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Miron Kaufman
Robert B. Griffiths, Carnegie Mellon University

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Thermodynamic model for tricritical mixtures with application to ammonium sulfate + water + ethanol + benzene

Miron Kaufman and Robert B. Griffiths

Physics Department, Carnegie-Mellon University, Pittsburgh, Pennsylvania 15213
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Procedures are developed for using composition data in the three-phase region and variations of meniscus heights to determine the parameters needed to relate a classical thermodynamic model for fluid mixtures near tricritical points to actual experiments. In the case of the mixture ammonium sulfate + water + ethanol + benzene the result is a reasonably good fit to a variety of data, including light scattering measurements of intensity and correlation length. There is some evidence for deviations from the classical theory, but it is not unambiguous.

I. INTRODUCTION

Tricritical points in multicomponent fluid mixtures arise when three coexisting phases become simultaneously identical to a single critical phase through a variation of temperature, pressure, and composition. In many respects they are analogous to the tricritical points observed in systems with symmetry-breaking phase transitions, such as the metamagnetic transition in FeCl₂, the order–disorder transition in NH₄Cl, or the superfluid transition in ⁴He–³He mixtures. The analysis of experimental data is much simpler in the case of symmetry-breaking phase transitions than it is for tricritical points. The absence of appropriate symmetries in the latter necessitates a rather extensive theoretical framework. It is the purpose of this paper to present the details of such a framework based on a "classical" phenomenological model (the expansion of a free energy in powers of an order parameter) and to apply it to the particular case of the mixture ammonium sulfate + water + ethanol + benzene.

The predictions of the classical model are actually fairly simple when stated in terms of an appropriate set of "scaling fields" (the αi of Sec. II below). The major complication comes about in trying to relate these scaling fields to physical thermodynamic variables such as temperature, pressure, and chemical potentials. One assumes that there is a smooth transformation from one set of variables to the other. However, the actual details of this relationship must be determined by using experimental data to determine explicit values for a large number of phenomenological parameters.

In the case of the quaternary mixture mentioned above, a large number of parameters can be determined with the help of the extensive data of Lang and Widom on the compositions of three coexisting phases at several values of overall composition and two different temperatures very near the tricritical point. (A similar analysis has been carried out by Bocko for the mixture water + acetonitrile + benzene + n-hexane.) The phenomenological theory can then be used to predict properties for other points of the three-phase region near the tricritical point; i.e., it serves to extrapolate as well as interpolate the experimental results.

However, there are also two-phase and one-phase regions in the vicinity of a tricritical point. For an appropriate description of these it is essential to add a "smooth" contribution to the appropriate thermodynamic potential. For the mixture in question we have used data on meniscus heights in closed tubes (thus fixed overall composition) as a function of temperature in order to fit the additional parameters present in the smooth part of the potential.

The choice of parameters has been checked by comparing the predictions of the classical model with the results of various optical experiments. The index of refraction can be calculated using the Clausius–Mossotti formula, provided the density of the phase is known along with its composition. Since densities have not been determined directly near the tricritical point, we have used a crude but not unreasonable estimate for the volume of mixing. The intensity of light scattering extrapolated to zero angle is determined by the thermodynamic fluctuation in the (optical) dielectric constant and we have worked out the appropriate formulas and compared them with experiment. The classical model can also be used to predict the correlation length, provided one is willing to supply values for additional phenomenological parameters. We have chosen these in order to provide reasonable agreement with the intensity of scattered light as a function of angle. In an earlier paper, we reported on the results of our computations for the three-phase region and compared them with optical experiments.

As a result of the procedures discussed above, we have, in effect, produced a model for the thermodynamic properties of this particular mixture near its tricritical point, a model which can be compared with future experiments or used to generate gedanken experiments. The results of one of the latter, the behavior of a mixture with precisely the tricritical composition, is discussed in Sec. IV G.

A classical model of the sort we employ has definite limitations, and it is well to recognize what they are. In the first place, it is well known that classical theories provide results which are quantitatively incorrect at "ordinary" critical points; in particular, the classi-
cal critical exponents are not correct. Second, the model is expected to give the correct tricritical exponents (in the sense of scaling) at the tricritical point, but it lacks the logarithmic corrections predicted by modern theory. Third, the classical model does not contain certain divergent susceptibilities which are allowed by scaling and which are observed experimentally in systems with symmetry breaking. And of course the classical model may be deficient in other respects. Despite these limitations our model seems to provide a remarkably good description of the available experimental data near the tricritical point of this mixture.

An outline of the paper is as follows. Section II is devoted to an exposition of the classical model, and Sec. III contains the formulas needed to apply it to a quaternary mixture at fixed pressure. The application to ammonium sulfate + water + ethanol + benzene will be found in Sec. IV, which describes both the methods we used to fit the parameters in the model, and comparisons between predictions of the model and various experimental data. The prediction for the behavior of a mixture with composition equal to the tricritical composition is at the end of this section. The conclusions of our study are summarized in Sec. V.

II. THE CLASSICAL MODEL

A. Basic formulas

In this section we present some of the basic formulas for a Landau theory employing a single order parameter. Although we are interested in liquid mixtures, we shall develop the formulas in a form which uses a set of thermodynamic field variables whose nature need not be specified in advance. (In Sec. IIIA we shall apply these formulas to a mixture where the fields are the temperature, pressure, and the chemical potentials.) A fundamental relation is provided by expressing one of these fields \( \Omega \) as a function of the remainder, which we denote by \( f_1, f_2, \ldots \).

We assume that \( \Omega \) is a sum

\[
\Omega = \Omega_r + \Omega_s
\]  

(2.1)

of a "regular" part \( \Omega_r \), which is a smooth function of the \( f \)'s, and a singular part

\[
\Omega_s = \min_\phi \Phi(\phi)
\]  

(2.2)

where

\[
\Phi = \sum_{k=1}^k a_k \phi^k
\]  

(2.3)

is a polynomial in the order parameter \( \phi \), with coefficients \( a_k \) which are smooth functions of the \( f \)'s. Since Eq. (2.2) is a global minimum for \(-\infty < \phi < \infty, k \) in (2.3) must be even and \( a_k \) must be positive. By rescaling \( \phi \) and shifting its origin, we can arrange to have \( a_1 = 1 \) and \( a_{k+1} = 0 \). A term \( a_k \) could be included in Eq. (2.2), but its only effect would be to add a term to \( \Omega_s \) which could equally well be included in \( \Omega_r \). Consequently, \( \Omega_s \) depends on the \( k-2 \) parameters \( a_1, a_2, \ldots, a_{k-2} \), whereas \( \Phi \) depends on these together with \( \phi \). If \( \phi \) has two or more equal minima, we shall say that the corresponding \( \phi \) values are associated with two or more coexisting phases.

The \( a \)'s in Eq. (2.3) act as thermodynamic field variables, and it is convenient to first work out the properties of the model in terms of these scaling fields before considering its relationship to the \( f \)'s, the "laboratory fields." Equation (2.2) may be written in the form

\[
\Omega_s(a_1, \ldots, a_{k-2}, \phi) = \Phi(a_1, \ldots, a_{k-2}, \psi),
\]  

(2.4)

where \( \psi \) on the right-hand side is the equilibrium value of the order parameter, the value which minimizes \( \Phi \) for this choice of the \( a \)'s, and is thus a function of \( a_1, \ldots, a_{k-2} \). If Eq. (2.4) is differentiated with respect to one of the \( a \)'s, the result is

\[
\frac{\partial \Phi}{\partial a_j} = \frac{\partial \Phi}{\partial a_j} + \frac{\partial \Phi}{\partial a_j} \frac{\partial a_j}{\partial a_j},
\]  

(2.5)

where the subscript \( a \) means that the (other) \( a \)'s are held fixed. Since at the minimum

\[
\frac{\partial \Phi}{\partial a_j} = \sum a_j \psi^{m-1} = 0,
\]  

(2.6)

we see that

\[
\frac{\partial \Phi}{\partial a_j} = \psi^j.
\]  

(2.7)

The matrix \( \chi_{ij} \) for the singular part of the susceptibility is defined as

\[
\chi_{ij} = -\frac{\partial^2 \Omega_s}{\partial a_i \partial a_j} = -j \frac{\partial^2 \Phi}{\partial a_i \partial a_j} = -j \frac{\partial^2 \Phi}{\partial a_j \partial a_i} - \frac{\partial \Phi}{\partial a_j} \frac{\partial a_j}{\partial a_i},
\]  

(2.8)

where \( i \) and \( j \) run from 1 to \( k-2 \). Upon differentiating Eq. (2.6) with respect to \( a_i \) (and noting that \( \psi \) depends on the \( a \)'s), we obtain

\[
\frac{\partial^2 \Phi}{\partial a_i \partial \psi} + \left( \frac{\partial^2 \Phi}{\partial \psi^2} \right) \frac{\partial \psi}{\partial a_i} = 0.
\]  

(2.9)

The first term can be evaluated using Eq. (2.3). When the resulting expression is inserted in Eq. (2.8) we obtain

\[
\chi_{ij} = ij \psi^{m-1} \left( \frac{\partial^2 \Phi}{\partial a_j \partial a_i} - \frac{\partial^2 \Phi}{\partial a_i \partial a_j} \right) = ij \psi^{m-2} \chi,
\]  

(2.10)

where the "order parameter susceptibility" \( \chi \) is defined by

\[
\chi = \chi_{11} = (\psi^2 \psi / \partial \psi^2) \chi \psi^2,
\]  

(2.11)

and is obviously positive since \( \Phi \) is a minimum at the equilibrium \( \psi \).

By means of Eq. (2.10) we can write the second differential of \( \Omega_s \) as

\[
d^2 \Omega_s = \sum_{ij} \frac{\partial^2 \Phi}{\partial a_i \partial a_j} da_i da_j = -\left( \sum_{ij} i j \psi^{m-1} \right)^2.
\]  

(2.12)

It is clear that \( d^2 \Omega_s \leq 0 \), which is consistent with the fact that \( \Omega_s \) is a concave function of the \( a \)'s. The latter is an immediate consequence of the fact that it is a minimum over \( \psi \) of \( \Phi(a_1, \ldots, a_{k-2}, \psi) \), and for fixed \( \psi, \Phi \) is a concave (actually, affine) function of the \( a \)'s. It is evident from Eq. (2.12) that there are nonzero \( da_i \) for which \( d^2 \Omega_s = 0 \), reflecting the fact that \( \Omega_s \) is not strictly concave. On the other hand, \( \Omega \) must be strictly con-
cave if the thermodynamic densities\textsuperscript{14} are to uniquely determine the fields, and this means $\Omega_4$ must be appropriately chosen.

Let $\varphi_i$ be the thermodynamic density conjugate to the field $f_i$. It is given by the formula
\[
\varphi_i = -\left(\frac{\delta H}{\delta f_i}\right) = -\left(\frac{\delta \Psi}{\delta f_i}\right) - \sum_{j \neq i} \left(\frac{\delta \varphi_j}{\delta f_i}\right) \varphi_j,
\]
where we have used Eqs. (2.1) and (2.7); the subscript $f$ indicates that the remaining $f$'s are held fixed. Next, let $\epsilon$ be some quantity (such as the dielectric constant) which is a function of the densities $\varphi_1, \varphi_2, \ldots$, and let $\delta \epsilon$ be the deviation of $\epsilon$ from its average value in some finite region whose linear dimensions exceed a typical correlation length. Its variance is given by the formula\textsuperscript{16}
\[
\langle (\delta \epsilon)^2 \rangle = \sum_{ij} \left(\frac{\partial \epsilon}{\partial \varphi_i}\right)\left(\frac{\partial \epsilon}{\partial \varphi_j}\right) \langle \varphi_i \varphi_j \rangle,
\]
where
\[
\langle \varphi_i \varphi_j \rangle = M \frac{\partial \varphi_i}{\partial f_i} \frac{\partial \varphi_j}{\partial f_j} = M \frac{\partial \varphi_i}{\partial f_i} \frac{\partial \varphi_j}{\partial f_j},
\]
and $M > 0$ is inversely proportional to the size of the region in question and a smooth function of the $f$'s.\textsuperscript{17}

Inserting Eq. (2.13) into Eq. (2.15) permits us to write
\[
\langle (\delta \epsilon)^2 \rangle = \langle (\delta \epsilon)^2 \rangle_0 + \langle (\delta \epsilon)^2 \rangle_1,
\]
where the nondivergent part is
\[
\langle (\delta \epsilon)^2 \rangle_0 = M \sum_{ij} \left(\frac{\partial \epsilon}{\partial \varphi_i}\right)\left(\frac{\partial \epsilon}{\partial \varphi_j}\right) \delta \varphi_i \delta \varphi_j,
\]
and the divergent part is
\[
\langle (\delta \epsilon)^2 \rangle_1 = -M \sum_{ij} \delta \varphi_i \delta \varphi_j \left(\frac{\partial \epsilon}{\partial \varphi_i}\right)\left(\frac{\partial \epsilon}{\partial \varphi_j}\right) + n \psi \psi^{-1} \left(\frac{\partial \psi}{\partial \varphi_i}\right)_0
\]
\[
= \chi M \left(\sum_n \delta \varphi_i \delta \varphi_j \psi^{-1}\right)^2.
\]
The last equality is obtained with the help of Eqs. (2.8) and (2.10).

The correlation length $\xi$ can be obtained within the context of a classical theory by assuming that $\psi$ depends upon position. If one adds a term
\[
\frac{1}{2} g(\nabla \psi)^2
\]
to the right side of Eq. (2.3), with $\nabla \psi$ the gradient of $\psi$ and $g > 0$ a smooth function of $\psi$, $\Phi$ becomes a (position-dependent) free energy density. For $\psi$ close to a minimum $\psi_0$ of Eq. (2.3), this free energy density is of the form [see Eq. (2.11)]
\[
\text{constant} + \frac{1}{2} \chi_n (\psi - \psi_0)^2 + \frac{1}{2} g_\alpha (\nabla \psi)^2,
\]
where $\chi_n$ and $g_\alpha$ are $\chi$ and $g$ evaluated at $\psi = \psi_0$. From this it follows that the corresponding correlation length is\textsuperscript{18}
\[
\xi_\alpha = \sqrt{\frac{g_\alpha}{\chi_\alpha}}.
\]

B. Parametric representation of the $\alpha$'s

In practice it is convenient to express the $\alpha_i$ in Eq. (2.3) as functions of the values of $\psi$ which minimize $\Phi$. If we imagine adding a constant to $\psi$ such that its minimum value is zero, the resulting polynomial can be factored in terms of its $k$ roots $\psi_0 \mp \sqrt{\psi_0}$, which are either real or occur in complex conjugate pairs. We can therefore write $\psi$ in the form
\[
\psi = \prod_{i=0}^k \left(\psi - \psi_i\right),
\]
with at least one of the $\psi_i$ equal to zero. Writing out the product enables one to express the $\alpha_i$ as functions of $\psi_0$ and $\psi_i$.

In the case $k = 6$, which is of interest for tricritical points, $\delta$ takes on the three values $\alpha$, $\beta$, and $\gamma$, and the requirement $\alpha_0 = 0$ (see Sec. II A) means that
\[
\psi_0 + \psi_1 + \psi_2 = 0.
\]
The expressions for $\alpha_1$, $\alpha_2$, $\alpha_3$, and $\alpha_4$, simplified with the help of Eq. (2.23), are given in Appendix A. We shall adopt Widom's convention that $\alpha$ is the phase of lowest density, followed by $\beta$ and then $\gamma$, and we shall assume that $\psi$ has its minimum (most negative) value in phase $\alpha$, so that
\[
\psi_0 = \psi_1 = \psi_2.
\]
When three phases coexist, $\overline{\psi}_{\alpha}$, $\overline{\psi}_0$, and $\overline{\psi}_0$ all vanish, and $\overline{\psi}_0$, $\overline{\psi}_0$, $\overline{\psi}_0$ can be expressed in the form
\[
\psi_0 = A \cos \phi \psi_1 = 120^\circ + \theta, \quad \delta = \alpha,
\]
\[
\psi_0 = 120^\circ - \theta, \quad \delta = \beta,
\]
where $\theta$ lies in the interval
\[
0^\circ \leq \theta \leq 60^\circ
\]
and
\[
A = \sqrt{2a_\epsilon^3}.
\]
(It is necessary to have $a_4 < 0$ for three coexisting phases.) Using the expressions in Appendix A one finds that
\[
a_1 = \frac{1}{2} A^5 \cos \theta,
\]
\[
a_2 = \frac{1}{2} A^4,
\]
\[
a_3 = -\frac{1}{2} A^3 \cos \theta.
\]
In the case of two coexisting phases, two of the $\overline{\psi}_0$ are zero and one is nonzero. If we let
\[
\Delta = -\frac{\overline{\psi}_0^2}{\epsilon_0^2}
\]
for the nonzero $\overline{\psi}_0$, and let $S$ and $P$ be the sum and product, respectively, of the $\overline{\psi}_0$ values in the two coexisting phases (where $\overline{\psi}_0 = 0$), then the $\alpha$'s may be written as follows:
\[
a_1 = 2PS(P - S^2) + A_2 S / 2,
\]
\[
a_2 = (S^2 - P^2) / 2 - \Delta(S^2 + 2P)/4,
\]
\[
a_3 = 2PS + A_3 S / 2, \quad a_4 = 2(P - S^2) - \Delta / 4.
\]
Note that by definition $\Delta \leq 0$ and $4P \leq \delta^2$.

Finally, let us note that if $\bar{y}_a = 0$, the susceptibility $\chi_a$ at $\psi = \bar{y}_a$, defined by Eq. (2.11), has the form

$$\chi_a = [2(\psi_a - \bar{y}_a)^2 + \bar{y}_a^2] \{(\psi_a - \bar{y}_a)^2 + \bar{y}_a^2\}^{-1},$$

(2.32)

and analogous expressions hold for $\chi_b$ or $\chi_c$ when $\bar{y}_a = 0$ or $\bar{y}_c = 0$.

C. Sum rules in the three-phase region

In the three-phase region near a tricritical point, the Landau theory predicts that the susceptibilities in the different phases are related by sum rules whose utility will be demonstrated in Sec. IV below. When three phases coexist, $\bar{y}_a = \bar{y}_b = \bar{y}_c = 0$, and Eq. (2.32) and the analogous expressions for $\chi_a$ and $\chi_c$ are relatively simple. It is then easily shown using Eqs. (2.23), (2.24), and (2.25) that

$$R_t = (\chi_a^{1/2} + \chi_{\psi}^{1/2})/\chi_{\psi}^{1/2} = 1$$

(2.33)

and

$$Q_t = \chi_a^{1/2} - \chi_{\psi}^{1/2} + \chi_{\psi}^{1/2} = -3a_t/\sqrt{2}.$$ 

(2.34)

We shall refer to Eq. (2.33) as the first and Eq. (2.34) as the second sum rule. Various other sum rules can be derived from these two.

Let $I$ denote the intensity of light, extrapolated to zero scattering angle, scattered by a mixture. Then $I$ is proportional to $I_{\text{dielectric}}(\epsilon_0 \epsilon)^2$, where $\epsilon$ is the dielectric constant (at optical frequencies), and near the tricritical point one expects the dominant contribution to come from $(\epsilon_0 \epsilon)^2$, as given by Eq. (2.18). That is, $I$ should be proportional to $\chi$ times a term which tends to a constant (independent of phase) at the tricritical point. Hence, in the immediate vicinity of the tricritical point, we expect that the scattering intensities in the three phases will satisfy the sum rules

$$R_t = (I_a^{1/2} + I_{\psi}^{1/2})/I_{\psi}^{1/2} = 1,$$

(2.35)

$$Q_t = I_a^{1/2} - I_{\psi}^{1/2} + I_{\psi}^{1/2} \propto (-a_t).$$

(2.36)

In addition, if we make the plausible assumption that $g$ in Eq. (2.19) tends to a constant near the tricritical point, then Eq. (2.21) and its analogs for phases $\beta$ and $\gamma$ lead to the correlation length sum rules

$$R_t = (\xi_a + \xi_{\psi})/\xi_{\psi} = 1,$$

(2.37)

$$Q_t = \xi_a - \xi_{\psi} + \xi_{\psi} \propto (-a_t).$$

(2.38)

in the three-phase region sufficiently near the tricritical point.

III. QUARTERNARY MIXTURES

A. Laboratory thermodynamic variables

We shall now show how the approach discussed in Sec. II can be implemented in the case of a quaternary mixture. Our formulation is chosen in part because of convenience in analyzing the experimental data discussed in Sec. IV below, but it is worth emphasizing that other choices for variables are possible.

Let $\mu_i$ be the chemical potential per unit mass for the $i$th component, and define

$$\Omega = \mu_4,$$

(3.1)

$$\bar{\mu}_i = \mu_i - \mu_4$$

(3.2)

for $i = 1, 2,$ and 3. We shall let $\Omega$ be the thermodynamic potential, and $\bar{\mu}_i$ together with $T$ (temperature) and $p$ (pressure) the independent thermodynamic fields. The Gibbs-Duhem equation yields the relation

$$d\Omega = -\sum_{i=1}^{3} x_id\bar{\mu}_i + vdp - sdT,$$

(3.3)

where $x_i$ is the weight fraction of component $i$, and $v$ and $s$ are the specific volume and entropy. In the notation of Sec. II, $\mu_1, \mu_2, \mu_3, -\beta$, and $T$ are the $f's$, while $x_1, x_2, x_3, v$, and $s$ are the corresponding $o's$.

In quaternary mixtures, we expect, in general, to have a one-parameter family of tricritical points, one for every $p$. Since the tricritical point occurs when the scaling fields vanish, i.e.,

$$a_1 = a_2 = a_3 = a_4 = 0,$$

(3.4)

we expect that to a first approximation the $a_i$ will be proportional to linear combinations of the deviations of $T$ and the $\bar{\mu}_i$ from their tricritical values $T_1$ and $\bar{\mu}_1$, which are, of course, functions of pressure. Since very near the tricritical point there should be considerable flexibility in choosing $a_4$, we shall assume that

$$a_1 = (3/2)\eta,$$

(3.5)

where

$$\eta = (T - T_1(p))/T_1$$

(3.6)

is the deviation of the temperature from its tricritical value, divided by a reference temperature $T_1$. When working at a fixed pressure, we shall let $T_1$ be equal to $T_1$ at that pressure. For $i = 1, 2, 3$, we let

$$a_i = -\sum_{j \neq i} b_{ij}(\bar{\mu}_j - \bar{\mu}_1) + F_i,$$

(3.7)

where the $b_{ij}$ and $F_i$ are assumed to be smooth functions of $T$ and $p$, and $F_i = 0$ on the tricritical line.

We shall assume that the regular part of $\Omega$, see Eq. (2.1), can be written in the form

$$\Omega = \Omega_0 + \sum_{i=1}^{3} \delta_i a_i - \frac{1}{2} \sum_{i=1}^{3} \sum_{j=1}^{3} \epsilon_{ij} a_i a_j,$$

(3.8)

in the neighborhood of the line of tricritical points, where $\Omega_0, \delta_i$, and $\epsilon_{ij} = \epsilon_{ji}$ are assumed to be smooth functions of $T$ and $p$. In addition, the matrix $\epsilon_{ij}$ is chosen to be positive definite so that $\Omega$ is a strictly concave function of the $o's$. [While the sums in Eq. (3.8) could be chosen to run from 1 to 4, it is just as convenient, given Eq. (3.5), to place the temperature dependence in the coefficients and $\Omega_0$.]

The weight fractions for $i = 1, 2, 3$ can now be written as [see Eqs. (2.13), (3.7), and (3.8)]

$$x_i = -\frac{\delta_i}{\delta_i^2} = \sum_{j \neq i} b_{ij} + \sum_{j=1}^{3} \psi_j = \sum_{j=1}^{3} \epsilon_{ij} a_j,$$

(3.9)

where

$$b_{ij} = \sum_{n=1}^{3} b_{in} \delta_n.$$

(3.10)
B. Approximation for \( \nu \)

In the experiments discussed in Sec. IV, the actual specific volume \( \nu \) of the mixtures was not directly determined. Since this quantity enters expressions for the index of refractions, we were forced to employ an approximation based on an estimate of the volume of mixing, Eq. (3.14) below.

If \( \nu_i \) is the specific volume of the \( i \)th pure component at the same temperature and pressure as the mixture whose weight fractions are \( x_i \), the volume of mixing \( V_m \) is defined by the equation

\[
\nu = (1 - V_m) \sum_i x_i \nu_i .
\]

Since \( V_m \) vanishes in any pure component, it is a plausible first approximation to suppose that

\[
V_m = \frac{1}{2} \sum_{i<j} C_{ij} x_i x_j ,
\]

where \( C_{ij} = C_{ji} \) is a set of temperature and pressure dependent coefficients. They can be determined provided volumes of mixing are known for the various binary mixtures involving the components which make up the quaternary mixture.

C. Mixtures with several phases

1. Introduction

If the fluid in a container consists of several coexisting phases, the value of a density \( \sigma_i \) for the mixture as a whole is given by the equation

\[
\sigma_i = \sum_{j} \lambda_j \sigma_j ,
\]

where \( \sigma_j \) is the value of this density in phase \( j \) and \( \lambda_j \) is the mass of phase \( j \) divided by the total mass of the mixture, so that

\[
\sum_{j} \lambda_j = 1 .
\]

When \( \sigma_i = x_i \), Eq. (3.15) applied to Eq. (3.9) yields

\[
x_i = b_{i0} + \sum_{j=1}^{n} b_{ij} x_j ,
\]

where

\[
u_i = u_i^0 - \sum_{j=1}^{n} \epsilon_i \nu_j
\]

and

\[
u_j^0 = \sum_{k=0}^{n} \lambda_k \nu_k^0 .
\]

Once the \( b_{ij} \) and the \( \epsilon_i \) are known, Eq. (3.17) can be used to calculate the overall composition for a given \( T \) and \( p \), provided \( x_1, x_2, x_3 \) and the \( \lambda_k \) are known. The inverse problem of calculating \( a_1, a_2, a_3 \) and the \( \lambda_k \), given an overall composition at a particular \( T \) and \( p \) (and assuming, as before, that \( b_{ij} \) and \( \epsilon_i \) are known) is much less trivial. Thus while one can solve Eq. (3.17) for the \( x_i \) given the \( \nu_i \), it is, in general, difficult or impossible to solve Eqs. (3.18) and (3.19) for the \( a_n \) and \( \lambda_k \) in closed form.

In order to simplify the inverse problem we shall choose

\[
\epsilon_{i1} = \epsilon_{i3} = 0 \quad (3.20)
\]

for all \( i \). In addition, we suppose that

\[
\epsilon_{22} > 0 , \quad \epsilon_{22} \epsilon_{33} > \epsilon_{23}^2 ,
\]

so that \( \Omega_s \) is a strictly concave function of \( a_2 \) and \( a_3 \), though not of \( a_1 \). However [see Eq. (2.12)] \( \Omega_s + \Omega_r \) will be strictly concave in \( a_1, a_2, a_3 \).

2. Inverse problem for the three-phase region

The sum over \( n \) in Eq. (3.18) may be restricted to \( n = 2,3 \) in view of Eq. (3.20). From Eqs. (2.29), (2.26), (2.26), and (2.25) we obtain the results

\[
a_2 = \frac{1}{2} ,
\]

\[
a_3 = -\frac{1}{2} (t - 1)^{1/2} \cos \theta = -\frac{1}{2} (t - 1)^{1/2} \cos \phi
\]

\[
= -2 \phi_0 - \frac{3}{2} t \phi_0 ,
\]

where, note, \( \phi_0 \) is the value of \( \phi \) in any of the three phases. Inserting these results in Eq. (3.18) and noting Eq. (3.16) allows us to rewrite Eq. (3.17) as

\[
x_i = b_{i0} + \sum_{j=1}^{3} b_{ij} x_j ,
\]

where

\[
b_{i0} = b_{i0} - \frac{9}{16} t^2 \sum_{j=0}^{2} b_{ij} \epsilon_{i_1} ,
\]

\[
b_{i1} = b_{i1} + \frac{3}{2} t \sum_{j=0}^{2} b_{ij} \epsilon_{i_2} ,
\]

\[
b_{i2} = b_{i2} ,
\]

\[
b_{i3} = b_{i3} + 2 \sum_{j=0}^{2} b_{ij} \epsilon_{i_3} .
\]

The procedure for obtaining the \( a_0 's \) and \( \lambda_k 's \), given the \( x_i 's \), is then the following. The coefficients \( b_{ij} 's \) are known (for a given \( T \) and \( p \)), so Eq. (3.24) may be solved


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where, note,

\[
\sum_{i} x_i = 1,
\]

It is also possible to write \( x_i \) in the form (3.9), provided the \( b_{ij} 's \) are chosen so that

\[
\sum_{i} b_{ij} = \delta_{ij}
\]

vanishes for \( j \neq 0 \) and is 1 for \( j = 0 \).

Similar expressions can be written down for \( v \) and \( s \), but as we shall not use them in Sec. IV, we shall not provide the explicit formulas here. Note that in computing \( v \) it is necessary to take into account the pressure dependence of \( T_{s} \) and \( \mu_{ij} \) as well as \( F_{ij}, \Omega_{s}, \Omega_{r}, \) etc.

[Note that in Ref. 10, Eq. (3.9) occurs with the \( \epsilon_m 's \) terms omitted. This is an adequate approximation in the three-phase region near the tricritical point, but not in the two- and one-phase regions.]

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for the $u_j$. Next, the formula
\[
\cos 3\xi = 4(-t)^{-3/2} u_j^2 - 3(-t)^{-1/2} u_j^3 ,
\]
(3.26)

which is obtained by multiplying Eq. (3.23) by $\lambda_{ij}$, summing over $i$, and using Eq. (3.23) can be solved for $\delta_j$ and $\psi_j$, and $\phi_j$ calculated from Eqs. (2.29), (2.25), and (2.26). The values of $\lambda_j$ are then obtained from Eqs. (3.19) and (3.16). Of course, if the right-hand side of Eq. (3.29) does not lie between -1 and 1, or if any of the $\lambda_j$ are negative, the overall composition does not lie in the three-phase region but rather in the one-phase or two-phase regions.

3. Inverse problem for the two-phase region

If we insert Eq. (3.5) into Eq. (2.31) and eliminate $\Delta$, the result is
\[
\Delta = 8(P - S^2) - 6t
\]
\[
a_1 = 6P(5S^2 - P^2 - \frac{1}{2}t),
\]
\[
a_2 = \frac{3}{2}(S^2 - P^2 + \frac{1}{2}t(S^2 + 2P))
\]
\[
a_3 = S(5P - 4S^2 - 3t),
\]
(3.27)
where $S$ and $P$ are equal to $\psi_1$ + $\psi_2$ and $\psi_1$ $\psi_2$, respective­ly. One can, in fact, write
\[
\psi_{j=2} = \frac{1}{2}(S + \frac{1}{2}(S - 4P)^{1/2}),
\]
(3.28)

where the + refers to phase 1 and the - to phase 2. If Eq. (3.28) is inserted into Eq. (3.19), and then Eqs. (3.19) and (3.27) are inserted into Eq. (3.18), the result is a set of three equations in the three unknowns $\lambda_{ij}$, $P$, and $S$ (note that $\lambda_1 = 1 - \lambda_1$). Eliminating $\lambda_{ij}$ yields two equations in $S$ and $P$ (Appendix B) and eliminating $P$ yields a polynomial equation
\[
\sum_{j=1}^{3} B_j S_j = 0
\]
(3.29)
in $S$ alone. The coefficients $B_j$, which are given in Appendix B, are functions of the $u_j$, $\epsilon_{j_n}$ and $t$.

To solve the inverse problem, we first find the real roots of Eq. (3.29) numerically, and for each $S$ compute the corresponding $P$. If $4P$ exceeds $S^2$ or if $4(P - S^2)$ exceeds $S$, the solution is discarded, since $\psi_1$ and $\psi_2$ must be real, Eq. (3.28), and $\Delta$, Eqs. (3.30) and (3.31), cannot be positive.

Once $S$ and $P$ are known, the $\sigma$s can be computed from Eq. (3.27) and inserted into Eq. (3.18) to provide the $u_j$, $\psi_1$ and $\psi_2$ can be calculated from Eq. (3.28). The values of $\lambda_1$ and $\lambda_2 = 1 - \lambda_1$ are then determined by Eq. (3.19), and of course an acceptable solution requires that both quantities be positive. If there is no solution satisfying all of these criteria, the overall composition does not correspond to two phases at the temperature and pressure of interest.

4. Inverse problem for the one-phase region

In contrast to the two- and three-phase regions, the inverse problem for the one-phase region is straightforward, given Eq. (3.20). Note that $u_j$ in this case is simply $\psi_j$, and setting $j = 1$ in Eq. (3.18) gives
\[
\psi = u_1
\]
(3.30)

so that $\psi$ and the $u_j$ are immediately determined by the $u_j$. Thus for $j = 2$ and 3, Eq. (3.18) is a pair of simultaneous linear equations in $a_2$ and $a_3$, and the solution is straightforward. Inserting these values along with $\psi$ in Eq. (3.6), which has the form
\[
a_1 + 2a_2 \psi + 3a_3 \psi^2 + 6\psi^3 = 0
\]
determines $a_1$.

That the result actually represents a minimum of $\Phi$ can be checked, to begin with, by seeing whether $\chi$ [Eq. (2.11)] is positive. To establish that it is a global minimum requires solving Eq. (3.31) numerically and evaluating $\Phi$ at each of the roots.

IV. THE MIXTURE AMMONIUM SELFATE + WATER + ETHANOL + BENZENE

A. Preliminary remarks

The tricritical point in the mixture ammonium sulfate + water + ethanol + benzene was discovered by Mertslin and Mochalov. Their work, that of Radishevskaya et al., and that mentioned below was carried out at atmospheric or near atmospheric pressure, so we have assumed a constant pressure in our analysis. Lang and Widom carried out a careful study of the compositions of three coexisting phases near the tricritical point. We have used their data in Sec. IV B as a principal source of the $b_{ij}$ coefficients defined in Sec. III, and in what follows we shall always use their convention on labeling the components: $i = 1$ for ammonium sulfate, $i = 2$ for water, $i = 3$ for ethanol, and $i = 4$ for benzene (the same order as in the title above).

We have used published and unpublished data on the heights of meniscuses separating the liquid phases in two sealed samples, here designated A and B, of fixed overall composition in order to estimate the $\epsilon_{i_n}$ coefficients in Eq. (3.8), as discussed in Sec. IV D below (following some remarks in Sec. IV C on our procedure for estimating the densities of the phases). Sample A was prepared with a composition (weight fractions) of $x_1 = 0.0175$, $x_2 = 0.3510$, $x_3 = 0.4500$, and $x_4 = 0.0185$, and sample B with $x_1 = 0.3510$, $x_2 = 0.3534$, $x_3 = 0.4471$, and $x_4 = 0.1817$. In order to reconcile the correlation lengths measured in sample B with those found for sample A, we increased the temperatures reported for sample B by 0.2°C. (This is not inconsistent with a possible uncertainty in the absolute temperature measurements for this sample; the relative temperatures were determined much more precisely.) We also assumed a slightly different set of compositions for sample A: $x_1 = 0.0180$, $x_2 = 0.3523$, $x_3 = 0.4467$, and $x_4 = 0.0180$. This change is not unreasonable in view of the difficulty of preparing samples of precise composition, and possible errors in the Lang and Widom results on which we have based our model parameters. No similar adjustments were made for sample A. The correlation lengths for sample B do not include corrections for multiple scattering, and the same is true of the correlation lengths for sample A as reported in Ref. 9; corrected values for sample A are in Ref. 7. We have used the uncorrected values for sample A in this paper, as these would seem to be more comparable with those for sample...
B, for which we did not have corrected values. (Some remarks on these corrections will be found in Sec. IV F.)

Light scattering measurements were also reported by Gollub et al., for two samples, and they published the meniscus heights as a function of temperature for one of these. We have not analyzed their data on linewidths or the corresponding data of Wu.

The light scattering data, for samples A and B is considered in Sec. IV F, following a discussion of indices of refraction in Sec. IV E. Finally, Sec. IV G presents the predictions of our model as to what would happen as the temperature varies in a mixture of composition precisely equal to the tricritical composition.

B. The three-phase data of Lang and Widom

Lang and Widom measured the composition of each of the three coexisting phases for four samples at a temperature of 20.9 °C, five at 21 °C, five at 44.91 °C, four at 48.04 °C, and one at 48.59 °C. The loci of the compositions of these coexisting phases at a given temperature form a (moderately) smooth curve in the composition tetrahedron.

At each temperature we analyzed the Lang and Widom data in the following manner. Each sample of three coexisting phases was assigned an angle \( \theta \), corresponding to the parametric representation Eq. (2.25), and the mass fraction \( x_i^\delta \) of component \( i \) in phase \( \delta \) was assumed to be of the form

\[
x_i^\delta = \sum_{J=0}^3 d_{iJ}(\cos \phi_J)^J,
\]

with \( \phi_J \) given by Eq. (2.26), and the \( d_{iJ} \) a set of coefficients. The motivation for Eq. (4.1) comes from Eq. (4.2) and from noting that according to Eq. (3.24) \( x_i^\delta \) should be a linear combination of \( \phi_0, \phi_1, \) and \( \phi_2 \) [since for phase \( \delta, \lambda_3 = 1 \) in Eq. (3.19) and the other \( \lambda's \) are zero].

<table>
<thead>
<tr>
<th>( T(\text{°C}) )</th>
<th>( i )</th>
<th>( 1 )</th>
<th>( 2 )</th>
<th>( 3 )</th>
<th>( 4 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>20.9</td>
<td>0</td>
<td>0.0244</td>
<td>0.3609</td>
<td>0.4173</td>
<td>0.1974</td>
</tr>
<tr>
<td>1</td>
<td>0.1011</td>
<td>0.4442</td>
<td>-0.1205</td>
<td>0.5529</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>0.1341</td>
<td>-0.0491</td>
<td>-0.3165</td>
<td>0.2316</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>0.0568</td>
<td>-0.2495</td>
<td>0.0902</td>
<td>0.1026</td>
<td></td>
</tr>
<tr>
<td>21</td>
<td>0</td>
<td>0.0465</td>
<td>0.3467</td>
<td>0.4909</td>
<td>0.1459</td>
</tr>
<tr>
<td>1</td>
<td>0.0390</td>
<td>0.5678</td>
<td>-0.0970</td>
<td>0.5045</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>0.1484</td>
<td>-0.0219</td>
<td>-0.4486</td>
<td>0.3221</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>0.0698</td>
<td>-0.2936</td>
<td>0.0920</td>
<td>0.1316</td>
<td></td>
</tr>
<tr>
<td>44.91</td>
<td>0</td>
<td>0.0143</td>
<td>0.3514</td>
<td>0.4629</td>
<td>0.1714</td>
</tr>
<tr>
<td>1</td>
<td>0.0311</td>
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<td>0.2393</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>0.0842</td>
<td>0.0116</td>
<td>-0.1307</td>
<td>0.0849</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>0.0146</td>
<td>-0.0226</td>
<td>0.0045</td>
<td>0.0033</td>
<td></td>
</tr>
<tr>
<td>48.04</td>
<td>0</td>
<td>0.0160</td>
<td>0.3535</td>
<td>0.4579</td>
<td>0.1727</td>
</tr>
<tr>
<td>1</td>
<td>0.0182</td>
<td>0.1309</td>
<td>-0.0253</td>
<td>0.1238</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>0.0079</td>
<td>0.0028</td>
<td>-0.0384</td>
<td>0.0282</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>0.0021</td>
<td>0.0059</td>
<td>-0.0012</td>
<td>0.0066</td>
<td></td>
</tr>
</tbody>
</table>

In practice, what we did was to assign a preliminary value of \( \theta \) to each of the three-phase samples and then adjust the \( d_{iJ} \) for a minimum deviation between the experimental compositions and those predicted by Eq. (4.1). The \( \theta's \) were then varied to improve the fit. Our choices for the \( d_{iJ} \) at the different temperatures are listed in Table I. A comparison of the computed and experimental \( x_i^\delta \) values is given in Table II in the following form. At each temperature we give the value of \( \theta \) (in degrees) which we assigned to a particular three-phase triangle studied by Lang and Widom, followed by the values of \( x_i^\delta \) computed using Eq. (4.1). The number beneath each of these values is the difference between it and the corresponding experimental value; the latter can be obtained by adding these two numbers. At 20.9 and 21 °C some of the calculated weight fractions are slightly negative for some cases in which the experimental values are small. The samples are listed in the same order as in Table I in Ref. 5, except that the values at 20.90 °C are all placed together.

Figure 1 shows the predicted weight fraction of benzene as a function of \( \cos \phi \) at a temperature of 44.91 °C plotted as a curve with the experimental values shown as points. This is typical of the quality of fit possible at the temperatures of 44.91 °C and above. Typical deviations of the measured from the computed weight fractions are 0.005 for the liquid components and 0.001 for the salt. At 21 °C the deviations are larger, typically 0.015 for the liquid components and 0.005 for the salt. An improved fit at 21 °C can, of course, be obtained by including a term \( 1\frac{J}{2} \) in Eq. (4.1). However, we only used the data above 40 °C in determining the \( b_{iJ} \) coefficients.

Given the choice in Eq. (3.5) for \( a_{it} \), it follows from Eqs. (2.28) and (2.25) that

\[
\psi_b = (-t)^{\frac{J}{2}} \cos \phi_b,
\]

where [see Eq. (3.6)]

\[
t = (T - T_t)/T_t.
\]

Hence, a comparison of Eqs. (3.24), (3.19), and (4.1) implies that

\[
d_{iJ} = (-t)^{\frac{J}{2}} b_{iJ},
\]

for \( 1 \leq i \leq 4 \) and \( 0 \leq j \leq 3 \). Now the \( b_{iJ} \) are smooth functions of the temperature (Sec. III A), and thus the same is true of the \( b_{iJ} \) [Eq. (3.25)]. We, therefore, assumed that

\[ b_{ij} = \tilde{b}_{ij} - \tilde{b}_{iJ} , \]

[Equations (4.4) and (4.5) differ from their counterparts in Ref. 10 because of the omission of the \( t^{2n} \) terms in Ref. 10, as noted above in Sec. IIIA.]

The quantities \( \tilde{b}_{iJ} \) and \( \tilde{b}_{iJ} \) were determined as follows. We assumed a value for the tricritical temperature \( T_t \), thereby fixing \( t \) for the Lang and Widom data. The values of \( \tilde{b}_{ij} \) were determined at 44.91 and 48.04 °C using Eq. (4.4), and from these the \( \tilde{b}_{iJ} \) which are listed in Table III. The procedure is sensitive to the choice of \( T_t \) because of the way \( t \) appears in Eq. (4.4); bad choices for \( T_t \) result in unreasonably large values

<table>
<thead>
<tr>
<th>T(°C)</th>
<th>x₁</th>
<th>x₂</th>
<th>x₃</th>
<th>x₄</th>
<th>x₁</th>
<th>x₂</th>
<th>x₃</th>
<th>x₄</th>
<th>x₁</th>
<th>x₂</th>
<th>x₃</th>
<th>x₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>20.9</td>
<td>0.0000</td>
<td>0.0908</td>
<td>0.3749</td>
<td>0.5344</td>
<td>0.0000</td>
<td>0.1263</td>
<td>0.3980</td>
<td>0.4749</td>
<td>0.3156</td>
<td>0.6069</td>
<td>0.0711</td>
<td>0.0064</td>
</tr>
<tr>
<td></td>
<td>+0.0009</td>
<td>+0.0062</td>
<td>-0.0084</td>
<td>+0.0013</td>
<td>+0.0001</td>
<td>-0.0094</td>
<td>+0.0041</td>
<td>-0.0044</td>
<td>-0.0009</td>
<td>+0.0031</td>
<td>+0.0043</td>
<td>-0.0064</td>
</tr>
<tr>
<td>3.7</td>
<td>0.0000</td>
<td>0.0864</td>
<td>0.3713</td>
<td>0.5425</td>
<td>0.0010</td>
<td>0.1318</td>
<td>0.4007</td>
<td>0.4666</td>
<td>0.3152</td>
<td>0.6072</td>
<td>0.0714</td>
<td>0.0062</td>
</tr>
<tr>
<td></td>
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<td>+0.0062</td>
<td>-0.0113</td>
<td>+0.0047</td>
<td>+0.0001</td>
<td>-0.0112</td>
<td>+0.0080</td>
<td>-0.0030</td>
<td>-0.0010</td>
<td>+0.0034</td>
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<td>46.</td>
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<td>0.8311</td>
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<td>0.5019</td>
<td>0.3619</td>
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</tr>
<tr>
<td></td>
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<td>-0.0075</td>
<td>-0.0020</td>
<td>+0.0192</td>
<td>+0.0210</td>
<td>-0.0381</td>
<td>+0.0052</td>
<td>-0.0143</td>
<td>-0.0163</td>
<td>+0.0243</td>
</tr>
<tr>
<td>57.6</td>
<td>0.0006</td>
<td>0.0169</td>
<td>0.1317</td>
<td>0.8507</td>
<td>0.1057</td>
<td>0.5777</td>
<td>0.3025</td>
<td>0.0142</td>
<td>0.1258</td>
<td>0.6000</td>
<td>0.2757</td>
<td>-0.0155</td>
</tr>
<tr>
<td></td>
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<td>-0.0002</td>
<td>+0.0122</td>
<td>-0.0113</td>
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<td>-0.0001</td>
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<td>-0.0014</td>
<td>-0.0001</td>
<td>+0.0044</td>
<td>+0.0139</td>
</tr>
</tbody>
</table>

TABLE II. Compositions of the Lang and Widom samples as predicted by our model. The difference between the experimental and computed value is listed in each case directly beneath the latter.
of \( \beta_{1f} \). We found that any \( T_1 \) between 49.0 and 49.3 °C gave reasonable coefficients. Those in Table III are based upon \( T_1 = 49.1 \) °C. This is slightly higher than the Lang and Widom estimate of 48.9 °C. Our estimates for the tricritical compositions are the \( \beta_{1f} \) in Table III. They differ slightly from those of Lang and Widom, which are as follows:

\[
\begin{align*}
  x_1 &= 0.0175 \pm 0.0005, & x_2 &= 0.351 \pm 0.002, \\
  x_3 &= 0.450 \pm 0.005, & x_4 &= 0.181 \pm 0.002.
\end{align*}
\]

The measurements of Kim et al. \(^7\) carried out at a composition nominally identical to the tricritical composition estimated by Lang and Widom, and discussed in Sec. IV D below, are consistent with our model calculations, and hence suggest that our tricritical composition estimate is better than that of Lang and Widom.

**TABLE III. Coefficients \( b_{14f} \) determined from experimental data.**

<table>
<thead>
<tr>
<th>Component</th>
<th>( b_{14f} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Salt)</td>
<td>(Water)</td>
</tr>
<tr>
<td>( i = 1 )</td>
<td>( i = 2 )</td>
</tr>
<tr>
<td>( j = 0 )</td>
<td>0.0166</td>
</tr>
<tr>
<td>( j = 1 )</td>
<td>0.3264</td>
</tr>
<tr>
<td>( j = 2 )</td>
<td>2.324</td>
</tr>
<tr>
<td>( j = 3 )</td>
<td>11.52</td>
</tr>
<tr>
<td>( j = 4 )</td>
<td></td>
</tr>
<tr>
<td>( i = 3 )</td>
<td>(Ethanol)</td>
</tr>
<tr>
<td>( j = 0 )</td>
<td>-0.1752</td>
</tr>
<tr>
<td>( j = 1 )</td>
<td>-2.784</td>
</tr>
<tr>
<td>( j = 2 )</td>
<td>23.54</td>
</tr>
<tr>
<td>( j = 3 )</td>
<td>-118.</td>
</tr>
<tr>
<td>( i = 4 )</td>
<td>(Benzene)</td>
</tr>
<tr>
<td>( j = 0 )</td>
<td>-0.1752</td>
</tr>
<tr>
<td>( j = 1 )</td>
<td>-2.784</td>
</tr>
<tr>
<td>( j = 2 )</td>
<td>23.54</td>
</tr>
<tr>
<td>( j = 3 )</td>
<td>-118.</td>
</tr>
</tbody>
</table>

*This row contains the estimated tricritical compositions.

*These values are only tentative estimates and they should not be taken very seriously.

Once the \( \beta_{1f} \) are determined, the model provides predictions for three-phase compositions at all temperatures near the tricritical temperature. As an example, Table II shows our prediction for the single Lang and Widom sample at 48.59 °C, with the parameter \( \theta \) adjusted for the best fit. Deviations from the experimental compositions are comparable to those found at 44.91 and 48.04 °C.

**C. Density of the mixtures**

The densities of a mixture with a given composition were computed from the densities of the pure components using Eq. (3.13) together with the approximation (3.14) for the volume of mixing. The densities \( \rho_1, \rho_2, \rho_3, \) and \( \rho_4 \) were set equal to zero. The precise value of \( \rho_1 \) is not very important.

The values of \( \rho_{1f} \) and \( \rho_{14} \) assuming \( T_1 = 49.1 \) °C, are given in Table IV, along with the value of \( \rho_4 \) assumed to be temperature independent, of crystalline ammonium sulfate. (We obtained these values from the data in Refs 23 and 24.) Note that at the tricritical composition there is very little ammonium sulfate in the mixture, so the precise value of \( \rho_1 \) is not very important.

The \( C_{14} \) in Eq. (3.14) could, in principle, be determined from the volumes of mixing of the different binary pairs. In fact, the only miscible pairs are water + ethanol, water + ammonium sulfate, and ethanol + benzene. Data for the volume of mixing of these pairs near the temperature of interest (45 to 50 °C) were analyzed to yield the corresponding \( C_{14} \), which are given in Table IV. The remaining \( C_{14} \) were simply set equal to zero. This obviously represents a rather crude approximation whose principal justification lies in the fact that corrections for the volume of mixing are in any case quite small. Including the nonzero values in Table IV in our computations did improve the agreement.
between the predicted and measured indices of refraction, as shown in Fig. 3.

D. Temperature dependence of volumes occupied by different phases in samples of fixed composition

The heights of the meniscuses separating the various phases inside a sealed tube were measured as a function of temperature in several different experiments.\(^7,8,21,22\) These measurements provide the fraction of volume occupied by phase \(\delta\) as a function of temperature in a mixture of fixed overall composition. (We assume that under the conditions of these experiments a negligible fraction of the volatile components was in the vapor phase.) We compared the results with our model, using the formula

\[
\dot{V}_\delta = \frac{\lambda_\delta v^\delta}{\sum \lambda_\delta v^\delta}, \tag{4.7}
\]

where \(\lambda_\delta\) is the fraction of the total mass in phase \(\delta\) and \(v^\delta\) is the volume of this phase divided by its mass. We included volume of mixing corrections (Sec. IV C) when calculating \(v^\delta\), but their effect is small and their omission would produce negligible changes.

Our procedure was to assume some overall composition, calculate the values of \(h_5\) for each phase using our model and the procedures described in Sec. III C, and see how well the results agreed with the measurements. Since the experiments included measurements in regions of two- as well as three-phase coexistence, it was necessary to adopt values for the \(\epsilon_{i\mu}\); these are shown in Table IV. In addition, we modified Eq. (4.5) by the addition of a quadratic term

\[
\tilde{\epsilon}_{i\mu} = \tilde{\epsilon}_{i\mu}(t) - \epsilon_{i\mu}(t), \tag{4.8}
\]

with \(t_1\) and \(t_2\) the values of \(t\) at 44.91 and 48.04 °C, respectively. A quadratic term is necessary, for otherwise the matrix \(\tilde{\epsilon}_{i\mu}\) in (3.7) becomes singular at about 52 °C, given the numerical values we used in Eq. (4.5). (This fact may, of course, reflect an important deficiency in our model.) The use of the particular form of the last term in Eq. (4.8) permitted us to retain the previous values of \(\tilde{\epsilon}_{i\mu}\) for \(h = 0\) and 1 which we obtained from Lang and Widom's data.

The introduction of the \(\epsilon_{i\mu}\) and \(\tilde{\epsilon}_{i\mu}\) had very little effect on the calculated heights of meniscuses in samples containing three phases, or on quantities, such as \(R_\mu\), calculated for comparison with light scattering measurements (Sec. IV F below) in the three-phase region. The values of these parameters must be regarded as very approximate, since they were determined by trial and error rather than by any systematic approach. From Eqs. (3, 8) and (2.8) it is evident that the \(\epsilon_{i\mu}\) are, in effect, smooth contributions to the "susceptibility" of the system, and it is gratifying to note that the values in Table IV are, in fact, quite small compared to the value of the singular order-parameter susceptibility \(\chi\) in the region near the tricritical point to which our calculations apply.

A comparison of the experimental and model values for the \(\dot{V}_\delta\) in samples A and B is given in Fig. 2. The lines can be thought of as indicating the heights of the meniscuses separating liquid phases, as a function of temperature, in a cylindrical tube with its (flat) bottom at \(h = 0\) and the liquid-vapor meniscus at \(h = 1\).

We have also carried out calculations of meniscus heights as a function of temperature for comparison with Fig. 1 of Ref. 21 and Fig. 1 of Ref. 22. Again, we are able to obtain reasonable agreement in the sense that with small shifts in overall composition the calculated and experimental curves as a function of temperature can be made to correspond quite closely. Even without any shifts in overall composition there is qualitative agreement in the sense that phase \(\beta\) disappears as temperature rises leaving \(\alpha\) and \(\gamma\) present, and the amount of \(\gamma\) thereafter decreases with increasing temperature.

FIG. 2. Fractional meniscus heights as a function of temperature for samples A and B. The curves represent the predictions of the model.
E. Index of refraction in samples of fixed composition

For comparison with experimental results, we computed the index of refraction $n$ for our model in the following manner. We assumed that

$$n = \sqrt{\epsilon},$$  \hspace{1cm} (4.9)

where $\epsilon$, the dielectric constant at optical frequencies, is given by the Clausius–Mossotti equation

$$\epsilon = \frac{1 + (8\pi/3)N\gamma}{1 - (4\pi/3)N\gamma}. \hspace{1cm} (4.10)$$

Here $N$ is the number of molecules per unit volume and $\gamma$ the average polarizability per molecule, determined by

$$N\gamma = \frac{4}{3} \sum_{i=1}^{4} \gamma_i x_i/v M_i, \hspace{1cm} (4.11)$$

with $N_A$ Avogadro’s number, $v$ the volume per unit mass, and $\gamma_i$ and $M_i$ the polarizability and molecular weight for molecules of component $i$. In turn, $\gamma_i$ is obtained from index of refraction measurements on pure component $i$ in the temperature range of interest, or in the case of ammonium sulfate from the index of refraction in an aqueous solution. Thus, the Clausius–Mossotti relation serves, in effect, as an interpolation formula to obtain the index of refraction of the mixtures from its values in the pure components.

Figure 3 shows the temperature dependence of the refractive index determined experimentally in samples A and B, along with theoretical curves which include a correction for the volume of mixing as noted in Sec. IV C. Calculations with $Y_n = 0$ in Eq. (3.13), i.e., with no volume of mixing corrections, produced curves parallel to those shown in the figure but displaced by an amount indicated by the dashed vertical lines towards lower $n$. It is clear that including the volume of mixing gives better agreement with experiment, suggesting that our corrections are in the right direction.

F. Light scattering

If one accepts the Ornstein–Zernike formula

$$I(q) = I_0/(1 + q^2 \xi^2), \hspace{1cm} (4.12)$$

for the intensity of scattered light as a function of wave vector

$$q = (4\pi n/\lambda) \sin(\theta/2), \hspace{1cm} (4.13)$$

where $\theta$ is the scattering angle, $n$ the index of refraction and $\lambda$ the wavelength of light in a vacuum, it is possible to use measurements of intensity as a function of $q$ to obtain both $\xi$, the scattering intensity extrapolated to $q = 0$, and the correlation length $\xi$. These quantities were extracted from their data by the authors of Refs. 7 and 9.

We have compared them with our theoretical model using the following procedures.

In order to calculate $I_0$, we have assumed\(^\text{18}\) that it is proportional to the fluctuations in the optical dielectric constant $\epsilon$, and that near the tricritical point these fluctuations are dominated by the divergent term $\langle \xi \rangle^2$ in Eq. (2.18). Note that in this equation (see Sec. IV A above), $f_1$, $f_2$, $f_3$, $f_4$, and $f_5$ are to be replaced by $\mu_1$, $\mu_2$, $\mu_3$, $-p$, and $T$, respectively, and $\sigma_1$, $\sigma_2$, $\sigma_3$, $\sigma_4$, and $\sigma_5$ by $x_1$, $x_2$, $x_3$, $v$, and $s$, respectively. It is reasonable to suppose that $\epsilon$ is roughly independent of temperature if the density and composition of the fluid are held fixed, since the molecular polarizabilities $\gamma_i$ should depend only weakly on the temperature, and this justifies the approximation

$$\frac{\partial \epsilon}{\partial T} = 0 \hspace{1cm} (4.14)$$

in Eq. (2.18). Consequently, there is no need to evaluate $\partial a_n^i/\partial T$. From Eqs. (3.7) and (3.8) we see that

$$\frac{\partial a_n^i/\partial T}{a_n^i} = b n^i, \hspace{1cm} i = n, 2, \text{ or } 3, \hspace{1cm} (4.15)$$

and

$$\frac{\partial a_n^i/\partial \mu_i}{a_n^i} = 0, \hspace{1cm} i = 1, 2, \text{ or } 3. \hspace{1cm} (4.16)$$

A similar direct calculation of $\partial a_n^i/\partial p$ is not possible, since the dependence of $T$, $\mu_n$, and $P_n$ on the pressure is not known. However, one can show (Appendix C) that to a good approximation

$$\sum_{n=1}^{4} \frac{\partial a_n}{\partial p} \xi^{n-1} = \frac{\partial a_n}{\partial \xi}, \hspace{1cm} (4.17)$$

and the right-hand side can be evaluated with the help of Eqs. (3.13) and (3.14). Note that various constants of proportionality, such as the $M$ in Eq. (2.18), are of no particular interest since we shall only be concerned with data in a small temperature range near the tricritical point, and in the experiments only relative, not absolute, intensities were measured.

Due to the fact that our estimates for the $\epsilon_i$ in Eq. (3.8) are very tentative, we set them equal to zero for the calculations reported below, after checking that the values shown in Table IV are in a small temperature range near the tricritical point.

It is interesting to note that the end result after all of these approximations, which seem to make negligible changes in the three-phase region near the tricritical point, is precisely the formula

$$I \propto \chi(\delta \epsilon/\partial \psi)^2 \hspace{1cm} (4.18)$$

employed in Ref. 10, where $\delta \epsilon/\partial \psi$ is to be understood in the following way. The vertices of the three-phase triangles of the three-phase region form a smooth curve in the composition tetrahedron at a fixed temperature (see, for example, Ref. 5). Our calculations supply values for both $\epsilon$ and $\psi$, and thus the derivative $\delta \epsilon/\partial \psi$ along this curve.

The experimental values of $I_{11}$, $I_{12}$, and $I_{13}$, the subscript referring to the phase in question, for samples A and B are shown as a function of $\Delta T = T - T_c$ on a logarithmic scale in Fig. 4, together with the theoretical predictions for $\langle \xi^2 \rangle_T$. For each sample we normalized the intensities by choosing a single constant, independent of temperature and independent of the phase. (In addition as noted earlier in Sec. IV A, we adjusted the temperature scale and also made a slight modification in the overall composition for sample B. The agreement between the experimental and theoretical values is generally satisfactory. Note that the theoretical predictions show a significant curvature.}

The light scattering data can also be used to check the sum rules in Eqs. (2.33) and (2.34). However, it is very important, as pointed out in previous publications,\textsuperscript{9,10} to take account of the fact that the term in parentheses on the right side of (2.18), while it tends to a constant at the tricritical point, does show a significant variation in the region near the tricritical point corresponding to the experiments on samples A and B. Thus, our model predicts that at a temperature of 47.55 °C the ratio $R_I$ defined in Eq. (2.35), with intensities proportional to $(\delta \phi)^2$, will vary with the parameter $\theta$ [see Eq. (2.36)] in the manner shown in Fig. 5, where the upper curve contains and the lower curve omits volume of mixing corrections. Note that each value of $\theta$ corresponds to one set of three coexisting phases, and that unless $\theta$ is near 0° or 60°, which is to say unless the sample is very near one of the two critical end points, our model predicts a significant deviation from the value 1 which would be expected if $I$ were proportional to $\chi$ in each phase with precisely the same proportionality constant.

Experimental values of $R_I$ for samples A and B, together with the predictions of our model, are shown in Fig. 6. (There are two theoretical curves because the two samples have different overall compositions.) The theoretical curves show $R_I$ decreasing with temperature, consistent with the fact that asymptotically close to the tricritical point $(\delta \phi)^2$ will be strictly proportional to $\chi$. The experimental values of $R_I$ show no such decrease and, indeed, may actually be increasing with temperature, though the size of the error estimates makes it hard to reach a definite conclusion.

Experimental values for $Q_I$, calculated from Eq. (2.36) using the intensity normalization referred to earlier, for samples A and B are shown in Fig. 7 along with the corresponding predictions of our model. Were $I$ strictly proportioned to $\chi$, the two theoretical curves would coincide and form a straight line intersecting the temperature axis at $T_A = 49.1$ K. The fact that the lines are displaced from each other and curved is an indication of the importance of the variation of the final factor in Eq. (2.18). Once again, while the agree-
The correlation length $\xi$ as a function of $\Delta T = T - T_t$ in the three-phase region. The circles, squares, and triangles (open for sample A, filled for sample B) are the experimental values for phases $\alpha$, $\beta$, and $\gamma$, respectively; the solid curves are calculated from Eq. (2.21).

In order to provide model predictions of the correlation length $\xi$ for comparison with the results from light scattering, we used Eq. (2.21) and assumed that the dependence of $g$ on composition could be approximated by writing it as a quadratic function of $\psi$:

$$g = g_0 + g_1 \psi + g_2 \psi^2. \quad (4.19)$$

The values of the coefficients $g_0$, $g_1$, $g_2$ given in Table IV were determined using the correlation lengths measured in the three coexisting phases in sample A at a temperature of 47.55°C, and reported in Ref. 9, along with the values of $\chi$ predicted by our model. It should be noted that these correlation lengths do not include the corrections for multiple scattering reported in Ref. 7 and that the experimental results shown in Figs. 8, 9, and 10 are based on uncorrected correlation lengths for both samples A and B (see Sec. IV A). We have checked that the corrected correlation lengths for sample A can be fitted equally well by our model using an alternative choice for the $g_i$'s. (The fractional corrections to $\xi$ are all of the same sign and of the same general magnitude, typically 7%, and thus they have very little effect on $R_\xi$ at least for the measurements on sample A.)

The $g_i$'s determined in the manner just described were then used to calculate $\xi$ as a function of temperature for each of the three phases in samples A and B, with the results shown in Fig. 8, which should be compared with Fig. 4. Again there is a noticeable curvature in the theoretical values in this logarithmic plot. Note that the experimental measurements yield values of $\xi$ directly, without arbitrary multiplicative factors, and thus the data for samples A and B are directly comparable, unlike the (absolute) intensities. Indeed, it is this comparison which motivated our applying a shift to the temperature values reported for sample B, as discussed above in Sec. IV A.

Experimental values and theoretical predictions for $R_\xi$ and $Q_\xi$ [Eqs. (2.37) and (2.38)] are shown in Figs. 9 and 10, respectively. In the case of $Q_\xi$, the two theoretical curves for samples A and B cannot be distinguished. Once again there is some evidence in the $R_\xi$ values for a systematic discrepancy between experiment and model calculations in that the latter show a definite decrease with temperature whereas the former do not.

There is no independent way (that we know of) to check the values of the $g_i$ which enter Eq. (4.19), and the coefficient $g_2$ is somewhat large, leading to a variation in $\sqrt{g}$ of about 30% over the range of compositions of three coexisting phases at 48°C. On the other hand, it would be implausible to assume that there is no dependence of $g$ on composition, and at the same temperature (48°C) $d\epsilon/d\psi$ [see Eq. (4.18)] varies by more than a factor of

$$\frac{Q_\xi}{(\text{number of A})}$$

for samples A and B. A single calculated curve is shown because the model indicates only very slight differences for the two compositions.
2 in the three-phase region. The dependence which we have assumed helps to explain an experimental "anomaly" in sample B: at several temperatures \( I_1 \) exceeds \( I_n \), whereas \( I_2 \) is less than \( I_2 \). This would, of course, be impossible were \( I \) and \( \xi \) strictly proportional to \( \chi \).

### G. Behavior of a sample with the tricritical composition

The thermodynamic model may be used to predict various properties of mixtures in the tricritical region. In this section we consider the behavior of a sample of fixed overall composition precisely equal to the tricritical composition, i.e., the case in which [see Eqs. (3.17), (3.25), and (4.5)]

\[
x_{1} = \frac{\xi_{0}}{\xi_{100}}.
\]  

(4.20)

The model predicts that this sample consists of three phases at temperatures below 46.5 °C, then two phases in the interval between 46.5 and the tricritical temperature at 49.1 °C, one phase in the interval of 49.1 to 49.9 °C, and again two phases above this temperature, or at least up to 51 °C; we do not place much confidence in our model at still higher temperatures. The meniscus heights are shown in Fig. 11. Note the break in the scale; over the entire temperature from 46 to 51 °C more than 90% of the volume is occupied by the single phase \( \beta \), i.e., the phase which evolves continuously in temperature from the \( \beta \) phase in the three-phase region. Such behavior is in marked contrast to what one finds in samples of fixed composition equal to the critical composition near an ordinary critical point, where two phases are, typically, present in roughly equal amounts.

We are not certain as to how much of the behavior just discussed depends on the particular choice of parameters in our analysis and to what extent it is to be anticipated for any system described by such a classical model and lacking special symmetries. However, some aspects can be readily analyzed in terms of the equations of Secs. III and IV as follows.

From Eqs. (4.20), (3.17), (3.25), and (4.8), one sees that

\[
x_{1} - b_{10} = \frac{\xi_{100} - b_{10}}{\xi_{100}} = \frac{\xi_{100} - b_{10}}{\xi_{100}} + O(\xi^{2})
\]  

(4.21)

will be proportional to \( t \) for small \( t \). Then by inverting Eq. (3.17) we conclude that the \( a_{1} \) are also proportional to \( t \) in general, i.e., apart from some special choice of parameters. Similarly, inverting Eq. (3.24) shows that in the three-phase region (if it exists), the \( a_{1} \) will be proportional to \( t \). But this is not possible in view of Eq. (3.26), since \( |\cos \theta| \) cannot exceed 1. Thus we conclude, in agreement with Ref. 4, that the three-phase region cannot extend all the way up to the tricritical temperature in a sample of fixed composition. [Of course, three-phase coexistence for \( T > T_{t} \) is impossible in our model, since \( a_{1} \) is a positive constant times \( T - T_{t} \), Eq. (3.5).]

If the \( a_{1} \) are asymptotically proportional to \( t \), the same is true of the coefficients \( B_{0}, B_{1}, \) and \( B_{2} \) (Appendix B) in Eq. (3.29), whereas \( B_{3}, B_{4}, B_{5}, \) and \( B_{6} \) tend to constant values at the tricritical point. Hence, we conclude that in the two-phase region (if it exists), \( S \) will vary asymptotically as

\[
S \propto |t|^{1/3},
\]  

(4.22)

whereas \( P \) (Appendix B) and \( \Delta \) [Eq. (3.27)] will behave as

\[
P \propto t, \quad \Delta \propto |t|^{2/3}.
\]  

(4.23)

These results can be used to show that the order parameter susceptibility \( \chi \) [see Eq. (2.32) and also Eqs. (2.23) and (2.30)] diverges as

\[
\chi \propto |t|^{-4/3}
\]  

(4.24)

upon approaching the tricritical point through the two-phase region and that, moreover, the ratio of \( \chi \) in the \( \beta \) phase [defined within the model by Eq. (2.24)] to that in the coexisting phase tends to 2 at the tricritical point.

The asymptotic behavior of \( \chi \) in the one-phase region (if it exists) can be determined using the methods of Sec. III C 4. In particular, Eq. (3.30) implies that \( \phi \) is proportional to \( \xi_{t} \), and Eq. (3.18) that \( a_{2} \) and \( a_{3} \) are proportional to \( t \). Hence, by use of Eq. (2.11) we infer that

\[
\chi \propto |t|^{-1}.
\]  

(4.25)

It should be noted that these results for the one- and two-phase regions depend on the assumption (3.20). Whereas we do not think they would be altered in the presence of nonzero \( \epsilon_{tt} \), we have not checked this.

Unfortunately, we have not been able to confirm that the situation shown in Fig. 11, two phases coexisting just below and only one phase just above the tricritical temperature, is a general feature of the classical model, nor to show the opposite, that other situations are possible by an alternative selection of the parameters.

### V. CONCLUSIONS

The basic conclusion of our calculation is that all the available experimental data on the static properties of the mixture ammonium sulfate + water + ethanol + benzene

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near its tricritical point can be fit remarkably well by a classical model based on the Landau expansion (2.3). Since this is a phenomenological model, it is necessary, in the nature of the case, to choose values for a large number of phenomenological constants which are free parameters within the framework of the model. Our choices are given in Tables III and IV, and with these we find that the classical model performs reasonably well for temperatures within three or four degrees of the tricritical temperature (if $I \leq 0.01$) and compositions sufficiently close to the tricritical value to exhibit three-phase coexistence within this temperature range.

The earlier analysis by Lang and Widom\textsuperscript{5} showed that the three-phase region near the tricritical point was in good qualitative and fairly good quantitative agreement with the classical model. Our own calculations have confirmed this result. The compositions given in Table I are based purely on the classical model, and we find no evidence of any substantial departure from classical behavior. Our estimate of the tricritical temperature (49.1°C) is slightly higher than that of Lang and Widom, and we suspect that their choice of a lower value may have been the source of their conclusion that their exponent $\beta_4$ was 0.4 instead of the classical 0.5.

In addition, however, we have shown that the classical model is in good agreement with the results of light-scattering measurements in the three-phase region. The prediction of the intensity $I$ of light scattered at zero angle (Fig. 4) is particularly impressive when one notes that the calculation requires a rather careful analysis of the dependence of the optical dielectric constant on the order parameter, and this analysis was carried out within the framework of the classical model. It is true that we found it necessary, in the absence of experimental data on the densities of the coexisting phases, to make a somewhat crude estimate for the volume of mixing; nonetheless, this estimate involved no additional free parameters since the $C_{ij}$ in Table IV were taken from other experiments.

To be sure, agreement between theory and experiment is not perfect. This is particularly apparent in the dimensionless quantity $R_{ij}$, defined in Eq. (2.35) and plotted in Fig. 6. The theoretical curves decrease with increasing temperature, and there is no evidence for such a decrease in the experimental values. Nonetheless, one needs to be cautious, both because the theoretical curves could be shifted somewhat (though they would probably still be monotone decreasing) if we had better estimates of the densities of the coexisting phases, and because of the substantial multiple-scattering effects in the experiments.

The agreement between our calculated values for the correlation length (Fig. 8) and the experimental values determined by light scattering is, once again, fairly good. We had to choose three adjustable parameters, the $g_i$ in Eq. (4.18), in order to carry out the comparison, but this choice could be made at a single temperature. (The comparison actually involves correlation lengths which have not been corrected for the effects of multiple scattering in the original data, for reasons explained in Sec. IV A. However, as noted in Sec. IV F, a different choice of the $g_i$'s leads to an equally good fit to the corrected correlation lengths\textsuperscript{3} of sample A. It should also be noted that we made an adjustment to the temperature scale and the composition for one of the samples, as discussed in Sec. IV.)

The agreement between our model predictions and available data in the two-phase region near the tricritical point is much less impressive. The reason is that we had very little data to work with and a large number of adjustable parameters (the $\epsilon_{ij}$ and $\bar{b}_{ij}$ of Table IV). Nonetheless, we think it is significant that the model was able to provide reasonable predictions for the meniscus height in the two-phase region for two samples of constant composition. Additional experiments in the two-phase region would help to refine the model parameters and might well uncover some deficiencies in the classical approach. It would also be interesting if experiments could be carried out at the tricritical composition or extremely close to it, in order to test the predictions of the model given in Sec. IV G.

Current theoretical ideas, and experiments near tricritical points in systems with symmetry breaking, strongly suggest that departures from classical tricritical behavior should occur in liquid mixtures of the sort considered in this paper. Thus the success of our analysis, whereas it is in one sense very gratifying, is in another sense a bit disappointing in that we find no solid evidence for nonclassical tricritical effects. It would be very useful to have an appropriate nonclassical equation of state near the tricritical point which could be fitted to available experimental data and which could provide indications of the magnitude and location of the most prominent nonclassical effects. We ourselves, however, have not been successful in developing such an equation of state.

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APPENDIX A: EXPRESSIONS FOR THE $a_i$

By multiplying out Eq. (2.22), comparing it with Eq. (2.3), and using Eq. (2.23), one obtains the expressions

$$a_1 = \psi_{xx} \psi_{xx} \left( \psi_{xx}^2 + \psi_{xy}^2 + \psi_{yy}^2 + 2 \left( \psi_{xx}^2 + \psi_{xy}^2 + \psi_{yy}^2 \right) \right) - 2 \left( \psi_{xx} \psi_{xy} \psi_{xx} + \psi_{xx} \psi_{xy} \psi_{yy} + \psi_{yy} \psi_{xy} \psi_{yy} \right),$$

$$a_2 = \frac{1}{2} \left( \psi_{xx}^2 + \psi_{xy}^2 + \psi_{yy}^2 \right)^2 - \left( \psi_{xx}^2 + \psi_{xy}^2 + \psi_{yy}^2 \right) \left( \psi_{xx}^2 + \psi_{xy}^2 + \psi_{yy}^2 \right) + 3 \left( \psi_{xx} \psi_{xy} \psi_{xx} + \psi_{xx} \psi_{xy} \psi_{yy} + \psi_{yy} \psi_{xy} \psi_{yy} \right),$$

$$a_3 = 2 \left( \psi_{xx}^2 + \psi_{xy}^2 + \psi_{yy}^2 \right) - \left( \psi_{xx}^2 + \psi_{xy}^2 + \psi_{yy}^2 \right),$$

$$a_4 = \psi_{xx}^2 + \psi_{xy}^2 + \psi_{yy}^2 - \left( \psi_{xx}^2 + \psi_{xy}^2 + \psi_{yy}^2 \right).$$

APPENDIX B: COEFFICIENTS $B_i$ IN EQ. (3.29)

In order to write the coefficients in a compact form, let us introduce the following symbols, employed (in the manner defined here) only in this appendix:

\[
\begin{align*}
 b &= \epsilon_{22}, \\
 c &= \epsilon_{33}, \\
 f &= \epsilon_{33}, \\
 g &= \epsilon_{22} - \epsilon_{33}, \\
 \alpha &= u_1, \\
 \beta &= u_2, \\
 \gamma &= u_3, \\
 \theta &= 3l/2.
\end{align*}
\]

The elimination procedure described in Sec. III C leads to the following two equations in $S$ and $P$:

\[
P[c - b\alpha + (6g - b)S] = by - c\beta + (2g\theta + c\alpha)S - b\alpha S^2 + 4gS^3,
\]

\[
\beta - P - \alpha S + cS(6P - 4S^2 - 2\theta) + b(3S^4 - 3P^2 + \theta(S^2 + 2P)) = 0.
\]

Solving the first equation for $P$ and inserting it in the second yields Eq. (3.29) with the coefficients $B_i$ given by the following expressions:

\[
B_0 = 3(by - c\beta)^2 + (by - c\beta)[2\theta(by - c\beta) + \gamma + \alpha],
\]

\[
B_1 = (by - c\beta)(1 + 6f + 2b\theta) + (by - c\beta)\{(\alpha + 2c\theta)^2 - 2\theta(1 + 6f)\},
\]

\[
B_2 = -6ba(by - c\beta) + (by - c\beta)\{(\alpha + 2c\theta)^2 - 2\theta(1 + 6f)\} + 3(4\alpha + 2g\theta)^2 + 3(by - c\beta)[\gamma + \alpha - \alpha S - (b \alpha - c\theta)],
\]

\[
B_3 = 2[2c f + 12g(by - c\beta) + \alpha(c - 4b\alpha) + f(b - 18g)] + 2\theta \{c(b - 8g) - b\alpha(b - 5g)\},
\]

\[
B_4 = 4\alpha(2b + 9g) - \theta(b - 2g) - b - 18g - 7c^2 - 4f(b - 6g),
\]

\[
B_5 = 10(b - 6g) - 6ba(b - 2g),
\]

\[
B_6 = -3(b - 2g) - 10g.
\]

APPENDIX C: DERIVATION OF EQ. (4.17)

If we choose $i = 4$ in Eq. (2.13) and make the identification (Sec. III A) of $\phi_i$ with $v$ and $f_j$ with $-\rho$, the result is

\[
v = v_r + \sum_{i \neq r} \left( \frac{\partial \phi_i}{\partial \rho} \right) \phi_i = \tilde{v}_r(\tilde{\mu}_1, \tilde{\mu}_2, \tilde{\mu}_3, \rho, T, \phi),
\]

where $v_r$ stands for $\partial \phi_i/\partial \rho$. The dependence of the function $\tilde{v}$ on $\phi$ is that given explicitly in Eq. (C1), while its dependence on $\tilde{\mu}_i$, $\rho$, and $T$ when $\phi$ is fixed comes about through the dependence of $v_r$ and $\partial \phi_i/\partial \rho$ on these quantities. Thus when $\phi$ is fixed, $\tilde{v}$ is a smooth function of all of its other arguments, and the same is true of its partial derivatives at fixed $\phi$. In a similar manner we can write Eq. (3.9) in the form

\[
x_i = \tilde{x}_i(\tilde{\mu}_1, \rho, T, \phi),
\]

where the dependence of $\tilde{x}_i$ on $\psi$ is shown explicitly in Eq. (3.9), and for fixed $\phi$, $\tilde{x}_i$ is a smooth function of its other arguments.

Of course, the equilibrium $\phi$ is itself a specific function of $\rho$, $T$, and the $\tilde{\mu}_i$'s. Thus $v$ is also a function of $\rho$, $T$, and the $\tilde{\mu}_i$'s or, equivalently, of $\rho$, $T$, and $x_1$, $x_2$, $x_3$. In the calculation which follows, we shall keep $\rho$ and $T$ fixed and therefore omit them from the arguments and subscripts. By differentiating (C1) with respect to $\tilde{\mu}_1$ at fixed $\tilde{\mu}_2$ and $\tilde{\mu}_3$ we obtain

\[
\sum_i \left( \frac{\partial \phi_i}{\partial \tilde{\mu}_1} \right) \frac{\partial \tilde{v}_r}{\partial \tilde{\mu}_1} + \left( \frac{\partial \phi_i}{\partial \mu_1} \right)_T \frac{\partial \tilde{v}_r}{\partial \mu_1}.
\]

where the subscripts $x$ and $\mu$ mean that the remaining $x$'s or $\mu$'s are held fixed. Similarly, from Eq. (C2), we obtain

\[
\left( \frac{\partial \phi_i}{\partial \tilde{\mu}_1} \right)_S + \left( \frac{\partial \phi_i}{\partial \mu_1} \right)_S.
\]

Combining Eq. (C3) with (C4) yields

\[
\left( \frac{\partial \phi_i}{\partial \tilde{\mu}_1} \right)_S + \left( \frac{\partial \phi_i}{\partial \mu_1} \right)_S - \left( \frac{\partial \phi_i}{\partial \psi} \right)_S.
\]

We expect the term in square brackets in Eq. (C5) to remain finite at the tricritical point, due to the properties of the $\chi_i$ and the $\tilde{v}_r$ functions previously discussed and the fact that we do not expect any divergences in $\partial \phi_i/\partial \psi$. On the other hand,

\[
\left( \frac{\partial \phi_i}{\partial \mu_1} \right)_S,
\]

should be proportional to $\chi$ [Eq. (2.11)] and diverge strongly at the tricritical point. Hence, it should be a good approximation to retain only the first sum on the right side of Eq. (C5). But then differentiating Eqs. (C1) and (3.9) with respect to $\psi$ and inserting the results in Eq. (C5) yields (in this approximation) Eq. (4.17).
The actual form of $M$ depends on the choice of thermodynamic variables. Some examples are given in Ref. 16.