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Spin-1 lattice-gas model. II. Condensation and phase separation in a binary fluid

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A spin-1 lattice-gas model is shown to describe condensation and phase separation in a binary fluid. The Ising-like Hamiltonian involves quadrupolar, dipolar, and crossed quadrupolar-dipolar interactions and is treated in the molecular-field approximation. Various experimental phase diagrams are reproduced qualitatively, exhibiting liquid-gas and liquid-liquid equilibrium lines, critical, azeotropic, and triple lines.

I. INTRODUCTION

In a preceding paper,[1] denoted paper I, we have studied a spin-1 lattice-gas model, similar to the Blume-Emery-Griffiths model[2] for ^{3}He-^{4}He mixtures, which describes the thermodynamical behavior of a simple fluid and other physical systems characterized by two order parameters. In this paper, the second of this series, we consider another spin-1 lattice-gas model in order to describe some thermodynamical properties of binary and ternary fluids, condensation and phase separation, which are ordinarily described by separate spin-$\frac{1}{2}$ Ising models.[3]

In paper I we considered an "active" pure compound A characterized by some cooperative ordering (configurational, orientational, superfluid, and magnetic), and the effect of pressure or dilution on this ordering. The states $|\pm 1\rangle$ were used to represent an "active" atom or molecule, and the state $|0\rangle$ either a vacancy or a "passive" atom or molecule. It was then possible to give a unified description of the cooperative ordering and condensation or phase separation.

In this paper the states $|+1\rangle$ or $|-1\rangle$ now represent an A or B atom or molecule (so that the cooperative ordering of paper I is now phase separation in an AB mixture), and the state $|0\rangle$ either a vacancy (binary mixtures) or a C atom or molecule of a third type (ternary mixtures kept at a fixed pressure). It is then possible to describe the interaction between A-B phase separation and condensation or A-C and B-C phase separations. Even if the state $|0\rangle$ represents a vacancy or a passive molecule, the interactions J_{AA}, J_{BB}, and J_{AB} play a role independently; three interaction parameters are then needed in this problem, whence the addition of a crossed quadrupolar-dipolar term to the model Hamiltonian used in paper I.

In Sec. II the applicability of the spin-1 lattice-gas model to binary fluids is discussed. The molecular field treatment is given in Sec. III. Condensation of a binary mixture is described in Sec. IV for the case where the liquid is always homogeneous. The interaction between condensation and phase separation is investigated in Sec. V. In the following paper (III),[4] it will be shown that the model also describes phase separations in a ternary liquid or solid kept at a fixed pressure. The occurrence of tricritical points in binary and ternary fluids will be discussed too.

II. LATTICE-GAS MODEL FOR BINARY FLUID

We consider a spin-1 lattice-gas model for a binary fluid, with the following interpretation of the state variables $Q_i = (S_i^z)^2$ and S_i^z. If $Q_i = 0$, the cell i is empty. If $Q_i = 1$, the cell i is occupied by one molecule, whose nature depends on the value of S_i^z; if $S_i^z = +1$ or -1, the molecule is of the type A or B. Thus, if N_A and N_B are the numbers of A and B condensed molecules, respectively, we have

$$N = N_A + N_B = \sum_i Q_i , \tag{1a}$$

$$N' = N_A - N_B = \sum_i S_i^z . \tag{1b}$$

Let v be the specific volume of homogeneous phase of the fluid and V the total volume of this phase. The volume of the unit cell is taken as unity, so that $V = N$ (total number of cells) and $Q = 1/v$ is the density, whence

$$N = VQ = V\langle Q_i \rangle , \tag{2a}$$

$$N' = VM = V\langle S_i^z \rangle . \tag{2b}$$

The quantity

$$y = M/Q = (N_A - N_B)/(N_A + N_B), \tag{3}$$

which will be called concentration, describes the deviation from equiconcentration [the concentration $x_A = N_A/(N_A + N_B)$, with $y = 2x_A - 1$, will not be used in this paper].

Three interactions between neighboring molecules must be introduced: J_{AA}, J_{BB}, and J_{AB}. J_{AA} and J_{BB} determine the critical temperatures T_A and T_B of the two pure liquids, respectively, while $J_{AA} + J_{BB} - 2J_{AB}$ determines the critical unmixing temperature in a liquid of density $Q = 1$. The Hamiltonian of the lattice model must also contain three independent interactions. In addition to the ordinary dipolar and quadrupolar interactions introduced in the Blume-Emery-Griffiths model,[2] the only possibility, since $S = 1$, is to introduce a crossed quadrupolar-dipolar interaction. Such an interaction is not time-reversal invariant, but this point is irrelevant since we are not considering a magnetic system.

Let us define operators P_i^A (or P_i^B) which equal one if the cell is occupied by an A (or B) molecule, and zero otherwise:

$$P_i^A = \tfrac{1}{2}(Q_i + S_i^z), \tag{4a}$$

$$P_i^B = \tfrac{1}{2}(Q_i - S_i^z). \tag{4b}$$

The Hamiltonian of the system is then

$$\mathcal{H} = -\sum_{i,j}\left[J_{AA}P_i^A P_j^A + J_{BB}P_i^B P_j^B + J_{AB}(P_i^A P_j^B + P_i^B P_j^A)\right] - \sum_i (\mu_A P_i^A + \mu_B P_i^B). \tag{5}$$

μ_A and μ_B are the chemical potentials of the molecules of type A and B, respectively, and must be introduced, since the number of A and B particles are not determined. Introducing the notations

$$K = \tfrac{1}{4}(J_{AA} + J_{BB} + 2J_{AB}), \tag{6a}$$

$$J = \tfrac{1}{4}(J_{AA} + J_{BB} - 2J_{AB}), \tag{6b}$$

$$L = \tfrac{1}{4}(J_{AA} - J_{BB}), \tag{6c}$$

or, conversely,

$$J_{AA} = K + J + 2L, \tag{7a}$$

$$J_{BB} = K + J - 2L, \tag{7b}$$

$$J_{AB} = K - J, \tag{7c}$$

and

$$D = \tfrac{1}{2}(\mu_A + \mu_B), \tag{8a}$$

$$H = \tfrac{1}{2}(\mu_A - \mu_B), \tag{8b}$$

the Hamiltonian $\mathcal{H}$ becomes

$$\mathcal{H} = -\sum_{i,j} K Q_i Q_j - \sum_{i,j} J S_i^z S_j^z - \sum_{i,j} L(S_i^z Q_j + Q_i S_j^z) - H\sum_i S_i^z - D\sum_i Q_i. \tag{9}$$

In the following we will have to use the Fourier transforms of the different interactions for $k = 0$, for instance, $K(0) = \sum_j K_{ij} = zK$, z being the number of neighbors of a given site. In order to simplify the notations, we put $z = 1$ below, which is equivalent to a renormalization of the interaction constants.

The interaction K is the mean interaction between the molecules in an equimolecular mixture, and drives condensation of the mixture. The interaction J describes the deviation from ideal behavior. If positive, it drives phase separation in the liquid state. The interaction L describes the difference between the pure A and B fluids (one can take $L > 0$ without any loss of generality). If accidentally $L = 0$, the two fluids have the same liquid-gas equilibrium curve in the P, T plane since, according to the Lee-Yang model, this curve depends only on the interaction parameter $J_{AA} = J_{BB}$ and not on the volume of the elementary cell.

We will use the effective interaction I between two molecules in homogeneous mixture of density Q and concentration $y = M/Q$. The probabilities Π_A and Π_B of finding a molecule A or B in an elementary cell are

$$\Pi_A = (Q + M)/2Q = \tfrac{1}{2}(1 + y), \tag{10a}$$

$$\Pi_B = (Q - M)/2Q = \tfrac{1}{2}(1 - y), \tag{10b}$$

whence the mean interaction I

$$I = \tfrac{1}{4}J_{AA}(1 + y)^2 + \tfrac{1}{4}J_{BB}(1 - y)^2 + 2J_{AB}(1 + y)(1 - y) \tag{11}$$

or

$$I = K + 2Ly + Jy^2. \tag{12}$$

For instance, if the molecules A and B are identical, $J = L = 0$ and $I \equiv K$. In an ideal mixture, $J = 0$ and I varies linearly with y. In a very dilute solution of B in A, $y = 1 - \epsilon$ ($\epsilon \ll 1$) and according to (12):

$$I \simeq (1 - \epsilon)J_{AA} + \epsilon(J_{AB} - J_{AA}). \tag{13}$$

Indeed, the probability of BB interactions is negligible and I is independent of J_{BB}.

The quantity $I(y)$ has an extremum equal to $I_e = K - L^2/J$ for $y_e = -L/J$. Since L is positive, y_e lies between -1 and 0 if $J_{AB} < J_{BB}$ and between 0 and $+1$ if $J_{AB} > J_{AA}$. If these conditions are satisfied, the interaction I_e is positive since if $J > 0$, $J_{AA}J_{BB} > J_{AB}^2$, and if $J < 0$, $J_{AA}J_{BB} < J_{AB}^2$. If $J_{BB} < J_{AB} < J_{AA}$, $I(y)$ has an extremum outside the interval $(-1, +1)$ and varies monotonically from J_{BB} to J_{AA} as y goes from -1 to $+1$. In the numerical calculations of the following sections, we choose $J_{AA} = 7$ and $J_{BB} = 5$, which determines the liquid-gas equilibrium curves of the pure-A and -B fluids ($T_A = 3.5$ and $T_B = 2.5$), and the value of L, $L = 0.5$. If we define $\bar{J} = \frac{1}{2}(J_{AA} + J_{BB}) = 6$, $J = 0$ if

$J_{AB} = \bar{J}$. Throughout the paper, we take $k = 1$ so that all interactions are given in deg K.

III. MOLECULAR-FIELD EQUATIONS

The Hamiltonian (9) can be treated in the molecular-field approximation, and the following equations for M and Q are found:

$$ZM = 2\exp[\beta(D + 2KQ + 2LM)]\sinh\beta(H + 2JM + 2LQ), \tag{14}$$

$$ZQ = 2\exp[\beta(D + 2KQ + 2LM)]\cosh\beta(H + 2JM + 2LQ), \tag{15}$$

where Z is the grand partition function of the system,

$$Z = 1 + 2\exp[\beta(D + 2KQ + 2LM)]\cosh\beta(H + 2JM + 2LQ), \tag{16}$$

and $\beta = 1/kT$. From (14) and (15), we deduce

$$y = M/Q = \tanh\beta(H + 2JM + 2LQ). \tag{17}$$

The equilibrium free energy is

$$\phi_e = -(1/\beta)\ln Z + JM^2 + KQ^2 + 2LMQ, \tag{18}$$

or, according to (12) and (15),

$$\phi_e = (1/\beta)\ln(1 - Q) + IQ^2. \tag{19}$$

From (15) we also deduce

$$D = -2KQ - 2LM + (1/\beta)\ln Q/2(1 - Q) - (1/\beta)\ln\cosh\beta(H + 2JM + 2LQ), \tag{20}$$

hence, using (17)

$$\frac{\partial D}{\partial Q} = -2K + \frac{1}{\beta}\,\frac{1}{Q(1 - Q)} - 2J\,\frac{M}{Q}\,\frac{\partial M}{\partial Q} - \frac{2L}{Q}\,\frac{\partial MQ}{\partial Q}. \tag{21}$$

In a liquid phase of maximum density ($Q = 1$ or $K = +\infty$), Eq. (17) becomes

$$M = \tanh\beta(H' + 2JM), \tag{22}$$

with

$$H' = \tfrac{1}{2}(\mu_A - \mu_B) + \tfrac{1}{2}(J_{AA} - J_{BB}). \tag{23}$$

This is the result found for the spin-$\frac{1}{2}$ lattice-gas model describing phase separation in a binary mixture, which omits pressure-volume effects. Conversely, if $L = J = 0$, we have a perfect solution in which the A and B molecules have the same interaction properties and need not be distinguished. From (15) the results of the Lee-Yang model for condensation of a simple fluid in a spin-1 formalism (see paper I) are immediately recovered.

We now want to construct the phase diagram of a binary mixture AB.[5-13] As in paper I, we get the pressure P of a homogeneous phase by noticing that in a lattice gas P is the opposite of the free energy,

$$P = -KQ^2 - JM^2 - 2LMQ - (1/\beta)\ln(1 - Q), \tag{24}$$

or, from (3) and (12),

$$P = -IQ^2 - (1/\beta)\ln(1 - Q). \tag{25}$$

Equation (25), where I is a function of y given by (12), is valid only if the fluid remains homogeneous along the isotherm, or of course if the molecules A and B are identical. Phase separation, however, is possible in the liquid state if $J > 0$. Moreover, Fig. 1(a) shows that, during the isothermal condensation of a mixture, the composition and pressure of the two phases at equilibrium vary; the concentration is y only in R and R'. In other words, a Maxwell plateau can be constructed on the isotherm, but it has a physical meaning only if the molecules A and B are identical [the cigarlike two-phase region of Fig. 1(a) is then a horizontal straight line] or if the mixture is azeotropic. In general the plateau is replaced by the surface $RSR'S'$, horizontal sections of which are shown in Figs. 1(a) and 1(b).

Equation (25) is not easy to handle and does not contain all the information on the system. It will be used only to determine the azeotropic mixtures. Consequently, we shall use Eqs. (15) and (17) directly. If only one solution (M, Q) is found at a given temperature T for given values of K, L, J, D, and H, it represents a homogeneous fluid. If n solutions (M_1, Q_1), (M_2, Q_2), ... are

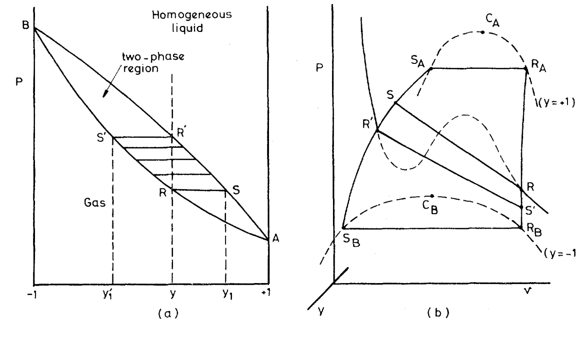

FIG. 1. (a) Isothermal liquid-gas equilibrium of a binary mixture ($T < T_A, T_B$). $ARS'B$ is the condensation curve, $ASR'B$ the ebullition curve. The phases R and S, R' and S' are in equilibrium and they have different compositions. (b) Isotherm of a binary mixture. Except between R and R', the isotherm is described by the van der Waals equation (29). Between R and R', the pressure varies and no phase has the concentration y. The figure also shows the binodal curves and the critical points of pure A and B fluids. R_AS_A and R_BS_B are Maxwell plateaux, while R_ARR_B and $S_AR'S_B$ are the saturation curves.

found with the same free energy, they represent n homogeneous phases at equilibrium: $T_1 = T_2 = \ldots$, $P_1 = P_2 = \ldots$ (since $\phi_1 = \phi_2 = \ldots$), $\mu_A^1 = \mu_A^2 = \ldots$, and $\mu_B^1 = \mu_B^2 = \ldots$ (because the n solutions correspond to the same values of D and H).

Consequently, in order to determine the phase diagram of the mixture, we choose some values of the interactions K, L, J and of the fields D and H. We look for a first-order transition in M and Q as temperature is varied. The two solutions at equilibrium determine either two liquids in equilibrium with different compositions, or a liquid and a gas in equilibrium, represented by two points such as R and S in Fig. 1(a) [the points A and B are determined from the phase diagram in the (P, T) plane of each pure component of the mixture]. In order to get other tie lines one must change the value of D and adjust the value of H, so that a first-order transition in M and Q occurs at the same temperature T.

Before describing the results of our calculations, we discuss the possible features of the phase diagram. According to the Gibbs rule for noncritical phases, the variance w of a state with coexisting AB phases is given by $w = 4 - n$, whence the following possibilities.

$n = 1$. Homogeneous phase; $w = 3$ (P, T, and y can be varied independently).

$n = 2$. Two-phase heterogeneous equilibrium (liquid-liquid or liquid-gas) represented by a tie line in a (P, y) or (T, y) plane; $w = 2$ (when P *or* T is varied, the tie line generates a surface, but when P *and* T are varied, the two extremities of the tie lines generate a surface; each tie line is replaced by a single point if y is replaced by the conjugated field H and this point also generates a surface in the P, T, H diagram).

$n = 3$. Three-phase heterogeneous equilibrium (three liquids or two liquids and a gas); $w = 1$ (when T or P is varied, such a triple point τ generates a line in the P, T, H diagram).

$n = 4$. Quadruple point; $w = 0$ (such a point may be found only for accidental values of the interactions parameters).

Moreover, according to the Gibbs rule for critical phases applied to binary mixtures, $w_c = 1$, so that we expect, in the P, T, H diagram, a liquid-gas critical curve and a liquid-liquid (unmixing) critical curve.

IV. CONDENSATION OF BINARY MIXTURE ($J \leq 0$)

We first consider the case $J \leq 0$. This condition implies that the liquid phase is always homogeneous (complete miscibility of A and B), and that there is no triple point: Only liquid-gas equilibrium is possible. We do not investigate the possibility of antiferromagneticlike ordering in the liquid state. The possibility of a phase separation in the liquid state will be discussed in Sec. V ($J > 0$).

$J = 0$. $J_{AB} = \bar{J} = 6$, hence $K = 6$. Since $L = 0.5 \neq 0$, the phase diagrams are never symmetrical in y. Figure 2 shows various isothermal liquid-gas equilibrium curves in the (P, y) plane. We say here that the solution is ideal. This definition does not correspond to the one given by Rowlinson,[12]—from which Raoult's law follows only as an approximation—but is introduced for the following reasons: According to our numerical calculations, Raoult's law is satisfied to a very good approximation for $J = 0$, at least for small values of L (we have not been able to prove the exact validity of the law for $J = 0$ and $L \neq 0$). Indeed the ebullition curve AB of Fig. 2 shows no appreciable deviation from a straight line. For $J > 0$ or $J < 0$ (see below) large positive or negative deviations from Raoult's

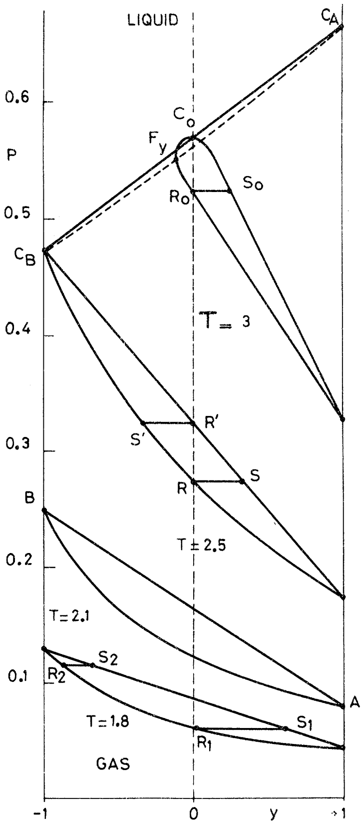

FIG. 2. Liquid-gas equilibrium at different temperatures ($T = 3$, 2.5, 2.1, 1.8) for $K = 6$, $L = 0.5$, $J = 0$ ($J_{AB} = 6$). $C_A C_0 C_B$ is the critical line, and $C_A F_y C_B$ the cricondentherm line (dashed). C_0 is the critical point for $y = 0$ and F_y the cricondentherm for $y \simeq 0.1$. The tie lines $R_1 S_1$ and $R_2 S_2$ are found for $D = -7.5$, $H = 0$ and $D = -7.5$, $H = -2$, respectively.

law are observed. The points A and B of Fig. 2 represent pure liquid and gaseous phases at equilibrium and are determined from the theory of paper I. As long as $T < T_A, T_B$, the points A and B exist. If $T_B < T < T_A$, B disappears and retrograde condensation becomes possible. The point C_0 is the critical point for equiconcentration $y = 0$; it corresponds to a second-order transition in M and Q as T varies for given values of D and H; in C_0 the two phases R and S at equilibrium have become identical. F_y is a cricondentherm point. If the temperature is increased, retrograde condensation disappears for a mixture of composition y.

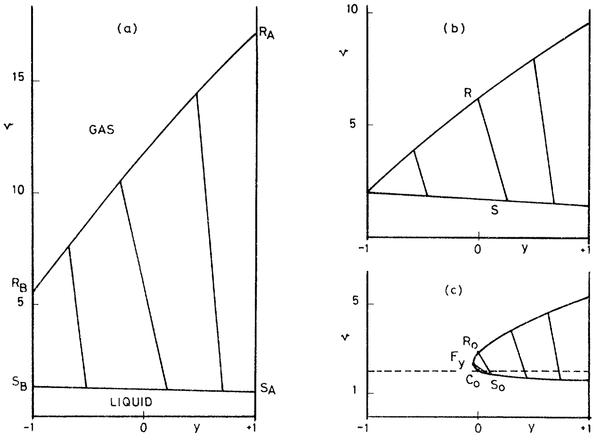

FIG. 4. Isothermal saturation curves in the (v, y) plane: (a) $T = 2.1$; (b) $T = 2.5 = T_B$; (c) $T = 3$ (the dashed line is the critical line). P varies from one tie line to the other. For $y = \pm 1$, the vertical tie line is a Maxwell plateau.

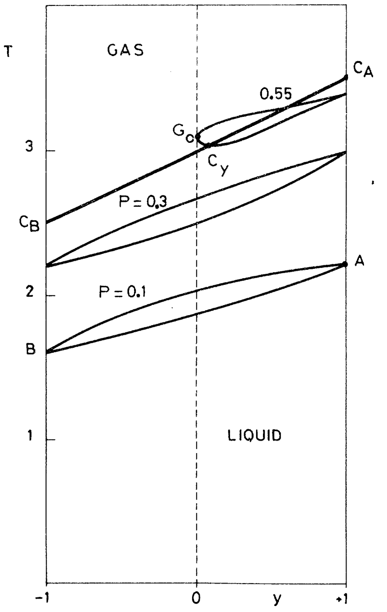

FIG. 3. Liquid-gas equilibrium at different pressures $(P = 0.55, 0.3, 0.1)$ for $J = 0$. G_0 is the cricondenbar for $y = 0$, C_y the critical point for $y \simeq 0.08$, $C_B C_Y C_A$ the critical line, and $C_B G_0 C_A$ the cricondenbar line.

From the numerical results leading to Fig. 2, one can construct as well the (T, y) phase diagram for given values of the pressure (Fig. 3). C_y is a critical point and G_0 is a cricondenbar point. If the pressure is increased, retrograde condensation disappears for a mixture of concentration $y = 0$. It is also possible to construct the phase diagram in the (v, y) plane considered by Prigogine and Defay[3] (Fig. 4). For each couple of solutions (M, Q) of Eqs. (15) and (17) at equilibrium, we know $v = 1/Q$ and $y = M/Q$. We can also place the points R and R' on the isotherms of Fig. 1(b) since the mean interaction $I(y)$ and the pressure are known for each of these points. Figure 5 represents schematically the locus Σ_0 of these points when T varies for $y = 0$ (the critical point of the isotherms is situated on the curve Σ only for $y = 0$). The curve Σ_0 plays the same role as the binodal curve for a simple fluid: It encloses unstable homogeneous states. If $T > T_F$, the mixture is always homogeneous. The cricondentherm line $C_A F_y C_B$ is represented in Fig. 2 $(P, y$ diagram). Figure 6 represents the liquid-gas equilibrium curves of the pure A and B fluids, and the liquid-gas equilibrium region of the mixture $y = 0$. R represents a gaseous phase $(y = 0)$ in equilibrium with a liquid phase S $(y > 0)$, and R' a liquid phase $(y = 0)$ in equilibrium with a gaseous phase $S'(y < 0)$. The phases R and R' become identical at the critical point C_0 so that two phases having the same composition are in equilibrium only if they are

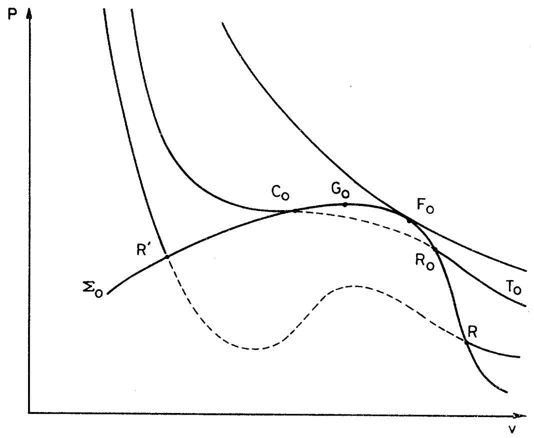

FIG. 5. Locus Σ_0 of R and R' for a given value of y $(y = 0$, for instance). The van der Waals isotherm is given by (25) with $I(0) = K$. R, R', C_0, and R_0 are shown also in Fig. 3. F_0 is the cricondentherm (figure not to scale). Dashed lines represent unstable states.

identical. The loop ORC_0R' is tangent to the critical line C_AC_B at the critical point C_0. ORC_0 is the condensation curve and $OR'C_0$ the ebullition curve. No phase of composition $y=0$ is found in the hatched region.

It should be noted that C_y, the critical point for the composition y, is not in general the critical point of the isotherm corresponding to $T=\frac{1}{2}I(y)$, since, as long as J and L are different from zero, Q is not equal to $\frac{1}{2}$ at the critical point C_y, except if C_y is a critical azeotrope (see below) or if $y=0$. Indeed if $y=0$, from (17) we deduce $H+2LQ=0$, and from (15)

$$Q=\frac{2\exp[\beta(D+2KQ)]}{1+2\exp[\beta(D+2KQ)]}\,. \tag{26}$$

According to the result of paper I, Q_c is then equal to $\frac{1}{2}$. One gets $Q_c=\frac{1}{2}$ for all values of y only if $J=L=0$. However, for small values of $|J|$, $Q\simeq\frac{1}{2}$ at C_y.

$J<0$. Figure 7 shows several phase diagrams at $T=2.5$ for various values of J. If $J=-0.25$ ($J<J_{AB}=6.5<J_{AA}$, $K=6.25$), the phase diagram exhibits negative deviation from the ideal behavior. The ebullition curve is no longer a straight line, so Raoult's law is not satisfied. But no azeotrope is found, and the critical temperature varies monotonically from T_B to T_A as y varies from -1 to $+1$. If $y\simeq+1$, the J_{BB} interactions play no role, and the slope of the liquefaction and ebullition curves near A change sign for $J_{AB}=J_{AA}$ or $J=-0.5$ and $K=6.5$.

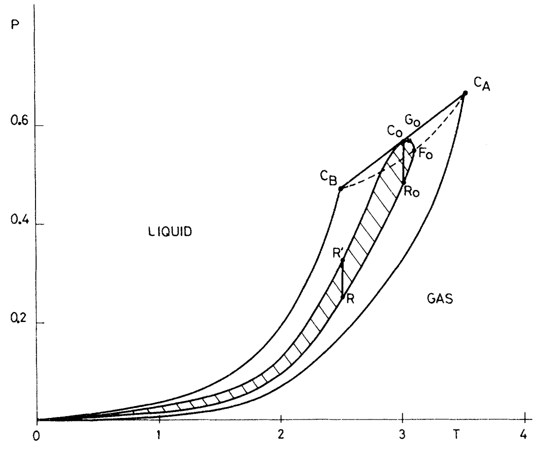

FIG. 6. Liquid-gas equilibrium curves in the (P,T) plane for pure-A and -B fluids, and for a mixture with $y=0$. The locus of R (gas) and R' (liquid) encloses a hatched region where two phases with $y\neq0$ coexist. R and R' are not in equilibrium. In C_0, the phases R and R' are identical. The critical line C_AC_B is the envelope of the curves ORC_yR' when y varies. The dashed line $C_AF_0C_B$ is the cricondentherm line. G_0 is the cricondenbar.

Figure 8 shows the phase diagram for $J=-1$ ($J_{AB}=8>J_{AA}$, $K=7$). Since $J<-0.5$, the slopes of the liquefaction and ebullition curves near A are negative, so that azeotropy is observed. The composition of the azeotrope is given by $\partial I(y)/\partial y=0$, or $y_{\text{az}}=-L/J=0.5$ (independent of temperature). Indeed, the larger the mean interaction $I(y)$, the lower the liquefaction pressure at any temperature. Also, a maximum critical temperature is found and at the critical point $C_{\max}$, the mean interaction $I(y)$ is maximum, $y_e=y_{\text{az}}=-L/J$, so that $C_{\max}$ is also the critical azeotrope. The azeotropic line is then a vertical line in the (P,y) plane, with an end point at $C_{\max}$. Since the azeotrope behaves as a simple fluid, the density at $C_{\max}$ is given by $Q=0.5$; $T_{\max}=\frac{1}{2}I(y_e)=\frac{1}{2}(K-L^2/J)=3.625$ and, according to (25), $P_{\max}\simeq0.70$. At each temperature, the pressure of the azeotrope can be calculated from the position of the Maxwell plateau on the van der Waals isotherm (25) (see paper I). Finally when $T_A<T<T_{\max}$, two critical points C_1 and C_2 are found at each temperature.

Figure 9 shows (v,y) diagrams at various temperatures. The azeotrope is represented by a tie line ZZ' parallel to the v axis, which is a true Maxwell plateau. Since $I(y_e)>J_{AA},J_{BB}$, this tie

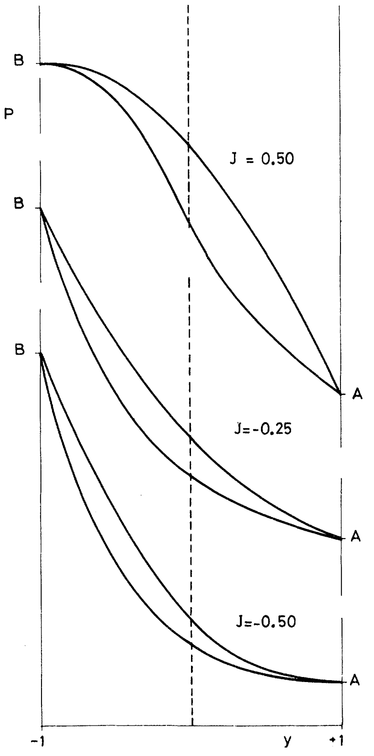

FIG. 7. Liquid-gas equilibrium at $T=2.5$ for different values of J ($J=-0.50$, -0.25, $+0.50$). Deviation from ideal behavior is found but there is no azeotropy.

line is longer than the Maxwell plateau of pure A and B at the same temperature. For $T_A < T < T_{\max}$, a closed loop with two critical points is found. Figure 10 shows the phase diagram in the (P, T) plane. The cricondentherm line is made of two branches: $C_B C_{\max}(y < y_e)$ and $C_{\max} C_A(y > y_e)$. The azeotropic line is nothing else than the Lee-Yang liquid-gas equilibrium curve for an intermolecular interaction equal to $K - L^2/J$. The critical point for $y = 0$ is at the same pressure as C_A, since $I(0) = K + 2L + J \equiv J_{AA}$.

When $|J|$ is very large, $J_{AB} \gg J_{AA}$, J_{BB} and therefore $T_{\max} \gg T_A, T_B$; $y_e \to 0$ and the phase diagrams are almost symmetrical in y.

V. CONDENSATION AND PHASE SEPARATION OF BINARY FLUID (J>0)

We consider the situation $J > 0$. The same method as in Sec. IV is used to construct the phase diagram. Unmixing in the liquid phase is now possible at low enough temperature, and triple points may be found (coexistence of two liquid phases L_1 and L_2 and a gaseous phase G) corresponding to the existence of three solutions of (15) and (17) at equilibrium.

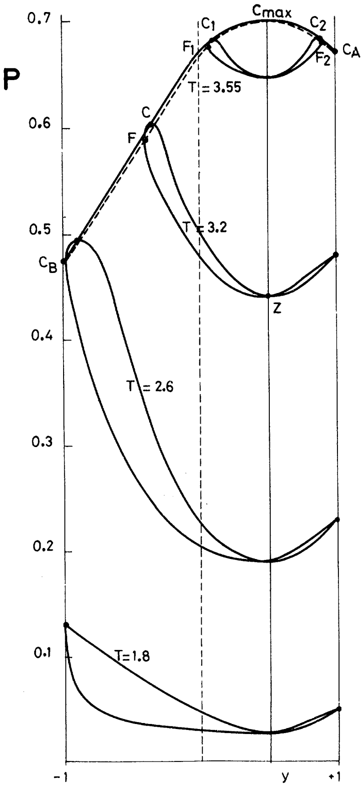

FIG. 8. Liquid-gas equilibrium at different temperatures ($T = 3.55$, 3.2, 2.6, 1.8) for $K = 7$, $L = 0.5$, and $J = -1$ ($J_{AB} = 8$). The dashed line is the cricondentherm line. Z is an azeotrope and $C_{\max}$ is the maximum critical point and also the critical azeotrope.

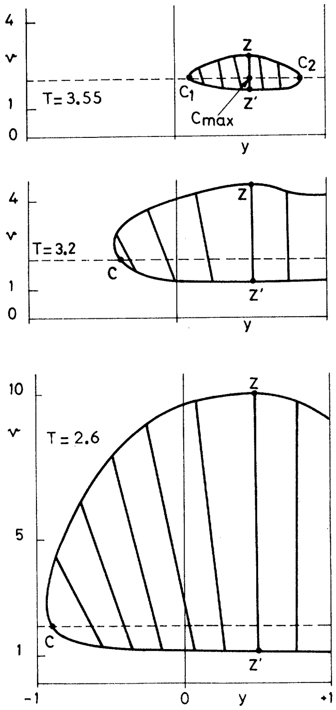

FIG. 9. Isothermal saturation curves at $T = 3.55$, 3.2, and 2.6 for $J = -1$. For $T_A < T < T_{\max}$, a closed loop with two critical points C_1 and C_2 is found. The dashed line is the critical curve. ZZ' is the Maxwell plateau of the azeotrope.

Figure 7 shows the phase diagram at $T = 2.5$ for $J = +0.5$. The slope of the liquefaction and ebulli-

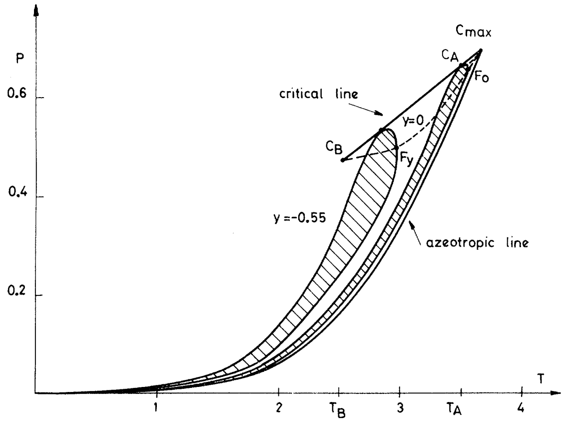

FIG. 10. Liquid-gas equilibrium in the (P, T) plane for $J = -1$ and $y = -0.55$, $y = 0$, and $y = y_{az} = -L/J$. The cricondentherm line (dashed) is composed of two branches: The low-pressure branch corresponds to $y < y_e$, the high-pressure one to $y > y_e$.

tion curves near B is zero. Indeed, if $y \simeq -1$, the J_{AA} interactions play no role and the sign of the slope changes sign for $J_{AB} = J_{BB}$ or $J = 0.5$ and $K = 5.5$, so that positive azeotropy is observed for $J > 0.5$.

$J = 0.45$ ($J_{AB} = 5.1$, $K = 5.55$). Figure 11 shows the phase diagram at various temperatures. At temperatures $T > 2J$, the phase diagrams are similar to those of Fig. 2 with a positive deviation from ideal behavior, and the critical temperature varies monotonically from T_B to T_A as y varies from -1 to $+1$. According to Eq. (17), as long as $T < 2J = 0.9$, phase separation is observed in the liquid state for high enough densities. When T is very close to 0.9, the phase diagram is a represented in Fig. 11(c): C_{AB} is the unmixing critical point. At a temperature $T \simeq 0.89$, the liquid-liquid binodal curve and the ebullition curve meet, and a triple point τ_1 is found. Figures 11(a) and 11(b) show peritecticlike phase diagrams. The (P, T) phase diagram is shown in Fig. 11(d): $0\tau_1$ is the triple line, $\tau_1 C_\infty$ the liquid-liquid critical line, and $C_A C_B$ the liquid-gas critical line.

$J = +1$ ($J_{AB} = 4$, $K = 5$). According to Eq. (17), the liquid phase is homogeneous for $T > 2J$, and the corresponding phase diagrams in the (P, y) plane are shown in Fig. 12. A minimum critical temperature is found at $T_{\min} = \frac{1}{2}(K - L^2/J) = 2.375$ and $y_e = -L/J = -0.5$. Since $J > 0.5$, positive azeotropy is observed at $y = y_e$. The azeotropic line is vertical and $C_{\min}$ is also the critical azeotrope. If $Q \simeq 1$, unmixing in the liquid state occurs for $T < 2JQ$ ($2J = T_{AB} < T_B < T_A$). Figure 13 shows the three possible types of phase diagrams. At $T = 1.9$ a liquid-liquid critical point C_{AB} is found, and the binodal curve is not symmetrical in y since $L \neq 0$. However, this symmetry is recovered as $P \to \infty$. At $T = 1.8$, a triple point (liquids L_1 and L_2 and gas G) is observed together with an azeotrope Z. At $T = 1.685$ only the triple point is observed. At $T \simeq 1.85$, C_{AB} lies on the ebullition curve (triple point τ_1 at which the liquids L_1 and L_2 are identical), and at $T \simeq 1.75$, the azeotrope Z disappears

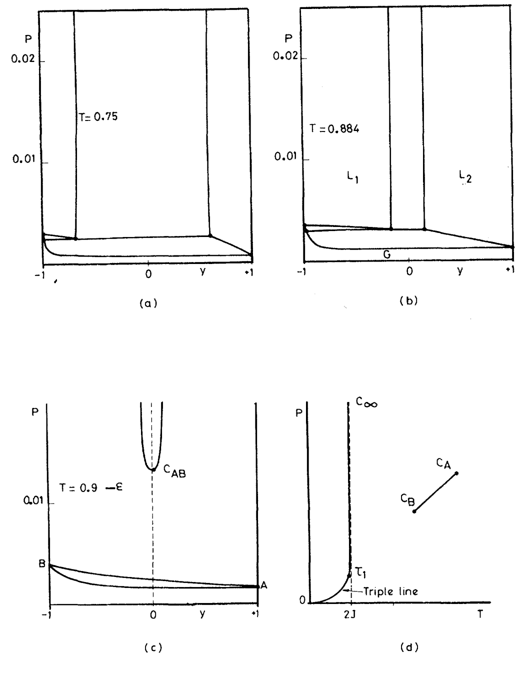

FIG. 11. Liquid-liquid and liquid-gas equilibrium curves for $K = 5.55$, $L = 0.5$, and $J = 0.45$ ($J_{AB} = 5.1$). (a) $T = 0.75$, (b) $T = 0.884$, (c) $T \lesssim 0.9$. L_1 and L_2 are two liquid phases and G is a gaseous phase. For $T \lesssim 0.9$, the triple point disappears and C_{AB} is a liquid-liquid critical point (not to scale). Liquid immiscibility disappears for $T > 2J = 0.9$. The equilibrium curves are then similar to that of Fig. 3. The (P, T) phase diagram is also given (not to scale). (d) (P, T) phase diagram: $\tau_1 C_\infty$ is the unmixing critical line, τ_1 is a critical end point.

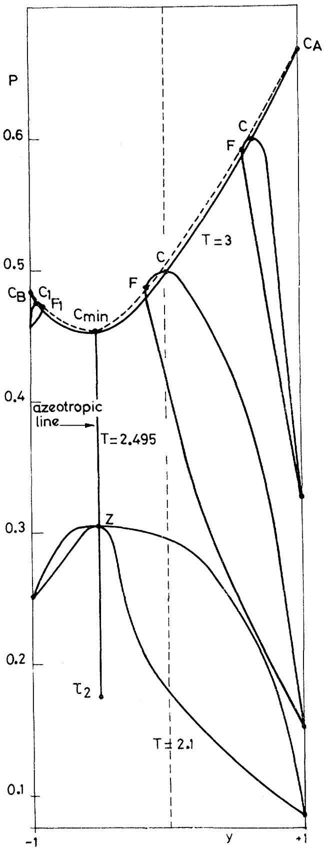

FIG. 12. Liquid-gas equilibrium at various temperatures ($T = 3$, 2.495, 2.1) for $K = 5$, $L = 0.5$, and $J = 1$ ($J_{AB} = 4$). The dashed line is the cricondentherm line. $C_{\min}$ is the minimum critical point and also the critical azeotrope. The azeotropic line has two end points $C_{\min}$ and τ_2.

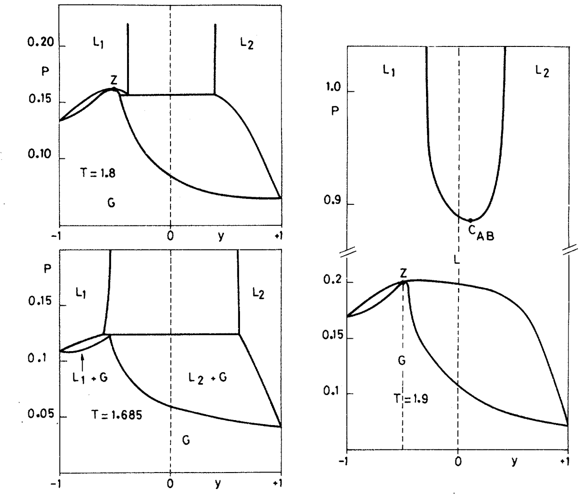

FIG. 13. Liquid-liquid and liquid-gas equilibrium in the (P,y) plane for $J=1$ at various temperatures ($T=1.9$, 1.8, 1.685). C_{AB} is an unmixing critical point and Z is an azeotropic point.

and three distinct phases are in equilibrium (triple point τ_2), so that the azeotropic line has two end points, $C_{\min}$ and τ_2. The saturation curves are given in Fig. 14 for various temperatures, and the phase diagrams in the (P,y) and (P,T) planes in Fig. 15. The (P,T) diagram exhibits two critical lines $C_AC_{\min}C_B$ and τ_1C_∞, an azeotropic line $C_{\min}\tau_2$, and a triple line $0\tau_2\tau_1$.

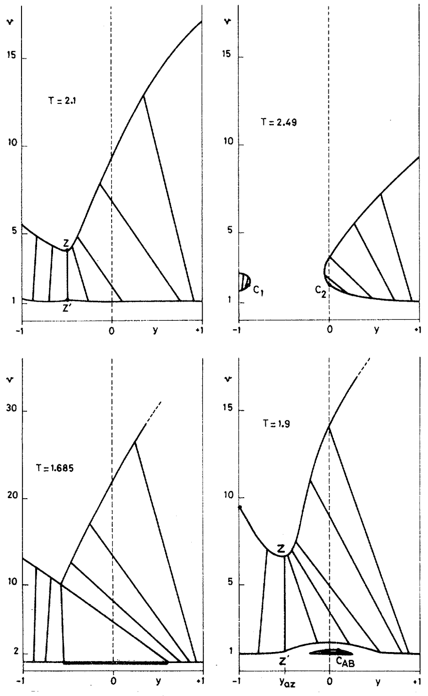

FIG. 14. Isothermal saturation curves for $J=1$ at $T=1.685$, 1.9, 2.1, and 2.49. For $T_{\min}<T<T_B$, the surface generated by the tie lines separates in two sheets, and two critical points are found.

$J=1.5$ ($J_{AB}=3$, $K=4.5$). (P,y) phase diagrams at various temperatures are given in Fig. 16. We have here $T_B<T_{AB}=3<T_A$, so that at $T=2.85$ liquid-liquid C_{AB} and liquid-gas C critical points are found. The two loops meet in C_α at a temperature T_α higher than T_B. At $T=2.4$, two loops are observed again. They meet in C_β at a temperature T_β higher than $T_{\min}=\frac{1}{2}(K-L^2/J)$, so that the minimum critical point and the azeotropic behavior are never observed, and the liquid-gas critical line is made of two branches C_AC_α and C_BC_β. Below T_β, a triple point is found. The phase diagrams in the (P,y) and (P,T) planes are given in Fig. 17.

Figure 18 shows the phase diagram at $T=2.35$ for $J=1.25$ ($J_{AB}=3.5$, $K=4.75$). Since $T_{AB}=T_B$ and $2J>\frac{1}{2}(K-L^2/J)=T_{\min}$, liquid immiscibility occurs in a temperature region in which two liquid-gas loops are observed, so that three loops are found in the (P,y) plane. At lower temperatures, two loops meet in C_α and then the two remaining loops meet at C_β. As for $J=1.5$, the minimum critical point and the azeotropic behavior are never observed and the liquid-gas critical curve is broken in two branches. $T_{\min}=T_{AB}$ for $J\simeq1.555$; for $J>J_0\simeq1.20$ $C_{\min}$ is not observed. For large values of J, $T_{AB}>T_A, T_B$ but the phase diagram remains similar to that of Fig. 16 for $J=1.5$.

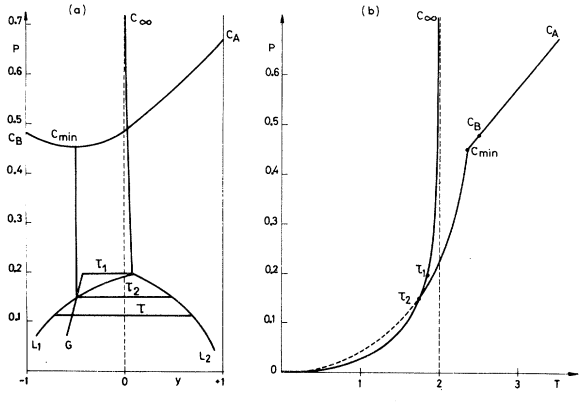

FIG. 15. Phase diagram for $J=1$ in the (P,y) and (P,T) planes. (a) τ_1 is the triple point found when C_{AB} lies on the ebullition curve ($T\simeq1.85$). The liquids L_1 and L_2 at equilibrium are then identical phases. τ_2 is the triple point found at $T\simeq1.75$: The azeotrope just disappears at this temperature while the gas G and the liquid L_1 at equilibrium are identical phases. The lines L_1, L_2, and G are the loci of the three phases at equilibrium at a triple point τ. (b) C_∞ is the unmixing critical point for $Q=1$. $0\tau_2\tau_1$ is the triple line, τ_1C_∞ the unmixing critical line, $\tau_2C_{\min}$ the azeotropic line, and $C_BC_{\min}C_A$ the liquid-gas critical line.

VI. CONCLUSION

We have shown that a spin-1 lattice-gas model with three interaction parameters (dipolar, quadrupolar, and crossed dipolar-quadrupolar interactions) describes many thermodynamic properties of a binary fluid, mainly condensation and phase separation. Many experimental phase diagrams have been reproduced theoretically. If $J=0$ ($J_{AB}=\bar{J}$), the solution is "ideal" and there is only one critical line. If $-0.5<J<0$ ($\bar{J}<J_{AB}<J_{AA}$), negative deviation from ideal behavior is found. If $J<-1$ ($J_{AA}<J_{AB}$), negative azeotropy and a maximum critical temperature are found. If $0<J<0.5$ ($J_{BB}<J_{AB}<\bar{J}$), then positive deviation from ideal behavior, phase separation in the liquid state, and a triple line are found. If $J>0.5$ ($J_{AB}<J_{BB}$), two critical lines, an azeotropic line, and a triple line are found, together with a minimum critical temperature. For larger values of J ($J_{AB}\ll J_{BB}$), the liquid-gas critical line is broken in two branches. All types of phase diagrams given in the literature[5-13] cannot be reproduced, however. For instance, the critical line C_AC_B in the P,T plane is generally not a straight line. Along a loop of constant composition in the P,T plane, the cricondentherm and cricondenbar points and the critical point may be found according to three different sequences (Figs. 6 and 9 of Ref. 12); also a critical azeotropic point is not always a minimum critical point (isotherms of Figs. 6 and 12 of Ref. 12 cannot be reproduced by our model). Similar limitations are found in the description of binary-liquid mixtures using the spin-$\frac{1}{2}$ Ising model: The binodal curve in the temperature-concentration plane is found to be symmetrical with respect

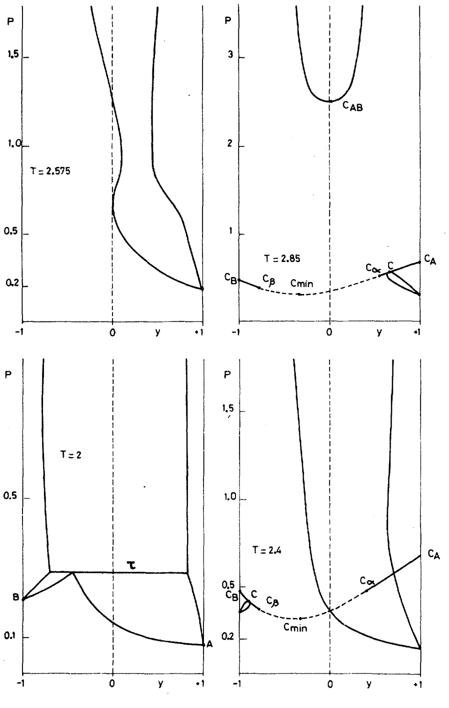

FIG. 16. Liquid-liquid and liquid-gas equilibrium for $K=4.5$, $L=0.5$, $J=1.5$ ($J_{AB}=3$) at different temperatures: $T=2$, 2.4, 2.575, and 2.85. C_α is the meeting point of the unmixing critical line and the liquid-gas critical line and C_β is the meeting point between the liquid-gas critical line and the triple line. The minimum critical point $C_{\min}$ is not observed since a triple point is found at $T_\beta > T_{\min}$. The critical line is made up of two branches C_AC_α and C_BC_β. The dashed line $C_\alpha C_\beta$ would be a part of the critical line if there were no unmixing in the liquid phase and no triple point τ.

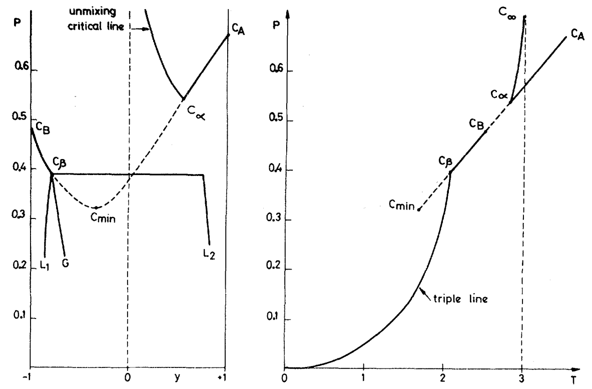

FIG. 17. Phase diagram for $J=1.5$ in the (P,y) and (P,T) planes. The liquid-gas critical line is made up of two branches.

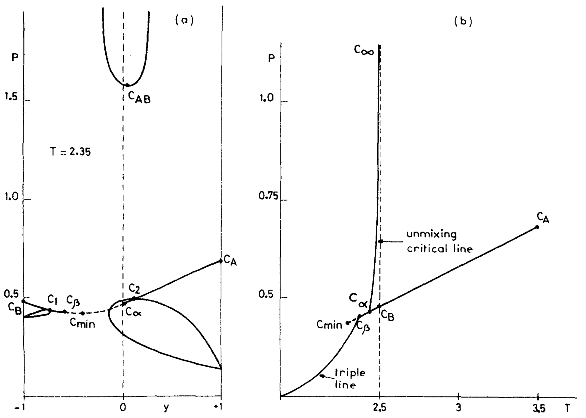

FIG. 18. (a) Liquid-liquid and liquid-gas equilibrium for $J=1.25$ at $T=2.35$. Two liquid-gas and one liquid-liquid critical points are found. As for $J=1$, the critical line is made up of two branches C_AC_α and C_BC_β, but here $T_\alpha < T_\beta$. The dashed line $C_\alpha C_\beta$ does not belong to the critical line because of unmixing in the liquid phase. (b) Phase diagram in the (P,T) plane. Each point of the line $C_\alpha C_\beta$ describes two critical points.

to equiconcentration, which is not always the experimental situation.

In conclusion, our model describes correctly regular solutions of spherical molecules, since only isotropic intermolecular interactions have been introduced. It does not take into account anisotropic- or position-dependent interactions or the possibility that the elementary volumes of the molecules A and B may be different. Let us consider finally the absorption of a binary gas. Our model with $L \neq 0$ represent not only the influence of pressure on the absorption, but also the possibility of a phase separation in the absorbed phase.[14] As stated in the Introduction, our model also describes ternary fluids kept at a constant pressure, and this point will be discussed in paper III,[4] together with the occurrence of tricritical points in binary and ternary mixtures.

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