Phase transitions in an asymmetrical Ising model

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An asymmetrical Ising model in which the eigenvalues of the operators S^z and $(S^z)^2$ are $1, 0, -\lambda$, and $1, 0, \lambda^2$ (λ being a parameter: $0 < \lambda < 1$) respectively is studied using Bragg-Williams approximation. It is shown that such an asymmetrical model is equivalent to a symmetrical model with renormalized coupling constants. The corresponding lattice-gas model is proposed which introduces four coupled ordering parameters: $m = \langle S^z \rangle$, $q = \langle (S^z)^2 \rangle$, $M = a_1 m + a_2 q$, and $Q = b_1 m + b_2 q$, where a's and b's are some λ-dependent parameters. The condensation of a Van der Waals–Boltzmann gas is studied and the variations of the critical pressure P_c and the critical temperature T_c with λ are analyzed. A study of the phase diagram shows that the isothermals shift downward as λ decreases from unity. The conditions for the occurrence of successive second-order liquid-gas and solid-liquid transitions are found and it is shown that a tricritical point may exist both in symmetrical and asymmetrical models at the liquid-gas transition depending on the strengths of interactions. Considering the different possible values of m, q, M, and Q four different possible solid phases can be conceived along with two different liquid phases so that the model permits five consequent solid-solid transitions and one liquid-liquid transition.

I. INTRODUCTION

Lee and Yang[1] developed the equation of state and the theory of condensation of a real gas by exploiting the complete analogy between an Ising model and a lattice gas. They observed that in Ising model one considers a lattice of interacting spins each of which having two mutually opposite orientations, whereas in a lattice gas one conceives a lattice with each lattice point either being occupied by an atom or lying vacant and that each configuration of lattice of spins corresponds formally to that of a lattice gas.

In fact, it has been found that a variety of cooperative physical phenomena can be simulated by a spin-$\frac{1}{2}$ Ising model. For example, the phase separation of a two-component liquid or solid,[2] the order-disorder transition in a binary alloy,[3] the freezing of a liquid,[4] magnetic and electric phase transition[5] can be simulated by spin-$\frac{1}{2}$ Ising models. The physical properties of the involved systems were successfully described by one-parameter models.

But the spin-$\frac{1}{2}$ one-parameter Ising models are really insufficient for describing more complicated physical phenomena. The thermodynamic behavior of ternary fluids was studied by Mukamel and Blume[6] using a lattice-gas model for spin-1 Ising system, by a generalization of an earlier work of Blume, Emery, and Griffiths[7] who interpreted the tricritical point in the mixture of two quantum fluids He^3 and He^4. Lajzerowicz and Sivardiere[8] and Sivardiere and

Lajzerowicz[9] developed a lattice-gas model for the condensation and solidification of a simple fluid. Their models were based on two kinds of ordering parameters m and q giving rise to phase transitions in a spin-1 Ising system. The parameters $m = \langle S^z \rangle$ and $q = \langle (S^z)^2 \rangle$ are responsible, respectively, for crystalline phase and the condensation. The parameter m is called the orientation parameter and q is an analogue of density called the condensation parameter. On the basis of this model, they developed the equation of state and the thermodynamics of phase transitions.

It may, however, be criticized that a two-parameter lattice-gas model as introduced and developed by Sivardiere and Lajzerowicz is not able to interpret the solid-solid and liquid-liquid transitions along with the solid-liquid and liquid-gas transitions. To interpret these various kinds of phase transitions one naturally attempts to introduce some three-parameter or four-parameter models for which the use of some high-spin Ising system ($S > 1$) becomes necessary. But it would be interesting to see that even within the spin-1 model one can introduce four coupled ordering parameters provided S^z and $(S^z)^2$ are assumed to possess asymmetrical eigenvalues.[10] In this context we mention several attempts where double spin-half Ising models were introduced,[11] with the motivation to employ more than two ordering parameters. The double spin-half Ising models were applied to magnetic liquids,[12] singlet-triplet magnetic systems,[13] degenerate Hubbard models,[14] Jahn-Teller systems,[15] and liquid crystal mixtures.[16]

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The purpose of the present paper is to develop the lattice-gas model of an asymmetrical Ising system[10] and to discuss the solid-solid, solid-liquid, liquid-gas, and liquid-liquid transitions. Following Huang[10] we assume that the eigenvalues of the operators S^z and $(S^z)^2$ are 1, 0, $-\lambda$, and 1, 0, λ^2 where λ is an asymmetry parameter: $0 < \lambda < 1$. The limiting case $\lambda = 1$ corresponds to a symmetrical system. Utilizing this assumption we have derived the Blume-Emery-Griffiths-Mukamel Hamiltonian appropriate for an asymmetrical system. Bragg-Williams approximation is then employed to derive the expression for the Helmholtz free energy $F(m,q,T)$. We have then utilized the concept of Sivardiere and Lajzerowicz to construct the appropriate lattice-gas model for an asymmetrical system. It is seen that the model automatically permits four coupled ordering parameters: m,q and $M = a_1 m + a_2 q$, $Q = b_1 m + b_2 q$, where a's and b's are λ-dependent parameters. Helmhotz free energy $F(M,Q,T)$ is then developed and is found to be identical with that of a symmetrical system with transformed spin operators. The equation of state of the asymmetrical system is derived from which the expressions for critical volume V_c^λ, critical pressure P_c^λ, and the critical temperature T_c^λ are found out. The possibility of second-order solid-liquid and liquid-gas transitions is studied and the conditions for successive occurrence of these two phase transitions are derived for both symmetrical and asymmetrical models. The thermodynamics of other kinds of transitions is also discussed.

II. BLUME-EMERY-GRIFFITHS-MUKAMEL HAMILTONIAN

We shall follow the method of Blume, Emery, and Griffiths[7] and Mukamel and Blume[6] to set up the Hamiltonian for an asymmetrical system. We introduce the number operators[17]

$$N_A = \frac{1}{1+\lambda} \sum_{i=1}^{N} (q_i + \lambda m_i) ,$$

$$N_B = \frac{1}{\lambda(1+\lambda)} \sum_{i=1}^{N} (q_i - m_i) , \quad (1)$$

$$N_O = \sum_{i=1}^{N} \left[1 - \frac{1}{\lambda} q_i + \frac{1-\lambda}{\lambda} m_i \right] ,$$

where $q_i = (S_i^z)^2$ and $m = S_i^z$ with the eigenvalues 1, 0, λ^2 and 1, 0, $-\lambda$, respectively.

The above expressions result from the natural extension of those of Mukamel and Blume. Let us suppose that the nearest-neighbor interaction between A- and B-type molecules is given by K_{AB}. Hence the Hamiltonian may be written

$$H = K_{AA}N_{AA} + K_{BB}N_{BB} + K_{AB}(N_{AB} + N_{BA}) + K_{OO}N_{OO}$$
$$+ K_{AO}(N_{AO} + N_{OA}) + K_{BO}(N_{BO} + N_{OB}) ,$$

where N_{AA}, N_{AB}, etc., are given by

$$N_{AA} = \frac{1}{(1+\lambda)^2} \sum_{\langle ij \rangle} (q_i + \lambda m_i)(q_j + \lambda m_j) ,$$

$$N_{AB} = \frac{1}{\lambda(1+\lambda)^2} \sum_{\langle ij \rangle} (q_i + \lambda m_i)(q_j - m_j) ,$$

according to Eq. (1).

After straightforward simplifications, the Hamiltonian may be written in the following form (apart from a constant factor):

$$H = -J \sum_{\langle ij \rangle} m_i m_j - j \sum_{\langle ij \rangle} q_i q_j - C \sum_{\langle ij \rangle} (m_i q_j + q_i m_j) - h \sum_i m_i - D \sum_i q_i , \quad (2)$$

where the interaction constants J, j, C, h, and D are given by

$$J = (1+\lambda)^{-2}\left[\lambda^2 K_{AA} + \frac{1}{\lambda^2}K_{BB} - 2K_{AB}\right] + (1-\lambda)^2\lambda^{-2}\left[K_{OO} + \frac{2\lambda^2}{1-\lambda^2}K_{AO} - \frac{2}{1-\lambda^2}K_{BO}\right] ,$$

$$j = (1+\lambda)^{-2}\left[K_{AA} + \frac{1}{\lambda^2}K_{BB} + \frac{2}{\lambda}K_{AB}\right] + \lambda^{-2}\left[K_{OO} - \frac{2\lambda}{1+\lambda}K_{AO} - \frac{2}{1+\lambda}K_{BO}\right] , \quad (3)$$

$$C = (1+\lambda)^{-2}\left[\lambda K_{AA} - \frac{1}{\lambda^2}K_{BB} - \frac{1-\lambda}{\lambda}K_{AB}\right] - (1-\lambda)\lambda^{-2}K_{OO} + \frac{1}{\lambda(1+\lambda)}K_{AO} + \frac{2-\lambda}{\lambda^2(1+\lambda)}K_{BO} ,$$

$$h = z\left[\frac{1-\lambda}{\lambda}K_{OO} + \frac{\lambda}{1+\lambda}K_{AO} - \frac{1}{\lambda(1+\lambda)}K_{BO}\right] , \quad D = z\left[\frac{1}{1+\lambda}K_{AO} + \frac{1}{\lambda(1+\lambda)}K_{BO} - K_{OO}\right] ,$$

z being the number of nearest neighbors.

We note here that Eq. (2) is identical with that of Mukamel and Blume but now the interaction constants occurring in the Hamiltonian depend on the asymmetry parameter λ. The interaction constants J,j,C,h, and D for $\lambda = 1$ coincide with those of Mukamel and Blume. The parameter h in the above Hamiltonian plays the role of an external field and D resembles a single-ion crystal-field anisotropy. In the corresponding lattice-gas model Lajzerowicz and Sivardiere (LS) identify D as the chemical potential, but they did not consider the crossed interaction C. We see from Eq. (3) that even for $\lambda = 1$ there is no justifiable assumption which can make $C = 0$ along with $D \neq 0$. On the contrary it becomes evident that if one assumes that $K_{AO} = K_{BO} = K_{OO} = 0$ then one gets $D = 0, h = 0, C \neq 0$. On the basis of this assumption we can show that the condensation does occur in this formalism also. In fact, we shall see later that the condensation for the asymmetrical case can be shown to be identical with that as appeared in LS formalism. The role played by the crossed interaction C is equivalent to that by D in LS formalism. The assumption that the interaction K_{AO}, K_{BO}, K_{OO} are zero does not evidently imply that $N_O = 0$. We have developed in Sec. IV an appropriate lattice-gas model which allows vacancies in the treatment so that the condensation and the solidification can be discussed.

III. FREE ENERGY IN BRAGG-WILLIAMS FORMALISM

The internal energy of the system described by the Hamiltonian (2) with $h = D = 0$ takes the following simple form in Bragg-Williams approximation:

$$U = -Nz[Jm^2 + jq^2 + 2cmq] , \tag{4}$$

where N is the total number of spins, and m and q are the dipolar and quadrupolar ordering parameters, respectively, which are given by $m = \langle S^z \rangle$ and $q = \langle (S^z)^2 \rangle$.

The entropy may be calculated from the expression

$$S = -Nk_B \sum_{m_s} p_{m_s} \ln p_{m_s} , \tag{5}$$

where k_B is the Boltzmann constant, and p_{m_s} is the probability of a spin to be in a quantum state whose eigenvalue is m_s, the latter taking the values $1, 0, -\lambda$. The parameters m and q may now be written in the forms

$$m = \sum_{m_s} m_s p_{m_s} , \tag{6}$$

$$q = \sum_{m_s} m_s^2 p_{m_s} . \tag{7}$$

The probabilities $p_1, p_0, p_{-\lambda}$ for each quantum state having the eigenvalues $1, 0, -\lambda$, respectively, can be calculated from Eqs. (6) and (7) with the additional condition

$$\sum_{m_s} p_{m_s} = 1 . \tag{8}$$

One gets after simplifications

$$p_1 = \frac{q + \lambda m}{1 + \lambda} ,$$

$$p_0 = 1 - \frac{1}{\lambda} q + \frac{1 - \lambda}{\lambda} m , \tag{9}$$

$$p_{-\lambda} = \frac{q - m}{\lambda(1 + \lambda)} .$$

The expression for the Helmholtz free energy per spin can now be written in the following form:

$$F(m,q,T) = -Jm^2 - jq^2 - 2cmq + T\left[\left[\frac{q + \lambda m}{1 + \lambda} \right] \ln\left[\frac{q + \lambda m}{1 + \lambda} \right] + \left[1 - \frac{1}{\lambda} q + \frac{1 - \lambda}{\lambda} m \right] \ln\left[1 - \frac{1}{\lambda} q + \frac{1 - \lambda}{\lambda} m \right] \right.$$

$$\left. + \left[\frac{q - m}{\lambda(1 + \lambda)} \right] \ln\left[\frac{q - m}{\lambda(1 + \lambda)} \right] \right] , \tag{10}$$

where we have written J for Jz, j for jz, C for Cz, and T for $k_B T$.

When the free energy of the system is given it becomes quite straightforward to develop the thermodynamics of phase transitions occurring in the system. One can make the development[18,19] of free energy and this may provide us some qualitative knowledge about phase transitions. But it is nevertheless evident that there exists a complicated coupling between the ordering parameters m and q;

hence no reliable information can be obtained from this method. The alternative procedure is to solve the equations obtained for m and q from the equilibrium conditions: $\partial F/\partial m = 0$, $\partial F/\partial q = 0$. We do not proceed to study the magnetic properties of the system and the related orderings in m and q. Instead, we shall develop the appropriate lattice-gas model with the help of which we shall discuss the thermodynamics of solid, liquid, and gaseous phases.

IV. LATTICE-GAS MODEL FOR ASYMMETRICAL SYSTEM

In constructing a lattice-gas model corresponding to a symmetrical Ising system, Sivardiere and Lajzerowicz considered m as the orientation parameter which describes the crystalline phase. The situation $m = 0$ therefore corresponds to the liquid phase and the temperature T_s at which m goes to zero describes the solid-liquid transition. The other ordering parameter q in their formalism is regarded as a density parameter and may be called the condensation parameter. In the corresponding magnetic problem transitions occur in both m and q leading to dipolar and quadrupolar transitions.[18-21] In the paramagnetic phase the ordering parameter $B_0 = (q - \frac{2}{3})$ is zero. In the lattice-gas model B_0 is, therefore, assumed to vanish at the liquid-gas transition.

The simple-lattice-gas model as stated above may be criticized in two respects: (i) one may easily note that the orientational ordering in gas as represented by nonzero m disappears in the liquid phase and (ii) the assumption that B_0 vanishes at the liquid-gas transition as envisaged in a symmetrical model is an oversimplification. In addition to this, the above model cannot be applied to more complicated phase transitions like the liquid-crystal transitions. The model is also incapable of interpreting the existence of so-called solid-solid transitions.

Before discussing the formal correspondence on which the present model is based we shall deal with an important aspect of the problem. We shall show below that our asymmetrical model corresponds to a symmetrical model with renormalized coupling constants and spin operators.

(a) *Transformation to a symmetrical model.* We introduce two ordering parameters M and Q defined

by

$$M = \langle N_A \rangle - \langle N_B \rangle ,$$
$$Q = \langle N_A \rangle + \langle N_B \rangle . \tag{11}$$

We shall call M "explicit orientation parameter" and Q "explicit condensation parameter" to distinguish them from the "implicit parameters" m and q. The relations between $m, M, q,$ and Q can easily be written down. Using Eq. (1) one can show that

$$M = \frac{1 + \lambda^2}{\lambda(1 + \lambda)} m - \frac{1 - \lambda}{\lambda(1 + \lambda)} q ,$$
$$Q = \frac{1}{\lambda} q - \frac{1 - \lambda}{\lambda(1 + \lambda)} m . \tag{12}$$

The inverse relations are

$$m = \tfrac{1}{2}(1 + \lambda) M + \tfrac{1}{2}(1 - \lambda) Q ,$$
$$q = \tfrac{1}{2}(1 - \lambda^2) M + \tfrac{1}{2}(1 + \lambda^2) Q . \tag{13}$$

We now define the solid phase by $M \neq 0, Q \neq \frac{2}{3}$, the liquid phase by $M = 0, Q \neq \frac{2}{3}$, and the gas phase by $M = 0, Q = \frac{2}{3}$. The internal structure of the crystalline phase or the liquid phase depends on the implicit parameters m and q. We see that in the gaseous phase

$$m = \tfrac{1}{3}(1 - \lambda) , \quad q = \tfrac{1}{3}(1 + \lambda^2) . \tag{14}$$

For $\lambda = 1$, we find $m = 0, q = \frac{2}{3}$.

It is also necessary to mention that Eq. (11) along with Eq. (1) yields $Q = 1/V$ whereas in the symmetrical model q is identified with the reciprocal of volume.

We shall now re-express the free energy in terms of the explicit parameters. Equation (10) with the help of Eq. (13) leads to

$$F(M,Q,T) = - XQ^2 - YM^2 - 2RQM + T\left[\frac{Q+m}{2} \ln \frac{Q+m}{2} + (1-Q)\ln(1-Q) + \frac{Q-M}{2} \ln \frac{Q-M}{2}\right], \tag{15}$$

where the interaction constants $X, Y,$ and R stand for

$$X = \tfrac{1}{4} J[(1 - \lambda)^2 + \alpha(1 + \lambda^2)^2$$
$$+ 2\gamma(1 - \lambda)(1 + \lambda^2)] ,$$
$$Y = \tfrac{1}{4} J[(1 + \lambda)^2 + \alpha(1 - \lambda^2)^2$$
$$+ 2\gamma(1 + \lambda)(1 - \lambda^2)] , \tag{16}$$
$$R = \tfrac{1}{4} J[(1 - \lambda^2) + \alpha(1 - \lambda^4)^2$$
$$+ 2\gamma(1 + \lambda^3)] ,$$

with $\alpha = j/J, \gamma = C/J$.

It is interesting to see that Eq. (15) can be derived

from a Hamiltonian

$$H = - X \sum_{\langle ij \rangle} Q_i Q_j - \gamma \sum_{\langle ij \rangle} M_i M_j$$
$$- R \sum_{\langle ij \rangle} (Q_i M_j + M_i Q_j) , \tag{17}$$

where M_i and Q_i are the effective spin operators defined by

$$M_i = \frac{1 + \lambda^2}{\lambda(1 + \lambda)} m_i - \frac{1 - \lambda}{\lambda(1 + \lambda)} q_i ,$$
$$Q_i = \frac{1}{\lambda} q_i - \frac{1 - \lambda}{\lambda} m_i . \tag{18}$$

One easily finds that the eigenvalues of M_i and Q_i

are 1, 0, −1 and 1, 0, 1, respectively. Equation (17), therefore, describes a symmetrical Ising system. An asymmetrical model can, therefore, be transformed to a symmetrical model with the interaction constants and the spin operators suitably renormalized.

The inverse relations of Eq. (18) are

$$m_i = \frac{1}{2}(1+\lambda)M_i + \frac{1}{2}(1-\lambda)Q_i \ ,$$

$$q_i = \frac{1}{2}(1-\lambda^2)M_i + \frac{1}{2}(1+\lambda^2)Q_i \ .$$

If we substitute these relations in Eq. (2) one would also get Eq. (17).

We shall now demonstrate that the new renormalized interaction constants possess some interesting properties. From Eq. (16) one can show the following relations:

$$X+Y+2R = K_{AA}, \quad X+Y-2R = K_{BB} \ ,$$

$$X-Y = K_{AB} \ ,$$

from which we get

$$4X = K_{AA}+K_{BB}+2K_{AB} \ ,$$

$$4Y = K_{AA}+K_{BB}-2K_{AB} \ ,$$

$$4R = K_{AA}-K_{BB} \ .$$

X may, therefore, be interpreted as the mean interatomic interaction in an equiatomic mixture, and Y as the parameter which gives us a measure of the tendency of phase separation. The parameter R measures the difference of AA and BB coupling.

(b) *Formal correspondence.* We propose below the following lattice-gas model appropriate for the present problem.

Let us imagine that a cell corresponding to the lattice site i with the effective spin operators M_i and Q_i is divided into two "compartments": right (+) and left (-) as shown in Fig. 1(a). The eigenvalues of M_i are 1, 0, −1. The situations $M_i = \pm 1$ correspond to a particle occupying the right and left compartments, respectively, and $M_i = 0$ corresponds to vacancy. On the other hand, Q_i possess the eigenvalues 1, 0, 1. The situation $Q_i = 1$ implies that the cell is occupied and $Q_i = 0$ implies that the cell is empty. This kind of formal correspondence was conceived in LS formalism where the implicit ordering parameters m_i and q_i were utilized.

To fit into the present formal picture the role played by the spin operators m_i and q_i we imagine that each "compartment" is divided into two subcells: left (L) and right (R) subcells as shown in Fig. 1(b). The subcells which belong to the right compartment
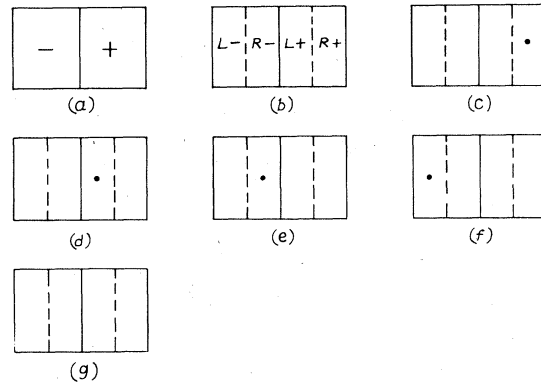

FIG. 1. Asymmetrical lattice-gas model: (a) a cell is divided into right (+) and left (-) compartments, (b) each compartment is divided into right (R) and left (L) subcells, (c) a particle occupies the position R_+ which corresponds to $M_i = 1$, $Q_i = 1$, $m_i = 1$, and $q_i = 1$, (d) a particle occupies the position L_+ which corresponds to $M_i = 1$, $Q_i = 1$, $m_i = -\lambda$, and $q_i = \lambda^2$, (e) a particle occupies the position R_- which corresponds to $M_i = -1$, $Q_i = 1$, $m_i = 1$, and $q_i = 1$, (f) the position L_- is occupied which refers to the situation $M_i = -1$, $Q_i = 1$, $m_i = -\lambda$, and $q_i = \lambda^2$, (g) the cell is vacant: $M_i = 0$, $Q_i = 0$, $m_i = 0$, and $q_i = 0$.

are denoted by R_+ and L_+, and those to the left by R_- and L_-. Now let us consider the situation $M_i = 1, Q_i = 1$ which implies that the right compartment is occupied by the particle. Which subcell of this compartment will be occupied by the particle is determined by the eigenvalues of m_i and q_i. Evidently there exist two possibilities: the particle may occupy the right subcell and it may also occupy the left subcell. We call the first possibility the "normal configuration" as shown in Fig. 1(c) which implies that if the particle goes to occupy the right subcell the situation may be represented by $m_i = 1$. But if the particle occupies the left subcell it corresponds to $m_i = -\lambda$ and we call it "asymmetry configuration" as shown in Fig. 1(d). We interpret m_i as the probability of occupation of a subcell by a particle and also the probability of a subcell to remain empty. In the normal configuration the probability $p(1)$ that the right subcell is occupied by a particle is unity and also the probability $p(2)$ that the left subcell will remain empty is also unity. In asymmetry configuration $p(1) = p(2) = -\lambda$. The joint probability of simultaneous occurrence of these two states (one subcell occupied and other empty) is therefore 1 in the normal configuration and λ^2 in the asymmetry configuration. We denote these situations by $q_i = 1$ and $q_i = \lambda^2$, respectively.

A similar picture holds for the case $M_i = -1$, $Q_i = 1$ and is demonstrated in Figs. 1(e) and 1(f). Figure 1(g) represents the situation $M_i = 0$ $Q_i = 0$, $m_i = 0$, $q_i = 0$, which implies that the cell is empty.

V. VAN DER WAALS–BOLTZMANN GAS

In this section we shall study the simple situation — the condensation of a Van der Waals–Boltzmann gas. We shall utilize Eq. (15) to find the equilibrium value of the free energy. We find that the condition

$$M\frac{\partial F}{\partial M} + Q\frac{\partial F}{\partial Q} = 0 \tag{19}$$

gives the identity

$$T\left[\frac{Q+M}{2}\ln\frac{Q+M}{2} + \frac{Q-M}{2}\ln\frac{Q-M}{2}\right]$$

$$= 2XQ^2 + 2YM^2 + 4RQM + TQ\ln(1-Q) . \tag{20}$$

Using this identity one gets from Eq. (15) the equilibrium value of the free energy

$$\phi_e = XQ^2 + YM^2 + T\ln(1-Q) . \tag{21}$$

Since we are considering only the case of condensation of a gas we put $M = 0$. The equation of state may, therefore, be written

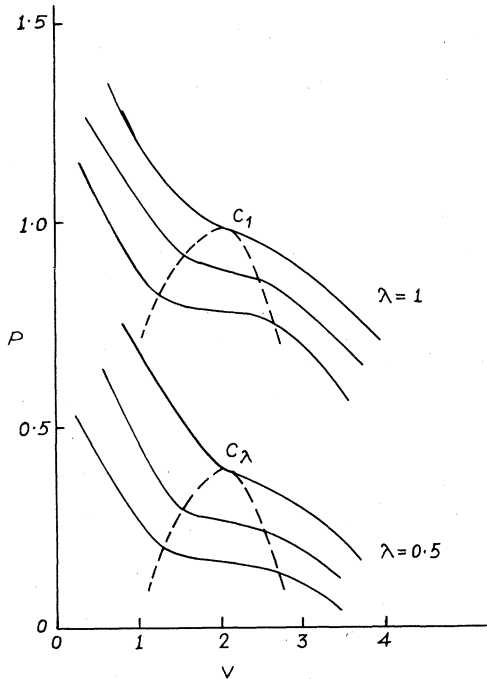$$P = -\frac{X}{V^2} - T\ln\left(1 - \frac{1}{V}\right) . \tag{22}$$

FIG. 2. Schematic phase diagram of an asymmetrical lattice gas. As λ increases, the isothermals are found to shift upward. Ordinates are scaled according to the relative shift of the critical point. As λ increases from 0.5 to 1, the relative shift is found to be 0.6 which refers to the combination $J = 0, C = 0, j \neq 0$.

The critical volume V_c^λ, the critical temperature T_c^λ, and the critical pressure P_c^λ can, therefore, be shown to be

$$V_c^\lambda = 2 , \quad t_c^\lambda = \tfrac{1}{2}X , \quad P_c^\lambda = \tfrac{1}{4}X(\ln 4 - 1) . \tag{23}$$

We see that the critical volume remains the same in both the symmetrical and asymmetrical models, but the critical pressure and temperature both vary with λ. For $J = 0, C = 0$, we get

$$P_c^\lambda/P_c = T_c^\lambda/T_c = \tfrac{1}{4}(1 + \lambda^2)^2 .$$

The phase diagram is shown in Fig. 2 which shows that the isothermals shift downward as λ decreases from unity. We should also mention that $P_c V_c/T_c$ is free from the interaction constants and is the same in both the symmetrical and asymmetrical models.

VI. SOLID-LIQUID AND LIQUID-GAS TRANSITIONS

In the symmetrical lattice-gas model the solid-liquid transitions and liquid-gas transitions may either be first order or second order depending on the strengths of interactions. Similar results are also obtained in the present asymmetrical model. Here we shall examine the possibilities of second-order solid-liquid and liquid-gas transitions to find the possibility of existence of a tricritical point, if any. For this purpose, we shall minimize the free energy $F(M,Q,T)$ with respect to M and Q so that we get

$$YM + RQ = \frac{T}{4}\ln\frac{Q+M}{Q-M} ,$$

$$XQ + RM = \frac{T}{4}\ln\frac{Q^2 - M^2}{(1-Q)^2} , \tag{24}$$

which can be combined to give

$$\frac{YM + RQ}{XQ + RM} = 2\ln\left|\frac{1-Q}{Q-M}\right| . \tag{25}$$

Taking the limit $M \to 0$ one gets the following expression for the volume $V_s = 1/Q_s$ at the solid-liquid transition:

$$V_s = 1 + e^{1/2\gamma'} , \tag{26}$$

where $\gamma' = R/X$.

The temperature T_s at which this transition occurs is obtained from Eq. (24).

$$\frac{T_s}{X} = \frac{2Q_s[1 - (R^2/XY)]}{\ln[Q_s/(1 - Q_s)]} . \tag{27}$$

Utilizing Eq. (26) in Eq. (27) we get

$$\frac{T_s}{X} = \left[2\left(\alpha' - \frac{1}{\gamma'}\right) \Big/ \cosh\left(\frac{\gamma'}{4}\right)\right] \exp\left(\frac{-\gamma'}{4}\right), \quad (28)$$

with $\alpha' = R / Y$.

Taking the limit $M \to 0$, $Q \to \frac{2}{3}$ one gets the temperature T_g at which the liquid-gas transition occurs

$$\frac{T_g}{X} = \frac{4(1 - \alpha'\gamma')}{3\ln 2}. \quad (29)$$

Equations (18) and (19) show that the solid-liquid and liquid-gas transitions may appear in the system as second-order transitions depending on the interaction parameters $X, Y,$ and R. An elementary discussion on the possibility of occurrence of second-order liquid-gas transitions in asymmetrical Ising model has been recently presented by the author.[17] Some of the results obtained in Ref. 17 are found to be modified in the present formalism. A detailed discussion of the results and the comparison of these results with those of Ref. 17 are given below.

It can be readily seen that a tricritical point may occur at T_g when the following condition is satisfied:

$$R^2/XY = 1 - (\tfrac{3}{8})\ln 2, \quad (30)$$

which results from the condition $T_c = T_g$.

It is to be noted that for $\lambda = 1$, $\gamma = 0$ the above condition is not satisifed. Thus for a symmetrical model a tricritical point cannot be found if the crossed dipole-quadrupole coupling vanishes. This result agrees with that of Ref. 17. For $\gamma = 0$ one gets $R = 0$ and thus $\alpha' = \gamma' = 0$ provided $X \neq 0, Y \neq 0$. Therefore, one gets

$$T_g = \frac{4j}{3\ln 2} \quad (31)$$

and thus a second-order liquid-gas transition is possible. It establishes the result of LS formalism. However, it should be noted that in this case T_s becomes infinite. Again, for $\gamma \neq 0$, $\lambda = 1$ one gets

$$T_g = \frac{4j}{3\ln 2}\left(1 - \frac{\gamma^2}{\alpha}\right),$$

$$T_s = \left[2j\left(\gamma - \frac{\alpha}{\gamma}\right) \Big/ \cosh\left(\frac{\gamma}{4\alpha}\right)\right] \exp\left(-\frac{\gamma}{4\alpha}\right), \quad (32)$$

$$T_c = \tfrac{1}{2}j.$$

We see that $T_g = T_s = 0$ when $\gamma^2 = \alpha$ and in this case only a first-order liquid-gas transition can occur at T_c provided $j > 0$. On the other hand, if $\gamma^2 \neq \alpha \neq 0$ all the above transitions become possible. It, therefore, modifies the previous conclusion of the author as obtained in Ref. 17. We find that both the first-order and second-order liquid-gas transitions may occur

even when the crossed interaction does not vanish and that there exists a tricritical point at the liquid-gas transition if $\gamma = \gamma_c$, where $\gamma_c = (0.74\alpha)^{1/2}$ which in turn, implies that both j and J must be positive.

We now consider the asymmetrical case. We first note that for $X = 1$ the critical temperature T_c is $\frac{1}{2}$, but in such case the second-order solid-liquid and liquid-gas transitions depend essentially on the values of R and Y. One finds that when $Y = R^2$ both T_s and T_g vanish. But for $Y <> R^2$ nonzero T_s and T_g are possible, and the condition which is necessary for the occurrence of successive solid-liquid and liquid-gas transitions is found to be

$$R[1 + \exp(R/2)] < 3\ln 2.$$

It is evident that for $R = 0$ this condition is not satisfied and therefore no successive T_s and T_g are possible. It implies that for successive T_s and T_g one should have $K_{AA} \neq K_{BB}$. For the critical case, that is, when $Y = R^2$ one finds $K_{AA} = K_{BB} = K_{AB} = 1$. One will find, conversely, $X = 1, R = 0$, and $Y = 0$ when $K_{AA} = K_{BB} = K_{AB} = 1$ so that in this case only a first-order transition occurs at T_c and no second-order transitions can come to occur at T_s and T_g. However, if $R \neq 0$ and $Y \neq 0$ but $Y = R^2$, one may get a tricritical point at T_c provided $X \simeq 1.35$. It is also to be noted, in general, that an asymmetrical model always permits both first-order and second-order liquid-gas transitions and that a tricritical point can exist depending on the interaction parameters and also on the values of λ. Considering all these results we conclude that the present lattice-gas model provides more general and more realistic information regarding the liquid-gas and solid-liquid transitions.

VII. SOLID-SOLID AND LIQUID-LIQUID TRANSITIONS

In Sec. VI we have discussed the thermodynamics of liquid-gas and solid-liquid transitions on the basis of the asymmetrical model. These kinds of transitions may also be discussed on the basis of a spin-1 symmetrical Ising model which permits only two ordering parameters. The thermodynamics of various solid-solid and liquid-liquid transitions is a difficult theoretical problem and cannot be discussed on the basis of a two-parameter model. Due to the involvement of two "explicit" and two "implicit" ordering parameters the asymmetrical model can be shown to give rise to solid-solid and liquid-liquid transitions along with the liquid-gas and solid-liquid transitions. We do not, however, attempt here to give detail statistical-mechanical calculations of all possible phases which may appear in the system, rather we shall mention some of the general consequences of the present lattice-gas model.

TABLE I. Different possible solid and liquid phases as permissible in the present lattice-gas model.

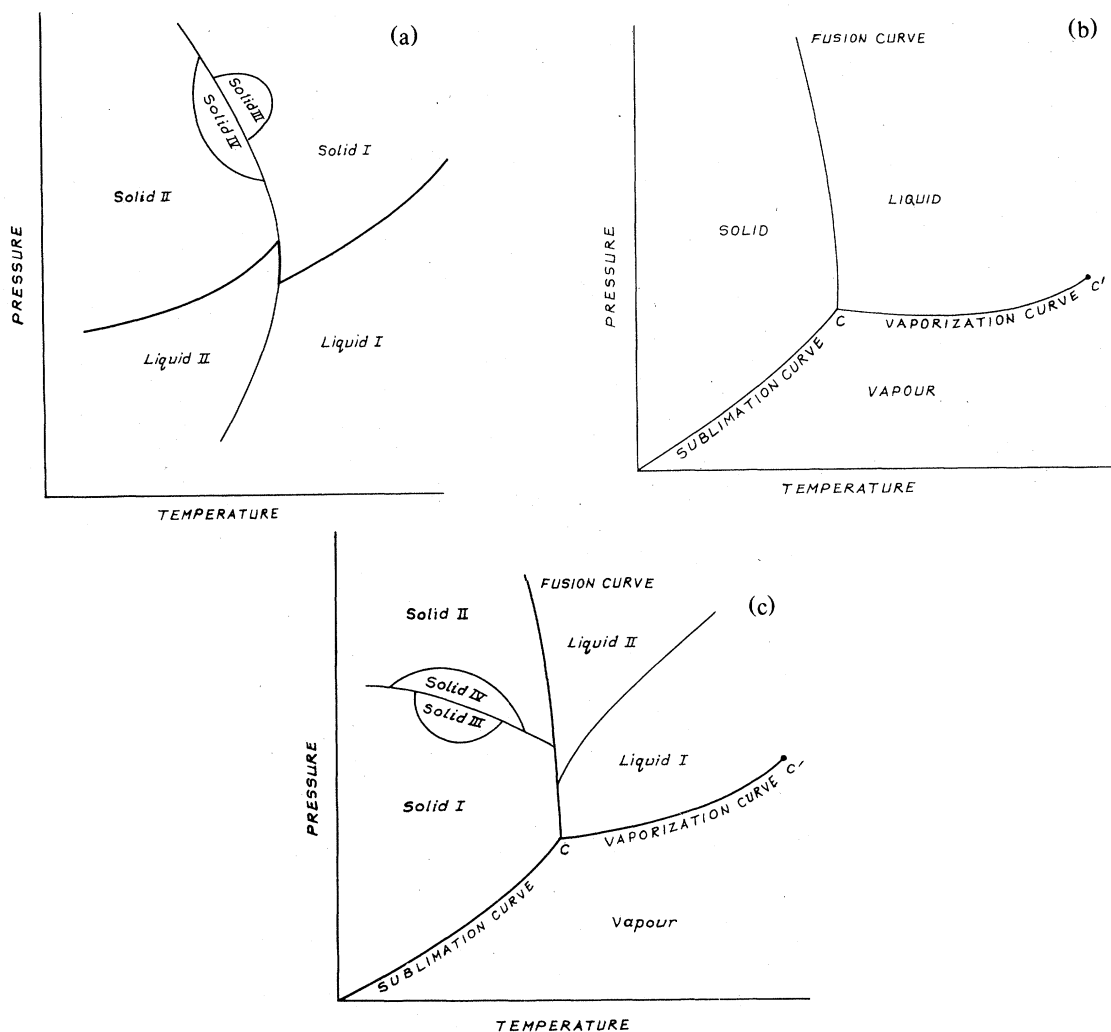| Phase	M	Q	m	q	Specification of the phase
			$\neq 0$	$\neq \frac{2}{3}$	S_1
			$\neq 0$	$\frac{2}{3}$	S_2
Solid	$\neq 0$	$\neq \frac{2}{3}$	0	$\neq \frac{2}{3}$	S_3
			0	$\frac{2}{3}$	S_4
			$\neq 0$	$\neq \frac{2}{3}$	L_1
Liquid	0	$\neq \frac{2}{3}$	$\neq 0$	$\frac{2}{3}$	L_2

FIG. 3. (a) Schematic phase diagrams for various possible solid and liquid phases as permissible in the asymmetrical lattice-gas model. (b) Schematic phase diagrams for solid, liquid, and vapor phase for $\lambda \simeq 1$. (c) Schematic phase diagrams for all possible solid, liquid, and vapor phases as permissible in the present model. The point C' is a critical point and C is one of many triple points.

If we consider different possible situations then the present model permits four different forms of solids S_1, S_2, S_3, S_4, and two liquids L_1, L_2. These are shown in Table I. An inspection of the table shows that five different solid-solid transitions are possible: $S_1 \to S_2, S_3, S_4$, $S_2 \to S_4$, and $S_3 \to S_4$. The transition $S_2 \to S_3$ is not permissible. In similar manner, only one liquid-liquid transition $(L_1 \to L_2)$ is allowed in the present model. The transition temperatures corresponding to the phase transitions $S_1 \to S_2, S_3$, and S_4 are obtained by taking the limits $(q \to \frac{2}{3})$, $(m \to 0)$, and $(m \to 0, q \to \frac{2}{3})$, respectively, and similarly for others. The whole situation is demonstrated in Fig. 3.

The transition temperatures at which various solid-solid and liquid-liquid transitions can occur may not be calculated easily. The procedure involves the derivation of molecular-field equations for M, Q, m, and q and the solution of these coupled equations. Detail calculations will be performed in future investigations. We shall present below a simple derivation of the transition temperature T_L at which the system undergoes the transition: $L_1 \to L_2$.

We differentiate $F(0, Q, T)$ with respect to Q and equate it to zero so that we get

$$\frac{\partial}{\partial Q} \{F(0, Q, T)\}$$

$$= -2XQ + T\left[1 - \ln 2 + \ln\left(\frac{Q}{1-Q}\right)\right] = 0 \quad (33)$$

in equilibrium. Taking the limits $M \to 0, q \to \frac{2}{3}$ one gets from Eq. (12)

$$m = \frac{2(1 - \lambda)}{3(1 + \lambda^2)},$$

$$Q = \frac{2}{3}\frac{3 + \lambda^2}{(1 + \lambda)(1 + \lambda^2)}. \quad (34)$$

Equation (33) therefore gives us the following expression for T_L:

$$\frac{T_L}{X} = \frac{4}{3}\left\{\frac{3 + \lambda^2}{(1 + \lambda)(1 + \lambda^2)}\right\}$$

$$\times \left\{1 + \ln\left(\frac{3 + \lambda^2}{3\lambda^3 + \lambda^2 + 3\lambda - 3}\right)\right\}^{-1}. \quad (35)$$

We note that the liquid-liquid transition which occurs at T_L is possible when $\lambda > 0.628$. It may also be noted that T_L is independent of the crossed interaction C.

VIII. CONCLUDING REMARKS

The asymmetrical Ising model as developed in Secs. I–VII is certainly more useful than a symmetrical spin-1 Ising model and also it works in a more simple way than a double spin-half Ising model. It can treat thermodynamics of phase transitions satisfactorily. However, it is insufficient in one respect. We have seen in Sec. VII that an asymmetrical Ising model permits four solid phases. In nature there exist more than four solid phases of a substance. Similarly more than two liquid phases may be possible. It follows, therefore, that an accurate model should allow more than four ordering parameters. The inclusion of a biaxiality parameter $P = \langle (S^x)^2 - (S^y)^2 \rangle$ may give rise to additional phases in the system.

It is also necessary to mention that the so-called mean-field or molecular-field calculations do not yield quantitatively accurate values of the thermodynamic functions. A Green's-function equation-of-motion method or a Green's-function diagrammatic technique is believed to reproduce much better results. Formulation of the problem in this manner has been currently taken up for investigation.

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