)^3} \int \frac{\tilde{c}(\mathbf{k}) \, d\mathbf{k}}{1 - R\tilde{c}(\mathbf{k})}$$

$$= \frac{1}{R} \left[-1 + \frac{1}{(2\pi)^3} \int \frac{d\mathbf{k}}{1 + 2RK - 2R\tilde{J}(\mathbf{k})} \right] \qquad (12)$$

or

$$\frac{1}{(2\pi)^3} \int \frac{d\mathbf{k}}{1 - (1/z)\tilde{J}(\mathbf{k})} = 2zR \qquad (13)$$

with

$$z = \frac{1 + 2RK}{2R} = \frac{1}{2R} + K$$

To determine the location of a phase transition we will need the pressure and the chemical potentials. The thermodynamics we obtain most easily by using the results of Høye and Stell [9]. There we find for a mixture: Internal energy per unit volume $\rho u = \sum_i \rho_i u_i$ where

$$-\beta \rho_i u_i = \frac{1}{2} \sum_j \rho_i \rho_j \int (h_{ij}(\mathbf{r}) + 1)\, c_{ij}(\mathbf{r})\, d\mathbf{r}$$

$$= \frac{1}{2}\left[\rho_i(h_{ii}(0) - c_{ii}(0)) + \sum_j \rho_i \rho_j \tilde{c}_{ij}(0) \right] \tag{14}$$

or in the present case

$$-\beta \rho u = RK + \tilde{J}(0)\, m^2 \tag{15}$$

For the excess free energy f^E, where $u = \beta(\partial f^E / \partial \beta)$, we have

$$-\beta \rho f^E = \frac{1}{2} \sum_{ij} \rho_i \rho_j [\tilde{c}_{ij}(0) - \tilde{c}_{0ij}(0)]$$

$$- \frac{1}{2}\frac{1}{(2\pi)^3} \text{Trace} \int \{\ln[1 - \rho\tilde{c}(\mathbf{k})] + \rho\tilde{c}(\mathbf{k})]\}\, d\mathbf{k}$$

$$+ \frac{1}{2}\frac{1}{(2\pi)^3} \text{Trace} \int \{\ln[1 - \rho\tilde{c}_0(\mathbf{k})] + \rho\tilde{c}_0(\mathbf{k})\}\, d\mathbf{k} \tag{16}$$

(where here $\rho\tilde{c}$ and $\rho\tilde{c}_0$ are matrices). In our case this becomes

$$-\beta \rho f^E = L + Am^2 + \rho K \tag{17}$$

where

$$A = \tfrac{1}{2}\tilde{c}(0) = -K + J; \qquad J = \tilde{J}(0) \tag{18}$$

and

$$L = -\frac{1}{2}\frac{1}{(2\pi)^3} \int \ln(1 - \rho\tilde{c}(\mathbf{k}))\, d\mathbf{k} \tag{19}$$

By use of (11) and (13) this can be written as

$$L = -\frac{1}{2}\frac{1}{(2\pi)^d} \int \ln\left(1 - \frac{1}{z}\tilde{J}(\mathbf{k})\right) d\mathbf{k} - \frac{1}{2}\ln I \tag{20}$$

where

$$I = \frac{1}{(2\pi)^3} \int \frac{d\mathbf{k}}{1 - (1/z)\,\tilde{J}(\mathbf{k})} = 1 + 2RK \tag{21}$$

Excess chemical potential is given by

$$-\beta\rho_l\mu_l^E = \rho_l \partial(-\beta\rho f^E)/\partial\rho_l = \tfrac{1}{2}\sum_i \rho_i\rho_l(\tilde{c}_{il}(0) - \tilde{c}_{0il}) - \beta\rho_l u_l$$

We get by use of (14) (since $\beta\rho_l u_l = 0$ for $J = 0$)

$$\begin{aligned} \beta\mu_1^E &= -K + 2mA \\ \beta\mu_2^E &= -K - 2mA \end{aligned} \tag{22}$$

Excess Gibbs free energy is given by

$$\beta\rho\mu^E = \sum_l \beta\rho_l\mu_l^E = -\rho K - 2m^2 A \tag{23}$$

Excess pressure follows from

$$\beta p^E = \beta\rho\mu^E - \beta\rho f^E = L - Am^2 \tag{24}$$

The pressure and chemical potentials of the hard-core reference system (or non-interacting spins) are well known;

$$\begin{aligned} \beta p^0 &= -\ln(1 - \rho) \\ \beta\mu_2^0 &= \ln \rho_1 - \ln(1 - \rho) \\ \beta\mu_2^0 &= \ln \rho_2 - \ln(1 - \rho) \end{aligned} \tag{25}$$

So in the MSA the total pressure and chemical potentials are given by

$$\begin{aligned} \beta p &= \beta p^0 + \beta p^E = -\ln(1 - \rho) - Am^2 + L \\ \beta\mu_1 &= \beta\mu_1^0 + \beta\mu_1^E = \ln \rho_1 - \ln(1 - \rho) - 2mA - K \\ \beta\mu_2 &= \beta\mu_2^0 + \beta\mu_2^E = \ln \rho_2 - \ln(1 - \rho) - 2mA - K \end{aligned} \tag{26}$$

We will now begin to consider phase transitions of the system. It is then convenient to take the difference between the two last equations of (26) to obtain the magnetic field of the corresponding spin system

$$\beta H = \frac{1}{2}(\beta\mu_2 - \beta\mu_1) = \frac{1}{2}\ln(\rho_2/\rho_1) - 2mA = \frac{1}{2}\ln\left(\frac{\rho + m}{\rho - m}\right) - 2mA \tag{27}$$

In our case the probabilities of up and down spins are equal so $\mu_1 = \mu_2$ or $H = 0$, i.e.,

$$4mA = \ln \frac{1 + m/\rho}{1 - m/\rho} \tag{28}$$

When ρ is not too small the system will behave as an ordinary spin one-half ferromagnetic system with up and down spin states, whose phase transition is determined by (28) for constant ρ (since the same ρ in both phases will satisfy (26)). By expansion of (28) we find

$$2\rho A = 1 + \frac{1}{3}\left(\frac{m}{\rho}\right)^2 + \cdots \tag{29}$$

The spontaneous magnetization is thus $m = \pm \rho(3(2\rho A - 1))^{1/2}$, which goes to zero as $2\rho A \to 1$. So the critical temperature is determined by

$$2\rho A = 1 \tag{30}$$

The J in Eq. (18) is proportional to inverse temperature β, so we may consider the J to be our measure of inverse temperature. Due to the K in (18), the A will depend upon m, β, and ρ. This m-dependence will have the effect that close to the critical point (29) will have several solutions for m which reflects the double loops of the MSA previously discussed in Section I.

However, if we let the inverse range of interaction γ go to zero then $K \to 0$ and $L \to 0$ and we obtain the "mean-field" limit where $A = J$.

When ρ drops below a certain value, the above ferromagnetic transition is no longer the stable solution. The change takes place where the previous critical point becomes tricritical. Instead of phases with equal ρ there will now be phases with unequal ρ. In one of the phases the $m = 0$ and $\rho < \rho_{tr}$ while in the other phase $m \neq 0$ and $\rho > \rho_{tr}$ where ρ_{tr} is the tricritical value of ρ. The tricritical point and the phase transition below is determined by equal pressures and chemical potentials in the two phases.

Denoting the quantities in the $m = 0$ phase by a subscript "o" we find from (26) ($\mu_1 = \mu_2$)

$$-\ln(1 - \rho_o) + L_o = -\ln(1 - \rho) - Am^2 + L$$

$$\ln(\tfrac{1}{2}\rho_o) - \ln(1 - \rho_o) - K_o = \ln \rho_1 - \ln(1 - \rho) + 2mA - K \tag{31}$$

$$\ln(\tfrac{1}{2}\rho_o) - \ln(1 - \rho_o) - K_o = \ln \rho_2 - \ln(1 - \rho) - 2mA - K$$

To make the analysis simpler we consider first the mean-field limit for which the results are well known. Then we have $L_o = L = 0$ and $K_o = K = 0$

$(A = J)$. From (31) we again obtain Eq. (28). The first one of Eqs. (31) means

$$1 - \rho_o = (1 - \rho)\, e^{Am^2} \tag{32}$$

while the sum to the last two means

$$\frac{\rho_o^2}{4(1 - \rho_o)^2} = \frac{\rho_1 \rho_2}{(1 - \rho)^2} = \frac{1}{4} \frac{\rho^2 - m^2}{(1 - \rho)^2}. \tag{33}$$

Eq. (28) can also be solved with respect to ρ

$$\rho = m\, \frac{\cosh(2mA)}{\sinh(2mA)} \tag{34}$$

Use of (32) and (34) in (33) gives

$$\rho_o = (\rho^2 - m^2)^{1/2}\, e^{Am^2} = \frac{m}{\sinh(2mA)}\, e^{Am^2} \tag{35}$$

Elimination of ρ and ρ_o in (32) then gives

$$1 - \frac{m}{\sinh(2mA)}\, e^{Am^2} = \left(1 - m\, \frac{\cosh(2mA)}{\sinh(2mA)}\right) e^{Am^2} \tag{36}$$

or

$$e^{-Am^2} + m\, \tanh(mA) - 1 = 0 \tag{37}$$

This equation determines A as function of m or vice versa $(\rho \neq \rho_o)$. The tricritical point will be determined by the resulting value of A when $m \to 0$. The tricritical point and the phase transition close to it can be determined explicitly by expansion. Numerically Eq. (37) can be solved in a straightforward way for any m or A. The expansion gives

$$1 - Am^2 + \tfrac{1}{2}A^2 m^4 - \tfrac{1}{6}A^3 m^6 + \cdots$$
$$+ m(mA - \tfrac{1}{3}(mA)^3 + \tfrac{2}{15}(mA)^5 + \cdots) - 1 = 0 \tag{38}$$

or

$$\tfrac{1}{2} - \tfrac{1}{3}A = (\tfrac{1}{6}A - \tfrac{2}{15}A^3)\, m^2 \tag{39}$$

Accordingly the tricritical value of A is

$$A_{tr} = A = 3/2 \tag{40}$$

and from (30) the tricritical density is thus

$$\rho_{tr} = 1/3 \tag{41}$$

For small m, (39) gives

$$A - \tfrac{3}{2} = 3(\tfrac{2}{15}A_{tr}^2 - \tfrac{1}{6})\, A_{tr} m^2 = \tfrac{3}{5} m^2 \tag{42}$$

and then from (34) and (35)

$$\begin{aligned}
\rho - \frac{1}{3} &= \frac{1}{2A} + m^2 - \frac{1}{3} = \frac{13}{15}\, m^2 \\[2mm]
\rho_o - \frac{1}{3} &= \frac{1}{2A} - \frac{1}{3} = -\frac{2}{15}\, m^2
\end{aligned} \tag{43}$$

From this solution we note that

$$1 - 2A\rho_o = O(m^4) \tag{44}$$

which to order m^2 is nothing but Eq. (30), which determines the ordinary critical point. In mean-field, where $A = J(\propto \beta)$, this means that the critical line and the line for the phase with density ρ_o $(m = 0)$ has a common tangent at the tricritical point (in a $\rho - T$ diagram). Thus the angle between these two lines will be 180 degrees, which is characteristic of mean-field theories of tricriticality.

Mean-field theory becomes exact for $J(\mathbf{r})$ of infinite range. We will now begin the analysis for forces of finite range. To do so we need a more explicit expression for the integral given by (13) or (21), at least close to the critical point. For forces of finite range γ^{-1}, where γ is the inverse range of $J(\mathbf{r})$,

$$\tilde{J}(\mathbf{k}) = \tilde{J}(0) - \text{const}(k/\gamma)^2 + \cdots \tag{45}$$

for small k, where $k = |\mathbf{k}|$. For small ε, where

$$\varepsilon^2 = 1 - \frac{1}{z}\tilde{J}(0) = 1 - \frac{2R}{I}(K + A) = \frac{1}{I}(1 - 2RA) \tag{46}$$

we thus find that the I of (21) can be expanded as

$$I = I_m(1 - 2b\varepsilon + \cdots) \tag{47}$$

where I_m and $b \propto \gamma^3$ are constants.

A convenient choice [10] of $J(\mathbf{r})$ is $P(\mathbf{r}, z)$, the Green's function for the (discretized) Helmholtz equation on the lattice [11],

$$P(\mathbf{r}, z) = \frac{1}{(2\pi)^3} \int d\mathbf{k} \frac{e^{i\mathbf{k}\mathbf{r}}}{1 - z\tilde{\psi}(\mathbf{k})}, \qquad (48)$$

where the integration is over a Brillouin zone and $\tilde{\psi}(\mathbf{k})$ is the characteristic function of the lattice. Then $\tilde{J}(\mathbf{k}) \sim [1 - z\tilde{\psi}(\mathbf{k})]^{-1}$ + const and γ^2 can be taken to be proportional to $z - 1$. When $z = 1$, $P(\mathbf{r}, z)$ becomes the Green's function for the discrete Laplace equation and so becomes an appropriate Coulombic $J(\mathbf{r})$ for the lattice, with $\tilde{J}(\mathbf{k}) \sim k^{-2}$ for small k, which we shall exploit in Section III. Finally the nearest-neighbor case corresponds to simply letting $\tilde{J}(\mathbf{k})$ be proportional to $\tilde{\psi}(\mathbf{k})$ itself. For instance, for the simple cubic lattice one has

$$\tilde{J}(\mathbf{k}) = J\tfrac{1}{3}(\cos k_x + \cos k_y + \cos k_z) = J(1 - \tfrac{1}{6}k^2 + \cdots) \qquad (49)$$

By a straightforward computation one then finds

$$2bI_m = \frac{3\sqrt{6}}{2\pi} = 1.17... \qquad (50)$$

The I_m has also been computed in an analytic way [12]. Its value in the literature is reported to be $I_m = 1.5163860591...$

Equation (30), which determines the critical line, will hold in general, not only in the mean-field case. Use of (9), (30), and (46) shows that $\varepsilon = 0$ on the critical line and at the tricritical point. Due to (47) the equation of state will thus have singular behavior in the neighborhood of this line.

If there is a magnetic field acting on the spin-one system, then Eq. (27) holds. We will study the critical isotherm for small m.

$$\beta H = \frac{m}{\rho} + \frac{1}{3}\left(\frac{m}{\rho}\right)^3 + \frac{1}{5}\left(\frac{m}{\rho}\right)^5 + \cdots - 2mA \qquad (51)$$

From (46) and (47)

$$\varepsilon^2 I = 1 - 2RA = 1 + 2RK - 2RJ = I - 2RJ = I_m(1 - 2b\varepsilon + \cdots) - 2(\rho - m^2)J \qquad (52)$$

At the critical point $\varepsilon = 0$ and $m = 0$ so $I_m = 2\rho J$. When a magnetic field is applied, the ρ as defined by (9) will vary along with m. However, for

simplicity we assume it fixed for the moment as this should not affect our conclusions. So for critical J and $m \neq 0$

$$\varepsilon^2 I = \varepsilon^2 I_m = -2bI_m\varepsilon + \frac{m^2}{\rho}I_m \tag{53}$$

or

$$\varepsilon = \frac{1}{2b}\frac{m^2}{\rho} \propto \frac{1}{\gamma^3}m^2 \tag{54}$$

for small $m^2(\sim \gamma^3)$. So with (46) and (51)

$$\beta H = \frac{m}{\rho} + \frac{1}{3}\left(\frac{m}{\rho}\right)^3 + \frac{1}{5}\left(\frac{m}{\rho}\right)^5 + \cdots - 2m\frac{1-\varepsilon^2 I}{2(\rho - m^2)}$$

$$= -\left(\rho - \frac{1}{3}\right)\left(\frac{m}{\rho}\right)^3 + \left(\frac{1}{5} - \rho^2\right)\left(\frac{m}{\rho}\right)^5 + \frac{m}{\rho}I_m\left(\frac{m^2}{2b\rho}\right)^2 + \cdots \tag{55}$$

This clearly shows the previously mentioned inconsistency of the ordinary MSA critical point. The critical behavior in an extended region is dominated by the $m\varepsilon^2$ term ($\sim m^5/\gamma^6$ as $m \to 0$). However, in a region where $m^2 \sim \gamma^3$, (55) has an irregular behavior since the m^3 term which has a negative coefficient will dominate for $\rho > 1/3$. When ρ approaches $1/3$ one sees that this inconsistency vanishes. At $\rho = 1/3$, which will be the tricritical point, (the same ρ as in mean field) this inconsistency does not exist any longer. Thus we have reason to expect that the MSA results close to the tricritical point are close to the exact ones and that we may obtain meaningful results arbitrarily close to this point. As we will show explicitly for our model, this will be true if the forces are not too short-ranged. Nearest-neighbor interaction only [Eq. (49)] will turn out to be too short-ranged in this respect.

Now we will begin to analyze the behavior close to the tricritical point. Along the critical line we from (52) find ($\varepsilon = 0$, $m = 0$, $R = \rho$)

$$0 = 1 - 2\rho A = I_m - 2\rho J \qquad \text{or} \qquad J = I_m A \tag{56}$$

Along the curve of coexistence below the tricritical point $\varepsilon \neq 0$ which means [Eq. (52) to $O(\varepsilon)$]

$$I_m(1 - 2b\varepsilon + \cdots) - 2(\rho - m^2)J = 0, \tag{57}$$

and for the branch with $m = 0$

$$I_m(1 - 2b\varepsilon_o + \cdots) - 2\rho_o J = 0 \tag{58}$$

Along the curves of coexistence away from the tricritical point ($p = 1/3$) we must expect J (inverse temperature) to grow to have meaningful results, i.e.,

$$2b\varepsilon_o < 2(\tfrac{1}{3} - p_o)\, J/I_m = 3(\tfrac{1}{3} - p_o) \tag{59}$$

For small m we expect $p_o - p_{tr}$, $p - p_{tr}$, and $A - A_{tr}$ to be of $O(m^2)$ as found in the mean-field case. Thus we must expect $\varepsilon^2 \sim m^4$ (not $\varepsilon^2 \sim m^2$) from (52) in order not to violate (59). Even with $\varepsilon \sim m^2$ Eq. (59) may still be violated if $b \sim \gamma^3$ is too large. When this is the case the MSA results cannot be expected to be meaningful arbitrarily close to the tricritical point, i.e., inconsistencies become too large.

A consequence of $\varepsilon_o \sim m^2$ and Eq. (58) is that

$$I_m - 2p_o J = 2bI_m\varepsilon_o \sim \gamma^3 m^2 \tag{60}$$

This differs from the mean-field result (44) (where $A = J$). The consequence of (60) is that the angle between the critical line and the line for the phase with density p_o becomes less than 180 degrees at the tricritical. This is due to the singular behavior (47) of the integral (21). The result of (60) is in accordance with both the results of renormalization-group analysis [13] and with the experimental situation for $He^3 - He^4$ mixtures [14], a feature which has not been possible to describe by mean-field theories.

We find that the equations of (31) can be handled exactly without too much trouble. This hinges very much on an expression for I that makes it possible to find L explicitly and at the same time makes it possible to eliminate ε_o and ε. The numerical problem reduces to solving two equations for the two unknown p_o and m with A considered known. [In mean-field we had only one such equation (37).] The suitable expression for I will be

$$I = \frac{I_m}{1 + 2b\varepsilon + c\varepsilon^2} = I_m(1 - 2b\varepsilon + \cdots) \tag{61}$$

where $I_m = 1 + 2b + c$ ($I = 1$ for $\varepsilon = 1$). We want to express all other quantities in terms of p_o, m, and A. Eq. (34) holds and by that we have an expression for p. Combining (9), (52), and (61) we find

$$\varepsilon^2 I = \alpha = 1 - 2(p - m^2)\,A$$
$$(I_m - c\alpha)\,\varepsilon^2 - 2b\alpha\varepsilon - \alpha = 0 \tag{62}$$

$$\varepsilon = \frac{1}{I_m - c\alpha}\,[\,b\alpha + \sqrt{(b\alpha)^2 + (I_m - c\alpha)\,\alpha}\,] \tag{63}$$

Eq. (52) also gives the inverse temperature J

$$J = \frac{I(1 - \varepsilon^2)}{2(\rho - m^2)} \tag{64}$$

where (61) and (63) gives I explicitly. For $R = \rho_o$ Eq. (52) becomes

$$\varepsilon_o^2 I_o = I_o - 2\rho_o J \tag{65}$$

or by use of (61)

$$\varepsilon_o^2 = 1 - q(1 + 2b\varepsilon_o + c\varepsilon_o^2) \tag{66}$$

where $q = 2\rho_o J/I_m$.
  So

$$\varepsilon_o = \frac{1}{1 + qc} \left[-qb + \sqrt{(qb)^2 + (1 - q)(1 + qc)} \right], \tag{67}$$

and by that we have K_o and K explicitly (see Eq. (21))

$$K = \frac{I - 1}{2(\rho - m^2)} \quad \text{and} \quad K_o = \frac{I_o - 1}{2\rho_o} \tag{68}$$

Finally we need L and L_o. From (20), (21), and the definition (46) of ε^2 we see that

$$\frac{dL}{d\sigma} = \frac{1}{2\sigma}(I - 1) - \frac{1}{2}\frac{d}{d\sigma}(\ln I) \tag{69}$$

where

$$\sigma = \frac{1}{z}J(0) = 1 - \varepsilon^2$$

$$d\sigma = -2\varepsilon d\varepsilon \tag{70}$$

Accordingly

$$L = -Q - \tfrac{1}{2}\ln I \tag{71}$$

The integral Q can be evaluated explicitly. (Constant of integration will be of no interest since we will only need $L_0 - L$.) We have

$$Q = \int_0^\varepsilon \frac{x}{(1-x^2)} \left[\frac{I_m}{1+2bx+cx^2} - 1 \right] dx$$

$$= \int_0^\varepsilon \frac{I_m}{c} \left\{ \frac{-1}{2(\varepsilon_1+1)(\varepsilon_2+1)} \frac{1}{x+1} - \frac{1}{2(\varepsilon_1-1)(\varepsilon_2-1)} \frac{1}{x-1} \right.$$

$$\left. + \frac{\varepsilon_1}{(1-\varepsilon_1^2)(\varepsilon_1-\varepsilon_2)} \frac{1}{x-\varepsilon_1} + \frac{\varepsilon_2}{(1-\varepsilon_2^2)(\varepsilon_2-\varepsilon_1)} \frac{1}{x-\varepsilon_2} \right\} dx + \frac{1}{2} \ln(1-\varepsilon^2)$$

$$= \frac{\varepsilon_1+\varepsilon_2}{(\varepsilon_1+1)(\varepsilon_2+1)} \ln(1+\varepsilon) + \frac{\varepsilon_2-1}{\varepsilon_1+1} \frac{\varepsilon_1}{\varepsilon_2-\varepsilon_1} \ln(|\varepsilon_1-\varepsilon|)$$

$$+ \frac{\varepsilon_1-1}{\varepsilon_2+1} \frac{\varepsilon_2}{\varepsilon_1-\varepsilon_2} \ln(|\varepsilon_2-\varepsilon|). \tag{72}$$

Here the ε_1 and ε_2 are the roots of $1+2bx+cx^2 = 0$.

$$\varepsilon_1 = \frac{1}{c} [-b + \sqrt{b^2-c}]$$

$$\varepsilon_2 = \frac{1}{c} [-b - \sqrt{b^2-c}] \tag{73}$$

$$\frac{I_m}{c} = \frac{1}{c} + \frac{2b}{c} + 1 = (\varepsilon_1-1)(\varepsilon_2-1)$$

By the use of the above expressions in (31) we arrive at two equations that can be solved numerically with respect to p_0 and m for given A. E.g., we may use the first expression of Eq. (31) and the sum of the last two (their difference gives (28) or (34) which we have already utilized.)

Finally we will expand the equations around the tricritical point, i.e., we will consider small $m \to 0$. For deviations from tricritical values we write

$$x = p - \tfrac{1}{3}; \qquad x_0 = p_0 - \tfrac{1}{3} \tag{74}$$

Expansion of (28) gives

$$A = \tfrac{3}{2}(1-3x+3m^2) \qquad \text{or} \qquad x = m^2 - \tfrac{2}{9}(A-\tfrac{3}{2}) \tag{75}$$

Equation (62) by use of (28) gives

$$\varepsilon^2 I = \varepsilon^2 I_m = 1 - 2(\rho - m^2) A$$

$$= 1 - \left[1 + \left(\frac{1}{3} \frac{1}{\rho^2} - \frac{1}{\rho} \right) m^2 + \left(\frac{1}{5} \frac{1}{\rho^4} - \frac{1}{3} \frac{1}{\rho^3} \right) m^4 \right]$$

$$= 9m^2 \left(x - \frac{4}{5} m^2 \right) \tag{76}$$

Equation (64) and (61) gives

$$J = \frac{I_m(1 - 2b\varepsilon)}{2((\rho - m^2)} = \frac{3}{2} I_m(1 - 2b\varepsilon - 3x + 3m^2) \tag{77}$$

and combined with (65)

$$\varepsilon_o = \varepsilon - \frac{3}{2b}(x_o - x + m^2) \tag{78}$$

Equation (28) or (75) is the result of the difference between the two last equations of (31). If we take their sum we instead get

$$\ln(\tfrac{1}{2}\rho_o) - \ln(1 - \rho_o) - K_o = \tfrac{1}{2}\ln(\rho_1\rho_2) - \ln(1 - \rho) - K \tag{79}$$

Here we need an expression for $K - K_o$ which we get from (18) and (62)

$$K = \frac{\varepsilon^2 I - 1}{2(\rho - m^2)} + J \tag{80}$$

From this, using (9) and (74), we finally obtain [through expansions in m/ρ and in x that are put into (79)]

$$\varepsilon^2 I_m - \varepsilon_o^2 I_m = \tfrac{27}{4}(x^2 - x_o^2) - \tfrac{9}{2} m^4 \tag{81}$$

To obtain the last equation we need we expand the first of Eqs. (31) and add to the result $-1/3$ times the left-hand-side of (79). We then use (61), (64), (69) and (80) to find an expression for $L + \tfrac{1}{3}K$. Expanding first in powers of m [with A given by (28)] and then in powers of $x[= \rho - 1/3]$ we finally obtain

$$-\tfrac{3}{2} x_o \varepsilon_o^2 I_m - \tfrac{1}{6} \varepsilon_o^3 (2b I_m) + \tfrac{27}{4} x_o^3$$

$$= -\tfrac{3}{2}(x - m^2) \varepsilon^2 I_m - \tfrac{1}{6}\varepsilon^3(2b I_m) + \tfrac{27}{4}x^3 - \tfrac{27}{2}xm^4 + \tfrac{36}{5}m^6 \tag{82}$$

The resulting equations to be solved close to the tricritical point are thus Eqs. (75)–(78), (81), and (82) with one of the parameters A, ε_o, ε, x, x_o, m^2, and J considered known. Besides these quantities the result also depends upon the parameters I_m and b. However, by a simple inspection of the equations it is easily seen that these two parameters reduce to only one parameter

$$B = \frac{b}{\sqrt{I_m}} \tag{83}$$

that affect the result since $\varepsilon \sqrt{I_m}$ and $\varepsilon_o \sqrt{I_m}$ can replace ε and ε_o respectively as parameters. The $B \sim b \sim \gamma^3$ where γ is the inverse range of interaction.

These equations for the phase transition close to the tricritical point can be solved explicitly in a straight-forward manner for arbitrary B on a computer. One finds that our MSA solution gives a well-defined phase transition close to the tricritical point. See Figs. 1 and 2 for the quantitative results. This is in contrast to the MSA behavior found from the energy
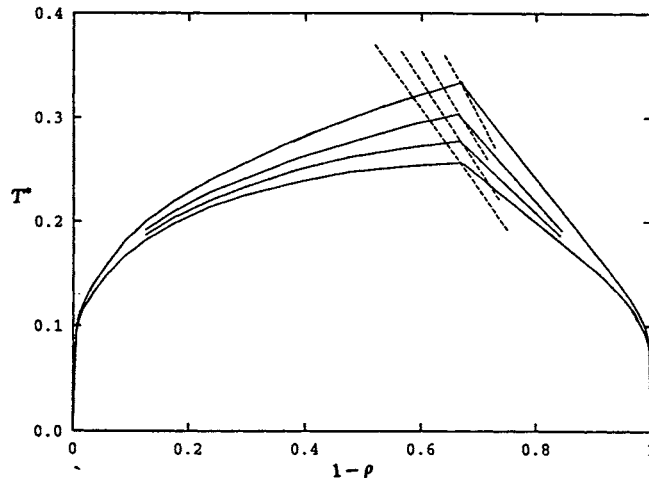

Fig. 1. The coexistence curve in the density-temperature plane. Here p is the fraction of sites occupied by spins and T^* is $k_B T/\tilde{J}(0)$, a dimensionless measure of temperature in units of interaction strength; see Eq. (11). The four sets of coexistence curves correspond to four increasing values of the inverse range of interaction given by B = 0.00, 0.07, 0.14, and 0.21 (from top to bottom, at the tricritical point). The coexistence-curve slope at the tricritical point on its left-hand side becomes zero at B = 0.22. The curve for the infinite-range value B = 0.00 is exact and coincides with the result of mean-field theory. B = 0.21 corresponds to a somewhat longer range than nearest-neighbor interaction. See Eqs. (21), (46), (47), and (83) for analytic details. The dashed lines represent the slopes of the λ-lines of Curie points at tricritical.
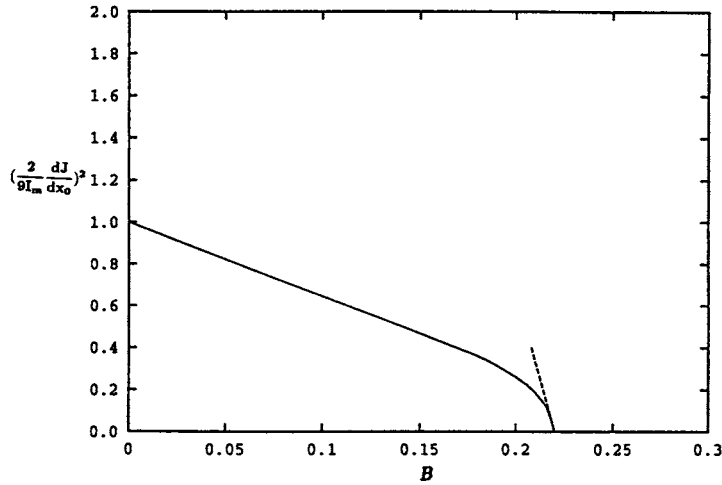
Fig. 2. Slope of coexistence curve squared (relative to its mean-field value) at the tricritical point on its low-density side, plotted against B, a dimensionless measure of inverse range of potential. The ordinate is given by $((2/9I_m)\,dJ/dx_o)^2$, which is $(1+(2/3)b\varepsilon_o/x_o)^2$. See Eqs. (77), (78), and (83) for further analytic details. The dashed line represents the limiting slope of the curve.

relation for the spin-1/2 Ising model (i.e., simple lattice gas) where irregularities and inconsistencies distort the description of the phase transition close to the critical point [2, 3].

For some special cases we may solve our equations in an analytic way. One such case is the mean-field limit $B \to 0(\gamma \to 0)$. In this case Eq. (78) gives

$$x_o - x + m^2 = 0 \tag{84}$$

This together with (81) can then be used in Eq. (82) to give

$$\tfrac{3}{2}x_o(\varepsilon^2 - \varepsilon_o^2)\,I_m + \tfrac{27}{4}(x_o^3 - x^3) + \tfrac{27}{2}xm^4 - \tfrac{36}{5}m^6 = 0$$

$$x_o[\tfrac{81}{8}(x^2 - x_o^2) - \tfrac{27}{4}m^4] + \tfrac{27}{4}(x_o^3 - x^3) + \tfrac{27}{2}xm^4 - \tfrac{36}{5}m^6 = 0$$

$$\tfrac{81}{8}(2x_o^2 m^2 + x_o m^4) - \tfrac{27}{4}x_o m^4 - \tfrac{27}{4}(3x_o^2 m^2 + 3x_o m^4 + m^6) \tag{85}$$

$$+ \tfrac{27}{2}(x_o + m^2)\,m^4 - \tfrac{36}{5}m^6 = 0$$

$$- \tfrac{27}{8}x_o m^4 - \tfrac{9}{20}m^6 = 0$$

Thus

$$x_o = -\tfrac{2}{15}m^2$$

$$x = \tfrac{13}{15}m^2 \tag{86}$$

This agrees with our previous result (43) as it should. In addition (76) and (81) further give

$$\varepsilon^2 I_m = 9m^2(\tfrac{13}{15} - \tfrac{4}{5})\, m^2 = \tfrac{3}{5} m^4$$

$$\varepsilon_o^2 I_m = \varepsilon^2 I_m - (\tfrac{27}{4}(x^2 - x_o^2) - \tfrac{9}{2} m^4) = \tfrac{3}{20} m^4 \tag{87}$$

and from (75) and (77) ($I_m = 1$)

$$J = A = \tfrac{3}{2}(1 - 3x + 3m^2) = \tfrac{3}{2} + \tfrac{3}{2} m^2 \tag{88}$$

Besides this $B = 0$ solution we also can find explicitly the value below which B has to be kept to have a solution of the equations that signals a phase transition close to the tricritical point. [Beyond that value of B the equations do not have a real solution. At an ordinary critical point the MSA always has such an inconsistency (for any γ).] The limiting B is determined by $\varepsilon_o = 0$ ($\varepsilon_o < \varepsilon$) which can be seen from Eq. (47) for instance to require ε (and ε_o) to be real and positive to be meaningful. As $\varepsilon_o \to 0$ the numerical solution indicates that $x_o \to 0$. So let us assume $x_o = 0$ for $\varepsilon_o = 0$. Eq. (76) put into (81) then gives

$$9m^2(x - \tfrac{4}{5} m^2) = \tfrac{27}{4} x^2 - \tfrac{9}{2} m^4$$

$$x^2 - \tfrac{4}{3} x m^2 + \tfrac{2}{5} m^4 = 0 \tag{89}$$

$$x = (\tfrac{2}{3} \pm \tfrac{\sqrt{10}}{15})\, m^2$$

Since $\varepsilon^2 > 0$ means $x > \tfrac{4}{5} m^2$ it is clear that the larger one of the roots is the proper one here, i.e.,

$$x/m^2 = \tfrac{2}{3} + \tfrac{\sqrt{10}}{15} = 0.877 \tag{90}$$

To verify that $x_o = 0$ is the proper value for $\varepsilon_o = 0$ we consider Eq. (82) too, where we eliminate $\varepsilon^2 I_m$ and $2b\varepsilon$ by means of Eqs. (76) and (78). By doing so we again recover Eq. (89). Thus $x_o = 0$ is indeed a solution.

From Eqs. (75)—(78) we then finally find for $\varepsilon_o = 0$

$$A - \frac{3}{2} = \frac{9}{2}(m^2 - x) = \frac{3(5 - \sqrt{10})}{10} m^2 = 0.551 m^2$$

$$\varepsilon^2 I_m = 9m^2 \left(x - \frac{4}{5} m^2\right) = \frac{3(\sqrt{10} - 2)}{5} m^4; \quad \varepsilon \sqrt{I_m} = 0.835 m^2 \tag{91}$$

$$B = b/\sqrt{I_m} = \frac{3}{2} \frac{m^2 - x}{\varepsilon \sqrt{I_m}} = \frac{5 - \sqrt{10}}{10} \sqrt{\frac{5}{3(\sqrt{10} - 2)}} = 0.220$$

This value of B we can compare with the one for nearest-neighbor interaction which from (49) and (50) means

$$B = \frac{2bI_m}{2I_m^{3/2}} = 0.314 \tag{92}$$

Since the latter B is the larger one, it is clear that the interaction must be a little more long-ranged than nearest-neighbor to get a proper phase transition just below the tricritical point when the MSA is utilized. However, for $0 < B < 0.220$, the MSA, in contrast to mean-field theories, gives a phase diagram that is in close accordance with experimental results as well as exact theoretical results for tricritical points [6–8]. This is consistent with the conclusion [8] that the phase diagram close to the tricritical point is characterized by the singular behavior resulting from the finite range of real interactions.

III. THE SPIN-1 SYSTEM AS A COULOMB GAS

On the simple cubic lattice with unit lattice spacing the Fourier transform of the discretized Coulomb interaction will be

$$\tilde{u}_c(\mathbf{k}) = \frac{4\pi e^2}{6(1 - \tilde{\psi}(\mathbf{k}))} \xrightarrow{k \to 0} \frac{4\pi e^2}{k^2 + \cdots} \tag{93}$$

where e is charge and $\tilde{\psi}(\mathbf{k}) = \frac{1}{3}(\cos k_x + \cos k_y + \cos k_z)$. The $\tilde{u}$ diverges when $k \to 0$, but is finite when $k_i \to \pm \pi$. We note that this Coulomb potential can be incorporated into the spin-one model studied in this work. For low temperatures one expects an ordering transition into a crystal lattice of antiferromagnetic type. This ordering will correspond to that of the ferromagnetic phase considered in this work if one changes the sign of the interaction for odd-numbered neighbors. Thus the equivalent ferromagnetic problem has the interaction

$$\tilde{u}_F(\mathbf{k}) = -\frac{4\pi e^2}{6(1 + \tilde{\psi}(\mathbf{k}))} \tag{94}$$

such that now

$$2\tilde{J}(\mathbf{k}) = -\beta \tilde{u}_F(\mathbf{k}) + \text{const}$$

where the const is adjusted so that $J(0) = 0$ is implied according to Eq. (11). The $\tilde{u}_F$ will represent a staggered interaction, and in terms of its γ dependence,

corresponds to a γ that is larger than for nearest-neighbor interaction (i.e., is formally a more short-ranged interaction, see Eq. (45)).

Evaluations for the Coulomb problem can now be closely related to the nearest-neighbor case. Thus one expects a line of critical points (which for the Coulomb case will be the antiferromagnetic line of Néel points) for $\rho \geqslant \frac{1}{3}$ with $\rho = 1/3$ being the MSA tricritical point. However, as we can expect the parameter B of Eq. (92) to be larger than 0.22 the MSA will not yield a well-defined tricritical point, as discussed earlier, when one obtains its thermodynamics through the energy relation. For this reason, the MSA does not appear to be useful in treating phase separation in the Coulomb lattice gas. On the other hand, it may well prove useful in treating thermo-dynamic states away from phase boundaries. Here we show explicitly that the standard Debye-Hückel low-density limit is found in the MSA Coulomb lattice gas. To obtain the close connection to the nearest-neighbor lattice gas we can consider the general lattice Green's function

$$\tilde{\varphi}(\mathbf{k}) = A \left(\frac{1}{1 - \alpha\tilde{\psi}} - I_\alpha \right) \tag{95}$$

with

$$A = \frac{1 - \alpha}{1 - (1 - \alpha) I_\alpha}$$

$$I_\alpha = \frac{1}{(2\pi)^3} \int \frac{d\mathbf{k}}{1 - \alpha\tilde{\psi}(\mathbf{k})} \tag{96}$$

The $\tilde{\varphi}(\mathbf{k})$ is normalized such that $\tilde{\varphi}(0) = 1$ and $\varphi(0) = 0$. The integral of interest is the one for I given by (21), to which (48) reduces at $\mathbf{r} = 0$. By rearrangement this integral can be related to integral (96). We find

$$P(z) = \frac{1}{(2\pi)^3} \int \frac{d\mathbf{k}}{1 - z\tilde{\varphi}(\mathbf{k})}$$

$$= \frac{1}{(2\pi)^3} \int \frac{d\mathbf{k}(1 - \alpha\tilde{\psi})}{1 - q(1 - I_\alpha) - \alpha(1 + qI_\alpha)\tilde{\psi}}$$

$$= \frac{1}{1 - q(1 - I_\alpha)} \frac{1}{(2\pi)^3} \int \frac{(\alpha/W (1 - W\tilde{\psi}) + 1 - (\alpha/W)}{1 - W\tilde{\psi}} d\mathbf{k}$$

$$= \frac{1}{1 - q(1 - I_\alpha)} \left[\frac{\alpha}{W} + \left(1 - \frac{\alpha}{W}\right) P_0(W) \right]$$

$$= \frac{1}{1 + qI_\alpha} \left[1 + \frac{q}{1 - q(1 - I_\alpha)} P_0(W) \right] \tag{97}$$

where

$$q = zA$$

$$W = \alpha \, \frac{1 + qI_\alpha}{1 - q(1 - I_\alpha)} \tag{98}$$

$$P_0(W) = I_W$$

Interaction (94) is obtained by putting $\alpha = -1$. This yields $(I_\alpha = I_{-\alpha})$

$$q = -\frac{2z}{2I_1 - 1}$$

$$W = -1 - \frac{2z}{2(1 - z)(I_1 - 1) + 1} \tag{99}$$

Now consider small densities such that z is small. Then we have (see Eq. (46))

$$-W = 1 - \varepsilon^2$$

$$\varepsilon^2 = \frac{2z}{2I_1 - 1} \tag{100}$$

$$P(z) - 1 = \frac{q}{1 + qI_\alpha} \left[\frac{1}{1 - q(1 - I_\alpha)} P_0(W) - I_\alpha \right]$$

$$\xrightarrow[q = -\varepsilon^2 \to 0]{} \varepsilon^2 (I_1 - P_0(1 - \varepsilon^2)) = \frac{3\sqrt{6}}{2\pi} \varepsilon^3 \tag{101}$$

utilizing (50) $(P_0(1) = I_1)$.

The excess chemical potential μ^{ex} is given by expression (26) for μ_1 and μ_2 for $m = 0$, i.e., the disordered or fluid state. So by use of Eqs. (26), (21), and (9) $(P(z) = I)$ we have

$$\beta \rho \mu^{ex} = -\rho K = -\rho \, \frac{I - 1}{2R} = -\frac{1}{2}(P(z) - 1) = -\frac{3\sqrt{6}}{4\pi} \varepsilon^3 \tag{102}$$

Finally the ε^2 should be identified in terms of the ionic fluid parameters. Eq. (95) for small Δk and $\alpha = -1$ is $(\Delta k_i = k_i - \pi$ and $(\Delta k)^2 = (\Delta k_x)^2 + (\Delta k_y)^2 + (\Delta k_z)^2)$

$$-z\tilde{\varphi}(\mathbf{k}) = -z \, \frac{6A}{(\Delta k)^2} = 6 \, \frac{2z}{2I_1 - 1} \, \frac{1}{(\Delta k)^2} = \frac{6\varepsilon^2}{(\Delta k)^2} \tag{103}$$

This can be identified with the Coulomb interaction. For small z (or $\beta\rho$) such that K is small one then has

$$-z\tilde{\varphi}(\mathbf{k}) = \beta\rho\tilde{u}_c(\mathbf{k}) = \frac{\kappa^2}{k^2} \tag{104}$$

with $\kappa^2 = 4\pi\beta\rho e^2$. Thus (with $\Delta k \leftrightarrow k$)

$$6\varepsilon^2 = \kappa^2 \tag{105}$$

which inserted into (102) yields

$$\beta\rho\mu^{ex} = -\frac{\kappa^3}{8\pi} \tag{106}$$

This is the well-known Debye–Hückel result for ionic fluids.

Finally we can evaluate the parameter B as given by (92). The $P(z)$ should then be investigated close to $z = 1$ so we put $z = 1 - \varepsilon^2$.

$$P(z) = (1 - 2I_1)(1 - 2P_0(W)) \tag{107}$$

as $q = -2/(2I_1 - 1)$ for $z = 1$. Expanding expression (99) for W we find

$$W = 1 - \varepsilon_W^2; \qquad \varepsilon_W^2 = 2(2I_1 - 1)\varepsilon^2 \tag{108}$$

Comparing with Eqs. (47)–(50) it follows that

$$P_0(W) = I_m(1 - 2b\varepsilon_W + \cdots)$$

So

$$P(z) = I_{1m}(1 - 2b_1\varepsilon + \cdots)$$

with

$$I_{1m} = (2I_1 - 1)^2$$

$$b_1 = 2I_1 b \sqrt{\frac{2}{2I_1 - 1}}$$

Inserted into (92) this yields $(I_m = I_1)$

$$B = \frac{b_1}{I_{1m}^{1/2}} = \left(\frac{2I_1}{2I_1 - 1}\right)^{3/2} \frac{b}{I_1^{1/2}} = 0.572$$

with b and B given by (49) and (50).

IV. DISCUSSION

As mentioned in our Introduction, one expects tricriticality in a spin-1 ferromagnet for all values of B. The fact that one finds MSA tricriticality confined to a range of B that ends at the value 0.220 on a simple cubic lattice is almost surely an artifact of the approximation. In light of the results of [7-9] and of [13] one would expect the zero slope to the left of the tricritical point to be realized only for $B \to \infty$ rather than for any finite value of B.

Except for this feature, the thermodynamic behavior of the MSA is very much like the exact behavior found in the spherical-model limit, $D \to \infty$, of a classical D-dimensional spin system with the spherical constraint $\sum_{i=1}^{N} s_i^2 = N$, which was studied in detail in reference [7] and [8]. In particular, the way the coexistence-curve geometry hinges upon the potential range in the $D \to \infty$ limit is closely mirrored by the MSA spin-1 behavior. We conclude from this study that when used judiciously, the MSA is a useful approximation for the study of spin-1 systems, and its solution deserves to be extended to the full BEG Hamiltonian studied in ref. [5].

We have used the correspondence (that follows the equivalence noted above Eq. (94)) between the thermodynamics for staggered and non-staggered potentials to argue that one should expect tricritical behavior in the spin-1 antiferromagnet with Coulombic $J(r)$, which is the lattice-gas version of the restricted primitive model (RPM) of a charged hard-sphere fluid of anions and cations of equal charge number and diameter. The suggestion that the RPM might have a tricritical point was made in 1993 by Kholodenko and Beyerlein [15] on the grounds that one might expect such behavior for a spin-1 antiferromagnet. Fisher [16] subsequently argued against the suggestion. He noted that there was no experimental evidence for systems believed to be well-modelled by the RPM or direct simulation evidence for the RPM itself of such tricriticality, and further argued that the theoretical grounds for expecting such tricriticality is weak.

There continues to be no direct evidence for tricriticality in continuum models of ionic fluids or in real electrolytes. However, unlike Fisher, we believe there are strong theoretical grounds for expecting tricriticality in the lattice-gas version of the RPM on the simple cubic lattice. We regard the argument we have put forward here as one of them, under the assumption that in an exact treatment tricriticality is preserved for B as large as 0.572, as the results of [7-9] and [13] strongly suggest. (Another is the fact that in the $\rho = 1$ limit in which all sites are occupied by ions, the antiferromagnetic spherical model with Coulombic $J(\mathbf{r})$ shows a Néel point on the simple cubic lattice [17].) We also believe that much could be learned by extending the results of [7] and [8] to a Coulombic $J(\mathbf{r})$.

Because of the absence of an underlying lattice structure in the RPM fluid that promotes the antiferromagnetic ordering of charges, it seems likely to us that the tricriticality we expect in the lattice gas may well not occur in the RPM fluid, where the usual gas-liquid appears to preempt the paramagnetic-antiferromagnetic ordering. The issue deserves further study, however, as does the possibility that a λ-line of Néel points persists in a solid phase of the RPM even if fluid tricriticality does not occur.

ACKNOWLEDGMENTS

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