Revised scaling variables in systems with many-body interactions

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Thermodynamic perturbation theory and the Kirkwood-Salsburg correlation function identities are used to study nearest-neighbor lattice gases with certain weak symmetry-breaking many-body interactions. It is shown that such systems may be mapped onto symmetric models by the introduction of suitable effective interactions and a shifted chemical potential, both of which depend explicitly on the temperature and fugacity of the original model. In the critical region, such a thermodynamic-state dependence implies the existence of a thermal scaling field which depends on the bare chemical potential, and this "field mixing" leads to a breakdown in the classical law of the rectilinear diameter. These results give a microscopic interpretation to a field-theoretic renormalization-group analysis which derives such a diameter singularity from the presence of terms cubic and higher in the order parameter and its gradients in an asymmetric Landau-Ginzburg-Wilson Hamiltonian. For a primarily repulsive three-body potential like the Axilrod-Teller interaction in classical insulating fluids, and in comparison with recent experiments, the analysis correctly describes the observed trends in the critical and near-critical behavior of the diameters with increasing particle polarizability.

I. INTRODUCTION

The lack of rigorous particle-hole symmetry in the Hamiltonian of a simple fluid suggests that certain aspects of its critical behavior should differ from those of the symmetric Ising model to whose universality class it belongs. In particular, the scaling variables of the fluid need not be the direct generalizations of those in the magnetic system, but may in fact be some linear combination. Such *thermodynamic field mixing* is found in continuum[1,2] and decorated-lattice models,[3,4] has been suggested on thermodynamic[5] and phenomenological[6] grounds, and appears in renormalization-group studies[7-9] of a Landau-Ginzburg-Wilson Hamiltonian with symmetry-breaking non-Ising terms.

One of the most important consequences of the presence of revised scaling variables is the existence of a weak critical singularity in the diameter ρ_d of the coexistence curve. With ρ_l and ρ_v the coexisting liquid and vapor densities, ρ_c the critical density, and $t = (T_c - T)/T_c$ the reduced temperature, it is predicted that as $t \rightarrow 0$,

$$\rho_d \equiv \frac{\rho_l + \rho_v}{2\rho_c} = 1 + A_{1-\alpha}t^{1-\alpha} + A_1 t + \cdots , \quad (1)$$

where α is the exponent which characterizes the critical divergence of the constant volume specific heat and the term linear in temperature is the universally observed analytic background. The coefficient $A_{1-\alpha}$ is identically zero for systems with particle-hole symmetry, but is finite in systems in which the effective thermal scaling field depends on the bare chemical potential.

For three-dimensional systems in the universality class of the Ising model, $\alpha \approx 0.11$, so that it is difficult experimentally to distinguish the presence of a linear term from the weakly-singular one. For many years, evidence was very weak for a breakdown in the classical law of the rec-

tilinear diameter,[10] an empirical observation which we use here to mean an *analytic* diameter,[11,12] that is, one varying like $\rho_d = 1 + A_1 t + \cdots$. Until recently, the only insulating fluid to show an appreciable departure from analyticity was SF_6.[13,14] However, Jüngst, Knuth, and Hensel[15] discovered that the coexistence curves of the alkali metals cesium and rubidium display anomalies with extremely large amplitudes, characterized by an exponent in excellent agreement with theory. It has been suggested[16] that the proximity of the liquid-vapor critical point to the metal-nonmetal transition which occurs in these systems upon expanding the liquid gives rise to a strong thermodynamic state dependence to the effective interparticle interactions and that this state dependence is the analog of field mixing.

Further observations of singular diameters in fluids were reported recently[17,18] for a series of insulating fluids (Ne, N_2, C_2H_4, and C_2H_6), and it was found that the amplitude of the diameter anomaly, as measured by the deviation of the critical density from that estimated by a linear extrapolation of the diameter from large t, scales with the critical temperature of the fluid, and is always such that $A_{1-\alpha} > 0$. This variation of the scaling variables with T_c has been attributed to the role of many-body dispersion forces, and in particular, to the three-body Axilrod-Teller interaction. It is also observed that the diameter slope outside the asymptotic critical region and the order parameter amplitude A_β, where $\Delta\rho \equiv (\rho_l - \rho_v)/2\rho_c \sim A_\beta t^\beta$, increase with T_c, or equivalently, with the molecular polarizability. These separate correlations may also be reinterpreted as a correlation between the two amplitudes A_1 and A_β, as shown in Fig. 1. Most of these correlations with fluid polarizability may be explained within a simple mean-field study of the critical behavior of a fluid with weak three-body interactions, the most significant of the many-body disper-
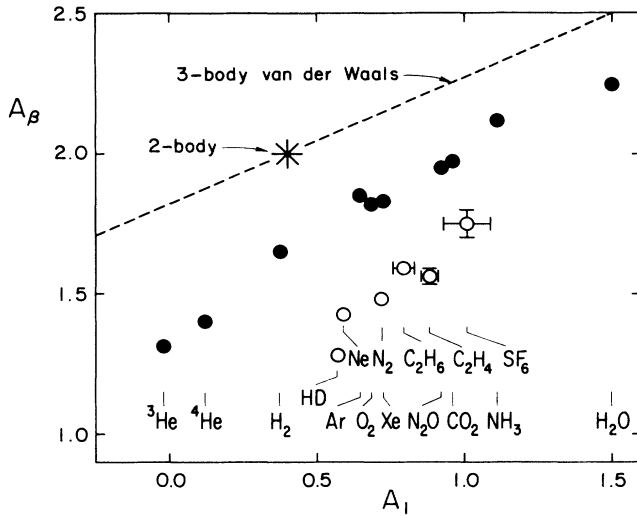
FIG. 1. Experimental correlation between order parameter amplitude and diameter slope, from Refs. 17 and 18.

sion forces. The dashed line in Fig. 1 is the prediction of a generalized van der Waals equation of state for such a fluid. That such interactions are important in the more polarizable fluids can be seen directly from the form of the triple-dipole potential[19] which is believed[20] to be the dominant many-body contribution to the thermodynamics of simple classical fluids. For a triad of particles at positions $(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)$, and with θ_i the interior angles of the triangle they form, the Axilrod-Teller potential is

$$V_{\text{AT}} = \tfrac{9}{16} I \alpha_p^3 \frac{3 \cos(\theta_1)\cos(\theta_2)\cos(\theta_3) + 1}{r_{12}^3 r_{13}^3 r_{23}^3} , \qquad (2)$$

where α_p is the polarizability (not to be confused with the critical exponent α) and I the first electronic excitation energy, often approximated by the ionization potential. On the other hand, the pairwise dispersion energy scales with the strength of the attractive part of the dominant two-body interaction $V_2(r) = -\tfrac{3}{4} I \alpha_p^2 / r^6$. The strength of three-body interactions relative to the pair potential is thus proportional to $\alpha_p / \bar{r}^3$, with $1/\bar{r}^3$ a typical inverse-cube interparticle separation. Setting $1/\bar{r}^3$ proportional to the density ρ, we arrive at the *critical polarizability product* $\alpha_p \rho_c$ as a dimensionless measure of the *relative* strength of triplet dispersion interactions in the critical region. Now, it is readily seen that the critical temperature scales with the strength of the pair potential, and so like $(\alpha_p \rho_c)^2$, so that $\alpha_p \rho_c \sim T_c^{1/2}$: Three-body dispersion interactions introduce a new energy scale which leads to deviations from a law of corresponding states. For most configurations of a triad of particles, this potential is *repulsive*, so that it tends to reduce the stability of the fluid below that estimated from pair potentials determined in the dilute-gas phase.

It was suggested by Reatto and Tau[21] in another context that three-body interactions could lead to field mixing, and a simple argument given by Pestak *et al.*[18] and a more rigorous calculation outlined previously[17] showed

that weak three-body forces in fluids could be accounted for within a pair-potential description, provided that two-body interaction has a suitable dependence on thermodynamic states, that is, temperature and fugacity. In the critical region, a fugacity dependence to an effective pair potential is the direct analog of an effective thermal scaling field which depends on the bare chemical potential, and therefore gives rise to a singular diameter.

Here we report in more detail the map[17] from a system with weak three-body interactions to one with an effective pairwise potential, by means of perturbation theory in the grand canonical ensemble supplemented with certain correlation-function identities. After reviewing the arguments which, in decorated-lattice models, lead to the prediction of a diameter anomaly and which, in field-theoretical studies, connect field mixing to cubic terms in the Hamiltonian, we describe in Sec. II how this map may be accomplished for nearest-neighbor spin-$\tfrac{1}{2}$ Ising models in two and three dimensions. For the particularly simple case of the honeycomb lattice in two dimensions, we obtain an explicit, analytic form for the dependence of the effective thermal scaling field on the bare chemical potential. This approach, yielding an *analytic* map from the full system onto that with only pair potentials, should be contrasted with others from the theory of fluids[22] which are carried out within the *canonical* ensemble, and yield effective potentials which depend parametrically on the *density*, rather than the chemical potential, its conjugate field. This distinction becomes important since the densities in the coexisting phases are themselves singular functions of temperature in the critical region, and if taken literally, the resulting singular effective potentials can be shown to lead to thermodynamic inconsistencies. As emphasized by Rowlinson,[23] thermodynamic-state-dependent potentials are most naturally derived in the grand canonical ensemble, as functions of the governing thermodynamic fields.

In the analysis of lattice models, we focus primarily on the two-dimensional cases, namely, the honeycomb and square lattice gases, for which the map is most easily constructed and mathematically clearest. The analysis of the simple-cubic lattice gas is rather lengthy, and we only comment on its general aspects. In Sec. III we discuss unresolved issues and the applicability of the perturbation theory described here to the study of many-body effects near other types of phase transitions, such as order-disorder transitions in binary metallic alloys.

II. THEORY

A. Field mixing

The way in which field mixing leads to a nonanalytic diameter is perhaps most easily seen by considering the free energy of a spin system which can be related, either exactly (as through the dedecoration procedure of a decorated-lattice calculation[24]), or as a phenomenological postulate,[25] to that of the simple nearest-neighbor Ising ferromagnet. Let $F(K, H)$ be the free energy per spin of the original system, and $F_I(K_I, H_I)$ be that of the Ising model, where $K_{(I)}$ is the nearest-neighbor spin-spin interaction and $H_{(I)}$ the applied external field of the origi-

nal (Ising) model. The two Hamiltonians are

$$\mathcal{H}_{(I)} = -\sum_i H_{(I)} s_i - \frac{1}{2!} \sum_{i,j}' K_{(I)} s_i s_j , \tag{3}$$

with $K_{(I)} > 0$ for ferromagnetic ordering, and where the prime restricts the summation to nearest-neighbor pairs. The most general map which relates F and F_I is then

$$F(K,H) = F_{(I)}(K_I(K,H), H_I(K,H)) + G(K,H) , \tag{4}$$

where the effective fields K_I and H_I, and the offset to the free energy G are *analytic* functions of their arguments. From Eqs. (3) and (4), and with $F_{(I)}$ related to the statistical trace through

$$F_{(I)} = -(1/N) k_B T \ln \sum_{\{s_i\}} e^{-\mathcal{H}_{(I)}/k_B T} ,$$

the magnetization $M = -(\partial F/\partial H)$ is

$$M = M_I \frac{\partial H_I}{\partial H} + E_I \frac{\partial K_I}{\partial H} - \frac{\partial G}{\partial H} , \tag{5}$$

where

$$M_I \equiv \frac{1}{N} \left\langle \sum_i s_i \right\rangle_I = \langle s_i \rangle_I \tag{6}$$

is the magnetization of the reference Ising model, and

$$E_I = \frac{1}{N} \left\langle \frac{1}{2} \sum_{i,j}' s_i s_j \right\rangle_I = \frac{1}{2} q \langle s_i s_j \rangle_I \tag{7}$$

is the nearest-neighbor spin-spin correlation function, with q the coordination number. The coexistence curve of the original model in (H,K) space is determined by that of the reference Ising model, namely $(H_I = 0, K_I)$. The magnetizations $M_\pm$ in the two branches of the coexistence curve are computed by evaluating Eq. (5) as $H_I \rightarrow 0^\pm$, at which M_I becomes the spontaneous magnetization of the Ising model (with a sign determined by that of the approach of H_I to zero) and E_I its dimensionless internal energy in zero field. The average of these two magnetizations defines the diameter $\overline{M}$, and recalling the analyticity of $K_I(K,H)$, $H_I(K,H)$, and G, we find

$$\overline{M} = E_I \frac{\partial K_I}{\partial H} - \frac{\partial G}{\partial H} . \tag{8}$$

Near the critical point of the reference Ising model, the spin-spin correlation function E_I deviates from its critical value $\langle s_i s_j \rangle_c$ as

$$\langle s_i s_j \rangle = \langle s_i s_j \rangle_c + e_{1-\alpha} t^{1-\alpha} + e_1 t + \cdots , \tag{9}$$

and in general, the derivative $\partial G/\partial H$ possesses a Taylor-series expansion around its value at the critical point, so that we recover the linear and singular terms in Eq. (1). The key result, also found in the present work, is that this "energylike" singularity appears in the diameter with an amplitude proportional the *field-mixing derivative* $\partial K_I/\partial H$.

Nicoll[7,9] has presented an argument for the generality of field mixing within a field-theoretic description of critical phenomena, using an Ising-like Landau-Ginzburg-Wilson (LGW) Hamiltonian supplemented by non-Ising, symmetry-breaking terms. The analysis we present in Sec.

II B below is similar in spirit, and so it is instructive to review this calculation.

Let $\varphi(x)$ be the spatially varying field whose average is the order parameter of the fluid. The symmetric LGW Hamiltonian in d dimensions is

$$\mathcal{H}_S = \int d^d x \left[\frac{1}{2} t(x) \varphi^2(x) + \frac{1}{2} [(\nabla \varphi(x)]^2 \right.$$
$$\left. + \frac{1}{4!} u \varphi^4(x) - h(x) \varphi(x) \right] , \tag{10}$$

where t is now the deviation from the mean-field critical temperature and $u > 0$. In the renormalization-group analysis, there exists an odd-order asymmetric operator which leads to field mixing:

$$\mathcal{H}_A = \int d^d x \left[\frac{1}{2} t(x) \varphi^3(x) - \frac{1}{2} \varphi^2(x) \nabla^2 \varphi(x) + \frac{1}{12} u \varphi^5(x) \right] . \tag{11}$$

The significance of this particular combination of operators can be seen through the equation of motion, an identity for all Hamiltonians,

$$\int D\varphi \frac{\delta}{\delta \varphi(x)} \exp(-\mathcal{H}/k_B T) = 0 . \tag{12}$$

For $\mathcal{H} = \mathcal{H}_S$, one finds

$$\left\langle t(x) \varphi(x) - \nabla^2 \varphi(x) + \frac{u}{3!} \varphi^3(x) - h(x) \right\rangle = 0 . \tag{13}$$

This equation of motion relates $h(x)$ to a quantity which is just the average of $[\frac{1}{2} \varphi^2(x)]^{-1}$ times the asymmetric operator $\mathcal{H}_A$. Applying the operator $\delta/\delta t(y)$ to Eq. (12), setting $y = x$, and integrating over x gives

$$\langle \mathcal{H}_A \rangle = \left\langle \int h(x) \frac{\delta}{\delta t(x)} \right\rangle + vM , \tag{14}$$

where M is the magnetization and v the volume of the Brillouin zone. Thus, the average of the asymmetric operator is equal to the average of the operator $\int h(\delta/\delta t)$, apart from a constant whose only effect is a global redefinition of the magnetic field.

Yet, from first-order perturbation theory, the change in the Gibbs free energy upon the introduction of $\lambda_A \mathcal{H}_A$ is just

$$\Delta G(h,t) \simeq \lambda_A \langle \mathcal{H}_A \rangle \simeq \lambda_A \int h \frac{\delta}{\delta t} G + \cdots . \tag{15}$$

To leading order this is completely equivalent to a Taylor-series expansion of $G(h, t + \lambda_A h)$, so that the effect of this asymmetric operator is to shift the scaling variables. It is important to realize that the correlation functions which enter into the middle relation in Eq. (15) are themselves singular at the critical point of the symmetric reference system, so that the perturbation theory formally involves singular corrections. The key point is the recognition that *these singularities arise from a singular function whose argument has been shifted analytically.* Note that the general asymmetric operator is not strictly proportional to $\mathcal{H}_A$, as the different cubic and quintic terms need not enter with coefficients precisely in the ratios given in Eq. (11). The more general operator can,

however, be resolved into its projection onto $\mathscr{H}_A$ and a remainder, the latter of which generates terms in the diameter less singular than $t^{1-\alpha}$.[7] In the lattice calculations discussed below, a similar phenomenon occurs, in that only certain three-body interactions may be accounted for in terms of revised scaling variables alone.

Implicit in this calculation is the assumption that the introduction of three-body interactions does not change the universality class of the transition, which is equivalent to the assumption that there exists an analytic map from the many-body problem to the symmetric Ising model. In the case of models such as that solved by Baxter and Wu,[26] with an important underlying lattice symmetry, this assumption is not true.

This derivation of field mixing thus involves two steps: (i) first-order perturbation theory applied to the asymmetric operator(s), and (ii) the reexpression of the expectation $\langle H_A \rangle$ in terms of the even-order energylike correlations of the reference system, allowing the change in free

energy to be interpreted as a change in the thermal field, or a change in the pair potential. It is this program which we follow below.

B. Perturbation theory

Consider a fluid or spin system characterized by a Hamiltonian which consists of a sum of pairwise interactions ϕ and three-body potentials ψ,

$$\mathscr{H} = \frac{1}{2!} \sum_{i,j} \phi(\mathbf{r}_i, \mathbf{r}_j) + \frac{1}{3!} \sum_{i,j,k} \psi(\mathbf{r}_i, \mathbf{r}_j, \mathbf{r}_k) \ , \tag{16}$$

where $\{\mathbf{r}_i\}$ denotes the positions of the fluid particles or the location of the lattice sites. We shall assume that the triplet potential is a weak perturbation to the system, and so its contribution to the grand free energy $\Omega = -k_B T \ln \Xi$, with Ξ the grand partition function and z the fugacity, can be computed within thermodynamic perturbation theory. The first-order result is

$$\Omega(z, \phi, \psi) \approx \Omega(z, \phi, 0) + \frac{1}{3!} \int d\mathbf{r}_1 \int d\mathbf{r}_2 \int d\mathbf{r}_3 \psi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \rho_0^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) + \cdots \ , \tag{17}$$

where $\rho_0^{(3)}$ is the three-body distribution function of the system with no triplet potential, hereafter referred to as the "reference system," and whose properties are denoted by the subscript 0. The essential point in the present analysis concerns the relationship between that triplet distribution and even-body correlations and the one-body density of the reference system, as expressed in the set of correlation function identities derived by Kirkwood and Salsburg[27] (KS). The general n-body distribution function $\rho^{(n)}$ of a fluid governed by a pair potential Hamiltonian $V_N(\{\mathbf{r}^N\})$ is[28]

$$\rho^{(n)}(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_n) = \frac{1}{\Xi} \sum_{N \geq n} \frac{z^N}{(N-n)!} \int d\mathbf{r}_{n+1} \int \cdots \int d\mathbf{r}_N \exp[-V_N(\{\mathbf{r}^N\})/k_B T] \ . \tag{18}$$

If we single out a particular particle, say, 1, the KS equations are

$$\rho^{(n)}(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_n) = z \exp\left[-\sum_{j=2}^{n} \phi(\mathbf{r}_1, \mathbf{r}_j)/k_B T \right] \left[\rho^{(n-1)}(\mathbf{r}_2, \mathbf{r}_3, \ldots, \mathbf{r}_n) \right.$$

$$+ \frac{1}{1!} \int d\mathbf{r}_{n+1} f(\mathbf{r}_1, \mathbf{r}_{n+1}) \rho^{(n)}(\mathbf{r}_2, \mathbf{r}_3, \ldots, \mathbf{r}_{n+1})$$

$$+ \frac{1}{2!} \int d\mathbf{r}_{n+1} \int d\mathbf{r}_{n+2} f(\mathbf{r}_1, \mathbf{r}_{n+1}) f(\mathbf{r}_1, \mathbf{r}_{n+2})$$

$$\left. \times \rho^{(n+1)}(\mathbf{r}_2, \mathbf{r}_3, \ldots, \mathbf{r}_{n+2}) + \frac{1}{3!} \cdots \right] \ , \tag{19}$$

where the Mayer f function is $f \equiv \exp(-\phi/k_B T) - 1$, and the fugacity $z = \exp(\mu/k_B T)$. For continuum systems with pair potentials extending to infinity, this is an integral equation involving an infinite number of correlation functions. However, if the potential $\phi(r)$ is *strictly zero* beyond some finite range R, then so too are the f functions. If, in addition, the particles have hard cores, then there is a maximum number of particles which can be accommodated within a sphere of radius R from the central one. In this case, Eq. (19) involves only a finite set of the $\rho^{(n)}$. The hierarchy is at its simplest in nearest-neighbor lattice problems, with the integral relations becoming linear *algebraic* equations. As we illustrate below for Ising models in two and three dimensions, it is possible to solve explicitly for the triplet distribution in terms of the density and near-neighbor spin-spin correlation functions of the reference system, so that

$$\rho_0^{(3)} = S_0^{(3)} + S_1^{(3)} \rho_0^{(1)} + S_2^{(3)} \rho_0^{(2)} \ , \tag{20}$$

where the coefficients S_i depend on the three coordinates, and the fugacity and pair potential, but are not themselves ensemble averages of density operators. To linear order, the shift in the free energy in Eq. (17) is then completely equivalent to redefinitions of the pair potential and the fugacity, since by a functional Taylor expansion,

$$\Omega_0(z + \Delta z, \phi + \Delta \phi) \approx \Omega_0(z, \phi) + \int d\mathbf{r} \frac{\delta \Omega_0}{\delta z(\mathbf{r})} \Delta z(\mathbf{r})$$

$$+ \int \int d\mathbf{r} \, d\mathbf{s} \frac{\delta \Omega_0}{\delta \phi(\mathbf{r}, \mathbf{s})} \Delta \phi(\mathbf{r}, \mathbf{s}) + \cdots \ . \tag{21}$$

We identify the functional derivates as[28]

$$\frac{\delta\Omega_0}{\delta z(\mathbf{r})} = -k_B T \frac{\rho_0^{(1)}(\mathbf{r})}{z(\mathbf{r})}$$ (22)

and

$$\frac{\delta\Omega_0}{\delta\phi(\mathbf{r},\mathbf{s})} = \frac{1}{2!}\rho_0^{(2)}(\mathbf{r},\mathbf{s}) .$$ (23)

The above shows that the perturbation expansion in Eq. (17) is equivalent to the expansion of the free energy of the reference system evaluated at a shifted fugacity and pair potential. Thus,

$$\Omega(z,\phi,\psi) \approx \Omega_0(z + \Delta z, \phi + \Delta\phi) + G(z,\phi) ,$$ (24)

where G is an analytic offset to the free energy, given in terms of $S_0^{(3)}$. We thus have mapped the system with triplet potentials onto one with only two-body forces, and the shifts $\Delta\phi$ and Δz are parametrized by the temperature and the fugacity. This then is the analog of the results from the decorated-lattice models and field-theoretic analysis.

1. Honeycomb lattice

As the first application of the above perturbation theory to a model system, we study the two-dimensional honeycomb lattice gas. A portion of this lattice is shown in Fig. 2 along with the three types of site-site couplings which are considered in the analysis; K between nearest neighbors, with $K < 0$ for an attractive potential, L for a triplet on sequential lattice sites, and M for the equilateral configuration of a trio of particles. With $n_i = 0,1$ the occupation variable at site i, and μ the chemical potential, the grand canonical Hamiltonian is

$$\mathcal{H} = \frac{1}{2!}\sum_{i,j} K n_i n_j + \frac{1}{3!}\sum_{i,j,k}' L n_i n_j n_k + \frac{1}{3!}\sum_{i,j,k}'' M n_i n_j n_k$$

$$-\mu \sum_i n_i ,$$ (25)

with the prime and double prime on the second and third sums denoting restrictions to the appropriate geometry trio configurations.

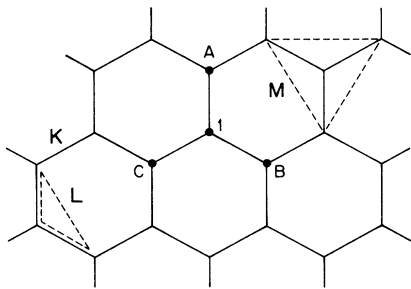The first-order expansion of the free energy per lattice

site $\omega = \Omega/N$ is

$$\omega(z,K,L,M) \approx \omega_0(z,K) + \frac{1}{3!N}\sum_{1AB}' L\rho_0^{(3)}(1AB)$$

$$+ \frac{1}{3!N}\sum_{ABC}'' M\rho_0^{(3)}(ABC) + \cdots ,$$ (26)

where the notation for the n-body distribution refers to the cluster of four sites in the center of Fig. 2.

In a translationally invariant lattice, the sums in Eq. (26) can be performed trivially, there being NC_{ijk} terms which are identical in each summation. The combinatorical factors C_{ijk} for the two triplet correlations are $C_{1AB} = 18$ and $C_{ABC} = 6$, giving

$$\omega(z,K,L,M) \approx \omega_0(z,K) + 3L\rho_0^{(3)}(1AB)$$

$$+ M\rho_0^{(3)}(ABC) + \cdots .$$ (27)

The Kirkwood-Salsburg equations are now used to express the particular triplet distribution functions in Eq. (27) in terms of lower-order correlations. For the model with nearest-neighbor interactions only, the Mayer f function takes on three possible values:

$$f(i,j) = \begin{cases} -1, & i = j , \\ f, & (i,j) \text{ nearest neighbors} , \\ 0, & \text{otherwise} , \end{cases}$$ (28)

where $f = \exp(-K/k_B T) - 1$. The four KS equations involving the central site are readily found to be

$$\rho^{(1)}(1) = z[1 + (3f - 1)\rho^{(1)}(1) - 3f\rho^{(2)}(1A)$$

$$+ 3f^2\rho^{(2)}(AB) - 3f^2\rho^{(3)}(1AB)$$

$$+ f^3\rho^{(3)}(ABC) - f^3\rho^{(4)}(1ABC)] ,$$ (29)

$$\rho^{(2)}(1A) = z(f + 1)[\rho^{(1)}(1) - \rho^{(2)}(1A)$$

$$+ 2f\rho^{(2)}(AB) - 2f\rho^{(3)}(1AB)$$

$$+ f^2\rho^{(3)}(ABC) - f^2\rho^{(4)}(1ABC)] ,$$ (30)

$$\rho^{(3)}(1AB) = z(f + 1)^2[\rho^{(2)}(AB) - \rho^{(3)}(1AB)$$

$$+ f\rho^{(3)}(ABC) - f\rho^{(4)}(1ABC)] ,$$ (31)

and

$$\rho^{(4)}(1ABC) = z(f + 1)^3[\rho^{(3)}(ABC) - \rho^{(4)}(1ABC)] .$$ (32)

In deriving these, it has been assumed that the lattice has translational invariance, so that $\rho^{(1)}(1) = \rho^{(1)}(A)$, etc. Figure 3 shows the six distribution functions which are related through Eqs. (29)—(32).

We have in Eqs. (29)—(32) *four* independent relations among the *six* distinct correlation functions involving the four sites in the cluster $1ABC$. This means that any four of the correlations may be expressed in terms of the other two. In general, as the coordination number of the lattice increases, so too does the number of correlations which play the role of parameters in solving the KS equations. In one dimension, with coordination number two, there is

FIG. 2. A section of the honeycomb lattice, indicating pair (K) and triplet (L,M) interactions considered in perturbation theory, with site labels given in central cluster.
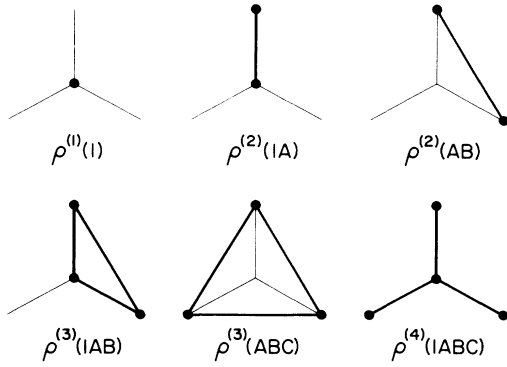
FIG. 3. The six correlation functions for a cluster of four sites which are related through the Kirkwood-Salsburg correlation identities.

a sufficient number of equations to solve explicitly for the density and pair correlation as functions of temperature and fugacity. In the present example, we may choose $\rho^{(1)}(1)$ and $\rho^{(2)}(1A)$ as parameters, thereby enabling the map from the full system with triplet interactions onto the symmetric nearest-neighbor honeycomb lattice gas. Solving for the triplet correlations, we find

$$\rho^{(3)}(1AB) = S_0^{(1AB)} + S_1^{(1AB)}\rho^{(1)}(1) + S_{1A}^{(1AB)}\rho^{(2)}(1A) , \qquad (33)$$

$$\rho^{(3)}(ABC) = S_0^{(ABC)} + S_1^{(ABC)}\rho^{(1)}(1) + S_{1A}^{(ABC)}\rho^{(2)}(1A) , \qquad (34)$$

where the coefficients are

$$
\begin{aligned}
S_0^{(1AB)} &= zf^{-2}(f+1)^2 , \\
S_1^{(1AB)} &= -f^{-2}(f+1)^2[1-z(f-1)] , \\
S_{1A}^{(1AB)} &= f^{-1}(f+1)[2-z(f+1)] , \\
S_0^{(ABC)} &= 2f^{-3}[1+z(f+1)^3] , \\
S_1^{(ABC)} &= -z^{-1}f^{-3}[1+z(f+1)^3][2-z(3f-2)] , \\
S_{1A}^{(ABC)} &= 3z^{-1}f^{-2}(f+1)^{-1}[1+z(f+1)^3][1-z(f+1)] .
\end{aligned}
\qquad (35)
$$

Substituting into the perturbation theory result, Eq. (27), we obtain

$$
\begin{aligned}
\omega(z,K,L,M) \approx \omega_0(z,K) &+ 3LS_0^{(1AB)} + MS_0^{(ABC)} \\
&+ (3LS_1^{(1AB)} + MS_1^{(ABC)})\rho_0^{(1)}(1) \\
&+ (3LS_{1A}^{(1AB)} + MS_{1A}^{(ABC)})\rho_0^{(2)}(1,A) + \cdots .
\end{aligned}
\qquad (36)
$$

This is to be compared to the change in the free energy of the reference system upon shifts in the fugacity and nearest-neighbor interaction, which is obtained from the lattice version of the general continuum result in Eqs. (21)–(23), namely,

$$
\omega_0(z+\Delta z, K+\Delta K) \approx \omega_0(z,K) - k_B T \frac{\Delta z}{z}\rho_0^{(1)}(1)
$$

$$
+ \tfrac{3}{2}\Delta K \rho_0^{(2)}(1A) .
$$

The shifts in the fugacity and nearest-neighbor interaction are therefore

$$\Delta z = -\frac{z}{k_B T}(3LS_1^{(1AB)} + MS_1^{(ABC)}) , \qquad (37)$$

and

$$\Delta K = \tfrac{2}{3}(3LS_{1A}^{(1AB)} + MS_{1A}^{(ABC)}) . \qquad (38)$$

Finally, we have

$$\omega(z,K,L,M) \approx \omega_0(z',K') + \omega_b(z,K,L,M) , \qquad (39)$$

where $z' = z + \Delta z$, $K' = K + \Delta K$, and the analytic background term $\omega_b = 3LS_0^{(1AB)} + MS_0^{(ABC)}$. Field mixing is readily apparent, as the effective thermal scaling field is proportional to $K' - K_c$ evaluated on the coexistence surface $z = z_{coex}$, and depends on the chemical potential as long as K' does.

While we have here imagined that only the triplet interactions are present as perturbations, it is clear that the four-spin coupling involving sites 1, A, B, and C, as well as the diagonal (AB) next-nearest-neighbor coupling could equally well have been accounted for in Δz and ΔK, since their conjugate correlations (Fig. 3) are expressible in terms of $\rho^{(1)}(1)$ and $\rho^{(2)}(1A)$. Yet, these compact many-body interactions whose conjugate correlations are linked to $\rho^{(1)}(1)$ and $\rho^{(2)}(1A)$ by the KS equations appear to be the only ones whose first-order effects may be completely subsumed into revised scaling variables. The correlations conjugate to other more extended many-body interactions are not expressible completely in terms of the density and nearest-neighbor correlations. This is the analog of the situation in the field-theoretic analysis, in which only a particular linear combination of cubic and quintic operators is equivalent, through the correlation identities arising from the equation of motion, to field mixing.

The thermodynamic density $\rho^{(1)}$ is

$$\rho^{(1)}(z,K,L,M) = -\frac{z}{k_B T}\frac{\partial\omega(z,K,L,M)}{\partial z} , \qquad (40)$$

which under the map becomes

$$
\begin{aligned}
\rho^{(1)} = &-\frac{z}{k_B T}\frac{\partial\omega_b}{\partial z} + \frac{z}{z'}\frac{\partial z'}{\partial z}\rho_0^{(1)}(z',K') \\
&-\frac{3}{2}\frac{z}{k_B T}\frac{\partial K'}{\partial z}\rho_0^{(2)}(z',K') .
\end{aligned}
\qquad (41)
$$

In order to make use of the known properties of the Ising model on the honeycomb lattice,[29] it is necessary to transform from the occupation-number variables $n_i = 0,1$ to spin variables $s_i = \pm 1$, using $n_i = (1+s_i)/2$, giving a mean density of

$$
\begin{aligned}
\bar{\rho}^{(1)} \equiv \frac{\rho_+^{(1)} + \rho_-^{(1)}}{2} = &-\frac{z}{k_B T}\frac{\partial\omega_b}{\partial z} + \frac{1}{2}\frac{z}{z'}\frac{\partial z'}{\partial z} \\
&-\frac{3}{8}\frac{z}{k_B T}\frac{\partial K'}{\partial z} - \frac{3}{8}\frac{z}{k_B T}\frac{\partial K'}{\partial z}\langle s_i s_j\rangle_I .
\end{aligned}
\qquad (42)
$$

It is readily verified that as $L,M \to 0$, $\bar{\rho} \to \tfrac{1}{2}$, and that the deviation from $\tfrac{1}{2}$ is linear in L and M. To leading order in the three-body interactions, we may evaluate the derivatives in Eq. (42) with $L = M = 0$, for which the

coexistence condition is

$$z_{\text{coex}} = (f+1)^{-3/2} , \quad (43)$$

and the critical temperature satisfies[29]

$$f_c = 6 + 4\sqrt{3} . \quad (44)$$

The field-mixing derivative is then

$$-\frac{3}{8}\frac{z}{k_BT}\frac{\partial K'}{\partial z} = \frac{3}{4k_BT}f^{-2}(f+1)^{1/2}[fL+(f+2)M] ,$$

(coexistence)

$$= 0.570\left[\frac{L}{-K}\right] + 0.658\left[\frac{M}{-K}\right], \quad (\text{at } T_c) .$$

(45)

which has the same sign as that of L and M. Thus, for repulsive three-body potentials, the singular deviation of the diameter from ρ_c is toward larger values as temperature decreases below T_c as shown in Fig. 4 for the case $-L/K = 0.02$, $M = 0$. From this particular numerical example, we see that even very small three-body interactions can introduce a measurable singularity, for the scale of the anomaly in Fig. 4 is like that seen in recent experiments.[17,18] The final expression for the field-mixing derivative in Eq. (45) illustrates the basic feature of three-body dispersion forces discussed in the Introduction, namely, that their effect is to introduce a new energy scale so that critical amplitudes scale with the ratio of triplet (e.g., L) to pair (K) interactions, and so like $T_c^{1/2}$.

The exact solution[29] of the honeycomb Ising model in zero external field gives the nearest-neighbor spin-spin correlation function

$$\langle s_i s_j \rangle = \tfrac{2}{3}[\coth(2\widetilde{K}) + a(\widetilde{K})E(b(\widetilde{K}))] , \quad (46)$$

where $\widetilde{K} = -K/k_BT$ and E is the complete elliptic integral of the second kind. For $T < T_c$, the functions a
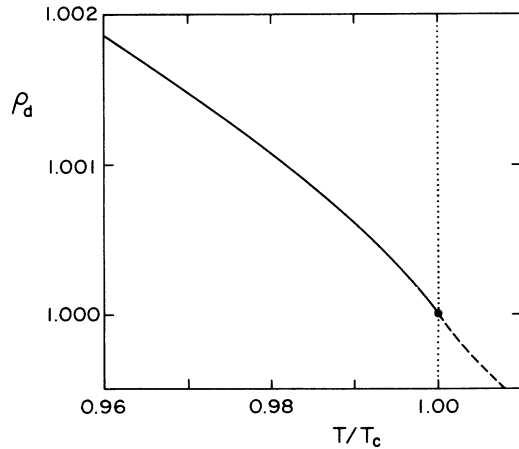

FIG. 4. Coexistence curve diameter for the honeycomb lattice gas with triplet interactions $(-L/K) = 0.02$, $(-M/K) = 0$. The dashed line is the mathematical continuation of the diameter into the one-phase region, and the dotted line is the coexistence curve.

and b are

$$a = \frac{(x^4-1)(x^2-4x+1)}{\pi(x^2-1)(x-1)^4} , \quad (47)$$

$$b = \frac{16(x^5-x^4+x^3)}{(x^2-1)^2(x-1)^4} , \quad (48)$$

where $x = \exp(2\widetilde{K})$. From Taylor expansions of the first three terms on the right-hand side of (42), each of which is linear in L and M, generating a term linear in reduced temperature, and from the asymptotic singular behavior of the elliptic integral in (46), we see that the diameter of the coexistence curve behaves as in Eq. (1), but with $\alpha = 0$ for the two-dimensional models, so that the singularity is actually of the form $t\ln t$. It is significant that both the amplitude of the singularity and that of the analytic background term are altered by the field mixing. This means that systems with larger three-body interactions will tend to have larger apparent slopes to their diameters outside the asymptotic critical region, as well as larger amplitude anomalies near $t = 0$. This correlation was noted before by Mulholland et al.[4] in the context of the decorated-lattice calculations, and is seen in experiment.[17,18]

It is informative to consider the properties of the coexistence curve to leading order in the strength of the triplet interaction. We find that the critical temperature is reduced,

$$\frac{T_c(L,M)}{T_c(0,0)} = 1 - 3.732\left[\frac{L}{-K}\right] - 1.732\left[\frac{M}{-K}\right] + \cdots , \quad (49)$$

along with the critical density,

$$\frac{\rho_c(L,M)}{\rho_c(0,0)} = 1 - 0.439\left[\frac{L}{-K}\right] - 0.380\left[\frac{M}{-K}\right] + \cdots . \quad (50)$$

The pressure P of the lattice gas can be found from the standard correspondence between the lattice gas and the Ising model, and in terms of the free energy per site it is $P = -(\omega_0 + \omega_b)$. Again considering small three-body forces, we find that the critical pressure is decreased by those interactions,

$$\frac{P_c(L,M)}{P_c(0,0)} = 1 - 4.72\left[\frac{L}{-K}\right] - 3.46\left[\frac{M}{-K}\right] + \cdots . \quad (51)$$

In combination with the above results for the critical temperature and density, we find that the critical compressibility product $Z_c = P_c/\rho_c k_B T_c$ also decreases with triplet interactions

$$\frac{Z_c(L,M)}{Z_c(0,0)} = 1 - 0.549\left[\frac{L}{-K}\right] - 1.34\left[\frac{M}{-K}\right] + \cdots , \quad (52)$$

where $Z_c(0,0) = 0.0738$ for the two-dimensional honeycomb lattice gas. All of these trends agree qualitatively with the results of the van der Waals theory of fluids with triplet interactions,[17,18] and with the intuitive notion that

a repulsive interaction tends both to lower the density and reduce the net cohesion, thereby lowering the critical temperature. The variation of the compressibility factor with triplet interactions is also in qualitative agreement with the experimental results reported by Pestak and co-workers.[17,18]

The order parameter $\Delta\rho \equiv (\rho_+ - \rho_-)/2\rho_c \sim A_\beta t^\beta$ has an amplitude which also increases with L and M,

$$\frac{A_\beta(L,M)}{A_\beta(0,0)} = 1 + 0.616 \left[\frac{-L}{K}\right] + 0.557 \left[\frac{-M}{K}\right] + \cdots , \tag{53}$$

where, from the exact calculation of Naya,[30] $A_\beta(0,0) = [-8\ln(2-\sqrt{3})/\sqrt{3}]^{1/8} = 1.25\ldots$ for the honeycomb lattice. Since the diameter slope A_1 outside the asymptotic critical region also increases with the triplet interactions, this implies a correlation between A_β and A_1 in the sense that systems with small diameter slopes also have small order parameter amplitudes, as is the case for the fluids in Fig. 1. The van der Waals theory of fluids with triplet interactions predicts $dA_\beta/dA_1 = \frac{5}{11}$, to leading order in the three-body interaction, as shown by the dotted line in the figure, with $A_\beta = 2$ and $A_1 = \frac{2}{5}$ in the absence of three-body forces. Of course, the lattice gas models with only pairwise forces are completely particle-hole symmetric, with $A_1 = 0$, identically. Nevertheless, in examining plots like that in Fig. 4, we may determine the slope of the apparently linear part of the diameter far from T_c, in the range $t \lesssim 0.02$, like that studied in experiment. We find that dA_β/dA_1 is of order unity, as appears to be the case with the newer data[17,18] in the figure (shown as open circles), which was analyzed with suitable corrections to scaling contributions and therefore presumably more accurately reflects the true

values of A_β than the older data (solid circles).

In addition to the scaling of the diameter singularity with the relative strength of three-body interactions, there is another property dependent on field mixing and which has been studied both theoretically and experimentally, namely, the *compressibility asymmetry*.[6] From revised scaling, decorated-lattice-type calculations, and the present work, it may be seen that while the leading order divergence of the compressibility is of precisely the same form in the liquid and vapor phases, there is a *singular difference* between them, characterized by a power-law divergence of the form $t^{\beta-1}$. We find that for repulsive triplet interactions, the singularity in the compressibility asymmetry is such that

$$\left[\frac{\partial\rho}{\partial\mu}\right]_{\text{liq}} - \left[\frac{\partial\rho}{\partial\mu}\right]_{\text{vap}} \sim \left[\frac{L}{-K}\right], \left[\frac{M}{-K}\right] > 0 . \tag{54}$$

Thus, the actual amplitude of the $t^{\beta-1}$ anomaly scales with the order parameter amplitude A_β, and also with the diameter slope, as was found by Mulholland et al.,[4] and has a sign in agreement with that found in experiment.[4,18,31]

2. Square lattice

Relative to the honeycomb lattice, the higher coordination number of the square lattice introduces added complexity into the perturbation theory. We consider a system characterized by a nearest-neighbor coupling K, and three distinct triplet interactions, L, M, and Q, as shown in Fig. 5. It also proves necessary to allow for two additional further-neighbor pair interactions, J between next-nearest neighbors along lattice bonds, and I coupling diagonal neighbors. Referring to the labeled cluster in Fig. 5, the six Kirkwood-Salsburg equations involving the central particle are

$$\rho^{(1)}(1) = z[1 + (4f-1)\rho^{(1)}(1) - 4f\rho^{(2)}(1A) + 4f^2\rho^{(2)}(AB) + 2f^2\rho^{(2)}(AC) - 4f^2\rho^{(3)}(1AB)$$
$$- 2f^2\rho^{(3)}(1AC) + 4f^3\rho^{(3)}(ABC) - 4f^3\rho^{(4)}(1ABC) + f^4\rho^{(4)}(ABCD) - f^4\rho^{(5)}(1ABCD)] , \tag{55}$$

$$\rho^{(2)}(1A) = z(f+1)[\rho^{(1)}(1) - \rho^{(2)}(1A) + 2f\rho^{(2)}(AB) + f\rho^{(2)}(AC) - 2f\rho^{(3)}(1AB) - f\rho^{(3)}(1AC)$$
$$+ 3f^2\rho^{(3)}(ABC) - 3f^2\rho^{(4)}(1ABC) + f^3\rho^{(4)}(ABCD) - f^3\rho^{(5)}(1ABCD)] , \tag{56}$$

$$\rho^{(3)}(1AB) = z(f+1)^2[\rho^{(2)}(AB) - \rho^{(3)}(1AB) + 2f\rho^{(3)}(ABC) - 2f\rho^{(4)}(1ABC) + f^2\rho^{(4)}(ABCD) - f^2\rho^{(5)}(1ABCD)] , \tag{57}$$

$$\rho^{(3)}(1AC) = z(f+1)^2[\rho^{(2)}(AC) - \rho^{(3)}(1AC) + 2f\rho^{(3)}(ABC) - 2f\rho^{(4)}(1ABC) + f^2\rho^{(4)}(ABCD) - f^2\rho^{(5)}(1ABCD)] , \tag{58}$$

$$\rho^{(4)}(1ABC) = z(f+1)^3[\rho^{(3)}(ABC) - \rho^{(4)}(1ABC) + f\rho^{(4)}(ABCD) - f\rho^{(5)}(1ABCD)] , \tag{59}$$

and

$$\rho^{(5)}(1ABCD) = z(f+1)^4[\rho^{(4)}(ABCD) - \rho^{(5)}(1ABCD)] . \tag{60}$$

In solving this set of equations for the ten unknown correlations, four become parameters, and we choose for these $\rho^{(1)}(1)$, $\rho^{(2)}(1A)$, $\rho^{(2)}(AB)$, and $\rho^{(2)}(AC)$, thus mapping the original model onto a symmetric Ising model with only pairwise interactions, albeit with some extending beyond nearest neighbors. In notation like that for the

honeycomb lattice calculation, we find that the three-body correlations may be decomposed as

$$\rho^{(3)}(1AB) = S_0^{(1AB)} + S_1^{(1AB)}\rho^{(1)}(1)$$
$$+ S_{1A}^{(1AB)}\rho^{(2)}(1A) + S_{AB}^{(1AB)}\rho^{(2)}(AB)$$
$$+ S_{AC}^{(1AB)}\rho^{(2)}(AC) , \tag{61}$$

with similar expression for $\rho^{(3)}(1AC)$ and $\rho^{(3)}(ABC)$. For the two compact clusters, the coefficients are
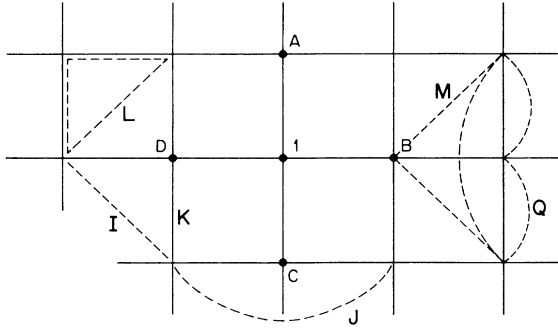
FIG. 5. As in Fig. 2, for the square lattice.

$$S_0^{(1AB)} = S_0^{(1AC)} = zf^{-2}(f+1)^2 D^{-1},$$

$$S_1^{(1AB)} = S_1^{(1AC)} = -f^{-2}(f+1)^2[1-z(2f-1)]D^{-1},$$

$$S_{1A}^{(1AB)} = S_{1A}^{(1AC)} = 2f^{-1}(f+1)[1-z(f+1)]D^{-1},$$

$$S_{AB}^{(1AB)} = S_{AC}^{(1AC)} = z(f+1)^2 D^{-1},$$

$$S_{AC}^{(1AB)} = S_{AB}^{(1AC)} = 0, \qquad (62)$$

where $D = z(f+1)^2$. As in the honeycomb lattice calculation, the S_{1A}'s are positive, lowering the critical temperature, and the z derivatives of the S_{1A}'s are negative, resulting in a lowered critical density and a downward-pointing diameter anomaly.

The first-order shift in the free energy density is

$$\omega(z,K,L,M,Q) \approx \omega_0(z,K) + \frac{1}{3!} C_{1AB} L \rho_0^{(3)}(1AB)$$

$$+ \frac{1}{3!} C_{ABC} M \rho_0^{(3)}(ABC)$$

$$+ \frac{1}{3!} C_{1AC} Q \rho_0^{(3)}(1AC). \qquad (63)$$

Using Eq. (62), the combinatorical results $C_{1AB} = 24$, $C_{1AC} = 12$, $C_{ABC} = 24$, and by comparison to the reference system free-energy expansion

$$\omega(z + \Delta z, K + \Delta K, I + \Delta I, J + \Delta J)$$

$$= \omega_0(z,K,I,J) - \frac{k_B T \Delta z}{z} \rho_0^{(1)}(1)$$

$$+ 2[\Delta K \rho_0^{(2)}(1A) + \Delta I \rho_0^{(2)}(AB) + \Delta J \rho_0^{(2)}(AC)], \qquad (64)$$

we obtain the map

$$\omega(z,K,L,M,Q) \approx \omega_0(z',K',I',J') + \omega_b(z,K,L,M,Q)$$

where, again, $K' = K + \Delta K$, etc., $\qquad (65)$

$$\Delta z = -\frac{z}{k_B T}(4LS_1^{(1AB)} + 4MS_1^{(ABC)} + 2QS_1^{(1AC)}), \qquad (66)$$

$$\Delta I = (2LS_{AB}^{(1AB)} + 2MS_{AB}^{(ABC)} + QS_{AB}^{(1AC)}),$$

$$\Delta J = (2LS_{AC}^{(1AB)} + 2MS_{AC}^{(ABC)} + QS_{AC}^{(1AC)}), \qquad (67)$$

$$\Delta K = (2LS_{1A}^{(1AB)} + 2MS_{1A}^{(ABC)} + QS_{1A}^{(1AC)}),$$

and

$$\omega_b = (4LS_0^{(1AB)} + 4MS_0^{(ABC)} + 2QS_0^{(1AC)}). \qquad (68)$$

Thus, even if there are no explicit higher-neighbor pair interactions I and J in the original Hamiltonian, they are *generated* by the perturbation theory. Explicit numerical calculations, which we do not present here, use the exact results for pairwise spin-spin correlation functions given in the papers of Onsager and Kaufman,[32] and the spontaneous magnetization derived by Yang.[33]

3. Simple-cubic lattice

The added complexity which arises from the sixfold coordination of the simple-cubic lattice renders the perturbation theory for it quite formidable. For the cluster of seven particles shown in Fig. 6, we find 10 KS equations for *18* distinct distribution functions, so that 8 of the latter must be taken as parameters. A convenient choice for these is the density $\rho^{(1)}(1)$, and the even-spin correlations $\rho^{(2)}(1A)$, $\rho^{(2)}(AB)$, $\rho^{(2)}(AC)$, $\rho^{(4)}(1ABC)$, $\rho^{(4)}(1ABE)$, $\rho^{(4)}(ABCD)$, and $\rho^{(4)}(ABCE)$. The many-body interactions conjugate to the ten remaining correlations may, to first-order, be absorbed into effective nearest-, further-neighbor, and several effective *four-body* interactions. Despite these complications, it is possible to map the system onto a symmetric model, and to demonstrate field mixing as above, with only quantitative differences in the results. In the absence of detailed information on the higher-order spin-spin correlations in the simple-cubic model, numerical calculations must introduce some sort of superposition approximations.

III. DISCUSSION

We have shown that the effects of certain weak symmetry-breaking many-body interactions in lattice systems are equivalent to those arising from symmetry-preserving interactions which depend on the thermodynamic state. In the language of lattice gases, this allows the asymmetric liquid-vapor phase diagrams of the former to be constructed from the known properties of the
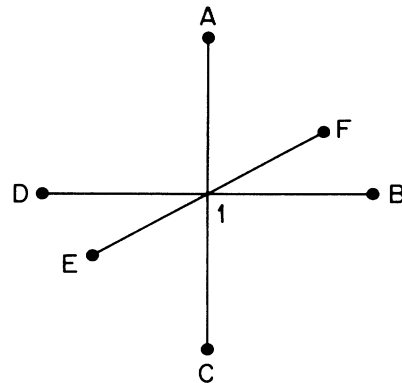

FIG. 6. Cluster of seven sites in the simple-cubic lattice, with site labels for correlation functions discussed in text.

simple up-down-symmetric Ising model, exhibiting the celebrated singular diameter as a direct consequence of an effective thermal scaling field which depends on the bare chemical potential. That dependence is parametrized by the relative strength of the many-body to pair potentials and is strongly supported by recent observations of diameter anomalies in a series of insulating fluids. In addition, certain critical amplitudes become correlated with each other as a consequence of the revision of scaling variables, and the existing data are consistent with these results.

The basis of our theoretical results is the set of Kirkwood-Salsburg correlation-function identities which play a role completely analogous to those which arise from the equation of motion in field theory. We have shown that these identities allow certain many-body interactions to be absorbed into revised scaling fields *to leading order,* but have not addressed the higher-order corrections, which presumably behave similarly to those found in the renormalization-group analysis, namely, producing additional, weaker diameter anomalies. On a fundamental level, then, it remains to establish in detail a connection between the KS equations and the equation-of-motion identities.

While the motivation for this work is primarily the behavior of liquid-vapor coexistence curves, there are other systems in which generalized *compositional* asymmetries have been attributed to many-body interactions. Perhaps the classic examples are binary fcc alloys such as copper plus gold which have loci of order-disorder transi-

tion temperatures which are quite far from being stoichiometrically symmetric.[34-36] Previous studies[37] of these systems have typically been with mean-field techniques and the cluster-variation method, neither of which is applicable in the neighborhood of critical points. The analysis outlined in this paper provides a perturbation theory for weak many-body interactions which is applicable over the entire phase diagram. Thus, it is possible to deduce the effects of compact many-body interactions on the critical density and the critical temperature knowing only the properties of a system governed solely by pair potentials. In addition, the behavior in the critical region may be addressed directly because of the grand canonical formulation of the approach, which should provide a rigorous starting point for the study of stronger many-body interactions.

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