A Self-Consistent Ornstein–Zernike Approximation for the Site-Diluted Ising Model

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We propose a theory for the site-diluted Ising model which is an extension to disordered systems of the self-consistent Ornstein–Zernike approximation of Hoye and Stell. By using the replica method in the context of liquid-state theory, we treat the concentration of impurities as an ordinary thermodynamic variable. This approach is not limited to the weak-disorder regime or to the vicinity of the percolation point. A preliminary analysis using series expansion shows that it can predict accurately the dependence of the critical temperature on dilution and can reproduce the nonuniversal behavior of the effective exponents. The theory also gives a reasonable estimate of the percolation threshold.

1. INTRODUCTION

Some time ago, Hoye and Stell[1] proposed a self-consistent Ornstein–Zernike approach (SCOZA) for lattice gas or continuum fluid systems in which the direct correlation function $c(r)$ that appears in the Ornstein–Zernike equation is chosen to ensure self-consistency between the compressibility and energy routes to the free energy. It has been shown only recently[2] that this approximation provides very accurate predictions for the nonuniversal properties of the three-dimensional nearest-neighbor lattice gas (and thus of the corresponding Ising model) over most of the parameter space. Moreover, although the asymptotic critical exponents as those of the spherical model, the predicted effective exponents, near, but not asymptotically close to the critical points are in remarkable agreement with the true exponents of the 3-d Ising model. Our objective is to extend

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this promising approach to magnetic or fluid systems in the presence of quenched disorder. In spite of the large body of work in this field over the last twenty years, the understanding of the influence of disorder on phase transitions is far from complete. In the present work, we consider the site-diluted Ising model that is probably the simplest example of such systems and has been studied both by analytical techniques and by numerical simulations (see ref. 3 and references therein). The former have been mostly used to investigate the critical behavior in the limits of weak or strong disorder (near the percolation threshold), which still remains a controversial issue. Although unable to give definite answers for the asymptotic critical behavior (because of the strong influence of finite-size effects and the dramatic increase of relaxation times with dilution), numerical simulations provide good estimates of the effective exponents and the critical temperature for some selected values of the dilution.[4-7] It would certainly be valuable to have a theory which yields quantitative predictions for these quantities at any dilution, even if it does not predict correctly the exact asymptotic critical behavior. We present in this paper the first steps we have made in this direction. The SCOZA scheme is generalized to study a site-disordered lattice gas model that has been recently proposed as a model for a fluid in a porous matrix.[8-10] The site-diluted Ising model corresponds to a special value of the matrix-fluid interaction parameter. We treat the quenched degrees of freedom by the replica method.

The paper is organized as follows. In Section II, we derive the SCOZA differential equations for this system. In Section III, we analyze the solution in terms of series expansion (both high-temperature and high-dilution series are considered) and we present some preliminary numerical results. A brief summary and a discussion are provided in Section IV.

II. DERIVATION OF THE SCOZA EQUATIONS

The starting point of our study is the lattice gas model for a fluid in a disordered matrix that has been introduced in ref. 8. We consider a d-dimensional hypercubic lattice where the sites can be occupied by two types of "particles", matrix (species 0) or fluid (species 1), with occupancy variables $1 - \eta_i$ and τ_i respectively. The site disorder variables η_i's are quenched and take the values 0,1 at random such that $\bar{\eta}_i = p$, where the overbar denotes the average over disorder. We exclude multiple occupancy of a site by assuming that the pair potentials all contain a point "hard-core". The Hamiltonian is

$$H = -w_{11} \sum_{\langle ij \rangle} \tau_i \tau_j \eta_i \eta_j - w_{01} \sum_{\langle ij \rangle} [\tau_i \eta_i (1 - \eta_j) + \tau_j \eta_j (1 - \eta_i)], \qquad (1)$$

where $w_{11} > 0$ and w_{01} are the fluid–fluid and fluid–matrix nearest-neighbor (n.n.) interactions and the sums are over n.n. pairs of sites. There are thus two independent variables, the dilution $1 - p$ and the interaction ratio $y = w_{01}/w_{11}$. This model encompasses the two effects exerted on a fluid by a disordered porous medium, namely the exclusion from the solid phase and the usually attractive interaction with the matrix walls. The matrix-dependent grand partition function for the fluid is given by

$$\Xi_1(\{\eta_i\}) = \sum_{N_1=0}^{\infty} \exp(\beta\mu_1 N_1) \sum_{\{\tau_i\}}^{*} \exp(-\beta H(\{\tau_i\}, \{\eta_i\})) \qquad (2)$$

where $\beta = (k_B T)^{-1}$ is the inverse temperature, μ_1 is the fluid chemical potential, and the summation $\sum^*$ signifies summation over the τ_i's subject to the restriction that $\sum_i \tau_i = N_1$. Introducing as usual spin variables instead of occupancy variables ($\tau_i = (1 + \sigma_i)/2$, with $\sigma_i = \pm 1$), the grand partition for the lattice gas becomes a multiple of the partition function for an Ising model with Hamiltonian

$$\mathcal{H} = -J \sum_{\langle ij \rangle} \sigma_i \sigma_j \eta_i \eta_j - K \sum_{\langle ij \rangle} [\sigma_i \eta_i(1 - \eta_j) + \sigma_j \eta_j(1 - \eta_i)] - h \sum_i \sigma_i \eta_i. \qquad (3)$$

with $J = w_{11}/4$, $K = J(2y - 1)$, and $h = 1/2(\mu_1 + qw_{11}/2)$ where q is the coordination number of the lattice. In this work, we shall restrict ourselves to the case $y = 1/2$ where $K = 0$. Then, the Hamiltonian in Eq. (3) reduces to that of the site-diluted Ising model.[3] For a study of the general case ($K \neq 0$) within the mean-spherical approximation see refs. 8–10.

In order to study the thermodynamics and the structure of the lattice gas described by Eq. (1), we use the replica method as discussed elsewhere.[11–13] The thermodynamics is obtained from the averaged fluid grand potential which is a self-averaging quantity and is expressed via the replica trick as[13]

$$-\beta\bar{\Omega}_1 = \overline{\ln \Xi_1(\{\eta_i\})} = -\beta \lim_{s \to 0} \frac{d}{ds} \Omega^{rep}(s) \qquad (4)$$

where $\Omega^{rep}(s)$ is the grand potential of an equilibrium mixture with $(s + 1)$ components: s fluid replicas plus the matrix particles which are now considered as annealed. The fluid replicas do not interact with each other but they do interact with the matrix (contrary to the standard replica approach to disordered spin systems, the average over disorder is not performed explicitly). One has thus replaced the study of the original quenched-annealed mixture by that of a multicomponent equilibrium mixture for which one can now use the standard methods of liquid-state statistical

mechanics. One can formally write integral equations, thermodynamic relations, closure approximations for the $(s+1)$-component equilibrium mixture and then take the appropriate limit $s \to 0$. This is how one derives the set of Ornstein–Zernike equations relating the total pair correlation functions h_{ij} of the quenched-annealed mixture to the corresponding direct correlation functions c_{ij}.[12] Since the approximation studied here does not allow for any replica symmetry breaking mechanism when taking the limit $s \to 0$, one only needs the replica-symmetric form of these equations (hereafter called the RSOZ equations), which writes in Fourier space as[8]

$$\hat{h}_{00}(\mathbf{k}) = \frac{\hat{c}_{00}(\mathbf{k})}{1 - \rho_0 \hat{c}_{00}(\mathbf{k})} \tag{5a}$$

$$\hat{h}_{01}(\mathbf{k}) = \frac{\hat{c}_{01}(\mathbf{k})}{[1 - \rho_0 \hat{c}_{00}(\mathbf{k})][1 - \rho_1 \hat{c}_c(\mathbf{k})]} \tag{5b}$$

$$\hat{h}_c(\mathbf{k}) = \frac{\hat{c}_c(\mathbf{k})}{1 - \rho_1 \hat{c}_c(\mathbf{k})} \tag{5c}$$

$$\hat{h}_b(\mathbf{k}) = \left[\hat{c}_b(\mathbf{k}) + \rho_0 \frac{\hat{c}_{01}^2(\mathbf{k})}{1 - \rho_0 \hat{c}_{00}(\mathbf{k})} \right] \frac{1}{[1 - \rho_1 \hat{c}_c(\mathbf{k})]^2} \tag{5d}$$

where ρ_1 is the average density of the fluid and $\rho_0 = 1 - p$ is the density of the matrix. $h_b \equiv h_{12}(s=0)$, $c_b \equiv c_{12}(s=0)$, $h_c \equiv h_{11}(s=0) - h_b$, and $c_c \equiv c_{11}(s=0) - c_b$ are the disconnected and connected parts of h_{11} and c_{11}, where 1 and 2 denote two different fluid replicas. Moreover, $h_{01} = h_{10}$ and $c_{01} = c_{10}$ by symmetry. It is also worthwhile to note the following relations which can be deduced from the symmetry properties of the Hamiltonian when $y = 1/2$,

$$\rho_1[\delta_{\mathbf{r}, 0} + \rho_1 h_c(\mathbf{r}, \rho_1)] = (p - \rho_1)[\delta_{\mathbf{r}, 0} + (p - \rho_1) h_c(\mathbf{r}, p - \rho_1)] \tag{6a}$$

$$\rho_1 h_{01}(\mathbf{r}, \rho_1) + (p - \rho_1) h_{01}(\mathbf{r}, p - \rho_1) = -p \delta_{\mathbf{r}, 0} \tag{6b}$$

$$\rho_1^2 h_b(\mathbf{r}, \rho_1) + (1 - p) \rho_1 h_{01}(\mathbf{r}, \rho_1)$$
$$= (p - \rho_1)^2 h_b(\mathbf{r}, p - \rho_1) + (1 - p)(p - \rho_1) h_{01}(\mathbf{r}, p - \rho_1). \tag{6c}$$

When $\rho_1 = p/2$ (or $h = 0$ in spin language), one has

$$h_{01}(\mathbf{r}, p/2) = -\delta_{\mathbf{r}, 0}, \tag{7a}$$

$$h_b(\mathbf{r}, p/2) = \frac{1 - p}{p} \delta_{\mathbf{r}, 0} \tag{7b}$$

which implies

$$c_{01}(\mathbf{r}, p/2) = \frac{1}{2} c_c(\mathbf{r}, p/2) - \frac{1}{p} \delta_{\mathbf{r}, \mathbf{0}}. \tag{8a}$$

$$c_b(\mathbf{r}, p/2) = 0 \tag{8b}$$

where we have used that $c_{00}(\mathbf{r}) = -\delta_{\mathbf{r}, \mathbf{0}}/p$ $(h_{00}(\mathbf{r}) = -\delta_{\mathbf{r}, \mathbf{0}}$ because of the core exclusion).

We now make an Ornstein–Zernike type of approximation by assuming that the direct correlation functions have the same range as the corresponding interaction potentials. In the present case of n.n. interactions, this gives

$$c_b(\mathbf{r}) = 0$$

$$c_c(\mathbf{r}) = c_c^0 \, \delta_{\mathbf{r}, \mathbf{0}} + c_c^1 \, \delta_{\mathbf{r}, \mathbf{e}} \tag{9}$$

$$c_{01}(\mathbf{r}) = c_{01}^0 \, \delta_{\mathbf{r}, \mathbf{0}} + c_{01}^1 \, \delta_{\mathbf{r}, \mathbf{e}}$$

where $\mathbf{e}$ denotes a vector from the origin to one of its nearest neighbors and δ is the Kronecker symbol (the first equation is a consequence of the fact that there is no interaction between two fluid replicas). The mean-spherical approximation (MSA)[8-10] consists in setting $c_c^1 = \beta w_{11}$ and $c_{01}^1 = \beta w_{01}$. In contrast, in SCOZA, we allow $c_c^1 = c_c^1(\rho_1, p, T)$ and $c_{01}^1 = c_{01}^1(\rho_1, p, T)$, and we determine these two functions by imposing thermodynamic self-consistency (see below), whereas $c_{01}^0(\rho_1, p, T)$ and $c_c^0(\rho_1, p, T)$ can be completely determined by imposing, as in MSA, the two core conditions $h_{01}(\mathbf{r} = 0) = h_{11}(\mathbf{r} = 0) = -1$ (note that h_c and h_b do not satisfy themselves the core requirement). Starting form the Gibbs–Helmholtz relation between the averaged internal energy per fluid particle $\bar{u}$ and the averaged Helmholtz free-energy per fluid particle $\bar{f}$,

$$\bar{u} = \frac{\partial \beta \bar{f}}{\partial \beta} \bigg|_{\rho_1, p}, \tag{10}$$

and differentiating with respect to ρ_1 and p, we get two self-consistency equations:

$$\frac{\partial^2 \rho_1 \bar{u}}{\partial \rho_1^2} \bigg|_{\beta} = -\frac{\partial \hat{c}_c(0)}{\partial \beta} \bigg|_{\rho_1, p} \tag{11}$$

and

$$\frac{\partial^2 \rho_1 \bar{u}}{\partial \rho_1 \, \partial p}\bigg|_\beta = \frac{\partial \hat{c}_{01}(0)}{\partial \beta}\bigg|_{\rho_1, p} \tag{12}$$

where we have used that $\hat{c}_{\alpha\beta}(0) = -\partial^2 \beta \bar{f}^{ex}/\partial \rho_\alpha \, \partial \rho_\beta (\alpha, \beta = 0, 1,..., s)$ in the "replicated" equilibrium mixture. As far as we know, Eq. (12) (or its translation in spin language) has never been considered in the context of dilute magnets. It is the originality of the present approach that p is treated via the replica trick as an ordinary thermodynamical variable ($\rho_0 = 1 - p$ is the concentration of the matrix particles) and not as an external parameter. $\bar{u}$ is given by[9]

$$\bar{u} = -\frac{q}{2}\left[\rho_1(1 + h_{11}^1) + (1 - p)(1 + h_{01}^1)\right] \tag{13}$$

where $h_{ij}^1 \equiv h_{ij}(\mathbf{r} = \mathbf{e})$ (in this equation and in the following we take $w_{11} = 1$). When $p = 1$, $c_c(\mathbf{k})$ is just the direct correlation function of the pure system and Eqs. (11) and (13) reduce to the SCOZA equations of ref. 2.

The MSA solution of the RSOZ equations for the correlation functions[8-10] is expressed in terms of the quantity $z = \rho_1 q c_c^1/(1 - \rho_1 c_c^0)$ and parametrized by $y = w_{01}/w_{11}$. The same expressions remain valid in SCOZA provided that y is now the state-dependent interaction ratio c_{01}^1/c_c^1. The two functions $z(\rho_1, p, T)$ and $y(\rho_1, p, T)$ are then obtained by solving the coupled partial differential equations, Eqs. (11) and (12). From refs. 9 and 10, and introducing the lattice Green's function

$$P(\mathbf{r}, z) = \frac{1}{(2\pi)^d} \int_{-\pi}^{\pi} d^d\mathbf{k} \, \frac{e^{i\mathbf{k}\cdot\mathbf{r}}}{1 - z\lambda(\mathbf{k})} \tag{14}$$

where $\lambda(\mathbf{k})$ is the characteristic function of the lattice,[14] we derive

$$\rho_1[\delta_{\mathbf{r}, 0} + \rho_1 h_c(\mathbf{r})] = p\left[\frac{1}{4} - \Delta\rho_1^2 - (1 - p) \, \theta^2 z^2 \psi'(z)\right]\frac{P(\mathbf{r}, z)}{P(z)} \tag{15}$$

$$\rho_1^2 h_b(\mathbf{r}) = p(1 - p)\left[y^2 \, \delta_{\mathbf{r}, 0} - 2y\theta \frac{P(\mathbf{r}, z)}{P(z)} + \theta^2 \frac{zP'(\mathbf{r}, z) + P(\mathbf{r}, z)}{P(z)^2}\right] \tag{16}$$

$$\rho_1 h_{01}(\mathbf{r}) = p\left[-y \, \delta_{\mathbf{r}, 0} + \theta \frac{P(\mathbf{r}, z)}{P(z)}\right] \tag{17}$$

where $\Delta\rho_1 \equiv \rho_1/p - 1/2$, $\theta \equiv y - \rho_1/p$, $P(z) \equiv P(0, z)$, $P'(\mathbf{r}, z) = \partial P(\mathbf{r}, z)/\partial z$, $\psi(z) = [1 - 1/P(z)]/z$, and $\psi'(z) = d\psi(z)/dz$.

After some calculations, this yields

$$\tilde{u} = \left[\Delta\rho_1 + \frac{1}{2}\right]\left[p\left(\Delta\rho_1 + \frac{1}{2}\right) + 1 - p\right] + \left(\frac{1}{4} - \Delta\rho_1^2\right)\psi(z)$$

$$+ (1-p)\,\theta\left[\theta\left(\frac{z}{P(z)}\,\psi'(z) - \psi(z)\right) - 2\,\Delta\rho_1\psi(z)\right] \qquad (18)$$

$$\hat{c}_c(0) = \frac{1}{p(\Delta\rho_1 + \frac{1}{2})} - \frac{1}{p}\frac{(1-z)\,P(z)}{(\frac{1}{4} - \Delta\rho_1^2) - (1-p)\,\theta^2 z^2\psi'(z)} \qquad (19)$$

$$\hat{c}_{01}(0) = -\frac{1}{p}\frac{(\theta + \Delta\rho_1 + 1/2)(1-z)\,P(z) - \theta}{(\frac{1}{4} - \Delta\rho_1^2) - (1-p)\,\theta^2 z^2\psi'(z)} \qquad (20)$$

where $\tilde{u} \equiv -2\rho_1\tilde{u}/(pq)$.

This completes the derivation of the SCOZA equations in the case where the lattice-gas model is isomorphic to the site-diluted Ising model (in fact, the preceding equations except Eqs. (13) and (18) remain valid when $w_{01}/w_{11} \neq 1/2$). It may be noticed from Eqs. (18)–(20) that the solution of Eqs. (11)–(12) satisfies the symmetry relations $z(\rho_1, p, T) = z(p - \rho_1, p, T)$ and $y(\rho_1, p, T) = 1 - y(p - \rho_1, p, T)$. Therefore the correlation functions given by Eqs. (15)–(17) satisfy the exact relations, Eqs. (6)–(7). Note also that we have

$$\left.\frac{\partial\hat{c}_c(0)}{\partial p}\right|_{\beta,\rho_1} = -\left.\frac{\partial\hat{c}_{01}(0)}{\partial\rho_1}\right|_{\beta,p} \qquad (21)$$

so that the self-consistency conditions, Eqs. (11)–(12), can be replaced by the equivalent system

$$\left.\frac{\partial p\hat{c}_c(0)}{\partial p}\right|_{\beta,\Delta\rho_1} = -\left.\frac{\partial[\hat{c}_{01}(0) - (\Delta\rho_1 + 1/2)\,\hat{c}_c(0)]}{\partial\,\Delta\rho_1}\right|_{\beta,p} \qquad (22)$$

$$\left.\frac{q}{2}\frac{\partial^2\tilde{u}}{\partial p\,\partial\Delta\rho_1}\right|_{\beta} = -\left.\frac{\partial[\hat{c}_{01}(0) - (\Delta\rho_1 + 1/2)\,\hat{c}_c(0)]}{\partial\beta}\right|_{\Delta\rho_1,p} \qquad (23)$$

where we have used $\Delta\rho_1$ as the density variable.

Once $z(\rho_1, p, T)$ and $y(\rho_1, p, T)$ are known, all thermodynamic properties (internal energy, pressure, entropy,...) can be obtained in a straightforward way. The inverse fluid compressibility is calculated from ref. 13

$$\frac{\beta}{\rho_1\chi_1} = 1 - \rho_1\hat{c}_c(0) \qquad (24)$$

and from Eq. (19) we readily see that χ_1^{-1} vanishes when $z = 1$, as in the pure case.[2] This defines the spinodal line and the critical point is reached when the spinodal meets the coexistence curve at $\rho_1 = p/2$ (i.e. $\Delta\rho_1 = 0$). Alternatively, we can locate the critical temperature by plotting χ_1^{-1} as a function of β along the critical isochore. An important consequence of $z_c = 1$ is that the present theory yields no phase transition in two dimensions because the Green's function $P(z)$ diverges at $z = 1$ for $d \leqslant 2$. For $2 < d \leqslant 4$, $P(1)$ is finite, but $P'(1)$ and, consequently, $\psi'(1)$ diverge, which also seems to prevent the existence of a bona fide spinodal in the SCOZA description of disordered systems. However, in the particular case of the site-diluted Ising model ($w_{01}/w_{11} = 1/2$), one has $y(p/2, p, T) = 1/2$ so that θ vanishes identically on the critical isochore $\Delta\rho_1 = 0$, allowing for the existence of a point $z_c = 1$ at a non-zero-temperature. Although we have so far no convincing proof of it, we speculate that there exists also a full spinodal curve that is characterized by $z = 1$ and $\theta = 0$. We expect the asymptotic critical exponents to be those of the spherical model, as in the pure case.

Finally we note that the critical internal energy can be readily obtained from Eq. (18):

$$\bar{u}_c = -\frac{q}{4}\left[3 - p - \frac{1}{P(1)} \right]. \tag{25}$$

In Appendix A, some more explicit expressions of $\bar{u}$, $\hat{c}_c(0)$, and $\hat{c}_{01}(0)$ are given in the case of the 3-d simple cubic lattice, using a nice approximation for the Green's function proposed some time ago by Jancovici.[15]

III. SERIES EXPANSIONS

The numerical solution of the coupled PDE's, Eqs. (11)–(12) or (22)–(23), is a difficult task which we defer to a later work. Here, we only give a qualitative analysis of the solution and some preliminary results obtained from series expansions.

A. High-Temperature Series

From Eqs. (11)–(12) and (18)–(20), it is straightforward to derive high-temperature series for $z(\rho_1, p, T)$ and $y(\rho_1, p, T)$. First, we note that when T goes to infinity the system must behave as a non-interacting lattice gas. Therefore, $c_c^1(\rho_1, p, T \to \infty) \to 0$ so that $z(\rho_1, p, T \to \infty) \to 0$. On the

other hand $y(\rho_1, p, T \to \infty) \to 1/2$, the bare value of the interaction ratio. Taking $v = \tanh(\beta J)$ as the high temperature variable, we thus write

$$z(\rho_1, p, v) = \sum_{n \geq 1} z_n(\rho_1, p) \, v^n$$

$$y(\rho_1, p, v) = \tfrac{1}{2} + \sum_{n \geq 1} y_n(\rho_1, p) \, v^n, \tag{26}$$

expand the Green's function $P(z)$ is powers of z

$$P(z) = 1 + \sum_{n \geq 2} P_n z^n \tag{27}$$

(with $P_2 = 1/q$), and substitute in the SCOZA equations. The coefficients $z_n(\rho_1, p)$ and $y_n(\rho_1, p)$ are polynomials in ρ_1 and p that can be evaluated very easily using a symbolic computation software such as MAPLE. We then deduce from Eq. (22) the compressibility along the critical isochore (i.e., the zero-field susceptibility for the spin system). The result for the 3-d face centered cubic lattice (FCC) for instance, is

$$kT\chi \left(\rho_1 = \frac{p}{2}, v \right)$$

$$= \frac{1}{p} + 12v + 132pv^2 + (1396p^2 + 16p - 8)\, v^3$$

$$+ (14436p^3 + 552p^2 - 360p + 24)\, v^4$$

$$+ \left(147160p^4 + 11800p^3 + \frac{43612}{5}\, p^2 + \frac{4944}{5}\, p - \frac{312}{5} \right) v^5$$

$$+ \left(\frac{22284736}{15}\, p^5 + \frac{1002396}{5}\, p^4 - \frac{790652}{5}\, p^3 + \frac{328268}{15}\, p^2 \right.$$

$$\left. - 2208p + \frac{968}{5} \right) v^6 + \left(\frac{74475612}{5}\, p^6 + \frac{103981372}{35}\, p^5 - \frac{16827836}{7}\, p^4 \right.$$

$$\left. + \frac{11411356}{35}\, p^3 - \frac{133756}{5}\, p^2 + \frac{186672}{35}\, p - \frac{26232}{35} \right) v^7$$

$$+ \left(\frac{5200266858}{35}\, p^7 + \frac{4225357904}{105}\, p^6 - \frac{1134125948}{35}\, p^5 + \frac{113281996}{35}\, p^4 \right.$$

$$\left. + \frac{7364330}{21}\, p^3 - \frac{1334636}{35}\, p^2 - \frac{590616}{35}\, p + \frac{125448}{35} \right) v^8 + O(v^9). \tag{28}$$

which can be compared to the exact series[16]

$$kT\chi\left(\rho_1 = \frac{p}{2}, v\right) = \frac{1}{p} + 12v + 132pv^2 + 1404p^2v^3 + (14700p^3 - 48p)\,v^4$$

$$+ (152532p^4 - 1368p^2 - 48p)\,v^5$$

$$+ (1573716p^5 - 25584p^3 - 1800p^2)\,v^6$$

$$+ (16172148p^6 - 397104p^4 - 40608p^3$$

$$- 24p^2 + 48p)\,v^7 + (165697044p^7 - 5549856p^5$$

$$- 723000p^4 - 2112p^3 + 3456p^2 + 48p)\,v^8 + O(v^9).$$

$$(29)$$

Our theory is thus exact through the $O(v^2)$ term (when $p = 1$, however, it is exact through order $O(v^4)$), and it can be checked that for higher-order terms the numerical values of the coefficients are very close to the exact ones when the dilution is in the range $0.5 \leqslant p \leqslant 1$ (the relative error on the $O(v^8)$ term is then smaller than 5%). Equally good results are obtained for the simple cubic (SC) and the body centered cubic (BCC) lattices.

As a first estimate of the accuracy of the theorem, we can extract the critical temperature and the critical exponent γ forming Padé approximants to the logarithmic derivative of $\chi(\rho_1 = p/2, v)$. A selection of results for the SC, BCC, and FCC lattices is shown in Tables I–III. Except for the two

Table I. Critical Temperature T_c and Effective Exponent γ for the Diluted Ising Model on a Simple Cubic Lattice from Padé Approximants to the SCOZA High-Temperature Series[a]

p	kT_c/J				γ			
	[4,5]	[5,5]	[6,5]	MC	[4,5]	[5,5]	[6,5]	MC
1	4.528	4.525	4.526	4.512	1.237	1.241	1.240	1.24
0.95	4.279	4.277	4.279	4.262	1.253	1.256	1.253	1.28
0.90	4.029	4.026	4.027	4.011	1.267	1.274	1.273	1.31
0.80	3.511	3.510	3.509	3.499	1.336	1.339	1.342	1.35
0.70	2.900	2.967	2.967	—	1.791	1.473	1.471	—
0.60	2.337	2.371	2.401	2.422	2.118	1.862	1.684	1.51
0.50	—	—	1.841	1.849	—	—	1.851	1.49
0.40	—	1.129	1.300	1.209	—	2.963	2.163	—

[a] The MC results are taken from ref. [6] except for $p = 0.40$ which is taken from ref. [7].

Table II. Critical Temperature T_c and Effective Exponent γ for the Diluted Ising Model on a Body Centred Cubic Lattice from Padé Approximants to the SCOZA High-Temperature Series

p	kT_c/J			γ		
	[4,5]	[5,5]	[6,5]	[4,5]	[5,5]	[6,5]
1	6.376	6.388	6.382	1.230	1.207	1.221
0.95	6.035	6.044	6.039	1.243	1.222	1.236
0.90	5.690	5.692	5.694	1.260	1.257	1.253
0.80	4.987	4.987	4.987	1.314	1.315	1.317
0.70	4.264	4.264	4.258	1.410	1.410	1.425
0.60	3.487	3.495	3.493	1.667	1.640	1.646
0.50	2.589	2.630	2.663	2.871	2.462	2.200
0.40	—	—	1.777	—	—	3.190

lowest values of p, we observe a reasonable convergence for the critical temperature between the different approximants and the predictions are in good agreement with the simulation data when those are available[6, 7] (note that for $p = 1$, our results are very close to those obtained from the solution of the SCOZA partial differential equation[2]). On the other hand, it is more difficult to obtain a reliable information on γ, as already observed in the analysis of the exact series.[16, 17] Clearly, what we get by this procedure is an *effective* exponent since spherical exponents are expected asymptotically. We observe a rapid increase of γ from the pure value, which is consistent with the behavior found in the simulations.

Table III. Critical Temperature T_c and Effective Exponent γ for the Diluted Ising Model on a Face Centred Cubic Lattice from Padé Approximants to the SCOZA High-Temperature Series

p	kT_c/J			γ		
	[4,5]	[5,5]	[6,5]	[4,5]	[5,5]	[6,5]
1	9.835	9.835	9.825	1.223	1.223	1.251
0.95	9.311	9.313	9.288	1.237	1.236	1.333
0.90	8.787	8.796	8.756	1.253	1.266	1.362
0.80	7.693	7.662	7.699	1.348	1.603	1.325
0.70	6.569	6.590	6.593	1.569	1.445	1.435
0.60	5.452	5.438	5.452	1.597	1.605	1.596
0.50	4.097	4.233	4.305	2.554	1.986	1.654
0.40	—	—	3.120	—	—	1.669

B. p-Expansion and Percolation

Although the above results show that the critical temperature decreases with p, it is not immediately obvious that T_c in this theory goes to zero at a finite value of the dilution corresponding to the geometric percolation threshold.[3] If such a critical p_c exists, the probability of finding an infinite cluster of spins is zero when $p < p_c$ and a transition becomes impossible. The zero temperature limit of the expansion

$$\chi\left(\rho_1 = \frac{p}{2}, p\right) = \sum_{n \geqslant 0} \chi_n(\beta)\, p^n \qquad (30)$$

then becomes the mean cluster size expansion for site percolation.

The p-expansion of $z(\rho_1, p, T)$ and $y(\rho_1, p, T)$ requires the solution of partial differential equations at each order in p, and here we shall content ourselves with the derivation of the lowest-order term only. When $p \to 0$, the fluid particles are isolated one from each others and we expect that $z \to 0$. On the other hand, the limiting value of y (or of $\theta = y - \rho_1/p$) is not trivial. We thus write

$$z(\rho_1, p, \beta) = \sum_{n \geqslant 1} z_n(\Delta\rho_1, \beta)\, p^n$$

$$\theta(\rho_1, p, \beta) = \theta_0(\Delta\rho_1, \beta) + \sum_{n \geqslant 1} \theta_n(\Delta\rho_1, \beta)\, p^n, \qquad (31)$$

expand again the Green's function in powers of z, and replace in Eqs. (22)-(23). At lowest order. Eq. (22) yields

$$\frac{z_1(\Delta\rho_1, \beta)}{\frac{1}{4} - \Delta\rho_1^2} = -\frac{\partial}{\partial\Delta\rho_1} \frac{\theta_0(\Delta\rho_1, \beta)\, z_1(\Delta\rho_1, \beta)}{\frac{1}{4} - \Delta\rho_1^2}, \qquad (32)$$

which has the solution

$$\theta_0(\Delta\rho_1, \beta) = -\frac{(\frac{1}{4} - \Delta\rho_1^2)}{z_1(\Delta\rho_1, \beta)} \int_0^{\Delta\rho_1} \frac{z_1(t, \beta)}{\frac{1}{4} - t^2}\, dt, \qquad (33)$$

where we have used $\theta_0(0, \beta) = 0$. Replacing into Eq. (23) and introducing the auxiliary variable $f(\Delta\rho_1, \beta) = \int_0^{\Delta\rho_1} z_1(t, \beta)/(1/4 - t^2)\, dt$, we get, at lowest order in p,

$$\frac{\partial f(\Delta\rho_1, \beta)}{\partial\beta} = q\,\Delta\rho_1 + \frac{1}{2} \frac{\partial}{\partial\Delta\rho_1} \left[\left(\frac{1}{4} - \Delta\rho_1^2\right)^2 \frac{\partial f(\Delta\rho_1, \beta)}{\partial\Delta\rho_1} \right.$$

$$\left. + 2\,\Delta\rho_1 \left(\frac{1}{4} - \Delta\rho_1^2\right) f(\Delta\rho_1, \beta) \right]. \qquad (34)$$

As shown in Appendix B, this second-order partial differential equation can be solved by taking the Laplace transform of $f(\Delta\rho_1, \beta)$ with respect to β. The solution is expressed in terms of associated Legendre functions and exhibits two noticable properties. First, the zero-temperature limit is well-defined and can be obtained by setting the l.h.s. of Eq. (34) to 0. Eq. (B8) yields

$$z_1(\Delta\rho_1, T=0) = 4q\left(\frac{1}{4} - \Delta\rho_1^2\right)\left(1 - \Delta\rho_1 \ln\frac{1/2 + \Delta\rho_1}{1/2 - \Delta\rho_1}\right), \qquad (35)$$

from which we get

$$\theta_0(\Delta\rho_1, T=0) = -\frac{\Delta\rho_1}{2} - \frac{1}{8}\frac{\ln\dfrac{1/2 + \Delta\rho_1}{1/2 - \Delta\rho_1}}{1 - \Delta\rho_1 \ln\dfrac{1/2 + \Delta\rho_1}{1/2 - \Delta\rho_1}}. \qquad (36)$$

Secondly, although $z_1(\Delta\rho_1, \beta)$ goes to 0 when $\Delta\rho_1 \to \pm 1/2$ as it should be, its behavior at $\Delta\rho_1 = \pm 1/2$ is nonanalytic (in other words, the virial expansion of z_1 in powers of ρ_1 has a radius of convergence equal to zero). We conjecture that these two properties hold at all orders in p when p is smaller than p_c.

We can now determine the value of p_c. If $z(\rho_1, p, T)$ and $y(\rho_1, p, T)$ remain finite when $T \to 0$, this is also true for $\hat{c}_c(0)$ and $\hat{c}_{01}(0)$ and their derivatives with respect to β go to 0 in this limit. Then Eq. (23) implies

$$\lim_{\beta \to \infty} \frac{\partial^2 \tilde{u}}{\partial p\, \partial \Delta\rho_1}\bigg|_\beta = 0. \qquad (37)$$

Therefore $\partial\tilde{u}/\partial\Delta\rho_1$ does not depend on p at $T=0$. Since $z(\rho_1, p=0, T) = 0$ and thus $\tilde{u}(\Delta\rho_1, p=0, T) = \Delta\rho_1 + 1/2$, we have

$$\tilde{u}(\rho_1, p, T=0) = \Delta\rho_1 + 1/2 + pF(p), \qquad (38)$$

where $F(p)$ is some function of p. But since the internal energy is zero when $\rho_1 = 0$, $F(p) = 0$ and we find from Eq. (18) that $z(\rho_1, p, T=0)$ and $\theta(\rho_1, p, T=0)$ are solutions of

$$\left(\frac{1}{4} - \Delta\rho_1^2\right)(\psi(z) - p) + (1-p)\,\theta\left[\theta\left(\frac{z}{P(z)}\psi'(z) - \psi(z)\right) - 2\Delta\rho_1\psi(z)\right] = 0$$

$$(39)$$

(it can be checked that $z_1(\Delta\rho_1, T=0)$ and $\theta_0(\Delta\rho_1, T=0)$ given by Eqs. (35) and (36) are indeed solutions of this equation when expanded at first order in p). In particular, on the isochore $\Delta\rho_1 = 0$ where $\theta = 0$, one has the simple relation

$$p = \psi(z). \tag{40}$$

The percolation threshold is reached when a phase transition for the fluid (or the magnetic spins) becomes possible, i.e., when $z = 1$. Hence

$$p_c = \psi(1) = 1 - \frac{1}{P(1)}. \tag{41}$$

Remarkably, this result is the same as the one obtained by using the MSA for the pair connectedness function.[18,19] It gives a reasonable prediction for p_c in 3 dimensions ($p_c = 0.3405, 0.2892$, and 0.2563 instead of 0.310, 0.243, and 0.195 for the SC, BCC and FCC lattices, respectively) and yields the spherical model values for the percolation exponents γ_p and ν_p (on the other hand, the upper critical dimension is 4 instead of the correct value 6). It happens that some Padé approximants to the high-temperature series are able to predict accurately these values of p_c. This is the case for instance of the [5,3] Padé for the SC lattice, which yields $p_c = 0.34533$, or, even better, the [4,3] Padé for the BCC lattice which yields $p_c = 0.28219$. We have not tried, however, to include this information more systematically by constructing biased approximants.

IV. CONCLUSION

This preliminary analysis of the SCOZA equations for the site-diluted Ising model is encouraging. The theory seems to predict accurately the variations of T_c with dilution and it may also describe the nonuniversal behavior of the effective exponents observed in the simulations or in experiments. Several important points, however, deserve a more extensive study, like for instance the existence of a spinodal, the behavior of $T_c(p)$ in the vicinity of $p = p_c$ or the possible occurence of Griffiths singularities. It should be also noticed that the theory presented here cannot account for the replica symmetry breaking mechanism which has been recently suggested in the literature.[20] For that purpose, one needs a closure relation to the Ornstein–Zernike equations that relates in a nonlinear fashion the direct correlation functions $c_{\alpha,\beta}(\mathbf{r})$'s to the total correlation functions $h_{\alpha,\beta}(\mathbf{r})$'s. Such a closure relation could be for instance the hypernetted chain equation.[21] Work in this direction is in progress.

APPENDIX A

Some time ago, Jancovici[15] proposed a simple approximation for the Green's function of the simple cubic lattice that reproduces the leading terms of the behavior at $z = 1$. It reads

$$P(z) - 1 = z\psi(z) \ P(z) = \frac{6\psi(z)^2}{1 + 3\psi(z)^2} \tag{A1}$$

which yields

$$P(z) = 3 \frac{1 - (1 - z^2)^{1/2}}{z^2 + 1 - (1 - z^2)^{1/2}} \tag{A2}$$

and

$$\psi(z) = \frac{1}{3z} (1 - (1 - z^2)^{1/2}). \tag{A3}$$

This approximation can be used to simplify the expressions of the internal energy and the correlation functions at $\mathbf{k} = 0$ given by Eqs. (18)–(20). It is now convenient to take $\psi(z) \equiv \psi(\Delta p_1, p, T)$ as the dependent variable instead of z in the differential equations (11)–(12) or (22)–(23) (θ being the other dependent variable). For instance, after some calculations, Eqs. (22)–(23) become

$$\frac{\partial}{\partial p} \left\{ \frac{(1 - 3\psi)^3 (1 + 3\psi)}{(1 + 3\psi^2)[(1/4 - \Delta p_1^2)(1 - 9\psi^2) + 6\psi^2(1 - p)\theta^2]} \right\}$$

$$= \frac{1}{p} \frac{\partial}{\partial \Delta p_1} \left\{ \frac{6\theta\psi(1 - \psi)(1 - 9\psi^2)}{[(1/4 - \Delta p_1^2)(1 - 9\psi^2) + 6\psi^2(1 - p) \theta^2]} \right\} \tag{A4}$$

and

$$q \Delta p_1 + \frac{q}{2} \frac{\partial^2}{\partial p \, \partial \Delta p_1} \left\{ \left(\frac{1}{4} - \Delta p_1^2 \right) \psi + 2(1 - p) \theta\psi \left[\frac{3\theta\psi^2}{1 - 9\psi^2} - \Delta p_1 \right] \right\}$$

$$= -\frac{1}{p} \frac{\partial}{\partial \beta} \left\{ \frac{6\theta\psi(1 - \psi)(1 - 9\psi^2)}{[(1/4 - \Delta p_1^2)(1 - 9\psi^2) + 6\psi^2(1 - p) \theta^2]} \right\}. \tag{A5}$$

APPENDIX B

In order to solve the partial differential equation, Eq. (34), we take the Laplace transform of $f(\varDelta\rho_1, \beta)$ with respect to β,

$$\hat{f}(\varDelta\rho_1, s) = \int_0^\infty e^{-\beta s} f(\varDelta\rho_1, \beta) \, d\beta. \tag{B1}$$

and we rewrite Eq. (34) as

$$(1-x^2) \frac{\partial^2 \hat{f}(x, s)}{\partial x^2} - 2x \frac{\partial \hat{f}(x, s)}{\partial x} + \left(6 - 4 \frac{1+2s}{1-x^2}\right) \hat{f}(x, s) = -\frac{4q}{s} \frac{x}{1-x^2}. \tag{B2}$$

where $x = 2 \varDelta\rho_1$. The corresponding homogeneous equation is a Legendre differential equation with regular singularities at 0,1 and ∞, whose solutions are the associated Legendre functions of the first and second kinds,[22] $P_\nu^\mu(x)$ and $Q_\nu^\mu(x)$, with $\nu = 2$ and $\mu = 2(1+2s)^{1/2}$. The solution of the inhomogeneous equation is then

$$\hat{f}(x, s) = -\frac{4q}{s} 2^{-2\mu} \frac{\Gamma(2-\mu/2) \, \Gamma(3/2-\mu/2)}{\Gamma(2+\mu/2) \, \Gamma(3/2+\mu/2)}$$

$$\times \left[Q_2^\mu(x) \int_0^x \frac{t P_2^\mu(t)}{1-t^2} dt - P_2^\mu(x) \int_0^x \frac{t Q_2^\mu(t)}{1-t^2} dt \right]$$

$$+ A(s) \, P_2^\mu(x) + B(s) \, Q_2^\mu(x), \tag{B3}$$

where Γ is the gamma function and $A(s)$ and $B(s)$ are two integration constants. Since the solution of Eq. (B2) is odd in x, we have

$$A(s) = -B(s) \frac{Q_2^\mu(0)}{P_2^\mu(0)} \tag{B4}$$

and we determine $B(s)$ by imposing that $\hat{f}(x, s)$ has a finite limit when $x \to \pm 1$. Using the following relation between Legendre functions,[23]

$$2 Q_\nu^\mu(x) \sin(\mu\pi) = \pi \left[P_\nu^\mu(x) \cos(\mu\pi) - \frac{\Gamma(\nu+\mu+1)}{\Gamma(\nu-\mu+1)} P_\nu^{-\mu}(x) \right], \tag{B5}$$

the duplication formula for the gamma function, and the explicit expression of $P_2^\mu(x)$,

$$P_2^\mu(x) = \frac{1}{\Gamma(1-\mu)} \left(\frac{1+x}{1-x}\right)^{\mu/2} \left[1 - \frac{3}{1-\mu} (1-x) + \frac{3}{(1-\mu)(2-\mu)} (1-x)^2 \right],$$

$$\tag{B6}$$

we obtain

$$B(s) = \frac{4q}{s} \int_0^1 \frac{t P_2^{-\mu}(t)}{1-t^2} \, dt \tag{B7}$$

and finally

$$\hat{f}(x, s) = \frac{2q\pi}{s \sin(\mu\pi)} \left[P_2^{-\mu}(x) \int_0^x \frac{t P_2^{\mu}(t)}{1-t^2} \, dt + P_2^{\mu}(x) \int_x^1 \frac{t P_2^{-\mu}(t)}{1-t^2} \, dt \right.$$

$$\left. - P_2^{-\mu}(x) \frac{\Gamma(3+\mu)}{\Gamma(3-\mu)} \int_0^1 \frac{t P_2^{-\mu}(t)}{1-t^2} \, dt \right]. \tag{B8}$$

The $\beta \to \infty$ limit of $f(x, \beta)$, if it exists, is given by $\lim_{s \to 0} s\hat{f}(x, s)$. It is readily obtained from Eqs. (B3), (B4) and (B7), using

$$P_2^2(x) = 3(1 - x^2)$$

$$Q_2^2(x) = \frac{3}{2}(1 - x^2) \ln \frac{1+x}{1-x} + x \frac{5 - 3x^2}{1 - x^2} \tag{B9}$$

The result is

$$f(x, \infty) = qx + \frac{q}{2}(1 - x^2) \ln \frac{1+x}{1-x} \tag{B10}$$

which is the solution of Eq. (34) when the l.h.s is 0.

As can be seen from Eqs. (B6) and (B8), the general solution of Eq. (B2) is nonanalytic at $x = \pm 1$, although it contains an analytic part that can be also obtained by expanding $f(x, \beta)$ in powers of $x \pm 1$ (virial expansion) and by solving the differential equation, Eq. (34), order by order.

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