Phase Transitions and Critical Points in a Model Three-Component System[1a]

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Abstract: A model of a three-component solution of difunctional ("diatomic") molecules of the types AA, AB, and BB is discussed. The postulated interactions are such as to favor the contacts of A ends with A ends and of B ends with B ends over the contacts of A ends with B ends. At low concentrations of the species AB there is phase separation into an AA-rich and a BB-rich phase, but a sufficiently high concentration of AB induces mutual solubility of AA and BB, and a plait point (critical point) is ultimately reached beyond which the solution is in equilibrium as a single phase. Near the plait point the shape of the binodal curve (two-phase coexistence curve) in the isothermal composition plane differs from the classical parabolic shape. The difference is analogous to that between the nearly cubic coexistence curves for liquid–vapor equilibrium found in real one-component fluids and the parabolic coexistence curves predicted by those equations of state of which the van der Waals equation is the prototype. Composition fluctuations in the neighborhood of the plait point, which are responsible for critical opalescence, are also discussed, and the rapidity with which the fluctuations diverge as the plait point is approached is likewise found to be nonclassical. At high concentrations of AB the model also shows an antiferromagnetic-like ordering in which the ordered state is roughly analogous to a liquid crystal or to the ordered state of a soap.

1. Introduction

Water and chloroform are almost completely immiscible, but when ethanol is added to the mixture the mutual solubility of the first two constituents is increased. As the concentration of ethanol is raised, the water-rich and chloroform-rich phases that are in equilibrium become progressively more alike until at some critical concentration of ethanol, which depends on the temperature, a plait point (critical point) is achieved where the two phases lose their separate identities and become a single, homogeneous liquid solution[2] (Figure 1). The action of the ethanol may perhaps be ascribed to its difunctionality. A number of ethanol molecules can surround a water molecule with the hydroxyl ends of the former pointing inward; the resulting complex consists outwardly of ethyl groups and is thus easily accommodated in the chloroform-rich phase. In this way water would have been made more soluble in chloroform than it would have been in the absence of ethanol, and the same argument with the roles of ethyl and hydroxyl reversed would account for the action of ethanol in increasing the solubility of chloroform in water. The point here is not to assert that this is the mode of action of the ethanol, for that is highly conjectural, but rather to observe that such a mechanism would be sufficient to produce a plait point of the character observed in the water–chloroform–ethanol system. This mechanism is reminiscent of one frequently invoked to explain the action of a soap. Its essential features are abstracted and incorporated in the model defined in section 2.

A one-component fluid near its liquid–vapor critical point is known to have properties deviating in important respects from those predicted by all the simple analytical equations of state, of which the van der Waals equation may be considered the prototype.[3] These "classical" equations of state either arise from some mean field approximation or they are empirical formulas based entirely on analytic functions. It may be supposed, analogously, that there would be signficant discrepancies between the behavior of a real ternary solution near a plait point and the predictions of the classical solution theories such as the multicomponent van der Waals equation of state or regular solution theory. As the critical point of a one-component fluid is approached, the density difference $\rho_l - \rho_g$ between coexistent liquid and vapor phases is predicted by all the classical equations of state to vanish proportionally to the square root of the difference $T_c - T$ between the temperature T and the critical temperature T_c

$$\rho_l - \rho_g \sim A(T_c - T)^{1/2} \qquad (1)$$

with some constant A characteristic of the substance. Thus, the coexistence curve in the temperature–density plane of the fluid is predicted to be parabolic in the neighborhood of the critical point, but in reality it is more nearly cubic

$$\rho_l - \rho_g \sim A(T_c - T)^{\beta} \qquad \beta \approx 1/3 \qquad (2)$$

Likewise, the mean-square fluctuation in the density, $\langle(\Delta\rho)^2\rangle$, which is determined by the isothermal compressibility and in turn determines the magnitude of the critical opalescence, is predicted by the classical equations of state to diverge proportionally to $(T - T_c)^{-1}$ as the critical point is approached from above

$$\langle(\Delta\rho)^2\rangle \sim B(T - T_c)^{-1} \qquad (3)$$

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(1) (a) Work supported by a grant from the Office of Saline Water, U. S. Department of the Interior. (b) National Science Foundation Predoctoral Fellow.

(2) A general description of the phenomenon may be found in most standard works on phase equilibrium, for example, A. Findlay, A. N. Campbell, and N. O. Smith, "The Phase Rule," 9th ed, Dover Publications, Inc., New York, N. Y., 1951, Chapter 14. For the water–chloroform–ethanol system, see Landolt-Börnstein, "Zahlenwerte und Funktionen," 6th ed, II/2c, Lösungsgleichgewichte II, Springer-Verlag, Heidelberg, 1964, p 548.

(3) For discussions of the inadequacies of the classical theories, as well as for summaries of the results of the Ising model (lattice gas) theories and the theoretical and experimental values of the critical point exponents which are quoted in this paper, see the recent reviews by M. E. Fisher, *Rept. Progr. Phys.*, **30**, 615 (1967); P. Heller, *ibid.*, **30**, 731 (1967); L. P. Kadanoff, *et al.*, *Rev. Mod. Phys.*, **39**, 395 (1967); and the recent analysis by M. S. Green, M. Vicentini-Missoni, and J. M. H. Levelt-Sengers, *Phys. Rev. Letters*, **18**, 1113 (1967).

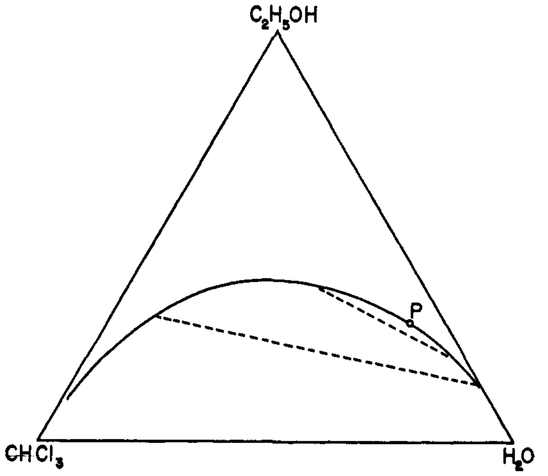

Figure 1. Schematic representation of the water–chloroform–ethanol system at a fixed temperature ~20°. Composition variables are mole fractions. Dashed lines are tie lines and the circle marks the plait point P.

with B another constant characteristic of the substance, but in reality the divergence is more rapid

$$\langle(\Delta\rho)^2\rangle \sim B(T - T_c)^{-\gamma} \qquad \gamma \approx 1.3 \tag{4}$$

Similarly, the classical solution theories all predict that the binodal curve (two-phase coexistence curve) in the isothermal composition plane of a ternary solution is parabolic in the neighborhood of the plait point, which is the analog of the incorrect eq 1, and that composition fluctuations diverge inversely proportionally to the first power of the distance from the plait point, which is the analog of the incorrect eq 3.

There are not yet experimental data of sufficient precision to confirm or deny the supposition that the neighborhood of a plait point, like the neighborhood of the critical point of a one-component system, is in reality nonclassical.[4] Theoretical models are now known, however, the partition functions of which can be found either numerically[5] or analytically,[6–9] but in any event without the approximations that lead inevitably to the classical results, and in all these models the supposition of nonclassical behavior is confirmed. Those which have been discussed analytically are all of one type, in that they are all reducible to the spin-$^1/_2$ Ising model by the "decoration" transformation.[10] The model introduced and analyzed in the present paper is again one which is reducible to the spin-$^1/_2$ Ising model, but is otherwise of a type essentially different from the earlier ones, and has as its physical basis the mechanism of difunctionality described above in connection with the water–chloroform–ethanol system. Its plait point behavior proves to be in exact accord with that of the earlier models, thus once more confirming the supposition of nonclassical behavior, and at the same time lending support to the conviction that the thermodynamic singularities at a plait point of a ternary system, like those at the critical point of a one-component system, are universal in character, not depending on the quantitative details of the molecular interactions that give rise to them.

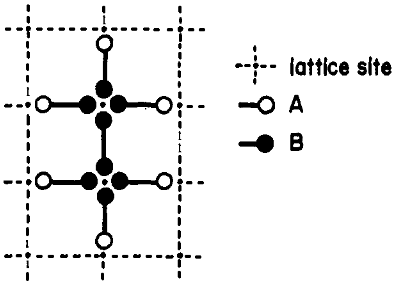

Figure 2. Two-dimensional illustration, based on the square-planar lattice, of an allowed configuration in which a BB molecule is surrounded by AB molecules so as to leave only A ends at the boundary of the complex.

The new model and the reduction of its partition function to that of the spin-$^1/_2$ Ising model are described in section 2. The binodal curve and the composition fluctuations in the neighborhood of the plait point are derived in section 3. In section 4 there is described another feature of the model which is interesting in its own right though irrelevant to the plait-point phenomenon. This is an antiferromagnetic-like ordering in which the ordered state is roughly analogous to a liquid crystal or to the ordered state of a soap, and it occurs at high concentrations of that species which, in the model, plays the role ascribed to the ethanol in the discussion above of the mechanism of difunctionality. The results are briefly summarized in section 5, where it is also pointed out that, though the model is a lattice model, this artificial aspect of it is probably not reflected in its plait-point behavior.

2. Model Three-Component Solution

Consider three species of difunctional ("diatomic") molecules AA, BB, and AB situated on, and completely filling, the bonds of a regular lattice such as the square planar in two dimensions or the simple cubic in three. Each end of a molecule is thus associated with a site of the lattice, and, if Z is the coordination number of the lattice (the number of bonds meeting at one site), then a total of Z molecule ends are associated with each site. The interaction energy between a pair of molecules is taken to be $+\infty$ if they are on the same bond of the lattice, so the bonds are forced to be singly occupied. Furthermore, the interaction energy is also taken to be $+\infty$ if the A end of one molecule and the B end of another are associated with the same site of the lattice, while the interaction energy is taken to be 0 otherwise. Thus, A ends may associate with each other, as may B ends with each other, but A's and B's repel infinitely strongly. In Figure 2 is shown an example of an allowed configuration in which a BB molecule is surrounded by AB molecules in such a way that the central BB is insulated; at the boundaries of the complex are only A ends so the complex as a

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[4] If it is granted that the plait point of a binary system at variable pressure is in principle the same as that of a ternary system at fixed pressure, with "vacuum" in the former case playing the role of a third component, then the measurements on the neon–argon system by W. B. Streett, *J. Chem. Phys.*, **46**, 3282 (1967), are relevant to the question raised here. Streett's data have been analyzed by J. Zollweg (private communication) who finds that the binodal curves near their plait points are indeed more nearly cubic than parabolic.

[5] F. H. Stillinger, Jr., and E. Helfand, *J. Chem. Phys.*, **41**, 2495 (1964).

[6] B. Widom, *ibid.*, **46**, 3324 (1967).

[7] G. Neece, *ibid.*, **47**, 4112 (1967).

[8] R. K. Clark, *ibid.*, **48**, 741 (1968).

[9] R. K. Clark and G. Neece, *ibid.*, in press.

[10] M. E. Fisher, *Phys. Rev.*, **113**, 969 (1959).

whole could be accommodated in a phase that was predominantly AA, while an uninsulated BB molecule could not have been. Moreover, as a consequence of the conditions that define the model, the Z molecule ends associated with each lattice site are either all A ends or all B ends, but never some of each, so that in any allowable configuration of the system every site may be unambiguously identified as an A site or a B site. It is this that allows a direct transcription to the spin-$^1/_2$ Ising model, where each lattice site is occupied by a spin in one of two possible spin states.

Because the potential energy in this system never varies, being always 0 in every allowable configuration, the temperature is not a significant variable in the model, and, in particular, the coexistence curve that one obtains in an isothermal composition plane at any one temperature is the same as that at any other.[6] The model can be extended to include temperature as a significant variable; it is then no longer related to the spin-$^1/_2$ Ising model on the original lattice, but rather to that on a decorated lattice in which each site is replaced by a cluster of sites, completely interconnected, with a coupling constant between clusters that differs from that within a cluster. We here restrict ourselves, however, to treating only the more primitive model.

Let N_{AA}, N_{BB}, and N_{AB} be the number of molecules of each species in the mixture, with x_{AA}, x_{BB}, and x_{AB} their respective mole fractions. If C is the total number of sites on the lattice, $^1/_2ZC$ is the total number of bonds, so

$$N_{AA} + N_{BB} + N_{AB} = {}^1/_2ZC \tag{5}$$

while

$$x_{AA} + x_{BB} + x_{AB} = 1 \tag{6}$$

The corresponding activities z_{AA}, z_{BB}, and z_{AB} are all infinite because by the definition of the model every available space on the lattice is occupied, but the ratio of any pair of these activities is in general finite, and modified activity variables ζ and ξ, defined by

$$\zeta = (z_{BB}/z_{AA})^{1/2} \qquad \xi = [z_{AB}/(z_{BB}z_{AA})^{1/2}]^{1/2} \tag{7}$$

are important variables in the theory. Likewise, the chemical potentials μ_{AA}, μ_{BB}, and μ_{AB}, related to the activities by

$$\mu_{AA} = kT \ln z_{AA}, \text{ etc.} \tag{8}$$

where k is Boltzmann's constant and T is the absolute temperature, are all infinite, but the difference of any pair of them is in general finite.

So long as $N_{AA} + N_{BB} + N_{AB}$ is fixed, so that

$$\mathrm{d}(N_{AA} + N_{BB} + N_{AB}) = 0$$

the relation

$$\begin{aligned}\mu_{AA}\,\mathrm{d}N_{AA} + \mu_{BB}\,\mathrm{d}N_{BB} + \mu_{AB}\,\mathrm{d}N_{AB} = \\ {}^1/_2(\mu_{BB} - \mu_{AA})\,\mathrm{d}(N_{BB} - N_{AA}) + \\ {}^1/_2[\mu_{AB} - {}^1/_2(\mu_{AA} + \mu_{BB})]\,\mathrm{d}(N_{AB} - N_{AA} - N_{BB})\end{aligned} \tag{9}$$

holds as an identity, and in the present model the differential coefficients on the right-hand side are manifestly finite for they involve only differences of the chemical potentials μ_{AA}, μ_{BB}, and μ_{AB} taken in pairs. If now $Q(N_{AA}, N_{BB}, N_{AB})$ is the number of distinguishable ways of placing the N_{AA} molecules AA, the N_{BB} molecules BB, and the N_{AB} molecules AB on the $^1/_2ZC$ bonds of the lattice, one molecule on each bond, and subject to condition that only A ends or only B ends meet at any one site, it is then a consequence of eq 9 and of the definitions in eq 7 and 8 that the partition function of the model solution, for the ensemble in which ζ, ξ, C are fixed, is

$$Y(\zeta,\xi,C) = \sum_{\substack{\text{all } N_{AA},\, N_{BB},\, N_{AB} \\ \text{such that} \\ N_{AA} + N_{BB} + N_{AB} = {}^1/_2ZC}} Q(N_{AA},N_{BB},N_{AB})\zeta^{N_{BB} - N_{AA}}\xi^{N_{AB} - N_{AA} - N_{BB}} \tag{10}$$

Fixed C, by eq 5, is equivalent to fixed $N_{AA} + N_{BB} + N_{AB}$. It is seen from the structure of the summand in eq 10 that composition variables δ and σ defined by

$$\begin{aligned}\delta &= x_{BB} - x_{AA} \\ \sigma &= x_{AB} - x_{AA} - x_{BB}\ (= 2x_{AB} - 1)\end{aligned} \tag{11}$$

are directly associated with the modified activities ζ and ξ, and these prove to be the significant composition variables in the model.

Now consider the same lattice, alternatively, as the underlying lattice of an Ising magnet, defined as follows. Let there be a spin ↑ or ↓ at each lattice site; let $N_\uparrow$ be the number of ↑ spins and $N_\downarrow$ the number of ↓ spins, so that $N_\uparrow + N_\downarrow = C$, the number of sites. The directions ↑ or ↓ are taken to be respectively parallel or antiparallel to the direction of an external magnetic field. Also let $N_{\uparrow\uparrow}$ be the number of pairs of neighboring ↑ spins, $N_{\downarrow\downarrow}$ the number of pairs of neighboring ↓ spins, and $N_{\uparrow\downarrow}$ the number of pairs of neighboring spins for which one member of the pair is ↑ and one ↓. The definition of the Ising model is then completed by taking the energy E associated with any configuration of the C spins to be

$$E = J(N_{\uparrow\downarrow} - N_{\uparrow\uparrow} - N_{\downarrow\downarrow}) - H(N_\uparrow - N_\downarrow) \tag{12}$$

with J a constant spin–spin coupling parameter with the dimensions of energy, and with H the product of the magnetic field strength and the constant magnetic moment per spin, so that it, too, has the dimensions of energy. Note that with Z the coordination number of the lattice, the relation

$$N_{\uparrow\uparrow} - N_{\downarrow\downarrow} = {}^1/_2Z(N_\uparrow - N_\downarrow) \tag{13}$$

is an identity, so that the energy of the Ising system can equally well be taken as

$$E = J(N_{\uparrow\downarrow} - N_{\uparrow\uparrow} - N_{\downarrow\downarrow}) - (2/Z)H(N_{\uparrow\uparrow} - N_{\downarrow\downarrow}) \tag{14}$$

and that the relation

$$N_{\uparrow\uparrow} + N_{\downarrow\downarrow} + N_{\uparrow\downarrow} = {}^1/_2Z(N_\uparrow + N_\downarrow) = {}^1/_2ZC \tag{15}$$

is also an identity.

If we now identify every A-end site in the solution model as a spin ↓ site and every B-end site as a spin ↑ site, then, because of eq 13 and 15, the summation in eq 10 is the same as a sum over all $N_\uparrow$ and $N_\downarrow$ subject to $N_\uparrow + N_\downarrow = C$, while the assignments of molecules to bonds in the solution model are in 1:1 correspondence with the assignments of spins to sites in the Ising model, so the combinatorial factor Q in the summand of eq 10 is identical with the combinatorial factor of the Ising model. It follows, upon also taking account of eq 14, that the fixed ζ, ξ, C partition function of the solution model in eq 10 is the same as the fixed H, θ, C partition function of the Ising model at temperature θ, with the activity variables ζ and ξ of the solution model related to the magnetic field and to the temperature of the equivalent Ising model by

$$\zeta^{1/2Z} = e^{H/k\theta} \tag{16}$$

$$\xi = e^{-J/k\theta} \tag{17}$$

It is convenient to symbolize $\exp(-J/k\theta)$ by X, so that the second of these relations is $\xi = X$. The solution composition variables δ and σ defined in eq 11 are related respectively to the magnetization per spin, I, and to the zero-field configurational energy, E_0, of the Ising model, defined by

$$I = (N_\uparrow - N_\downarrow)/C$$

$$E_0 = E_{H=0} = J(N_{\uparrow\downarrow} - N_{\uparrow\uparrow} - N_{\downarrow\downarrow}) \tag{18}$$

The various connections and equivalences, and some of the definitions, are summarized in Table I. It should be noted that the only variable temperature and configurational energy that appear are those of the equivalent Ising model; as pointed out before, the temperature of the solution model is irrelevant and its configurational energy is always 0.

Table I. Equivalences between the Variables of the Solution Model and Those of the Spin-$^1/_2$ Ising Model

Solution model	Ising model
$\delta = x_{\mathrm{BB}} - x_{\mathrm{AA}}$	I
$\sigma = 2x_{\mathrm{AB}} - 1$	$(2/ZJC)E_0$
ξ	$X = \exp(-J/k\theta)$
$\zeta^{1/2Z}$	$\exp(H/k\theta)$

3. Binodal Curve and Composition Fluctuations in the Neighborhood of the Plait Point

The spontaneous magnetization of the equivalent Ising model is reflected in phase separation in the solution model, and the Curie point of the ferromagnet, where the spontaneous magnetization vanishes, becomes a plait point in the ternary system. If E_c is the value of the zero-field configurational energy of the Ising model at its Curie point, then the plait point in the composition plane of the solution model occurs at $\delta = 0$ and $\sigma = (2/ZJC)E_c$. That $\delta = 0$ at the plait point implies $x_{\mathrm{AA}} = x_{\mathrm{BB}}$ there, an obvious consequence of the symmetry of the model with respect to the species AA and BB. The value of E_c/JC in the Ising model, hence also the value of x_{AB} at the plait point of the solution model, depends only on the dimensionality and topology of the underlying lattice, but on nothing else. For the common three-dimensional lattices $(2/ZJC)E_c$ ranges between about[11] -0.33 and -0.24, so the value of x_{AB} at the plait point is in the range 0.34–0.38, and correspondingly the common value of x_{AA} and x_{BB} at the plait point is in the range 0.33–0.31. Thus, in this solution model the plait point lies close to the centroid of the equilateral x_{AA}, x_{BB}, x_{AB} composition triangle.

The ferromagnetic phase transition occurs only in zero field and at temperatures θ less than the Curie temperature θ_c. The magnitude I_0 of the spontaneous magnetization is a function of temperature, $\mathrm{f}(X)$ say

$$I_0 = |I_{H=0}| = \mathrm{f}(X)$$

which is defined for $\theta \leq \theta_c$ and vanishes at $\theta = \theta_c$. Then from the correspondences in Table I, the bindoal curve is determined by

$$|\delta| = \mathrm{f}(\xi) \tag{19}$$

and at every point on the binodal curve and within the two-phase region

$$\zeta = 1 \tag{20}$$

Equation 19 is not yet fully explicit, for to know the form of the binodal curve as it would appear in a diagram such as that of Figure 1 would require knowing δ as a function of the second composition variable σ rather than as a function of the activity variable ξ. However, the zero-field configurational energy E_0 of the Ising model is also a function of temperature, so that

$$(2/ZJC)E_0 = \mathrm{g}(X)$$

say. Then throughout the two-phase region of the solution model, including all points of the binodal curve

$$\sigma = \mathrm{g}(\xi) \tag{21}$$

In principle, with the functions f and g known from the Ising model, the activity variable ξ could be eliminated from eq 19 and 21 to yield the equation of the binodal curve in the δ–σ composition plane of the solution. This will now be done, but only for the immediate neighborhood of the critical point.

For temperatures θ less than but close to the Curie temperature θ_c, the zero-field energy of the Ising model deviates from its value at the critical point proportionally to a power of $\theta_c - \theta$ or, equivalently, of $X_c - X$

$$\mathrm{g}(X_c) - \mathrm{g}(X) \sim (X_c - X)^{1-\alpha'} \tag{22}$$

$$[X < X_c = \exp(-J/k\theta_c)]$$

The exponent α' is the index of the divergence of the specific heat of the Ising system as $\theta \rightarrow \theta_c$ from below; *i.e.*, the specific heat diverges as $(X_c - X)^{-\alpha'}$. The spontaneous magnetization of the ferromagnet is likewise proportional, near the Curie point, to a power of $\theta_c - \theta$ or, equivalently, of $X_c - X$

$$\mathrm{f}(X) \sim (X_c - X)^{\beta} \tag{23}$$

which is analogous to the difference in density between coexistent phases of a one-component fluid near its critical point, as given by eq 2. From eq 19 and 21–23 it follows that near the plait point the binodal curve in the δ–σ composition plane of the mixture is given by

$$|\delta| \sim (\sigma_c - \sigma)^{\beta/(1-\alpha')} \tag{24}$$

where σ_c is the value of $\sigma = 2x_{\mathrm{AB}} - 1$ at the plait point. In the event that $\alpha' = 0$, corresponding to a logarithmic divergence of the Ising model specific heat, the right-hand side of eq 24 must be slightly modified.[6]

The binodal curve and plait point are shown schematically in the lower part of the composition triangle

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[11] These are the negatives of the quantities called U_c/U_0 in the table given by M. E. Fisher, *J. Math. Phys.*, **4**, 278 (1963).

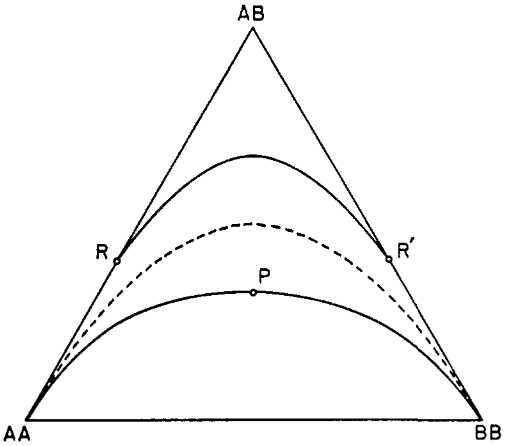

Figure 3. Phase diagram of the model system. Composition variables are mole fractions. The lowest curve is the binodal, with the plait point P; tie lines (not shown) are horizontal. The dashed curve, not a locus of phase transitions, separates the region of compositions where the solution is analogous to a ferromagnet (lower region) from that in which it is analogous to an antiferromagnet (upper region). The curve RR′ is the locus of phase transitions associated with the onset of long-range order.

in Figure 3. The binodal curve is symmetric about the vertical line $x_{AA} = x_{BB}$. Near the plait point it is characterized by the exponent $\beta/(1 - \alpha')$, just as are the coexistence curves of the earlier models.[6-9] Because α' is small, if not zero, $\beta/(1 - \alpha')$ is close to β, the exponent that characterizes the temperature dependence of the spontaneous magnetization of the Ising model; and this β, in turn, is close to $^1/_3$, just as is the experimental value of the exponent that characterizes the temperature–density coexistence curve of a one-component fluid, as given by eq 2. The plait point is nonclassical, for $\beta/(1 - \alpha')$ is in any event not $^1/_2$.

We may also determine the way in which the mean-square composition fluctuations $\langle(\Delta\delta)^2\rangle$ and $\langle(\Delta\sigma)^2\rangle$ in any small but fixed subvolume of the system (or, alternatively, in the whole system at fixed ζ, ξ, and C) diverge as the plait point is approached through the one-phase region. The first of these, which proves to be the more rapidly divergent of the two, is the major factor in determining the extent of the critical opalescence, or, more specifically, the magnitude of the zero-angle light scattering, in the neighborhood of the plait point.

Consider first those states of the system that, in Figure 3, would be represented by points above the plait point on the vertical line $x_{AA} = x_{BB}$, where the fluctuations in δ that occur are then fluctuations from the mean value 0. In the equivalent Ising model the mean-square fluctuations $\langle(\Delta E_0)^2\rangle$ in the zero-field configurational energy of the system, at fixed temperature, are determined by, and are proportional to, the zero-field specific heat. The latter, in turn, diverges proportionally to a negative power, $-\alpha$ say, of $\theta - \theta_c$ or of $X - X_c$, as the Curie temperature is approached from above. (Like the exponent α' that characterizes the divergence of the specific heat when the Curie point is approached from below, α is small or zero; if zero, the divergence is logarithmic and the formulas given below would again require slight modification.[6]) Thus

$$\langle(\Delta E_0)^2\rangle \sim (X - X_c)^{-\alpha} \quad (25)$$

Likewise, the mean-square fluctuations $\langle(\Delta I)^2\rangle$ in the magnetization are determined by, and are proportional to, the magnetic susceptibility. The latter, in turn, in the absence of an external magnetic field, diverges proportionally to a negative power, $-\gamma$ say, of $\theta - \theta_c$ or of $X - X_c$, as the Curie temperature is approached from above. Thus, as the Curie point is approached from above, in zero field, the mean-square fluctuations of the magnetization away from the value 0 are given by

$$\langle(\Delta I)^2\rangle \sim (X - X_c)^{-\gamma} \quad (26)$$

From the correspondences in Table I, these formulas for $\langle(\Delta E_0)^2\rangle$ and $\langle(\Delta I)^2\rangle$ in the Ising model become

$$\langle(\Delta\sigma)^2\rangle \sim (\xi - \xi_c)^{-\alpha}$$

and

$$\langle(\Delta\delta)^2\rangle \sim (\xi - \xi_c)^{-\gamma}$$

in the solution model, giving the mean-square fluctuations in σ and δ as the plait point is approached through the one-phase region along the line $x_{AA} = x_{BB}$ in the composition plane. But because the exponent α characterizes the divergence of the zero-field specific heat of the Ising model as $\theta \rightarrow \theta_c$ from above, the function $g(X)$ that yields the zero-field configurational energy is such that

$$g(X) - g(X_c) \sim (X - X_c)^{1-\alpha} \qquad (X > X_c)$$

in analogy with eq 22. Therefore, in the solution model, along the line $x_{AA} = x_{BB}$

$$\sigma - \sigma_c = 2(x_{AB} - x_{AB}{}^c) \sim (\xi - \xi_c)^{1-\alpha}$$

where $x_{AB}{}^c$ is the value of x_{AB} at the plait point, so the mean-square composition fluctuations are

$$\langle(\Delta\sigma)^2\rangle \sim (x_{AB} - x_{AB}{}^c)^{-\alpha/(1-\alpha)} \quad (27)$$

$$\langle(\Delta\delta)^2\rangle \sim (x_{AB} - x_{AB}{}^c)^{-\gamma/(1-\alpha)} \quad (28)$$

having been expressed finally in terms of the distance $x_{AB} - x_{AB}{}^c$ from the plait point as measured along the line $x_{AA} = x_{BB}$ in the composition triangle. These expressions for the mean-square fluctuations in composition are identical with their analogs in the earlier models.[6,8]

Because α is small, if not zero, $\gamma/(1 - \alpha)$ is close to γ, the exponent that characterizes the temperature dependence of the magnetic susceptibility of the Ising model, and this γ, in turn, is close to 1.3, just as is the experimental value of the exponent that characterizes the compressibility (and hence the mean-square fluctuations in density) of a one-component fluid, as given by eq 4. The plait point is then also nonclassical with respect to composition fluctuations, for in the classical theories the analog of $\langle(\Delta\delta)^2\rangle$ diverges proportionally to the reciprocal of the distance from the plait point, whereas $\gamma/(1 - \alpha)$ is in any event not 1.

Because $\alpha \ll \gamma$, the divergence of $\langle(\Delta\sigma)^2\rangle$ is much weaker than that of $\langle(\Delta\delta)^2\rangle$. The mean-square fluctuations in any composition variable which is not merely a function of x_{AB} alone, *i.e.*, of σ alone, but depends also on δ, would show the stronger divergence, proportional to the power $-\gamma/(1 - \alpha)$ of the distance from the plait point. This result is undoubtedly general; that is, in any three-component solution there will be one composition variable (not necessarily the mole fraction of one of the components), fluctuations in which, like those in x_{AB} in the present model, are only weakly divergent, their divergence being characterized by the exponent $\alpha/(1 - \alpha)$, while all composition variables that are not merely functions of that one alone would undergo the more strongly divergent fluctuations characterized by the exponent $\gamma/(1 - \alpha)$.

In either of the two spontaneously magnetized states (either net spin $\uparrow$ or net spin $\downarrow$) below the Curie point, in zero field, the mean-square fluctuations in the magnetization of the Ising model diverge proportionally to a power $-\gamma'$ of $\theta_c - \theta$ or of $X_c - X$

$$\langle(\Delta I)^2\rangle \sim (X_c - X)^{-\gamma'}$$

The exponent γ' may in principle differ from the exponent γ in eq 26 that determines $\langle(\Delta I)^2\rangle$ when the critical point is approached from the high-temperature side, and there are indeed suggestions that γ' may be slightly greater than γ, perhaps $\gamma' \approx 1.32$ as opposed to $\gamma \approx 1.25$. According to eq 23 the spontaneous magnetization itself is proportional to $(X_c - X)^\beta$. Therefore, from the correspondences in Table I, and from the known form of the binodal curve as given by eq 24, the mean-square fluctuations in δ that occur in solutions of mean composition x_{AA}, x_{BB}, x_{AB}, just at the coexistence curve near the plait point, may be described by

$$\langle(\Delta\delta)^2\rangle \sim |\delta|^{-\gamma'/\beta} \sim |x_{\mathrm{BB}} - x_{\mathrm{AA}}|^{-\gamma'/\beta}$$

or alternatively by

$$\langle(\Delta\delta)^2\rangle \sim (\sigma_c - \sigma)^{-\gamma'/(1-\alpha')} \sim (x_{\mathrm{AB}}{}^{c} - x_{\mathrm{AB}})^{-\gamma'/(1-\alpha')}$$

The second of these is to be compared with eq 28, which determines the nature of the divergence of the composition fluctuations as the plait point is approached from above, rather than along, the binodal curve.

As the plait point is approached the distance over which the local composition at once point of the solution is correlated with that at another increases without limit, and the divergence of the fluctuations in composition may be ascribed to the divergence of this correlation distance. Close to the plait point the correlation length is much larger than the lattice spacing, and it is this that allows us to argue in section 5 that the presence of the underlying lattice is probably irrelevant to the plait-point behavior of the model.

4. Antiferromagnetic-Like Ordering

The dashed curve in Figure 3 is the locus $\xi = 1$, that is, by the definition of ξ in eq 7, the locus of solution compositions at which the activity of the species AB is the geometric mean of the activities of AA and *BB*. The condition $\xi = 1$ occurs at $J/\theta = 0$ in the equivalent Ising model and so marks the transition between those states of the solution ($\xi < 1$) that are in correspondence with states of a ferromagnetic Ising model ($J/\theta > 0$) and those ($\xi > 1$) that are in correspondence with states of an antiferromagnetic Ising model ($J/\theta < 0$). The plait point and binodal curve lie below this locus and reflect the spontaneous magnetization and Curie point of an equivalent ferromagnet, but above it there must be another phase-transition curve reflecting the onset of sublattice magnetization in an equivalent antiferromagnet.[12] Unlike the binodal curve, this would not be a coexistence curve bounding a two-phase region, for the transitions it would mark would be of higher than first order and would not be accompanied by phase separation.

The demarcation line $\xi = 1$, or $J/\theta = 0$, is not itself a locus of phase transitions but rather may be looked upon as the locus of points representing the equilibrium states that a ferromagnet ($J > 0$) and an antiferromagnet ($J < 0$) have in common at infinite temperature, but also at infinite magnetic field, with H/θ finite and variable. In this condition there is in general a nonvanishing net spin determined by H/θ, but there is no correlation between spins, so that $\mathrm{N}_{\uparrow\uparrow} = {}^1\!/_2 ZC\cdot(N_\uparrow/C)^2$, $N_{\downarrow\downarrow} = {}^1\!/_2 ZC(N_\downarrow/C)^2$ and $N_{\uparrow\downarrow} = ZC(N_\uparrow\cdot N_\downarrow/C^2)$, and hence $N_{\uparrow\downarrow}{}^2/N_{\uparrow\uparrow}N_{\downarrow\downarrow} = 4$. Thus, the equation of the locus $\xi = 1$ in the composition plane of the solution is

$$x_{\mathrm{AB}}{}^2/x_{\mathrm{AA}}x_{\mathrm{BB}} = 4 \tag{29}$$

and it is this which is plotted as the dashed curve in Figure 3. At the highest point on the locus $x_{\mathrm{AA}} = x_{\mathrm{BB}} = {}^1\!/_4$, $x_{\mathrm{AB}} = {}^1\!/_2$. (The condition $\xi = 1$, it was observed, is $z_{\mathrm{AB}}{}^2 = z_{\mathrm{AA}}z_{\mathrm{BB}}$, which is equivalent to $2\mu_{\mathrm{AB}} = \mu_{\mathrm{AA}} + \mu_{\mathrm{BB}}$; this, together with eq 29, means that on the locus in question the chemical potentials and concentrations satisfy the same relations as would be satisfied if the solution were an ideal mixture of diatomic molecules with A and B heavy isotopes of the same element and with the three constituents related by the mobile chemical equilibrium AA + BB $\rightleftarrows$ 2AB. This is a purely formal analogy, however, and holds only on the locus $\xi = 1$; the solution is in reality not ideal, and the three constituents are in reality independent, not in chemical equilibrium.)

We now consider the ordering process that occurs at high ξ, or high x_{AB}. In the extreme where $x_{\mathrm{AB}} = 1$, in any allowable configuration of the molecules every A site necessarily has only B sites for its Z neighbors, and *vice versa*. If the lattice is composed of two interpenetrating sublattices, such that the neighbors of the sites of one of the sublattices are all to be found on the other (the simple cubic lattice, for example, is of this nature), then in the extreme $x_{\mathrm{AB}} = 1$ all the A sites are on one sublattice and all the B sites on the other. At low concentrations of AB, by contrast, such inequalities in the sublattice occupancies can be at most short-ranged, and each infinite sublattice contains half of all the A sites and half of all the B sites. There is a transition curve, such as the curve RR′ in Figure 3, discussed below, which marks the onset of long-range sublattice ordering; in states of the system represented by points above, but close to, the transition curve, slightly more than half the A sites and slightly less than half the B sites are to be found on one sublattice, and *vice versa* on the other. This inequality in sublattice occupancy becomes more extreme the more deeply one penetrates into the upper region of the phase diagram, until at $x_{\mathrm{AB}} = 1$ the sublattice ordering is complete. In the equivalent Ising antiferromagnet ($J < 0$), it is energetically favorable for neighboring spins to be antiparallel. At temperatures below an antiferromagnetic phase transition temperature that depends on the magnetic field, one sublattice will contain more than half of all

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(12) We are grateful to J. F. Nagle for a helpful discussion of this question.

the $\uparrow$ spins and less than half of all the $\downarrow$ spins, and *vice versa* on the other sublattice. As $\theta \rightarrow 0$ in the absence of an external field (analogous to $x_{AB} \rightarrow 1$ in the solution), the antiferromagnet approaches the extreme condition in which every site on one sublattice is a spin $\uparrow$ site and every site on the other is a spin $\downarrow$ site; there is then exact and perfect $\uparrow, \downarrow$ alternation from site to site of the composite lattice.

In zero field the mean magnetization of the antiferromagnet vanishes, so $N_\uparrow = N_\downarrow$, and in this condition the onset of unequal sublattice occupancy is known to occur when the configurational energy has the same value, E_c, that it has at the Curie point of the corresponding ferromagnet, *i.e.*, of the ferromagnet which has a coupling constant J of the same magnitude but opposite (now positive) sign. Thus, one point on the phase-transition curve we are seeking in the upper region of the composition triangle must be the point $\delta = 0$, $\sigma = -\sigma_c$, that is, the point

$$x_{AA} = x_{BB} = {}^1/_2 x_{AB}{}^c \qquad x_{AB} = 1 - x_{AB}{}^c \quad (30)$$

where $x_{AB}{}^c$, as before, is the value of x_{AB} at the plait point of the binodal curve that appears in the lower region of the composition triangle.

At $\theta = 0$ in a nonvanishing external magnetic field, the equilibrium configuration of the Ising antiferromagnet is either that of perfect parallel spin alignment or perfect spin alternation, according to the relative values of H and $|J|$. The transition between these two possibilities occurs when $H = {}^1/_2 Z|J|$, for then the energies of the two competing configurations are equal. This condition of the antiferromagnet corresponds not to a single point in the composition triangle of the solution but to the whole of the sides opposite the AA and BB vertices, whereas, still at $\theta = 0$, all values of H greater than ${}^1/_2 Z|J|$ correspond only to the AA and BB vertices, while all values of H less than ${}^1/_2 Z|J|$ correspond only to the AB vertex. The points R and R′ in Figure 3, where the phase transition curve we are seeking intersects the sides of the composition triangle, are known, then, to correspond to the condition $\theta = 0$, $H = {}^1/_2 Z|J|$ of the equivalent antiferromagnet. But to know the location of these points on the sides of the composition triangle requires a knowledge not of θ and H there but of E and I, which is equivalent to locating the transition density of the hard-core lattice gas. The value of x_{AB} at the points R and R′ is, more specifically, the ratio of the transition density to the close-packed density of the hard-core lattice gas, and is[13] 0.43 for the simple cubic lattice and 0.36 for the body-centered cubic lattice. These points R and R′, together with the one point given by eq 30, are the only points of the entire phase-transition curve which are known, and, furthermore, it is only at these points that the sublattice ordering has been quantitatively characterized.

The whole of the phase-transition curve can be found in the Bethe–Guggenheim approximation. Either from the potential distribution formulation of statistical mechanics[14] as applied to a certain pseudo-lattice (a Cayley tree), or by rearrangement of an equation given by Kasteleijn[15] in connection with the statistical mechanics of an adsorbed monolayer, one may find the transition curve in question to be given in the Bethe–Guggenheim approximation by

$$1 + \sigma = \frac{Z}{Z - 1}(1 - \delta^2)$$

that is, by

$$2x_{AB} = \frac{Z}{Z - 1}[1 - (x_{BB} - x_{AA})^2]$$

This approximation constitutes one of the classical, mean-field solution theories, however, so its account of the sublattice ordering, like its description of the shape of the binodal curve near the plait point, is certain to be erroneous.

5. Summary and Discussion

The major results of this theory are those on the nonclassical nature of the plait-point phenomenon. The binodal curve in the neighborhood of the plait point is not parabolic, which contradicts the predictions of all the classical solution theories; instead, the binodal curve is described by eq 24, which shows it to be more nearly cubic. Likewise, composition fluctuations diverge not as the reciprocal of the distance from the plait point, which is the prediction of the classical theories, but more rapidly, as given by eq 28. These nonclassical results are in exact accord with those found in other solution models that, like the present one, avoid approximations of the mean-field type. That the nonclassical results have so far been found only in lattice models does not make them inapplicable to real liquid solutions. It was pointed out in section 3 that, as the plait point is approached, the composition correlation length becomes much larger than the lattice spacing. It is, therefore, highly probable that the underlying lattice, as well as the specific form of the short-ranged intermolecular forces and other model-dependent details, are all quite irrelevant in the neighborhood of the plait point, and that the behavior expressed by eq 24 and 28 is universal. In these respects the situation may be like that at the liquid–vapor critical point of a one-component fluid, where the thermodynamic singularities are nonclassical and apparently universal, and are described with great fidelity by the lattice gas model.

The present model was also seen to imply, at certain compositions, a transition to an ordered state. Though ternary liquid solutions do not in general undergo the sublattice ordering found in section 4, it should be noted that many organic soaps do exhibit liquid crystal and other ordered phases. Since the action of the AB molecules in increasing the mutual solubility of AA and BB is suggestive of the action of a soap, as mentioned earlier, it may be significant that the model solution undergoes this transition at high concentrations of AB. Here, however, the character of the transition may well depend on the details of the model. We have seen that the long-range order of the model's lattice structure does not in itself imply long-range order in the composition of the solution, which is all that could have affected the plait point; but the structural order of the lattice does imply long-range correlations of molecular orientations, for in the present model the molecules are constrained to lie along bonds of the lattice, and such crystalline order in the molecular orientations might well enhance the tendency toward unequal sublattice

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occupancies. Thus, while not relevant to the plait point, the orientational constraints imposed by the model may play an important role in the antiferromagnetic-like ordering, and the details of this phase transition might well be model dependent in a way that the plait-point phenomenon is not.

The Dielectric Constants of Mixtures and of the Supercritical Region of Some Hydrogen-Bonded Fluids

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Abstract: Recently, the domain theory of the dielectric constants of hydrogen-bonded liquids proposed by Hobbs, Jhon, and Eyring has been successfully applied to the system of light and heavy water, various forms of ice, and to the lower aliphatic alcohols. In this paper, we apply the theory to the supercritical region of water. The theory is also developed for the calculation of the dielectric constant of mixtures such as water–methanol and water–dioxane. The model is quite satisfactory in all cases.

Recently, Hobbs, Jhon, and Eyring[2a] developed the domain theory of the dielectric constants of hydrogen-bonded liquids in which the following assumptions were made.

(1) Liquid water and other hydrogen-bonded liquids are made up of a mosaic of roughly bricklike domains with the dipoles in a particular domain having an average resultant moment $\mu \cos \theta$ along the direction of maximum polarization for the domain, while the direction of maximum polarization of neighboring domains tend to be rotated through 180° with respect to the first in the same way magnets juxtapose south poles against north poles. For perfect tetrahedral bonding $\cos \theta$ gives the value of 1, while for bent hydrogen bonds[2b] $\cos \theta$ is correspondingly smaller.

(2) Under the electric field, those domains which are favorably oriented with respect to the field grow at the expense of the less favorably oriented domains until the steady state is reached. The relaxation process involves only the molecules at the interface between domains.

The resulting mean dipole moment for solid-like molecules is then $\bar{\mu} = \mu^2 \cos^2 \theta F/kT$, while for the gas-like molecules, $\bar{\mu} = \mu^2 F/3kT$ since such molecules orient freely in the local field F.[3]

The use of the foregoing assumptions and the concept of the significant structure theory of liquids[4] lead to the following equation for the dielectric constants of hydrogen-bonded liquids such as liquid water.

$$\frac{(\epsilon - n^2)(2\epsilon + n^2)}{3\epsilon} = 4\pi \frac{N}{V}\left(\frac{n^2 + 2}{3}\right)^2 \left(\frac{V_s}{V}\frac{\mu^2 G}{kT} + \frac{V - V_s}{V}\frac{\mu^2}{3kT}\right) \quad (1)$$

Here ϵ, n, and μ are the dielectric constant, the index of refraction, and the dipole moment, respectively, and V_s and V are the molar volume of the solid-like structure in the liquid and the molar volume of the liquid, respectively.

This model differs from the Onsager[5] and Kirkwood[6] models in an essential point. This is in the account taken of the forces due to neighboring molecules. Equation 1 was tested for the dielectric constants[2a] of the various forms of ice and of light and heavy water where excellent agreement between experiment and theory was found.

The fact that the values found for G are nearly equal to unity is an extremely satisfying result in conjunction with the proposed model.

Following our early work, Jhon, *et al.*,[7] calculated the dielectric constants of various lower aliphatic alcohols by a similar scheme to that used for liquid water, and G values which were found to be slightly greater than unity were interpreted as indicating a slight degree of polymerization of alcohol molecules.

In this paper, we extend the theory to the supercritical regions of hydrogen-bonded liquids for which no satisfactory theoretical studies appear to have been made; second, the theory of the dielectric constant of some of the hydrogen-bonded liquid mixtures is developed.

Dielectric Constant of Water in the Supercritical Region

For the calculation of the dielectric constant of steam at supercritical temperatures under high pressure, we have to consider the pressure effect in eq 1.

In a compressed region of dense gas or liquid, the pressure effect[8] on V_s is not negligible, since some solids are fairly compressible. Thus, the pressure dependence

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