

Spin-1 lattice-gas model. I. Condensation and solidification of a simple fluid

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A spin-1 lattice-gas model, similar to the Blume-Emery-Griffiths model for ^3He - ^4He mixtures, is shown to describe condensation and solidification of a simple fluid. The Ising-like Hamiltonian of the system involves quadrupolar and dipolar interactions, which are responsible for condensation and solidification, respectively. The molecular-field approximation is used, and the ordinary phase diagram of a simple fluid is reproduced. However, for some range of the parameters, the liquid-gas equilibrium curve disappears. Also, the melting curve may exhibit a tricritical point: For pressures larger than the tricritical pressure, critical melting is found. Other physical applications of the model are briefly discussed.

I. INTRODUCTION

It is well known that the thermodynamical behavior of various cooperative physical systems can be simulated by a spin- $\frac{1}{2}$ Ising model. For instance, a spin- $\frac{1}{2}$ lattice-gas model describes the condensation of a fluid,^{1,2} or the adsorption³ or absorption⁴ of a gas. Similarly, a spin- $\frac{1}{2}$ Ising model simulates the phase separation of a two-component liquid or solid,⁵ the order-disorder phase transition in a binary alloy,⁶ the freezing of a liquid,⁷ and other cooperative phenomena such as order-disorder and magnetic and electric⁸ phase transitions.

The above phase transitions are characterized by a single order parameter: density, concentration, crystallographic order parameter, magnetization, or electric polarization. Many physical systems, however, cannot be completely described by a single order parameter. For instance, in a magnetic alloy two types of ordering processes can take place: a magnetic ordering and a structural ordering. Such systems must be described by at least two order parameters, and their interest lies in the mutual interaction between the two ordering processes.

To represent some physical systems characterized by two order parameters, a spin-1 Ising model with dipolar and quadrupolar interactions can be used. The order parameters are represented by $M = \langle S^z \rangle$ and $Q = \langle (S^z)^2 \rangle$; they are not independent in the sense that $M \neq 0$ implies $Q \neq 0$ (kinematical coupling). This model has been considered in order to describe phase separation and superfluid ordering in ^3He - ^4He mixtures,⁹ or phase separation and ferromagnetism in binary alloys.^{10,11} We show in this article that the same model can also describe the condensation and freezing of a simple fluid,

which can otherwise be described only by two separate spin- $\frac{1}{2}$ models.

This paper is organized as follows: In Sec. II we discuss the possibility of dipolar and quadrupolar ordering in a spin-1 Ising magnetic system in order to illustrate some properties of the model Hamiltonian. The molecular-field approximation is used. In Secs. III and IV we describe the condensation and freezing of a simple fluid, and in Sec. V we discuss some peculiarities of the phase diagram. Finally, in Sec. VI other physical applications of the model are briefly reviewed, some of which will be presented in the second and third papers of this series,¹² referred to as papers II and III.

II. DIPOLAR AND QUADRUPOLAR ORDERING IN A MAGNETIC SYSTEM

We consider the following Hamiltonian for $S=1$ ions on a lattice:

$$\begin{aligned} \mathcal{H} = & -H \sum_i S_i^z - \sum_{i,j} J_{ij} S_i^z S_j^z \\ & - D \sum_i Q_i - \sum_{i,j} K_{ij} Q_i Q_j, \end{aligned} \quad (1)$$

where $Q_i = (S_i^z)^2$ is the single-ion quadrupolar operator, H is a magnetic field along z , and D represents a single-ion anisotropy energy. We shall later use the quantities

$$J = J(0) = \sum_j J_{ij}, \quad (2a)$$

$$K = K(0) = \sum_j K_{ij}. \quad (2b)$$

[If $D = -\frac{4}{3}K$, the quadrupolar part of (1) is

$$-\sum_{i,j} (Q_i - \frac{2}{3})(Q_j - \frac{2}{3}),$$

where $Q_i - \frac{2}{3}$ is a traceless operator.]

The quantities J , K , H , and D will be given various physical interpretations in the following sections. In this section we discuss briefly the properties of a magnetic system described by the Ising-like Hamiltonian (1), and look for possible dipolar and quadrupolar phase transitions in the parameters M and Q . This problem has already been considered^{13,14} in the case of isotropic interactions. The results presented here will be used in paper II.¹² They could also be used to study a three-well ferroelectric model¹⁵ similar to the de Gennes model for order-disorder ferroelectrics⁸ if single-ion tunneling energies are added to the Hamiltonian.

Let us first consider the purely quadrupolar case ($J=H=0$). In order to derive an equation for the order parameter Q , we use the molecular-field approximation in the Bragg-Williams formalism. The Bragg-Williams free energy of the system is given per site by

$$\phi = -DQ - KQ^2 - (kT/\mathcal{N}) \ln W, \quad (3)$$

with

$$W = 2^{7Q} \mathcal{N}! / [(\mathcal{N} - \mathcal{N}Q)! (\mathcal{N}Q)!] \quad (4)$$

(\mathcal{N} is the number of sites). Using the Stirling formula we get

$$\phi \approx -DQ - KQ^2 + kT[Q \ln Q + (1-Q) \ln(1-Q) - Q \ln 2], \quad (5)$$

and minimizing ϕ with respect to Q we get

$$D = -2KQ + kT \ln[Q/2(1-Q)] \quad (6)$$

or

$$Q = \frac{2e^{\beta(D+2KQ)}}{1+2e^{\beta(D+2KQ)}} \quad (7)$$

($\beta = 1/kT$). The equilibrium value ϕ_e of ϕ is then

$$\phi_e = KQ^2 + kT \ln(1-Q), \quad (8)$$

Q being a solution of Eqs. (6) or (7). If this equation has more than one solution, we consider only the solution with the lowest free energy.

Equation (7) has been solved numerically. The thermal variation of Q is represented in Fig. 1 for various values of D . For $D < D_c = -1.346$ K, $|0\rangle$ is always the single-ion ground state and there is no phase transition. For $D_c < D < -K$, a first-order phase transition in Q is found. For $-\frac{4}{3}K < D < -K$, the transition is, in fact, a supertransition as defined by Chestnut.¹⁶ Finally for $-K < D$, $|\pm 1\rangle$ is always the single-ion ground state and there is no longer a phase transition. In the (D, T) plane, the

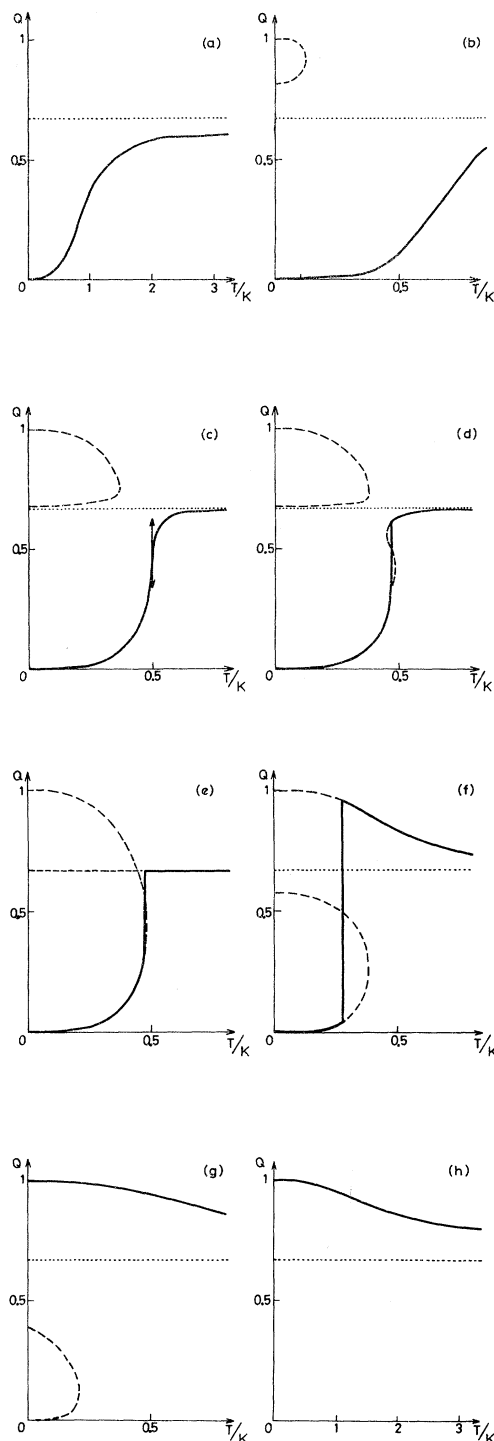


FIG. 1. Thermal variation of order parameter Q according to Eq. (7): (a) $D/K = -2.0$; (b) $D/K = -1.6$; (c) $D = D_c$; (d) $D/K = -1.34$; (e) $D/K = -\frac{4}{3}$; (f) $D/K = -1.2$; (g) $D/K = -0.8$; (h) $D/K = 0.4$. Dashed lines represent unstable solutions. The horizontal dotted line corresponds to $Q = \frac{2}{3}$.

equilibrium curve terminates at a liquid-vapor-like critical point; see Ref. 17 for a very similar situation.

It is interesting to represent the curves $D(Q)$ for various values of T . Equation (6) is then solved by considering the intersection of a curve $D(Q)$ with the horizontal line $D = \text{const}$. All curves intersect at the point $Q = \frac{2}{3}$, $D = -\frac{4}{3}K$. Each curve has an inflexion point at $Q = \frac{1}{2}$, $D = -K - kT \ln 2$, which is also its inversion center. The derivative dD/dQ can be zero only if $kT < kT_c = \frac{1}{2}K$. If $D < -2K$ or $D > -K$, or if $T > T_c$, Eq. (6) has only one root. If $-2K < D < -K$ and $T < T_c$, three roots $-Q_1$, Q_2 , and Q_3 are found, and at the first-order transition temperature T_Q , one must have $\phi_1 = \phi_3 < \phi_2$, which is satisfied for $Q_1 = 1 - Q_3$, $Q_2 = 0.5$. Consequently, the value of D is that of the inversion center A_2 , and the line A_1A_3 is similar to the Maxwell plateau of the isotherm of the van der Waals gas (see Fig. 2).

We consider now the Hamiltonian (1) with $J \neq 0$ and $H = 0$, and look for the possibility of successive quadrupolar and dipolar phase transitions. For $K = 0$ and $D < 0$, the Hamiltonian is that of the Blume¹⁸-Capel¹⁹ model; a first- or second-order magnetic transition is found. In the general case $J \neq 0$, the Bragg-Williams free energy per site is

$$\phi = -DQ - KQ^2 - JM^2 - (kT/\mathcal{N}) \ln W, \tag{9}$$

with

$$W = \frac{\mathcal{N}!}{(\mathcal{N} - \mathcal{N}Q)! (\mathcal{N}Q)!} \frac{(\mathcal{N}Q)!}{[\frac{1}{2}\mathcal{N}(Q+M)]! [\frac{1}{2}\mathcal{N}(Q-M)]!} \tag{10}$$

The fact that linear combinations $Q \pm M$ are found in the second factor of the expression of W is a consequence of the kinematical coupling between M and Q . From (9) and (10) we deduce the molecular field equations for M and Q :

$$M = \frac{2e^{\beta(D+2KQ)} \sinh 2\beta JM}{1 + 2e^{\beta(D+2KQ)} \cosh 2\beta JM}, \tag{11}$$

$$Q = \frac{2e^{\beta(D+2KQ)} \cosh 2\beta JM}{1 + 2e^{\beta(D+2KQ)} \cosh 2\beta JM}, \tag{12}$$

whence

$$M = Q \tanh 2\beta JM. \tag{13}$$

The equilibrium value of the free energy ϕ is given by

$$\phi_e = KQ^2 + JM^2 + kT \ln(1 - Q), \tag{14}$$

M and Q being solutions of Eqs. (11) and (12), or equivalently (12) and (13).

These equations have been solved numerically, and Fig. 3 shows the phase diagram in the

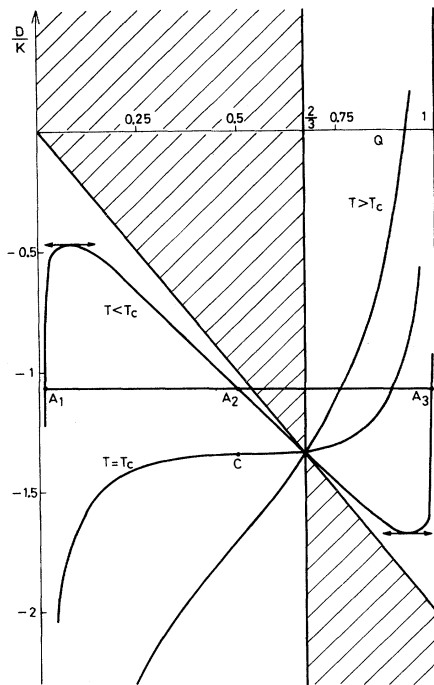


FIG. 2. Curves $D(Q)$ according to Eq. (6) for various values of T ($K = 1$). These curves do not enter the hatched area. $A_1A_2A_3$ is a Maxwell plateau. $D(Q)$ is given in units of K .

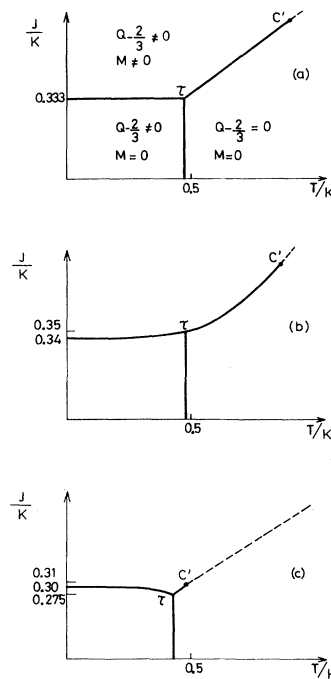


FIG. 3. Phase diagram in the $(T/K, J/K)$ plane for Hamiltonian (1) with $H = 0$. (a) $D/K = -\frac{4}{3}$; (b) $D/K = -1.34$; (c) $D/K = -1.30$. Dashed lines are second-order transition lines. τ is a quadruple point, $\tau C'$ is a triple line.

($J/K, T/K$) plane for various values of D . When $D/K = -\frac{4}{3}$, either a dipolar or a quadrupolar transition is found. When D/K is slightly less than $-\frac{4}{3}$, a first-order quadrupolar transition can be followed by a first-order dipolar transition, which is similar to the dipolar transition of the Blume-Capel magnet. When $D < D_c$, the quadrupolar transition disappears. When D/K is slightly greater than $-\frac{4}{3}$, a second-order dipolar transition can be followed by a transition from the dipolar state to a purely quadrupolar state.

When $D/K > -1$, this second transition disappears (the point τ goes to the origin). Figures 4(a) and 4(b) show the thermal variation of M and Q in the cases of two successive transitions. The limiting situations where a triple point τ is found are easily deduced from them when the intermediate phase disappears. τ is in fact a quadruple point if the domains $+M$ and $-M$ are considered as distinct phases. Similar results have been found²⁰ for the case when the dipolar interaction is replaced by the nonaxial quadrupolar interaction,

$$- \sum_{i,j} L_{ij} P_i P_j,$$

with

$$P_i = (S_i^x)^2 - (S_i^y)^2. \quad (15)$$

In fact, the operator P has the same form in the basis

$$\left(\frac{|1\rangle + |-1\rangle}{\sqrt{2}}, \frac{|1\rangle - |-1\rangle}{\sqrt{2}}, |0\rangle \right)$$

as the operator S^z in the basis $(|1\rangle, |-1\rangle, |0\rangle)$.

III. SPIN-1 LATTICE-GAS MODEL FOR CONDENSATION

We now reconsider the Lee-Yang lattice-gas model¹ for the condensation of a fluid using a spin-1 formalism. We use the variable Q_i , which is zero if the cell i is empty and 1 if the cell is occupied by a molecule (we are not interested here in the value of S_i^z). If D is the chemical potential of the fluid, the system is described by the Hamiltonian (1) with $H=J=0$. The order parameter $Q = \langle Q_i \rangle$ is the density of the fluid:

$$Q = 1/v = N/V, \quad (16)$$

v being the specific volume, N the number of occupied cells, and V the volume of the fluid (the volume of the elementary cell is taken as the unit volume, whence $V = \mathcal{N}$, the total number of cells). For each temperature, we look for the possibility of having two phases in equilibrium, hence having the same chemical potential D and the same free energy ϕ . For $kT > kT_c = \frac{1}{2}K$ there is no such possibility. For $T < T_c$, the phases described by the

parameters Q_1 and Q_3 of Fig. 2 are in equilibrium, so the chemical potential is

$$D = -kT \ln 2 - K. \quad (17)$$

Consequently, T_c is the critical temperature of the fluid (for $T > T_c$, the fluid is always homogeneous at equilibrium) and we know how to determine the Maxwell plateau.

We now calculate the equation of the isotherms of the fluid in the (P, v) plane. The free energy ϕ_e per site in the magnetic system is also the generalized potential Ω per cell of the fluid. It is well known that in a lattice gas the pressure is the opposite of Ω , so we immediately get

$$P = -KQ^2 - kT \ln(1 - Q), \quad (18)$$

or

$$P = -K/v^2 - kT \ln(v - 1)/v. \quad (19)$$

Equations (8) and (19) are in agreement since ϕ_e is the free energy per site in the magnetic system and the generalized potential Ω per cell of the fluid. The results are the same as those of Temperley^{2,21}: We obtain the equation of the Boltzmann-van der Waals gas. The critical point is defined by

$$v_c = 2, \quad kT_c = \frac{1}{2}K, \quad P_c = \frac{1}{4}K(\ln 4 - 1). \quad (20)$$

The chemical potential, however, has different definitions in the $S = \frac{1}{2}$ and $S = 1$ models. In partic-

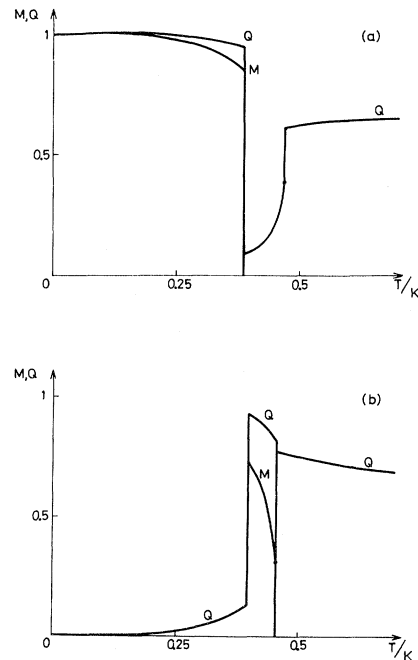


FIG. 4. Thermal variation of the order parameters M and Q according to the Hamiltonian (1) with $H=0$. (a) $D/K = -1.34$, $J/K = 0.341$; (b) $D/K = -1.30$, $J/K = 0.29$.

ular, the condition $D = -kT \ln 2$ for the Maxwell plateau corresponds to the condition $H = 0$ in the Lee-Yang model.⁶ We note here two advantages of the spin-1 model. The chemical potential D varies from one Maxwell plateau to another as it should, and no extra symmetry is introduced by the model (the paramagnetic symmetry breaking of the Lee-Yang model has no physical counterpart in the fluid, since the liquid-gas transition involves no symmetry change, as a quadrupolar transition in Q in the spin-1 model).

The spinodal line²² ($\partial P/\partial V = 0$) can be computed easily. It is also easy to get the equation of the binodal line.²² Along this line, Q is solution of (6) with $D = -kT \ln 2 - K$, whence

$$kT \ln[Q/(1-Q)] = K(2Q-1). \quad (21)$$

Putting $Q = \frac{1}{2} + \alpha$, α is solution of the equation

$$2\alpha = \tanh \alpha / T. \quad (22)$$

For each T α is calculated, whence the specific volumes

$$v_1 = 2/(1+2\alpha), \quad v_3 = 2/(1-2\alpha). \quad (23)$$

IV. SPIN-1 LATTICE-GAS MODEL FOR CONDENSATION AND SOLIDIFICATION

We now use the spin-1 lattice-gas model to describe the condensation and solidification of a simple fluid. We can use the following picture: Each cell of the lattice is made of two subcells. If $S_i^z = Q_i = 0$, the cell is empty. If $Q_i = 1$, the cell is occupied and the two possible values of S_i^z can be interpreted in the following way: If $S_i^z = +1$ (-1) the molecule occupies the right (left) subcell.

The preferential occupation of the right (left) subcells may simulate crystallographic ordering of the fluid as in the model of Lennard-Jones and Devonshire.⁷ On the other hand when $\langle S_i^z \rangle = 0$, the two subcells are occupied indifferently and this disorder simulates the orientational disorder of the molecules in a liquid or a gas; vacancies and partial orientational disorder are allowed in the solid phase.

The Hamiltonian (1) can be used to describe the above situation. J and K are two isotropic molecular interactions, i.e., independent of the orientations of the molecules if they are elongated or platelike. K favors the condensed state irrespective of the occupied subcell; J , if positive, favors the preferential occupation of the right (or left) subcell. If J is negative, antiferromagneticlike configurational ordering is favored (crystallographic ordering with "doubling" of the unit cell). $K + J$ is the interaction of two "right" neighboring molecules. We put $H = 0$ in (1), since in general

there is no physical field conjugated to the crystallographic order parameter M/Q . The two possible opposite values of M describe different twins or grains. M and Q are solutions of Eqs. (12) and (13). $M = 0$ is always a solution (liquid or gas) and the pressure P of the fluid is given by (18). We now need to calculate the pressure P for any value of M .

Using again the fact that in a lattice gas the pressure is the opposite of the free energy, we immediately get

$$P = -KQ^2 - JM^2 - kT \ln(1-Q), \quad (24)$$

with $Q = 1/v$ and M given by (13).

To draw the isotherms of the fluid for given values of J and K for each temperature, we choose a value v of the specific volume. Then $Q = 1/v$ and M is given by (13), whence the value of P from (24). $M = 0$ is always a solution of (13) but, if $v < v_B = 2J/T$, (13) also has a nonzero solution in M and $P(M \neq 0) < P(M = 0)$. There is a branching point B on the isotherm and, for $v < v_B$, only the low-pressure branch may represent stable states of the fluid.

The derivative in B of the branch $M \neq 0$ of the isotherm is positive if

$$T < 2J(J+2)/(3J+2), \quad (25)$$

or $J > J_0(T)$ with

$$J_0(T) = \frac{1}{4} [3T - 4 + (gT^2 - 8T + 16)^{1/2}]. \quad (26)$$

If (25) is not satisfied (negative derivative in B), which is the case at high temperatures, one goes from the isotropic fluid to the solid without any volume change Δv_s ; the fluid-solid transition is second order [(Fig. 5(a)]. At low temperatures (25) can be satisfied. It is then possible to construct a Maxwell plateau corresponding to the isothermal solidification of the fluid [(Fig. 5(b)]. Consequently, we find along the solidification line in the (P, T) plane a tricritical point C' at which the liquid-solid transition switches from first to second order.

The above considerations are entirely valid as long as $T > T_c$ since no complication arises from the existence of a condensation plateau. Let us suppose now that $T < T_c$, and discuss the possibility of constructing a condensation plateau and a solidification plateau as in Fig. 5(b). In addition to the conditions $T < T_c$ and (25), we must have $v_B < v_1 = 1/Q_1$, which is equivalent to $J < J_1(T)$ with

$$J_1(T) = T/[1 + 2\alpha(T)], \quad (27)$$

where $\alpha(T)$ is given by Eq. (22). Moreover, the pressure P_{sol} of the solidification plateau must be higher than that (P_{cond}) of the condensation plateau.

If $T < T_c$, $J < J_1(T)$ but $J < J_0(T)$, condensation is followed by a second-order solidification [Fig. 5(a)]. If $T < T_c$, $J > J_0(T)$, and $J < J_1(T)$ but $P_{\text{sol}} < P_{\text{cond}}$ [Fig. 5(c)] or $T < T_c$ but $J > J_1(T)$, then a single plateau must be constructed. It corresponds to the gas-solid transition (sublimation). If $T < T_c$, $J > J_0(T)$, and $J < J_1(T)$ coupled with $P_{\text{sol}} = P_{\text{cond}}$, we have a triple point at which three phases coexist [Fig. 5(d)] (four phases in fact, if we consider the twins $\pm M$ as distinct phases).

Equations (12) and (13) then have three solutions $Q_1: M_1=0$, $Q_3: M_3=0$, and $Q: M \neq 0$ which have the same free energy. Another type of "triple point" τ' is found for $J = J_1(T)$ and $J < J_0(T)$. In τ' , the pressure at the branching point is equal to that of the condensation plateau, and the liquid and solid phases are identical. The curves $J_0(T)$ and $J_1(T)$ are represented in Fig. 6. $J_0(T)$ determines the tricritical temperature as a function of J ; $J_1(T)$ is defined only for $T < T_c = \frac{1}{2}K$. Triple points τ are found only if $J_0(T) < J < J_1(T)$ (hatched region of Fig. 6) and their locus AD has been computed numerically (dotted line). The locus of the "triple points" τ' is the curve $J_1(T)$ between O and A.

Finally, we discuss the various aspects of the phase diagram for different values of the parameter J (Fig. 7). We take $K = 1$ to simplify ($T_c = 0.5$). When $J > J_D \sim 0.365$, there is no triple point,

or critical point, and the solid-fluid equilibrium curve in the (P, T) plane is never determined by the isotherms with $M = 0$ alone. There is only a tricritical point C' [Fig. 7(a)]. The temperature $T = 0.5$ has no special meaning since if $J > 0.5$, then $v_B > 2$ and the slope in B is positive, but if $J < 0.5$, $v_B < 2$ and the slope in B is still positive. For $J = 0.5$, B is in C , and for $J = 0.365$, the triple point τ and the critical point C coincide. In the case where $J_D > J > J_A \sim 0.26$ there is a triple point τ , a critical point C , and a tricritical point C' [see Figs. 7(b) and 7(c) and also Fig. 6(c) of Ref. (9)]. The sublimation curve and the melting curve $\tau C'$ are triple lines. If $J > J_E$, then $T_{C'} > T_c$ and if $J_A < J < J_E$, we find $T_{C'} < T_c$. If $J = J_A$, τ and C' coincide when $J < J_A$. Solidification is always a second-order transition (as long as $J < J_D$, sublimation is always a first-order transition). At the triple point τ' , the liquid and solid phases are identical, and τ' is a critical end point.

Finally, we see that the locus of τ in the (P, T) plane, when J varies from 0 to J_D , is nothing else than the Lee-Yang liquid-vapor equilibrium curve. We note also that, whatever the value of J , the solidification curve has a positive derivative which tends to infinity at very high pressures as the curve goes closer to the asymptote $T = 2J$.

V. DISCUSSION OF PHASE DIAGRAM OF FLUID

Figure 7(b) corresponds to a common experimental situation. Two successive transitions, condensation and solidification, can be found along

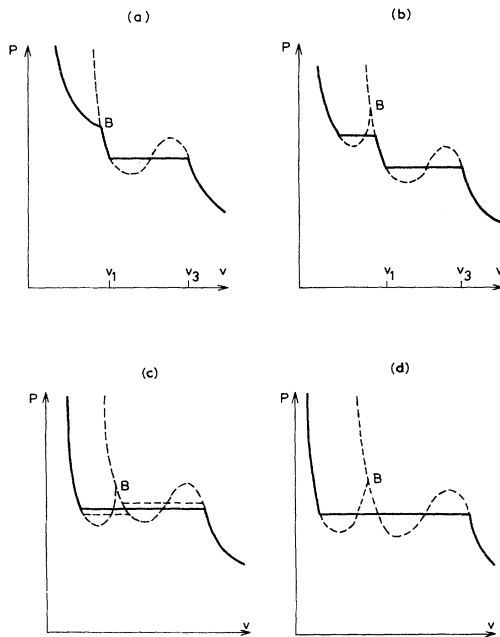


FIG. 5. Schematic aspect of the isotherm of a fluid for various values of T and J . (a) $T < T_c$, $v_B < v_1$, $\Delta v_s = 0$; (b) $T < T_c$, $v_B < v_1$, $\Delta v_s \neq 0$; (c) $T < T_c$, $v_B < v_1$, $\Delta v_s \neq 0$, $P_{\text{sol}} < P_{\text{cond}}$; (d) $T < T_c$, $v_B < v_1$, $\Delta v_s \neq 0$, $P_{\text{sol}} = P_{\text{cond}}$. Dashed lines represent unstable or metastable states.

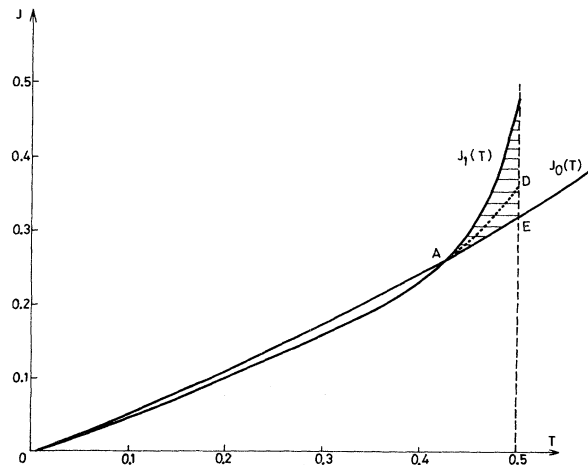


FIG. 6. Discussion of the aspect of the phase diagram of the fluid. $J_0(T)$ defines the tricritical temperature and $J_1(T)$ corresponds to the condition $v_B = v_1$. The dotted line AD is the locus of the triple points τ and the part OA of $J_1(T)$ is the locus of the triple points τ' . T is measured in units of K . The dashed line corresponds to $T = 0.5$.

an isobar line if $P < P_c$ (this situation cannot be exactly compared to successive quadrupolar and dipolar ordering in a magnetic system—see Fig. 4—since here P , and not D , is kept constant). The slope of the solidification curve in the (P, T) plane is always positive in our model, which is not always the case for some fluids such as H_2O . The reason is the following: Because of the kinematical coupling between M and Q , ordering in M increases the saturation of Q , so that the specific volume of the solid is smaller than that of the liquid. A striking property of our model is the occurrence of critical melting and, at least for some range of the ratio J/K , the existence of a tricritical point C' along the liquid-solid equilibrium curve. When the density is high ($Q \sim 1$), the fluid is in a liquidlike phase and solidification is second order, as in the ordinary magnetic transition in S^z of the spin- $\frac{1}{2}$ Ising model. Solidification, however, may become first order at lower pressures. Sublimation, on the other hand, always occurs at low pressures and is always first order.

In their description of the liquid-solid phase transition, Lennard-Jones and Devonshire (see Ref. 7) used a spin- $\frac{1}{2}$ compressible Ising model in which the two values of the state variable correspond to two possible positions of a molecule in a unit cell (they did not allow for vacancies). In order to make the transition first order, they introduced *ad hoc* volume-dependent interactions in the form of a direct coupling between the order parameter M and the volume V of the fluid. In their model, solidification involves a sudden change of the elementary volume occupied by a molecule of the fluid as long as the pressure is lower than some critical value.

The above coupling between M and V does not need to be considered in our model to provide the possibility of a first-order solidification, since our model allows for the existence of vacancies and then for density variations of the fluid. If first order, solidification involves no sudden change of the volume of the unit cell, which is kept constant by construction, but a sudden change of the density of vacancies. This result is not unrealistic since the typical 10–15% expansion of a substance on melting is accompanied by a decrease in the coordination number and virtually no change in intermolecular distances. If introduced with the correct sign, the M - V coupling could also change the sign of the slope of the liquid-solid equilibrium curve and possibly lead to a critical curve maximum.

Our model displays the possibility of critical melting, and this result contradicts a general statement by Landau.²³ This apparent contradiction is investigated in the Appendix. Critical melting,

and in particular a tricritical point C' , have never been observed experimentally, although the point C' might be masked by the occurrence of solid-solid transitions along the liquid-solid equilibrium curve. Ubbelohde²⁴ has considered the physical origins of the entropy and volume changes at the liquid-solid transition and has discussed the possibility of critical melting.

We have also found a range of values of J/K for which there is no critical point. Although no experimental example of this behavior has yet been found, to our knowledge, this result is not surprising since some fluids are known²⁴ for which the ratio T_c/T_τ is very close to 1 (for most fluids, this ratio lies between 1 and 4).

Perhaps the main weakness of the spin-one lattice-gas model is the low value—of the order of $k \ln 2$ per particle—of the entropy change at the liquid-solid transition, as compared to experimental values.⁷ This discrepancy is due to the fact that the local parameter S_i^z can take only two values ± 1 once the cell is occupied by a molecule. It could be of course removed by dividing the elementary cell of the lattice model by a number of subcells larger than two: This would allow for a higher disorder of the molecules in the liquid

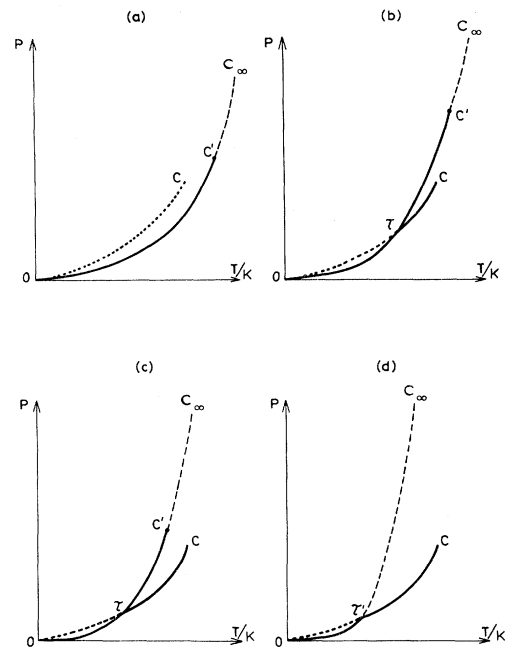


FIG. 7. Different aspects of the phase diagram of the fluid when J varies. (a) $J > J_0$: The dotted line τc is the liquid-gas equilibrium curve as given by the Lee-Yang theory; (b) $J_E < J < J_D$; (c) $J_A < J < J_E$; (d) $J < J_A$. $C' C_\infty$ is the second-order liquid-solid transition line. OC is the locus of the triple point τ or τ' when J varies.

phase. Suppose finally that a physical field H has some influence on the crystallographic ordering process. The molecular-field equations for M and Q are similar to (12) and (13), except that $2\beta JM$ must be replaced by $H + 2\beta JM$. The pressure is still given by Eq. (24), with

$$M/Q = \tanh\beta(H + 2\beta JM). \quad (28)$$

$M = 0$ is no longer a solution because the fluid is always partly solidified. Figure 8 shows that the position and even the existence of the solidification and condensation plateaus can be strongly affected by the applied field.

VI. OTHER POSSIBLE APPLICATIONS OF MODEL

Let us consider a spin- $\frac{1}{2}$ Ising model describing some cooperative phenomenon in a fluid, such as solidification, nematic ordering, superfluid ordering, magnetic ordering, etc. (In these simplified models of course, the order parameter M has only two possible phases, positive and negative, whereas the position or orientation of molecules, the phase of the superfluid order parameter, in addition to the direction of magnetic moments, can be varied continuously.) Suppose now that we want to describe the influence of the pressure of the fluid on these different cooperative phenomena. We have to switch from a spin- $\frac{1}{2}$ to a spin-1 model. The new available state $|0\rangle$ represents a vacancy, and this procedure introduces the new order parameter Q , which is the density. If we now forget about the internal degree of freedom inside the doublet $|\pm 1\rangle$, we return to the Lee-Yang lattice-gas model in a spin-1 formalism (Sec. III); only condensation is described. Conversely, we may start with a spin-1 lattice-gas model for condensation and ask which property of the molecules the internal degree of freedom of the doublet may represent. Condensation and a second cooperative transition will then be described by our model.

The internal degree of freedom of the doublet can represent the orientational freedom of the molecules. If the molecules are elongated, they may have a random orientation in the liquid phase. At low temperatures, an isotropic-nematic phase transition becomes possible. Our model may then describe the condensation and nematic transition of an anisotropic fluid. Only two possible orientations ($S^z = \pm 1$) of each molecule are retained and K and J describe the isotropic and anisotropic parts of the interaction between two neighboring molecules, respectively: $K + J$ is the interaction between two parallel molecules and $K - J$ between two perpendicular ones. A second-order nematic transition can be found at large pressures, and

the result, although in agreement with the symmetry change from isotropic to axial, contradicts the Landau theory.^{23,25} However, the contradiction could be removed by considering more than two orientations of the molecules. The Zeeman part of the Hamiltonian represents the influence of an external electric or magnetic field on the nematic transition. Such a field induces an axial symmetry of the fluid at any temperature, so that in large fields the first-order nematic transition disappears. Incidentally, the smectic A - cholesteric or nematic transition may be compared to the solid-liquid transition (crystallographic disordering along one direction without any orientational disordering). It has been shown recently²⁶ that this transition can change from first to second order under increasing pressure. However, this one-dimensional density-wave transition is permitted to be second order by symmetry.

Our model also describes the influence of pressure on the superfluid transition in ^4He . $S^z = 0$ describes a vacancy in the lattice. $S^z = \pm 1$ describes a cell occupied by a ^4He atom, and this internal degree of freedom allows for the description of the superfluid transition as in the Blume-Emery-Griffiths model.⁹ Superfluid ordering, which is simulated by dipolar ordering, is a second-order phase transition (it involves no volume change). The situation is then illustrated qualitatively by Fig. 7(d), although the slope of normal liquid-superfluid liquid-equilibrium curve (the so-called λ line) does not have the correct sign (see Ref. 6, p. 375) and the solid phase is not described.

A third possibility of our model, already noticed by Bernasconi and Rys,¹¹ is the description of a paramagnetic gas which exhibits a coupling between the density and the magnetization. Isothermal compression may induce a first- or sec-

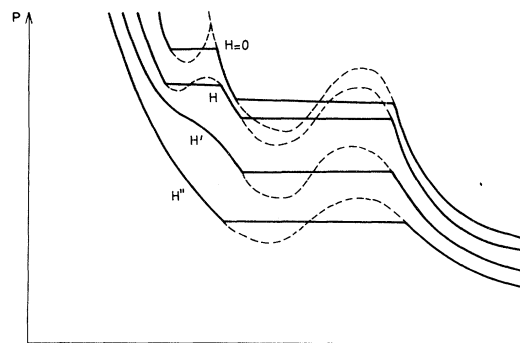


FIG. 8. Schematic influence of a field on the phase diagram. In the field H , two plateaus are found. In the field H' a single "condensation" plateau is found and in the field H'' , a single "sublimation" plateau is found.

ond-order magnetic transition: The fluid is ferromagnetic when the density is large enough, whatever the values of $T < 2J$, where J is the exchange integral. The situation is similar to that of a compressible magnetic system. At high pressures, a second-order ferromagnetic transition is found, involving a symmetry change of the system. When the pressure is lowered, the ferromagnetic transition switches from second to first order. The application of an external field H suppresses the second-order-line $C'C_\infty$ shifts and shortens the lines τC and $\tau C'$ (Fig. 9), which generate symmetrical "wings" limited by critical lines, and reduces the jump of M at the ferromagnetic transition until a critical point is reached. As in the Griffiths picture of a tricritical point,²⁷ three critical lines ($H = 0$, $H > 0$, and $H < 0$) meet at C' . $C'\tau$ is in fact a triple line along which a paramagnetic phase coexists with two magnetic phases of opposite magnetizations, and τ is a quadruple point.

Another situation described by the spin-1 model is that of the absorption or adsorption of a gas at the sites of a two- or three-dimensional lattice. A first-order adsorption or absorption can be followed by an order-disorder (configurational, orientational, superfluid, magnetic) transition. For instance, our model might describe absorption of hydrogen in palladium and superconductivity in the Pd-H system.^{28, 29}

In the preceding examples, the state $|0\rangle$ was used to represent a vacancy on a given site of the lattice, and the model described the effect of pressure on some cooperative phenomenon. A second possibility is to consider a mixture AB . The pure- A (active) compound is characterized by some cooperative ordering described ordinarily by a spin- $\frac{1}{2}$ Ising model, whereas the pure- B (passive) compound is insensitive to it. In order to describe the influence of dilution of A by B on the cooperative transition of A , the state $|0\rangle$ is now used to represent a B atom, and the states $|\pm 1\rangle$ represent an A atom. Phase separation is then the analog of condensation and concentration in A the analog of density. The procedure has been used to describe ^3He - ^4He mixtures⁹ and magnetic alloys.¹⁰ It could be used similarly to describe phase separation and nematic ordering in nematic mixtures³⁰: The A molecules are elongated with only two possible orientations; the B molecules are spherical and hinder the nematic phase transition. The spin-1 model describes the dilution effect on nematic ordering and phase separation, either induced by intermolecular forces in the isotropic liquid or driven by nematic ordering (see the various possibilities of Fig. 5 of Ref. 9).

Similarly, let us consider a binary liquid AB . The singlet state $|0\rangle$ may represent a "big" B molecule, the doublet state $|\pm 1\rangle$ a "small" A molecule. A "big" molecule occupies the two subcells of a given cell, a "small" molecule occupies either the left or right subcell. Suppose the interaction between two neighboring A and B molecules does not depend on the subcell occupied by A , neglecting the possibility that $J^{++} \neq J^{--} \neq -J^{+-}$ (the Hamiltonian of paper II¹² should then be used). We may use the Hamiltonian (1) to describe the influence of dilution on the solidification of A (in this model, solidification of A is second order at $kT_A = 2J$ and B does not solidify) and phase separation (either induced by intermolecular forces or triggered by solidification).

VII. CONCLUSION

We have shown in this paper that the thermodynamical behavior of a simple fluid can be simulated by use of a spin-1 Ising model with Hamiltonian (1), similar to the Blume-Emery-Griffiths model.⁹ Although the model has some unusual features discussed in Sec. V, the qualitative aspect of the phase diagram is reproduced correctly for some range of the parameters J and K . We have predicted the existence of compounds without any liquid-gas equilibrium and the existence of compounds exhibiting the transition from first-order melting to critical melting. The possibility of having more than one solid phase³¹ has not been introduced.

Various applications of the same model have

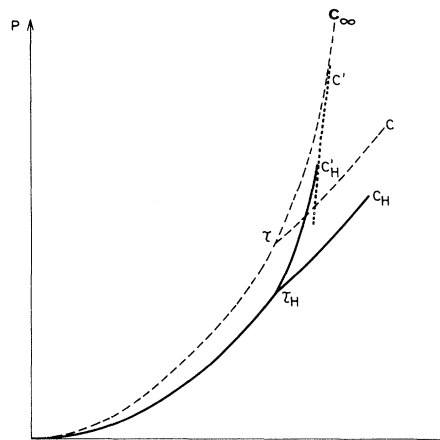


FIG. 9. Schematic phase diagram of a paramagnetic gas. The dashed lines correspond to $H = 0$; τ is a quadruple point. The full lines correspond to $|H| \neq 0$ and C_H and C'_H are critical points, τ_H is a triple point. The dotted line C'_H is the projection of the two critical lines ($H > 0$ and $H < 0$) which meet with the critical line $C'C_\infty$ ($H = 0$) at the tricritical point.

been considered in Sec. VI. In papers II and III we show that, provided a new term is added to the Hamiltonian (1), the model also describes condensation and phase separation in binary mixtures, phase separation in ternary mixtures and, in particular, the effect of pressure and dilution on phase separation in binary mixtures.

APPENDIX

As with the Lennard-Jones and Devonshire model, our model indicates the possibility of critical melting. This contradicts a well-known result of Landau,²³ who has shown that the liquid-solid transition is first order except in isolated points. We must then reexamine the applicability of our model to the description of the liquid-solid transition.

Melting corresponds in general to the disappearance of both positional and orientational orderings. For simple monatomic solids, only positional ordering is concerned. For more complex crystals such as molecular crystals, orientational ordering must be considered too. In our model, a single orientational parameter M is introduced to describe the crystalline phase. This is mostly justified at high pressures, when the liquid is closely packed (the main mechanism for the transition is then orientational) and leads to a second-order transition. At lower pressures, the coupling between M and Q changes the order of the transition. Using terminology found in the field of ferroelectric phase transitions,³² solidification is described as an "improper" transition. The volume change, if any, at solidification is a consequence of ordering in M .

Suppose that a system undergoes a transition from a phase of symmetry G_0 to a phase of symmetry G (G being a subgroup of G_0). According to Landau²³ if a transition is second order, the three following conditions must be satisfied.

(a) The order parameter must transform as a basis function of a single irreducible representation Γ_α of G_0 .

(b) The symmetric direct cube $[\Gamma_\alpha^3]$ must not contain the identity representation Γ_1 , so that the Landau free-energy expansion contains no third-order term.

(c) The antisymmetric direct product $\{\Gamma_\alpha^2\}$ must not contain the vector representation of G_0 (stability condition).

In our problem, M transforms in the representation D_1^- of the rotational group $R^3 \times 1$ (while the density Q transforms in the identity representation D_0) and condition (a) is satisfied. Since M is odd with respect to inversion, odd-order terms cannot be found in the free-energy expansion and condition (b) is satisfied [indeed, $[(D_1^-)^3] = D_1^- + D_3^-$]. Finally, since we are using a lattice model for the fluid, the stability condition (c) is irrelevant.

The three Landau conditions being satisfied in our model, solidification may be second order, as found at high pressures. M is the leading order parameter and not Q —otherwise the transition would always be first order. Our result proves that the first-order character of solidification is not necessarily due to the violation of condition (b), which was the only possibility investigated by Landau.²³ We may also think that the third-order term in the leading order parameter will always be missing for a transition from a liquid to a noncentrosymmetric crystal.

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