Critical Curves and Thermodynamic Phases of Lattice Fluids and Antiferromagnets with Structured Interactions*

Michael Plischke and Daniel Mattis

Belfer Graduate School of Science, Yeshiva University, New York, New York 10033

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We study the classical lattice gas with hard cores, nearest-neighbor repulsive forces, and next-nearest-neighbor attractive forces. We find several thermodynamic phases (vapor, liquid, and solid) and unusually shaped critical curves, yet no critical point or triple point. We find and discuss discontinuities in $m(h)$ in the analogous magnetic systems. The principal calculational tool is molecular field theory but accurate numerical solutions of the transfer matrix are also obtained as a check on some of the results. It is conjectured that the critical line separating vapor and liquid phases (bounded by the triple point on one end and the critical point on the other) exists in the exact solution of a lattice gas with structured, relatively long-ranged interactions, but cannot be found in the molecular field approximation.

I. INTRODUCTION

Lattice gases have been extensively studied analytically and numerically. For example, Runnels and Combs[1] have studied two-dimensional systems of hard squares by the transfer-matrix method. Runnels, Salvant, and Streiffer[2] have studied hard squares with both positive and negative finite interaction between third nearest neighbors. They find a first-order phase transition for a temperature range $0 \leq T < T_0$ and a second-order transition in the range $T_0 \leq T < T_c$ for attractive coupling between third nearest neighbors. Orban, van Craen, and Bellemans[3] have studied a two-dimensional system with hard cores extending to the third-nearest-neighbor sites and attractive potentials to the fourth and fifth nearest neighbors. Gaunt and Fisher[4] and Gaunt[5] have studied hard-square systems by the series-expansion method.

We have two principal aims in this paper. One is to investigate the properties of lattice gases having a soft-core repulsive potential as well as a nonextended hard core. The basis system, in magnetic language, is the nearest-neighbor Ising antiferromagnet. In zero magnetic field this sys-

tem has the same thermodynamic properties as the Ising ferromagnet which was solved exactly in two dimensions by Onsager.[6] Mazo[7] solved the Ising antiferromagnet in a finite field in the spherical-model approximation and obtained the corresponding lattice gas properties. Garrett[8] also treated the Ising antiferromagnet in a finite field using molecular field theory (MFT). He obtained, for $T < T_N$, a second-order phase transition at a finite critical field $H_c(T)$ at which point the magnetization is continuous but the susceptibility is discontinuous. In Sec. II we also use MFT to obtain the properties of the lattice gas. In Sec. III we analyze the transfer matrix of the two-dimensional antiferromagnet for strips of infinite length but finite width. For strips M sites wide the transfer matrix is a $2^M \times 2^M$ matrix whose largest eigenvalue may be obtained by an iterative process already used by us to treat the Ising ferromagnet. We are able to treat strips up to 10 sites wide and find MFT to be qualitatively correct, with possibly one important exception, discussed below.

In Sec. IV we discuss our other principal aim, a study of the antiferromagnet with various ferromagnetic interactions between next nearest neigh-

bors. In lattice gas language this is a system with hard cores, soft cores, and a longer-range attractive force. Hemmer and Stell[9] have recently treated exactly a one-dimensional continuum fluid with hard core, soft core, and a long-range attractive potential. They found either a single first-order phase transition or two first-order transitions depending on the values of certain parameters in their model. They have also argued that if the attractive part of the interaction is capable of producing a first-order phase transition in the lattice gas, then the soft-core repulsion should bring about two first-order phase transitions. In MFT, however, we find that while there are always two phase transitions the nature of these transitions is variable. Notably, there is a temperature $T_1 < T_c$ above which the transitions are second order, whereas below T_1 the transitions are first order. These results are expected to hold for an exact calculation as well. While it might moreover be expected that this model would at least qualitatively reproduce the properties of the rare gases, we find in MFT no critical line (or critical point or triple point) even for interactions with more structure than the ones reported on here. In view of the fact that Hemmer and Stell have found the possibility of such a critical line already in one dimension, it seems to us that MFT *is the culprit*. Thus the major improvement of an exact transfer-matrix solution, in two or three dimensions, over the molecular field approximation, will be the precise delineation of the critical lines and their dependence on the structure of the interactions (depth and width of attractive potentials and radius of repulsive core). It is our opinion, from the present calculations, that only a "blend" of repulsive and attractive forces comparable to the forces between two argon atoms can yield a thermodynamic phase diagram comparable to the experiments on argon. We have not yet found this blend.

Orban, van Craen, and Bellemans[3] on the other hand have reported a phase diagram similar to that found in the rare gases.[10,11] They have studied, by the transfer matrix method, a two-dimensional model having a hard-core potential extending to the third-nearest-neighbor sites and attractive potentials of decreasing magnitude extending to the fourth- and fifth-nearest-neighbor sites. Their results indicate that the system has a triple point and a "critical line" which may or may not terminate at a critical point.

In Sec. V we apply the transfer-matrix method to the antiferromagnet with ferromagnetic interactions along crossed bonds. While at the present time we cannot yet verify the existence of the temperature T_1 we present evidence that MFT does indeed give the correct picture concerning the order of the phase transitions. Any subsequent re-

sults will be incorporated into the Ph.D. thesis of Plischke and in future publications on this subject.

II. ISING ANTIFERROMAGNET: MOLECULAR FIELD THEORY

The Ising antiferromagnet on an isotropic square lattice has the Hamiltonian

$$H = J \sum_{ij} (S_{i,j} S_{i,j+1} + S_{i,j} S_{i+1,j}) - H \sum_{ij} S_{i,j}, \tag{1}$$

where $S_{ij} = \pm 1$ and $J > 0$.

The magnetic properties of the antiferromagnet (AF) have been previously derived in MFT by Garrett.[8] Dividing the lattice into A and B sublattices and designating the sublattice magnetizations as m_A and m_B we have

$$m_A = -\tanh\beta[zJm_B - H] = -[\tanh(m_B - h)/t],$$
$$\tag{2}$$
$$m_B = -\tanh\beta[zJm_A - H] = -[\tanh(m_A - h)/t],$$

where $h = H/zJ$, $t = kT/zJ$, and z is the number of nearest neighbors. The free energy per spin is given by

$$f/zJ = -t\ln 2 - \tfrac{1}{2}m_A m_B - \tfrac{1}{2}t\ln[\cosh(m_B - h)/t]$$

$$- \tfrac{1}{2}t\ln[\cosh(m_A - h)/t]. \tag{3}$$

Equations (2) admit two types of solution: (a) $m_A \neq m_B$ with free energy f_a and (b) $m_A = m_B$ with free energy f_b.

As was shown by Garrett,[8] $f_a < f_b$ whenever the (a)-type solution of Eqs. (2) exists. As the magnetic field is increased from zero at constant temperature we pass through a critical field $h_c(t)$ at which the (a) solution ceases to exist. The sublattice magnetizations m_A, m_B approach each other continuously and the magnetization $m = \tfrac{1}{2}(m_A + m_B)$ is continuous. The susceptibility $\chi = (\partial m/\partial h)_t$ is discontinuous and the transition is second order. In Fig. 1(a) we show some magnetic isotherms. The temperature dependence of the critical field is given by

$$h_c(t) = (1 - t)^{1/2} + t\tanh^{-1}(1 - t)^{1/2}. \tag{4}$$

This curve is plotted in Fig. 2.

The properties of the lattice gas are obtained from the magnetic properties via

$$v = 2/[1 - m(H, T)], \quad p = -f - H + \tfrac{1}{2}zJ. \tag{5}$$

Since the magnetization is everywhere continuous, the lattice gas can have no discontinuous change in volume and thus no first-order phase transition. However, there are two second-order phase transitions along each isotherm with $T < T_c = zJ$ and we have three distinct phases in the system. In Fig. 1(b) we plot P/kT as function of $\rho = 1/v$ for several
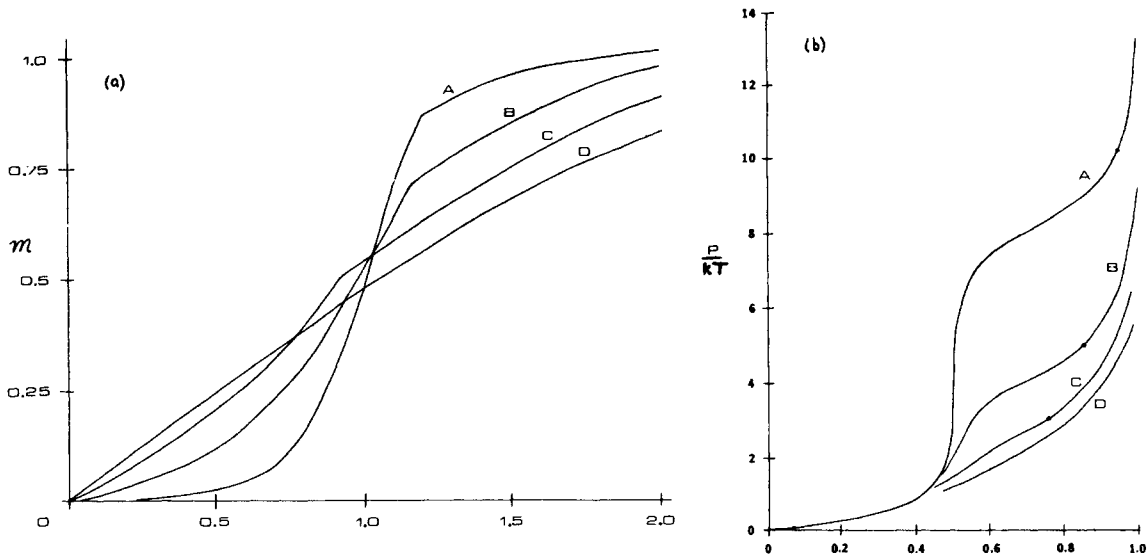
FIG. 1. (a) Plot of $m(h)$ obtained from MFT as function of h for the simple antiferromagnet at several temperatures. Curve A: $t=0.25$; B: $t=0.5$; C: $t=0.75$; and D: $t=1.0$. (b) Plot of P/kT obtained from MFT as function of $\rho=1/v$ for several temperatures. The dots mark the transition points. Curve A: $t=0.25$; B: $t=0.5$; C: $t=0.75$; and D: $t=1.0$.

temperatures. The transition points are indicated by dots. At these points there is a discontinuity in $(\partial P/\partial \rho)_T$. Note that there is a region in which increasing temperature causes the pressure to decrease. In Fig. 3 the coexistence curve in the pt plane is shown.

The identification of the various phases is as

follows: (a) is degenerate because for any solution $m_A=S$, $m_B=Q$ with $S \neq Q$ we can find a second equally valid solution $m_A=Q$, $m_B=S$. (The existence of degeneracy is the *sine qua non* of long-range order, as is well known.) Then whenever (a) is the solution, a crystal is formed, having twice the basic lattice parameter of the original lattice. (b) The solution being unique, there is no long-range order. The identification of vapor versus liquid is merely a question of density.

III. ISING ANTIFERROMAGNET: TRANSFER-MATRIX METHOD

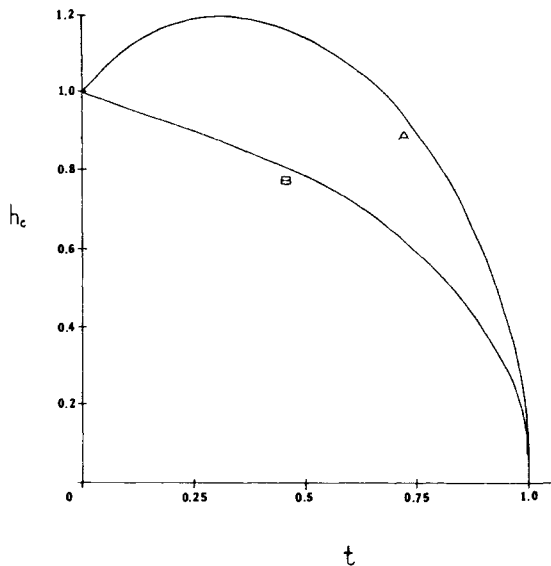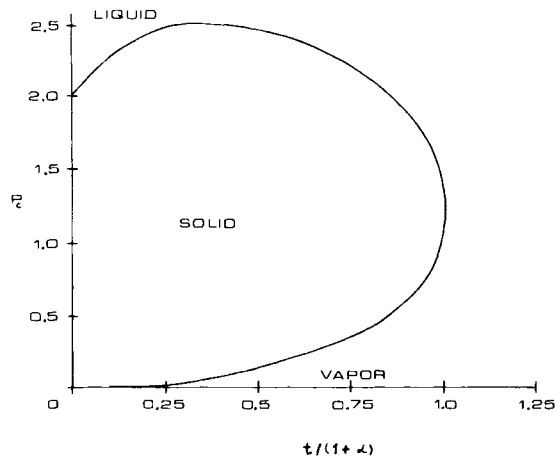The Ising AF on an $M \times N$ square lattice has the

FIG. 2. Plot of the critical field $h_c(t)$ as function of temperature for the antiferromagnet. Curve A: MFT and B: transfer matrix for $N=8$. For curve B the variable t is defined $t = T/2.269\,185J$; for curve A, $t = T/zJ$.

FIG. 3. Coexistence curve for the anitferromagnet in the pT plane obtained from MFT.

transfer matrix

$$V = (V_2 V_3)^{1/2} V_1 (V_2 V_3)^{1/2}, \tag{6}$$

where

$$V_1 = e^{-MK} \prod_{j=1}^{M} (1 + \sigma_j^x e^{2K}),$$

$$V_2 = \exp\left(-K \sum_{j=1}^{M} \sigma_{j+1}^z \sigma_j^z\right),$$

$$V_3 = \exp\left(\beta H \sum_{j=1}^{M} \sigma_j^z\right),$$

$K \equiv \beta J$, and σ^x, σ^z are the Pauli matrices. The thermodynamics is given by the partition function

$$Z(M, N, H, T) \equiv Z = \mathrm{Tr}\, V^N = \Lambda_{\max}^N (M, H, T), \tag{7}$$

where $\Lambda_{\max}$ is the largest eigenvalue of V. In zero magnetic field the transfer matrix may be exactly diagonalized[6] and the thermodynamic properties are exactly the same as those of the Ising ferromagnet with the same interaction strength. In particular the specific heat $C(0, T)$ is logarithmically infinite at $T = T_N \stackrel{.}{=} 2.269\,185J$.

In a previous paper[12] we used a simple iterative prodedure to obtain $\Lambda_{\max}$ and the corresponding eigenvector for the ferromagnet on strips of infinite length and width up to 10 spins. We now use this procedure to analyze the transfer matrix of the AF for strips of width 2, 4, 6, 8, and 10 spins. In Fig. 4 we plot the magnetization $M(H)$ as a function of H for several temperatures for the case $N = 6$. All isotherms are smooth as is to be expected for a lattice which is infinite in only one direction. That a phase transition is developing is indicated, however, by the specific heat $C_H(N, T)$. For strips of width N the specific heat $C_H(N, T)$, which we obtain by numerical differentiation of the internal energy $U(N, H, T)$, has a maximum at

a temperature $T_c(N, H)$. As $N \to \infty$, $T_c(N, H) \to T_c(H)$, where $T_c(H)$ is the critical temperature of the infinite two-dimensional lattice in field H. We estimate that the numerical differentiation introduces a possible error of 1% in the specific heat. Using T_c for eight spins, we nevertheless find that in any field H

$$C_H(N, T_c(8, H)) \sim \ln N$$

up to the largest value of N which we are able to treat leading to the conjecture that the infinity which is known to exist at $H = 0$ persists at finite field. A plot of $C_H(N, T_c(8, H))$ vs $\ln N$ is shown in Fig. 5. From the maxima of the specific heat we obtain the curve $h_c(t)$ in successively better approximation. Here we define $t \equiv T/T_c$ (rather than $t = kT/zJ$) and $h = H/zJ$. We plot it in Fig. 2 for $N = 8$ together with the MFT version of $h_c(t)$. It is clear that the initial increase in h_c at $t = 0$ in MFT is an artifact of the mean field approximation.

Various thermodynamic phases can be identified using the degeneracy (or nondegeneracy) of $\Lambda_{\max}$, following the arguments given at the conclusion of Sec. II. The exact results agree with MFT in the essential qualitative features.

IV. ISING ANTIFERROMAGNET WITH NEXT-NEAREST-NEIGHBOR FERROMAGNET INTERACTIONS: MOLECULAR FIELD THEORY

We consider the AF with next-nearest-neighbor ferromagnetic interactions. In anticipation of the transfer-matrix treatment we let the ferromagnetic interactions be along crossed bonds. This type of system has been studied by Padé approximant techniques by Domb and Dalton[13] and analytically by Fan and Wu.[14]

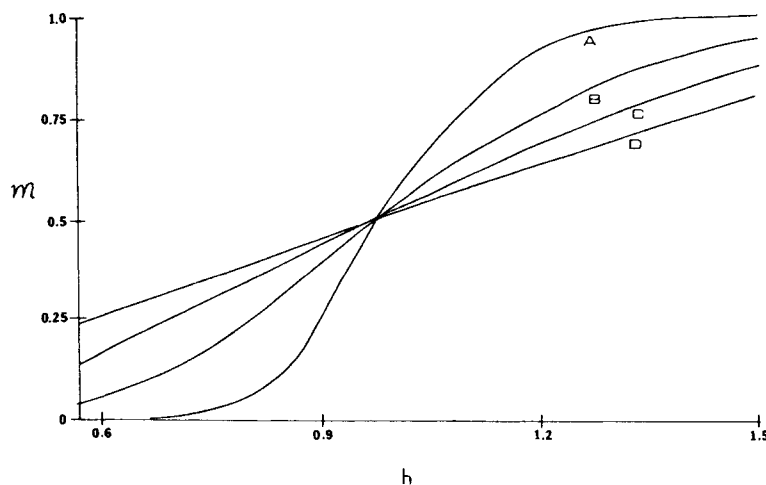$$H = J \sum_{i,j} (S_{i,j} S_{i,j+1} + S_{i,j} S_{i+1,j})$$

FIG. 4. Plot of some magnetization isotherms for the antiferromagnet obtained by the transfer-matrix method for $N = 6$. Curve A: $t = 0.25$; B: $t = 0.5$; C: $t = 0.75$; and D: $t = 1.0$. Here $t = T/2.269\,185J$.
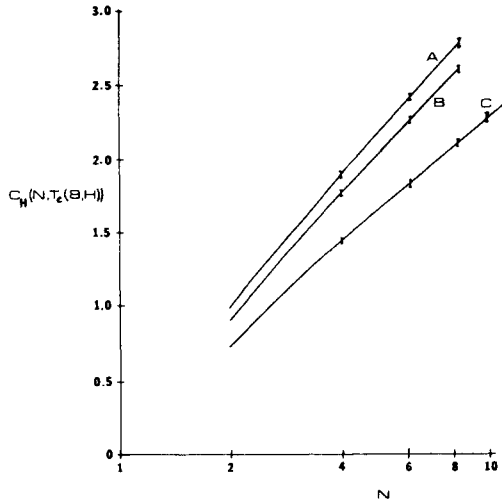
FIG. 5. Plot of $C_h(N, T_c(8, H))$ as function of N on a logarithmic scale. Curve A: $h = 0$; B: $h = 0.4$; and C: $h = 0.8$. The error bars correspond to an estimated error of 1% in C_H.

$$-\alpha J\sum_{i,j} S_{ij}\,(S_{i+1,j+1} + S_{i+1,j-1}) - H\sum_{i,j} S_{ij} \ . \qquad (8)$$

Here $\alpha > 0$ is a parameter specifying the strength of the ferromagnetic coupling. In lattice-gas language this Hamiltonian describes particles with a hard core, a soft core, and a longer-range attraction. If the soft-core part of the interaction were not there the attraction would be sufficient to bring about a first-order phase transition in the lattice gas in two or more dimensions. Hemmer and Stell[9] have argued that the soft core should then cause the system to undergo *two* first-order phase transitions. In the MFT approximation we find that, while there are always two phase transitions, they are first order only below some temperature $T_1(\alpha) < T_c(\alpha)$. Between T_1 and T_c the transitions are second order and above T_c there is no transition at all.

Dividing the lattice into A and B sublattices with magnetizations m_A, m_B we obtain the equations

$$m_A = -\ \tanh\left[\beta(zJm_B - \alpha zJm_A - H)\right]$$

$$\equiv -\tanh[(m_B - \alpha m_A - h)/t]\,,$$

$$m_B = -\tanh\left[\beta(zJm_A - \alpha zJm_B - H)\right] \qquad (9)$$

$$\equiv -\tanh[(m_A - \alpha m_B - h)/t]$$

for the magnetizations and

$$f \equiv F/zJN = -\ t\ln2 - \tfrac{1}{2}m_A m_B + \tfrac{1}{4}\alpha(m_A^2 + m_B^2)$$

$$-\ \tfrac{1}{2}t\ln\cosh[(m_B - \alpha m_A - h)/t]$$

$$-\ \tfrac{1}{2}t\ln\cosh[(m_A - \alpha m_B - h)/t] \qquad (10)$$

for the free energy. Again $t = kT/zJ$, $h = H/zJ$. The critical temperature $t_c = 1 + \alpha$. Equations 9 admit the two types of solution: (a) $m = m_A = m_B$ with free energy f_a and (b) $m_A \neq m_B$ with free energy f_b.

Except at $t = 0$, the (a) state is always a solution with $m \neq 0$. At $t = 0$ we need $h > 1 - \alpha$, for $\alpha < 1$, for the (a) state to exist. At $h = 0$ the (b) state has the solution $m_A = -\ m_B \neq 0$ for $t < t_c$. Moreover at $h = 0$ the (b) state always has the lower free energy. As h is raised we reach a value $h_c(t)$ where $f_a = f_b$. However, unlike the antiferromagnetic case, this does not mean that $m_A = m_B$. The (b) state may continue to be a solution of Eqs. (9) after the free energies have crossed. The situation is illustrated in Fig. 6(a) for the case $\alpha = 0.5$. The dashed curve is the locus of $f_a(h, T) = f_b(h, T)$ and the solid curve represents the mathematical limit of the (b) state. The two curves merge at a temperature state to the (a) state with a discontinuous change of
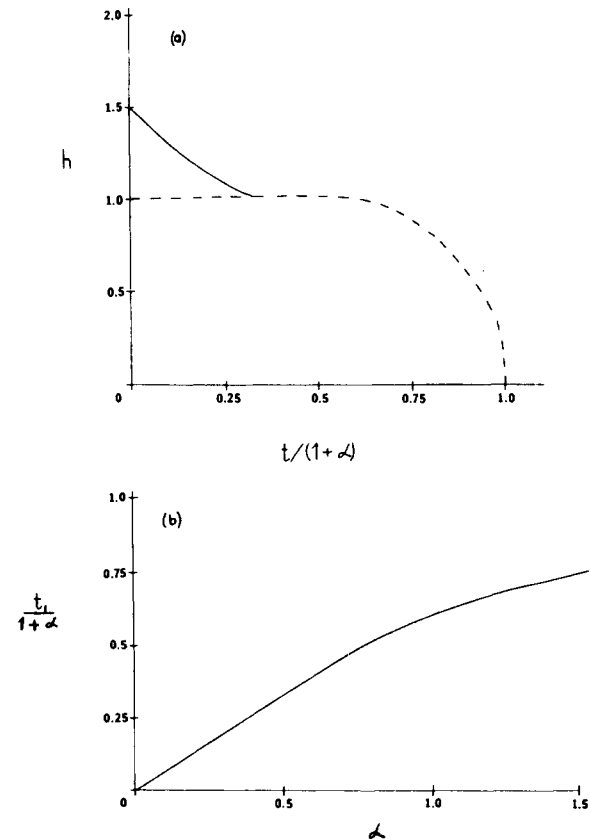

FIG. 6. (a) Critical field $h_c(t)$ obtained from MFT is plotted against $t/(1 + \alpha)$ for the antiferromagnet with next-nearest-neighbor ferromagnetic coupling of strength $\alpha = 0.5$. The dashed curve is the locus of $f_a(h, t) = f_b(h, t)$, and the solid curve is the mathematical limit of the b state for $t < t_1$. (b) Plot of $t_1/1 + \alpha$ as function of α. For $t < t_1$, $m(h)$ has a discontinuity at $h_c(t)$.
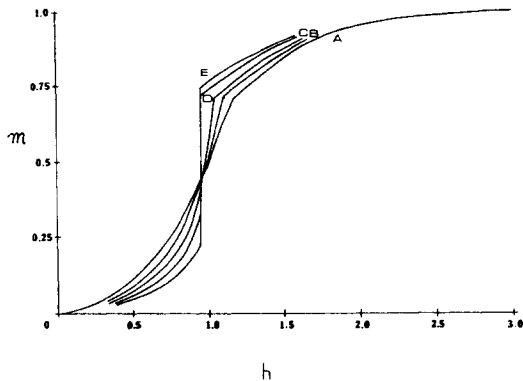
FIG. 7. Plot of $m(h)$ as obtained from MFT for several values of α at fixed $t/1 + \alpha = 0.5$. Curve A: $\alpha = 0$; B: $\alpha = 0.25$; C: $\alpha = 0.5$; D: $\alpha = 0.75$; and E: $\alpha = 1.0$.

magnetization. For $t > t_1(\alpha)$ there is no discontinuity in m and only the kink, familiar from the pure antiferromagnet, remains. In Fig. 6(b), $t_1(\alpha)/1 + \alpha$ is plotted as a function of α. As $\alpha \to \infty$, i.e., the limit of purely ferromagnetic interactions, $t_1 \to \alpha$ which is the critical temperature of a molecular field ferromagnet with interaction strength α. In Fig. 7 we show $m(h, t)$ as function of h for several values of α for a fixed ratio $t/1 + \alpha = 0.5$. As $t_1(\alpha)$ becomes greater than 0.5 it can be seen that the magnetization changes from a continuous function to a discontinuous one.

We make the transformation (5) to obtain the properties of the lattice gas. The jump in the magnetization at $\pm h_c(t)$ implies two first-order phase transitions for the lattice gas. In Fig. 8 we show
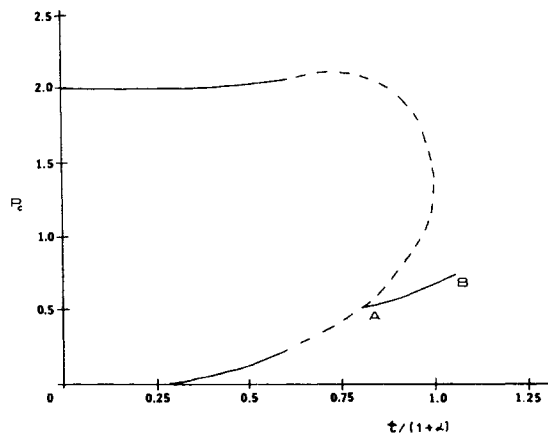

FIG. 8. Coexistence curve in the pT plane for the lattice gas at $\alpha = 1.0$. The solid part of the curve corresponds to first-order phase transitions along an isotherm. AB is the critical line which is not given by MFT, extending from the triple point A to the critical point B, which should appear in a better theory.
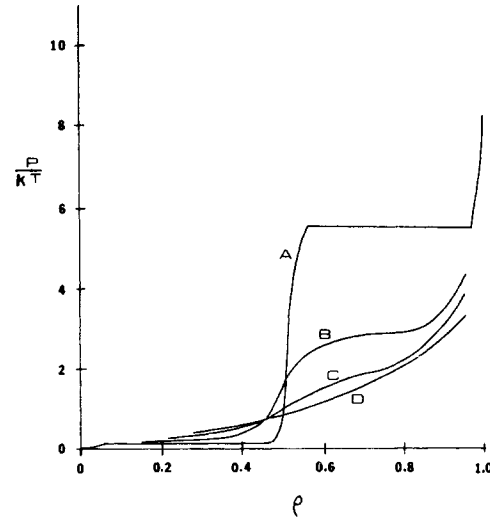

FIG. 9. Plot of P/kT vs $\rho = 1/v$ for the lattice gas with soft-core repulsion and next-nearest-neighbor attraction with strength $\alpha = 0.5$. Curve A: $t = 0.25$; B: $t = 0.5$; C: $t = 0.75$; D: $t = 1.0$. The straight lines in curve A correspond to first-order phase transitions.

the coexistence curve in the pT plane. We interpret the enclosed region as a solid phase, for reasons given in Sec. II. The lattice (fcc) spacing is twice the length of the basis lattice parameter. The second phase transition takes the system to a liquid phase. In Fig. 9 we plot P/kT as function of $\rho = 1/v$ for $\alpha = 0.5$ at several temperatures. Again, as in the $\alpha = 0$ case, there is considerable structure for $t < 1 + \alpha$. Moreover, for $t < t_1$ there are two straight-line segments corresponding to constant p and discontinuous change in v.

We also find that MFT is incapable of predicting the type of phase diagram found in the rare gases,[10,11] i.e., a triple point at p_t, $T_t(A)$ a liquid-gas transition line terminating at T_c, $p_c(B)$ as sketched in Fig. 8. Assuming that the enclosed region in Fig. 8 correctly limits the solid phase, we are still missing the liquid–gas transition line extending from A to B. In magnetic language we would need a region $T_t \le T \le T_c$ where the critical field $h_c(T)$ is zero, i.e., where the ordering is ferromagnetic rather than antiferromagnetic. In MFT, however, if the ground state is antiferromagnetically ordered then this type of ordering also exists just below the highest critical temperature. This theorem can easily be proved by Fourier transforming the interaction $J(R_{ij})$.

V. ISING AF WITH NEXT-NEAREST-NEIGHBOR FERROMAGNETIC INTERACTION TRANSFER MATRIX

We write the transfer matrix for the crossed bond problem with Hamiltonian (8) as
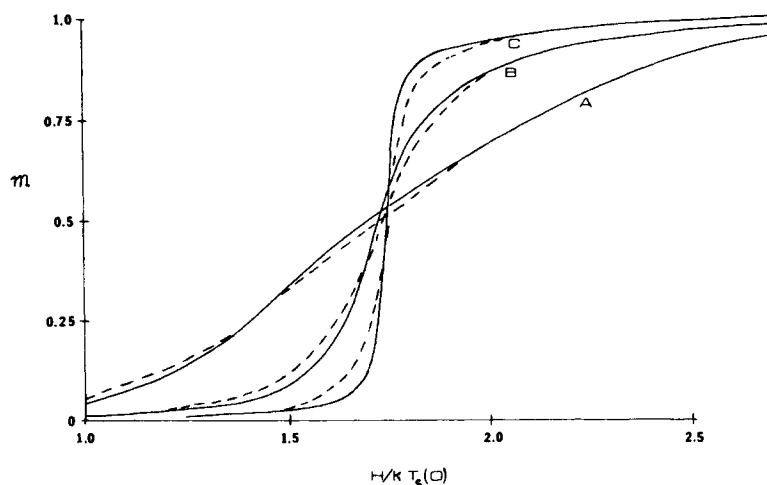
$$V = (V_2 V_3)^{1/2} V_1' (V_2 V_3)^{1/2}. \tag{11}$$

FIG. 10. Plot of $m(h)$ against h for several values of α at fixed ratio of $T/2.269\,185J(1+\alpha)=0.5$. The solid curves are obtained from a six-site transfer matrix, the dashed curves from a four-site transfer matrix. Curve A: $\alpha=0$; B: $\alpha=0.5$; and C: $\alpha=1.0$.

V_2 and V_3 are the same as for the AF. It is inconvenient to express the matrix V_1' in closed form in terms of Pauli matrices. This is not required, as we know all matrix elements of V in the direct product representation. Let $|\mu_i\rangle$ be some configuration of the N spins corresponding to a row. Then

$$\langle\mu_i|\,V_1'\,|\mu_j\rangle = \prod_{k=1}^{N} e^{\alpha K\sigma_{ik}\sigma_{jk}}e^{\alpha K\sigma_{ik}(\sigma_{jk+1}+\sigma_{jk-1})}, \quad (12)$$

where $\sigma_{ik}=\pm 1$ is the orientation of the kth spin in configuration i.

It is clear that the crossed bond coupling supports both ferromagnetism and antiferromagnetism so that at $H=0$ we always expect the ordering to be predominantly antiferromagnetic. At $t=0$ the critical field can be exactly determined to be $H=zJ$ (or $h=1$) by examination of the matrix elements of V. Again we compute the largest eigenvalue for strips up to 6 spins wide for several values of α. From the maxima of the specific heat we find that $T_c(\alpha)\cong(1+\alpha)\,T_c(0)$, where $T_c(\alpha)$ is the critical temperature for the crossed bond model with coupling

strength α. This confirms the molecular field result. We show, in Fig. 10, the effect of increasing α on the magnetization $m(h)$ at fixed value of $t=T/(1+\alpha)T_c(0)=0.5$. The solid curves are the $N=6$ isotherms and the dashed curves are the $N=4$ isotherms at the same t, α. While the data so far obtained is inconclusive, it seems likely that at $t=0.5$, $\alpha=0$, and $\alpha=0.5$ there is no first-order phase transition, whereas, judging from the change in slope of $m(h)$ in going from $N=4$ to $N=6$, there is a first-order transition at $\alpha=1.0$.

Our results on the transfer matrix are not yet sufficiently extensive to discuss the existence (or lack thereof) of a critical line, nor its dependence on the various parameters. We have found that two repulsive step potentials, of decreasing magnitude, do not give any indication of a triple point or critical line for strips up to 8 sites wide. This may be due to the finite size of the strip or to an inopportune choice of potentials. We hope to report on calculations done on larger strips soon, and plan to study this peculiar problem from other points of view as well.

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