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Thermodynamic Model and Sum Rules for Three-Phase Coexistence near the Tricritical Point in a Liquid Mixture

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(Received 24 August 1979)

Two sum rules for order-parameter susceptibilities are derived for the classical theory of the three-phase region near a tricritical point in ordinary liquid mixtures. The classical theory can also be fitted in a quantitative way to the composition data of Lang and Widom near the tricritical point in the mixture ethanol + benzene + water + ammonium sulfate.

In principle, it should be possible to obtain a wealth of information about tricritical points by carrying out experiments on ordinary liquid mixtures.[1] Variations in composition, temperature, and pressure permit one to alter thermodynamic parameters whose counterparts at a typical symmetry-breaking tricritical point (such as in $FeCl_2$ or ^3He-^4He mixtures) are not under experimental control. However, in practice it is difficult to interpret experimental data for ordinary mixtures near tricritical points precisely because of the large number of thermodynamic degrees of freedom: Four variables must be adjusted to achieve the tricritical state, in place of the two which suffice for a symmetry-breaking system, and phase diagrams should, ideally, be drawn in four dimensions! Thus the task of understanding such experiments can be greatly assisted by the development of *quantitative* theoretical and phenomenological descriptions which can be compared with, or applied to, the laboratory data.

In this Letter we report two results which should be quite useful in interpreting experimental data in the region of three-phase coexistence near a tricritical point. The first is a pair of sum rules for the order-parameter susceptibility. Experimental tests of these sum rules are reported in an accompanying Letter.[2] The second is a practical method of choosing parameters in a thermodynamic model to fit data on compositions of three coexisting phases in a four-component mixture. We have applied it to the data of Lang and Widom[3] for the mixture ethanol + benzene + water + ammonium sulfate, and the results near the tricritical point are very encouraging.

Both results are based on the classical theory[4] of tricritical points and thus do not include nonclassical effects such as the expected logarithmic corrections to scaling.[5,6] Thus far there has been no clear-cut experimental evidence of nonclassical tricritical effects in ordinary mixtures. Of course, one way of looking for such effects is to find where the predictions reported here break down.

In the classical theory the stable thermodynamic state is given by that value of an order parameter ψ which minimizes a free energy Ψ which we assume is a polynomial of the form

$$\Psi = \sum_{j=0}^{6} a_j \psi^j. \qquad (1)$$

We choose $a_6 = 1$, so that for three coexisting phases Ψ has the form

$$\Psi = (\psi - \psi_\alpha)^2(\psi - \psi_\beta)^2(\psi - \psi_\gamma)^2 + \text{const}, \tag{2}$$

where

$$\psi_\alpha < \psi_\beta < \psi_\gamma \tag{3}$$

are the values of ψ in phases α, β, and γ, respectively. If the origin for ψ is chosen so that[4]

$$a_5 = 0 = \psi_\alpha + \psi_\beta + \psi_\gamma, \tag{4}$$

it follows that

$$a_4 = 2(\psi_\alpha\psi_\beta + \psi_\alpha\psi_\gamma + \psi_\beta\psi_\gamma). \tag{5}$$

Let us define the susceptibility χ_α in phase α by

$$\chi_\alpha^{-1} = [d^2\Psi/d\psi^2]_{\psi=\psi_\alpha} = 2(\psi_\alpha - \psi_\beta)^2(\psi_\alpha - \psi_\gamma)^2, \tag{6}$$

and similarly χ_β and χ_γ. *The first sum rule*

$$\chi_\alpha^{1/2} + \chi_\gamma^{1/2} - \chi_\beta^{1/2} = 0 \tag{7}$$

is a consequence of (6) and its analogs for the other phases, where (3) should be noted when square roots are taken. *The second sum rule*

$$\chi_\alpha^{-1/2} + \chi_\gamma^{-1/2} - \chi_\beta^{-1/2} = -3a_4/\sqrt{2} \tag{8}$$

comes from combining (4), (5), and (6) and its analogs. Various other results, such as

$$\chi_\alpha^{-1} + \chi_\beta^{-1} + \chi_\gamma^{-1} = 9a_4^2/2 \tag{9}$$

can be obtained by combining (7) and (8).

The sum rules are of practical interest because (7) should hold throughout the three-phase region, and the right-hand side of (8) depends only on temperature if we make the identification in (10) below. Thus certain combinations of quantities in the three phases should be independent of the compositions of the individual phases, and this is an advantage because these compositions are difficult to measure.

Lang and Widom[3] have carried out careful measurements of the compositions of a number of cases of three coexisting phases in the mixture water + ethanol + benzene + ammonium sulfate. We shall show how such information can be combined with (1) in order to produce a thermodynamic model which can make predictions of properties throughout the three-phase region near the tricritical point. The basic problem is to find the relationship between the a_j, ψ, and quantities observed experimentally.

First we let a_4 be a measure of temperature[4]:

$$a_4 = \tfrac{3}{2}t = 3/2(T/T_t - 1), \tag{10}$$

where T is the sample and T_t the tricritical temperature (in degrees Kelvin). Next we suppose that the weight fraction x_i of the ith component in the mixture has the form

$$x_i = b_{i0} + \sum_{j=1}^{3} b_{ij}\psi^j, \tag{11}$$

where the b_{ij} are smooth functions of T.

For a fixed $t < 0$ there is a one-parameter family of regions of three-phase coexistence. (It may be visualized as a stack of triangles in the space of compositions.[3]) We can label each member of this family (i.e., each three-phase triangle) with a parameter θ in the range $0° < \theta < 60°$. The order parameter ψ_δ in phase δ [$\delta = \alpha$ or β or γ] is given by inserting

$$\varphi_\alpha = 120° + \theta, \quad \varphi_\beta = 120° - \theta, \quad \varphi_\gamma = \theta, \tag{12}$$

in the formula

$$\psi_\delta/(-t)^{1/2} = \cos\varphi_\delta. \tag{13}$$

One can check that this representation[7] is consistent with (4), (5), and (10), and that $\theta = 0°$ and $60°$ are the α-β and β-γ critical end points.

To determine the b_{ij} in (11), we used the following procedure. At a fixed temperature we assigned a preliminary value of θ to each three-phase triangle whose compositions had been measured by Lang and Widom, in such a way that for each component the points $x_i(\varphi)$, as determined by (12), lay close to a smooth curve in the interval $0° < \varphi < 180°$. The coefficients d_{ij} in

$$x_i(\varphi) = d_{i0} + \sum_{j=1}^{3} d_{ij}(\cos\varphi)^j \tag{14}$$

were adjusted to produce a least-squares fit to the data points. The values of θ were then readjusted to improve the fit, etc. By this technique we were able to fit the Lang and Widom weight fractions with typical deviations of ±0.004 for the liquids and ±0.001 for the salt at 44.91 and 48.04 °C, and ±0.02 for the liquids and ±0.003 for the salt at 20.9 and 21.0 °C.

Next we carried out an interpolation for the Lang and Widom measurements above 44 °C with use of the functional form [see (11), (13), and (14)]

$$\begin{aligned} d_{ij} &= (-t)^{j/2} b_{ij}, \\ b_{ij} &= b_{ij0} + (-t) b_{ij1}. \end{aligned} \tag{15}$$

In seeking an optimal form for the coefficients, we treated T_t as an adjustable parameter. While any value between 49.0 and 49.3 °C gave acceptable results, the values of the b_{ijk} in Table I are

TABLE I. Coefficients b_{ijk} determined from experimental data.

(j,k)	$i = 1$ (salt)	$i = 2$ (water)	$i = 3$ (ethanol)	$i = 4$ (benzene)
(0,0)	0.0166	0.3542	0.4562	0.1730
(1,0)	0.3264	2.290	-0.4373	-2.179
(2,0)	2.324	0.634	-12.224	9.266
(3,0)	11.52	47.01	-9.54	-48.98
(0,1)	-0.1752	-0.2159	0.5146	-0.1235
(1,1)	-2.784	-2.214	-1.174	6.173
(2,1)	23.54	19.86	167.0	-210.4
(3,1)	-118	-4783	967	3934

based on

$$T_t = 49.1\,^\circ\mathrm{C}. \tag{16}$$

This is somewhat higher than the Lang and Widom estimate of 48.9 ± 0.1 °C, and the b_{i00} in Table I, which are our estimates for the tricritical compositions, also differ slightly from those of Lang and Widom.

The results just described have been used for various calculations. One of considerable interest in connection with the accompanying Letter[2] was a calculation of the derivative $d\epsilon/d\psi$ which enters the formula

$$I \propto (d\epsilon/d\psi)^2\chi \tag{17}$$

for the intensity of light scattered at zero angle near the tricritical point. The value of the dielectric constant ϵ can be obtained from the Clausius-Mossotti formula if the density as well as the composition of a phase is known. Since the densities were not measured by Lang and Widom, we estimated them as follows. We assumed that the volume occupied by 1 g is given by

$$V = (\textstyle\sum_i V_i)(1 - \sum_{j<k} c_{jk} x_j x_k), \tag{18}$$

where V_i is the volume occupied at the same temperature by an amount of pure component i equal to that in 1 g of the phase of interest. The coefficients c_{jk} for the pairs ammonium-sulfate–water, water-ethanol, and ethanol-benzene were set equal to 0.07, 0.1, and 0.007, respectively; these values were obtained from published data on the volume of mixing in the corresponding *binary* mixtures. The other c_{jk} were set equal to zero. This is a crude approximation whose main justification lies in the fact that employing these nonzero c_{jk} in (18) did not produce very large changes in the value of R_I in (19) below (see Fig. 1) but did give values for the index of refraction in better agreement with experiment.

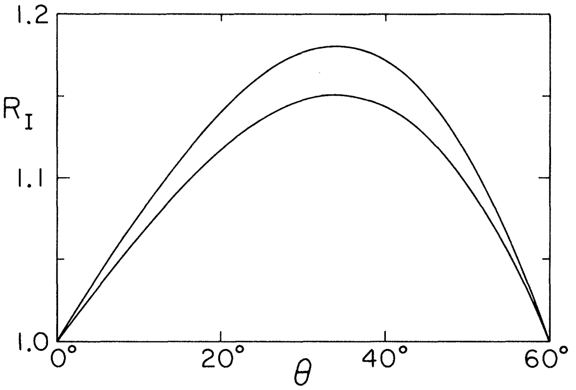

FIG. 1. Calculated R_I as a function of θ at 47.55 °C. The lower curve is calculated without volume of mixing corrections, and the upper curve includes these corrections.

From the Clausius-Mossotti formula, with use of polarizabilities as determined from optical measurements on the pure components (and solutions of ammonium sulfate in water) near the temperatures of interest, we calculated ϵ as a function of the mass fractions at a fixed temperature, and then $d\epsilon/d\psi$ with the dependence of these mass fractions on ψ given by (11). Then with the help of (17) we calculated

$$R_I = (I_\alpha^{1/2} + I_\gamma^{1/2})/I_\beta^{1/2} \tag{19}$$

as a function of θ; the results at $T = 47.55\,^\circ\mathrm{C}$ are shown in Fig. 1. Note that R_I has a smooth maximum near $\theta = 30^\circ$ at a value, 1.18, which is not too different from experiments[2] carried out at this temperature. However, the maximum value of R_I decreases linearly to 1 as $|t|$ goes to zero near the tricritical point, a result not confirmed by experiment.

A corresponding "classical" attempt to explain why experiments[2] give a value of

$$R_\xi = (\xi_\alpha + \xi_\gamma)/\xi_\beta \tag{20}$$

significantly larger than 1 can be carried out by assuming that the correlation length ξ is proportional to $(g\chi)^{1/2}$, where

$$g = g_0 + g_1\psi + g_2\psi^2 \tag{21}$$

is a ψ-dependent coefficient of the $(\nabla\psi)^2$ term in a Landau-Ginzburg theory. By making g_2 sufficiently large it is possible to produce values of R_ξ as large as those found experimentally. However, as there is no independent basis for determining the g_j, and as the maximum value of R_ξ

at a given temperature is predicted to decrease to 1 as $|t|$ goes to zero, a result not supported by experiments, one must view this explanation with some skepticism.

Once the model parameters have been fixed, as in Table I, it is possible to run "computer experiments" on samples of fixed compositions, similar to those used in the light-scattering experiments, and to predict meniscus heights and relative scattering intensities as a function of temperature. We found that by choosing compositions close to those reported for the experiments we could obtain reasonable agreement for meniscus heights and somewhat worse agreement for intensities in the three-phase region, but that the model was not nearly as good in the two-phase regions adjoining the three-phase region. Details of these calculations will be published separately.

We are grateful to Dr. Goldburg, Dr. Kim, Dr. Levelt Sengers, Dr. Esfandiari, and Dr. Wu for providing us with their experimental data before publication (Ref. 2). Dr. Levelt Sengers gave us major assistance in the calculation of $d\epsilon/d\psi$. Our research was supported by the National Science Foundation through Grant Nos. DMR 76-23071 and DMR 78-20394.

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Light Scattering and Sum Rules in Three Phases of a Liquid Mixture near Its Tricritical Point

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(Received 24 August 1979)

Measurements of light-scattering intensity and correlation lengths in all three coexisting phases in the mixture water + benzene + ethanol + ammonium sulfate are reported for temperatures near the tricritical point. A comparison with two sum rules predicted by a classical theory shows fairly good agreement in one case and significant deviations in the other. Possible explanations of the latter are discussed.

Tricritical points are the only multicritical points which have thus far been observed in ordinary liquid mixtures.[1-5] Light scattering is a useful probe for studying tricritical points, and in the case of ordinary mixtures it provides direct information about fluctuations in the principal order parameter. The interpretation of previous studies[2,3] of intensity and linewidth has been hindered, however, by the fact that these quantities depend not only on the temperature, but also, in a fairly complicated way, on the precise composition of the liquid sample, a variable which is not easy to measure or to control.

In this Letter we report measurements of intensity and correlation length in *each* of three coexisting phases near the tricritical point in the system[4,5] water + ethanol + benzene + ammonium sulfate, and analyze the data with use of two sum rules predicted by the classical theory[6] of tricritical points and derived in the accompanying Letter.[7] These rules predict that, independent of composition, certain functions of measured