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Asymmetry in Critical Light Scattering from Binary Mixtures of Phenol and Water in the Two-Phase Region*

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Previously reported experiments by Pusey, Bak, and Goldburg showed an asymmetry in the light scattering in the high- (h) and low- (l) density phases of critical mixtures of phenol and water at temperatures below the critical temperature T_c. Those experiments have been reanalyzed to evaluate the exponents τ and θ in the asymptotic expressions $I_{h(l)} \propto (|t|^{-\gamma} \pm B'|t|^{-\theta})$ and $\Gamma_{h(l)} \propto (|t|^{\nu^*} \mp B|t|^{\tau})$, where I and Γ are, respectively, the intensity and spectral width of the scattered light and $t=(T-T_c)/T_c$. The experimental results are discussed in terms of recent ideas concerning expected nonsymmetric behavior in pure fluids and binary mixtures. The value of τ the experiments yield can be accounted for in terms of simple linear dependence of the viscosity on concentration.

I. INTRODUCTION

Recent light-scattering measurements by Pusey, Bak, and Goldburg[1] have indicated asymmetric behavior of the scattered light intensity (I) and the spectral width (Γ) below the critical temperature T_c in a critical binary mixture of phenol and water. In Fig. 1 we show a log plot of T/I vs $|\Delta T| = |T-T_c|$ for pure phenol water indicating a small difference in slope between the phenol-rich high-density (h) and the water-rich low-density (l) phases. In the original analysis, over the temperature range in which experimental data were available, the two phases were characterized by different critical exponents.[2] For example, with

$$t=(T-T_c)/T_c\ , \tag{1.1}$$

it was found that over the range of the data

$$I_{h(l)}(|t|) \sim |t|^{-\gamma_{h(l)}}\ ,\quad T<T_c \tag{1.2}$$

with $\gamma_l - \gamma_h \simeq 0.08$. In the case of impure (5.7 wt% H_3PO_2) phenol water, this difference was even larger, as may be seen in Fig. 2, and well outside estimated experimental limits.

Over a somewhat larger temperature range the spectral width in pure phenol water was found to behave similarly, with

$$\Gamma_{h(l)}(|t|) \sim |t|^{\nu^*_{h(l)}}\ ,\quad 10^{-4} \lesssim |t| \lesssim 10^{-2} \tag{1.3}$$

and $\nu^*_l - \nu^*_h \simeq 0.08$. Again the impure phenol-water system gave measurably different values of ν^*_h and ν^*_l. It was observed, however, that in both the pure and impure phenol-water systems

$$\Delta\Gamma(|t|) \equiv \Gamma_l(|t|) - \Gamma_h(|t|) \to 0 \quad \text{as } t \to 0-\ , \tag{1.4}$$

and at the lower-temperature limit ($|t| \simeq 10^{-4}$) the differences were approaching the accuracy of the individual data points.[3]

There is at present no firm theoretical or experimental evidence that separate critical exponents need be defined for the two coexisting phases. In the light of recent theoretical ideas on the behavior of nonsymmetric systems near the critical point,[4–8] we reanalyze the original data (along with some previously unpublished data[3]) to present a consistent description of the available information without requiring separate exponents.

The measurements of the scattered intensity I, while more amenable to theoretical interpretation, are less precise and over a smaller temperature range than measurements of Γ; hence we concentrate on the latter for quantitative interpretation. In order to make contact with the thermodynamic functions, on which our interest centers, an appeal must be made to the results of a dynamical theory.[9] The difficulty with this approach is that relations which come out of dynamical theories are not rigorous; however, agreement with experiment is often quite good. Furthermore, parameters appear (e.g., the viscosity) which can have analytic

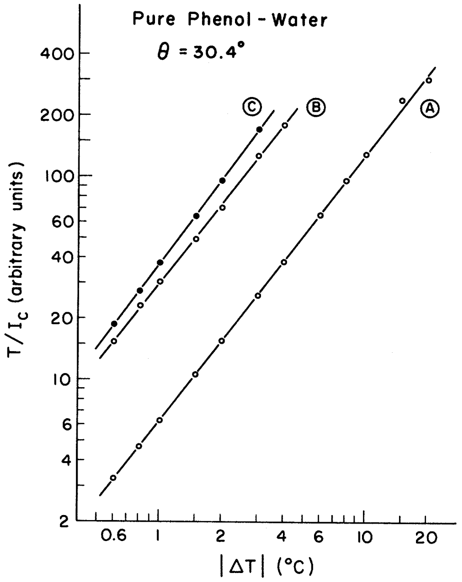

FIG. 1. Temperature dependence of the inverse scattered light intensity in a critical mixture of pure phenol water at a scattering angle of 30.4° curves A, B, and C correspond, respectively, to $T > T_c$, $T < T_c$ (high-density phase), and $T < T_c$ (low-density phase). The intensity has been corrected for background effects as discussed by Pusey and Goldburg (Ref. 1.)

background and anomalous contributions[10] that have not been completely studied or understood. The relevant expression [see (4.1) below] for the spectral width involves the range of correlations as well as the viscosity. We shall find that because of a strong concentration dependence, the viscosity cannot be treated as a constant for $T \lesssim T_c$ and, in fact, may be the determining factor in the asymmetry observed in the spectral widths. Aside from questions of asymmetry, there may be other difficulties in properly interpreting spectral-width measurements (even above T_c) for the purpose of extracting critical exponents.[10]

The results of the reanalysis are as follows. For both pure and impure phenol-water mixtures we find a consistent fit over the range of available data with the form

$$\Gamma_{h(l)}(|t|) \approx A(|t|^{\nu^*} \mp B|t|^{\tau}) , \qquad (1.5)$$

with the upper (lower) sign corresponding to the high- (low-) density phase throughout. The exponent ν^* approximately equals the spectral-width index for $T > T_c$ as quoted in Ref. 1, and the data indicate

$$\tau - \nu^* \simeq \tfrac{1}{3} , \qquad (1.6a)$$

$$\tau \simeq 1 , \qquad (1.6b)$$

the estimate in (1.6b) following from a somewhat less precise direct determination (see below). The analysis of the intensity is not given in detail here. It is worth noting that the form (with k_B Boltzmann's constant)

$$(k_BT)^{-1} I_{h(l)}(|t|) \approx A'(|t|^{-\gamma} \pm B'|t|^{-\theta}) \qquad (1.7)$$

is possible, but the accuracy is insufficient to make the important distinction between $\theta = 1 - \beta$ and $\theta = \gamma - \beta$, the former providing a slightly better fit.[11] As we shall discuss in Sec. II, one might expect the value $\theta = 1 - \beta$ if a "most symmetric" description of a two-component fluid is possible. This description is obtained by generalizing from the observed behavior of simple fluids and their lattice-gas analogies. Accepting the result of the dynamical theory,[9] $\Gamma \propto \xi^{-1}$ (ignoring any temperature dependence of the viscosity near T_c), and the Ornstein–Zernike equation, $I \propto \xi^2$, the results (1.6) then favor the latter possibility $\theta = \gamma - \beta$. These possibilities will be discussed further in Sec. IV in which we estimate the effect of the background viscosity. In Sec. II we discuss asymmetry in two-component fluids, and in Sec. III we present the analysis of the spectral width of the phenol-water system. Section V is devoted to summary and further discussion.

II. LIGHT SCATTERING IN TWO-COMPONENT FLUID

In a two-component fluid the intensity of scattered light[12] is essentially proportional to fluctuations of the dielectric constant ϵ,

$$I \propto \langle \delta\epsilon^2 \rangle_V , \qquad (2.1)$$

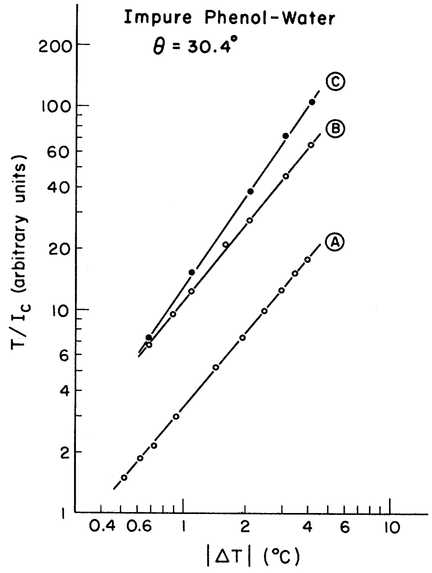

FIG. 2. Inverse corrected light intensity vs temperature in a critical mixture of phenol, water, and 5.7 wt% H_3PO_2, for (A) $T > T_c$, (B) $T < T_c$ (high-density phase), and (C) $T < T_c$ (low-density phase). The scattering angle is $\theta = 30.4°$.

where $\langle \cdots \rangle_V$ indicates an appropriate (grand-canonical) average for a fixed volume of fluid exposed to the light beam. Equation (2.1) is a Born-approximation result. One further approximates

$$\delta\epsilon = (4\pi/V)(\alpha_A\,\delta N_A + \alpha_B\,\delta N_B)\ , \tag{2.2}$$

where $\alpha_{A(B)}$ is the polarizability of a molecule $A(B)$ and $\delta N_{A(B)}$ is the number fluctuation for the $A(B)$ species.[13] Rather than work with the separate chemical potentials $\mu_{A(B)}$ it is convenient to define sum and differences,

$$\nu = \tfrac{1}{2}(\mu_A + \mu_B)\ , \quad \Delta = \tfrac{1}{2}(\mu_A - \mu_B) \tag{2.3}$$

and

$$N = N_A + N_B\ , \qquad n = N_A - N_B\ . \tag{2.4}$$

Then in terms of thermodynamic derivatives, the dielectric constant fluctuation is given by

$$\langle \delta\epsilon^2 \rangle_V = \left(\frac{4\pi}{V}\right)^2 k_B T \left[\lambda^2 \left(\frac{\partial n}{\partial \Delta}\right)_{VT\nu} + \overline{\alpha}^2 \left(\frac{\partial N}{\partial \nu}\right)_{VT\Delta} - 2\overline{\alpha}\,\lambda \left(\frac{\partial n}{\partial \nu}\right)_{VT\Delta}\right], \tag{2.5}$$

with

$$\overline{\alpha} = \tfrac{1}{2}(\alpha_A + \alpha_B)\ , \quad \lambda = \tfrac{1}{2}(\alpha_A - \alpha_B)\ . \tag{2.6}$$

The derivative $(\partial N/\partial \nu)_{VT\Delta}$ is essentially a compressibility, measuring over all density fluctuations, while $(\partial n/\partial \Delta)_{VT\nu}$ contains contributions from concentration as well as density fluctuations. Defining the number concentration x, and the average density ρ,

$$x = N_A/N, \quad \rho = N/V\ , \tag{2.7}$$

one can express $\langle \delta\epsilon^2 \rangle_V$ entirely in terms of the compressibility

$$\rho^2 K_{T,\Delta} = \left(\frac{\partial \rho}{\partial \nu}\right)_{T,\Delta} \tag{2.8}$$

and the thermodynamic derivative $(\partial x/\partial \Delta)_{T,P}$. Though it is frequently overlooked, the compressibility (2.8) as well as $(\partial x/\partial \Delta)_{T,P}$ is, in general, expected to have an asymptotic strong divergence (γ divergence).[7,12] In the present experimental situation the amplitudes of both contributions appear to be the same order of magnitude and cannot be separated. Equivalently, all three terms in (2.5) are second derivatives of the thermodynamic potential (in this case the pressure), and all should have γ divergences according to the Griffiths–Wheeler hypothesis.[7]

The description of nonsymmetric systems is, in general, not straightforward.[8] The most symmetric formulation for a two-component fluid is a generalization of the prescription of Mermin and Rehr[6] to the present situation. To generalize the one-component fluid treatment we describe a real two-component fluid as if it were based on an underlying "ideal" (but physically unrealizable) symmetric system. The hypotheses used in this procedure are essentially statements of a form of critical-point stability or universality.[8]

The independent variables for the present case may be chosen to be T, μ_A, and μ_B. This is the natural generalization, since taking one of the chemical potentials to $-\infty$ reproduces the one-component fluid. Equivalently, we have chosen the combinations T, Δ, and ν which were defined in (2.3). The difference in chemical potentials, Δ, plays the role of an ordering field, its conjugate order parameter being $n = N_A - N_B$. The "ideal" underlying system is presumed to have a free energy $F^0(T, \Delta, \nu)$ defined by the equations

$$\left(\frac{\partial F^0}{\partial \Delta}\right)_{T\nu} = n^0\ , \quad \left(\frac{\partial F^0}{\partial \nu}\right)_{T\Delta} = N^0\ . \tag{2.9}$$

The ideal phase boundary is assumed to be the plane $\Delta_\sigma^0(T, \nu) = \Delta_c^0$ in the space of thermodynamic variables T, Δ, ν. As in the case of a symmetric system, Δ_c^0 can be taken as $\Delta_c^0 = 0$. (This is analogous to the plane $H' = 0$, with H' the staggered magnetic field and ν corresponding to the magnetic field H, in an ordinary Ising antiferromagnet.) We consider the system at constant volume (which variable we do not exhibit explicitly) since this corresponds to the situation indicated in (2.5). The free energy F^0 is essentially the pressure of the ideal system. According to the Griffiths–Wheeler[7] hypothesis, the derivative

$$\chi^0(T, \Delta, \nu) = \left(\frac{\partial^2 F^0}{\partial \Delta^2}\right)_{T\nu} \tag{2.10}$$

is expected to exhibit a strong (γ-type) singularity at the phase transition, the derivative being in a direction which is not parallel to the ideal phase boundary $\Delta = \Delta_c^0 = 0$. On the other hand, the derivatives $(\partial^2 F^0/\partial T^2)_{\Delta\nu}$ and $(\partial^2 F^0/\partial \nu^2)_{T\Delta}$ are expected to show weak (α-type) specific-heat singularities.[7]

Before discussing the thermodynamics of the nonsymmetric system we note that a spin-1 Ising-like lattice-gas model for a two-component fluid (allowing for independent density variations) can be formulated quite easily. The correspondences with $\sigma_i = \pm 1, 0$ are $n_i^A = \frac{1}{2}(\sigma_i + \sigma_i^2)$, $n_i^B = \frac{1}{2}(-\sigma_i + \sigma_i^2)$ representing occupation variables for species A and B in the ith cell, and $n_i^c = 1 - \sigma_i^2$ representing the absence of a molecule in the ith cell. In the grand canonical ensemble, the chemical potentials Δ and ν couple to $n_i^A - n_i^B$ and $n_i^A + n_i^B$, respectively. The model is made symmetric (to correspond to F^0) by choosing the lattice-gas interactions ϵ_{AA} and ϵ_{BB} to be equal.[2] Studies of such a Hamiltonian in mean-field theory[14] and through high- and low-temperature series expansions[15] indicate that there is a region of parameter space in which ν acts as a nonordering field coupling to a local "energy density" $\sigma_i^2 = n_i^A + n_i^B$. In this region a fixed value ν

does not change the basic Ising ($s = 1$) character of the phase transition but merely produces a λ line, $T_c(\nu)$. The available information[15] and phenomenological arguments based equivalently on "hidden-variable" theory,[16] critical-point stability or universality,[8] or indeed other qualitative arguments, strongly suggest, in the context of the model, the validity of the Griffiths–Wheeler predictions on the thermodynamic derivatives pertaining to the symmetric system.

To introduce the effect of asymmetry we carry the above ideas one step further, in effect generalizing the one-component fluid results. The hypothesis we make is that the true free energy $F(T, \Delta, \nu)$ and the "ideal" or symmetric underlying free energy $F^0(T, \Delta, \nu)$ are related by the transformation

$$F(T, \Delta, \nu) = f F^0(\overline{T}, \overline{\Delta}, \overline{\nu}) + g \ , \qquad (2.11)$$

where the *analytic* functions f, g, $\overline{T}$, $\overline{\Delta}$, $\overline{\nu}$ are each functions of T, Δ, and ν. Mermin and Rehr[5,6] have shown the connection (2.11) to be rigorously true in a variety of one-component models which have explicit underlying symmetries. In the present context there is nothing rigorous about (2.11); it is the natural generalization of the earlier results[5,6] based on the assumption that the real system has an additional field term (not exhibited explicitly) in the Hamiltonian which simply draws the coexistence surface out of the plane $\Delta = \Delta_c^0 = 0$. In the spin model described above, such a term could be of the form

$$J_2 \sum_{\langle ij \rangle} (\sigma_i \sigma_j^2 + \sigma_j \sigma_i^2) \ , \qquad (2.12)$$

when $\epsilon_{AA} \neq \epsilon_{BB}$, the sum being over nearest-neighbor spins.

The consequences of the generalization (2.11) are straightforward,[8] and we do not spell out the details. We merely note that the phase boundary in the real system $\Delta_\sigma(T, \nu)$ is determined implicitly by

$$\overline{\Delta}(T, \Delta_\sigma, \nu) = 0 \ , \qquad (2.13)$$

and the critical temperature by

$$\overline{T}(\Delta_\sigma, T_c, \nu) = T_c^0 \ . \qquad (2.14)$$

The structure of these equations produces the weak singularity $|\Delta T|^{1-\alpha'}$ in the coexistence diameter, $\frac{1}{2}[n_h(|t|) + n_l(|t|)]$. More importantly, now *both* $(\partial^2 F/\partial\Delta^2)_{T\nu} = (\partial n/\partial\Delta)_{T\nu}$ and $(\partial^2 F/\partial\nu^2)_{T\Delta} = (\partial N/\partial\nu)_{T\Delta}$ will have strong (γ-type) singularities asymptotically; this is consistent with the Griffiths–Wheeler hypothesis[7] in that neither derivative is parallel to the phase boundary in the nonsymmetric system. Such a result also follows from mean-field theory when density fluctuations are considered.[8] We also note that each of these derivatives is asymmetrical for the two coexisting phases, for example,

$$\left(\frac{\partial^2 F}{\partial \Delta^2}\right)_{h(l)} \approx (a|t|^{-\gamma} \pm b|t|^{-(1-\beta)}) \ , \qquad (2.15)$$

where

$$\left(\frac{\partial^2 F}{\partial \Delta^2}\right)_{h(l)} = \lim_{\Delta \to \Delta_\sigma^\pm} \left(\frac{\partial^2 F}{\partial \Delta^2}\right)_{T\nu} \ . \qquad (2.16)$$

The same form (2.15) holds for the second ν derivative and the mixed derivative $(\partial^2 F/\partial\Delta\partial\nu)_T$.[17] Returning to (2.1)–(2.5), and the arguments presented above, it follows that the generalization of the one-component fluid analysis predicts that the scattered light intensity should have the form (1.7) with $\theta = 1 - \beta$.

This prediction represents the simplest possibility, namely, that a real two-component fluid can be described in terms of an underlying symmetric system with the variables T, Δ, ν playing special roles. This would be the case if the spin-1 Ising-like model mentioned above described a two-component fluid as well as, say, the spin-$\frac{1}{2}$ Ising model describes β-brass. At present the evidence is that continuum systems are not so well mapped onto simple Ising models; real systems, for example, are characterized by values $\gamma \simeq \frac{4}{3}$ rather than $\gamma = \frac{5}{4}$. Nonetheless it is possible that T, Δ, ν (or equivalently, T, μ_A, μ_B) represent the most symmetric variables with which to describe a real two-component fluid, this being the generalization of experimental results on one-component systems.

III. SPECTRAL-WIDTH ANALYSIS

As mentioned previously, the data for the spectral widths are reliable enough to extract an asymmetry exponent. One defines the symmetric and antisymmetric parts

$$\begin{aligned} \Gamma_s(|t|) &= \Gamma_l(|t|) + \Gamma_h(|t|) \ , \\ \Gamma_a(|t|) &= \Gamma_l(|t|) - \Gamma_h(|t|), \qquad T < T_c \end{aligned} \qquad (3.1)$$

combining the experimental results for the high- and low-density phases. Γ_s for both pure and impure phenol water is plotted vs $|t|$ in Fig. 3.[1,3] The straight lines through the data indicate that the leading terms in Γ_s are characterized by the exponent ν^* [see (1.5)],

$$\begin{aligned} \nu^* &= 0.65 \pm 0.03 \ \text{(pure)} \ , \\ \nu^* &= 0.63 \pm 0.04 \ \text{(impure)} \ , \end{aligned} \qquad (3.2)$$

which are to be compared with the $T > T_c$ values ν^* (pure) $= 0.68 \pm 0.03$ and ν^* (impure) $= 0.70 \pm 0.03$. Within experimental margins there can be agreement in the exponents above and below T_c, although this need not be assumed.

The plots for Γ_a, the antisymmetric part, are shown in Fig. 4. The pure case covers a wider

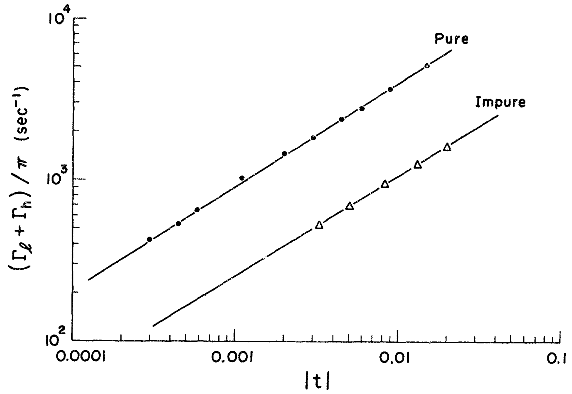

FIG. 3. Temperature dependence of the symmetric part of the decay rate, $\Gamma_s = \Gamma_h + \Gamma_l$, for both pure and impure phenol water. The slopes of the two straight lines determine the exponents ν^* (pure) and ν^* (impure) in Eq. (1.5).

temperature range, but the error bars grow at the low-temperature end. The straight lines through the data give the leading asymmetric term in (1.5),

$$\tau = 1.0 \pm 0.07 \quad \text{(pure)}\,,$$
$$\tau = 0.91 \pm 0.08 \quad \text{(impure)} \quad . \qquad (3.3)$$

The above-quoted values of τ are somewhat imprecise, and the value $\tau \simeq 1$ represents a working hypothesis. An over-all numerical fit determining $\tau - \nu^*$ can be found by plotting

$$\Gamma_l(|t|)/\Gamma_h(|t|) - 1 \text{ vs } |t|$$

and fitting to the form following from (1.5),

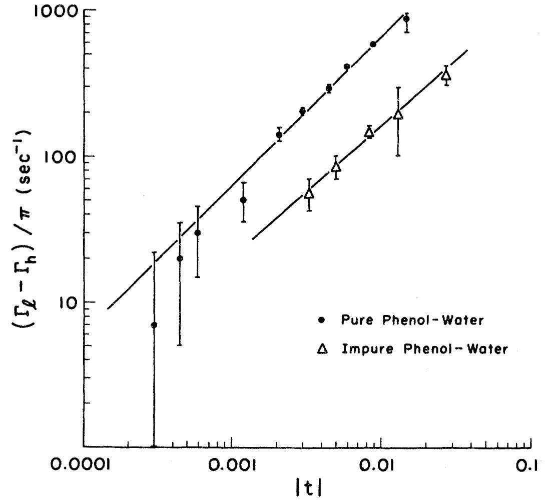

FIG. 4. Temperature dependence of the asymmetric part of the decay rate, $\Gamma_a = \Gamma_l - \Gamma_h$, in pure and impure phenol water. The straight lines are reasonable fits to the data points and determine the exponents τ (pure) and τ (impure) in Eq. (1.5).

$$G(|t|; B, \omega) = (1 + B|t|^{\omega})/(1 - B|t|^{\omega}) - 1\,. \qquad (3.4)$$

The data for both pure and impure phenol water together with plots of the function G for several values of B and ω are shown in Fig. 5. A reasonably good fit is found with $B \simeq 0.75$ and $\omega \simeq \frac{1}{3}$. This is indeed consistent with our previous choice $\tau \simeq 1$. The data indicate that $\omega = \frac{2}{3}$ is probably ruled out. Further comment will be made below on the numerical value of the coefficient B. At this point we have satisfactorily characterized the asymmetry in Γ and turn next to an interpretation of these results.

IV. INTERPRETATION OF SPECTRAL-WIDTH MEASUREMENTS

As noted in Sec. I a connection between the spectral width and the intensity requires the results of a dynamical theory of critical behavior.[9] We shall use the Kawasaki–Ferrell relation[9]

$$\Gamma = (k_B T/6\pi\eta\xi)\,k^2 \qquad (k\xi \ll 1)\,, \qquad (4.1)$$

where ξ is the correlation range, η the viscosity,[18] and k the value of the photon momentum transfer. This is basically Stokes's law for a sphere of radius ξ falling through the fluid. The relation (4.1) has been examined in several experimental cases.[19] In the present system there may be several correlations which become long ranged, i.e., $\langle \delta n(\vec{r})\, \delta n(\vec{r}\,')\rangle$, $\langle \delta N(\vec{r})\, \delta N(\vec{r}\,')\rangle$, and $\langle \delta N(\vec{r})\, \delta n(\vec{r}\,')\rangle$, since each is expected to have a γ divergence for the total fluctuation, for example,

$$k_B T\left(\frac{\partial n}{\partial \Delta}\right)_{VT\nu} = \int d\vec{r}\, d\vec{r}\,'\, \langle \delta n(\vec{r})\, \delta n(\vec{r}\,')\rangle\,. \qquad (4.2)$$

We make the usual assumption that all of the diverging correlation lengths ξ are proportional. Furthermore, in the spirit of Ornstein–Zernike theory[20] we may take

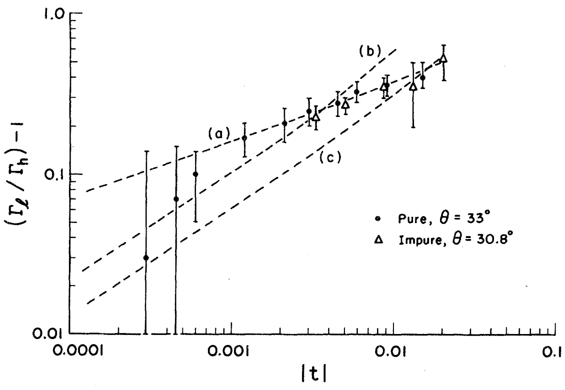

FIG. 5. $(\Gamma_l/\Gamma_h) - 1$ vs temperature for pure and impure phenol water. The dashed lines are the functions (a) $G(|t|;\, 0.75,\, \frac{1}{3})$, (b) $G(|t|;\, 5,\, \frac{2}{3})$, and (c) $G(|t|;\, 3,\, \frac{2}{3})$, the function $G(|t|;\, B,\, \omega)$ defined in Eq. (3.4).

$$I/k_BT \propto \xi^2/b\ , \qquad (4.3)$$

where b represents an average second moment of direct correlation functions. (We refer to an average here to include fluctuations in both n and N.) Combining (4.1) and (4.3) we have a relation between the measured spectral width and intensity:

$$\Gamma \propto I^{-1/2}/(b^{1/2}\eta)\ , \qquad (4.4)$$

ignoring constants which cannot affect the observed asymmetry and the slowly varying factor k_BT.

Viscosity measurements below the critical point are virtually nonexistent, and the question of a weak anomaly in η as $T \rightarrow T_c+$ is not well settled. In any case, for phenol water, the viscosity anomaly appears to be broad and weak. The available data for this system[21] come to within $t \simeq 0.003$ and show no sign of a divergence at the critical point, but may indicate some kind of weakly anomalous behavior in the one-phase region (there being no measurements below T_c). To estimate numerically the low-temperature smoothly varying background viscosity, one can attempt to extrapolate the data of Ref. 21 to $T < T_c$. Alternatively, reasonable numerical agreement with the above extrapolation procedure can be obtained by a "perfect-fluid" approach, namely, to approximate

$$\eta(|t|) \simeq \eta_{\text{ph}}\tilde{x} + (1 - \tilde{x})\eta_w \qquad (4.5)$$

in the two-phase region, where $\eta_{\text{ph}} = 26 \times 10^{-3}$ g cm^{-1} sec^{-1} and $\eta_w \simeq 5 \times 10^{-3}$ g cm^{-1} sec^{-1} at $T = 60\ ^\circ\text{C}$ ($\simeq T_c$ in pure phenol water), and $\tilde{x}$ is the weight fraction of phenol. The coexistence curve is given by

$$\tilde{x} = \tilde{x} \pm c_1|t|^\beta\ , \qquad (4.6)$$

with $\beta \simeq \frac{1}{3}$, $c_1 \simeq 0.8 - 0.9$, and $\tilde{x}_c = 0.34$.[22] Then (4.5) and (4.6) indicate that for $t \lesssim 0$ we may approximate

$$\eta \simeq \eta_c(1 \pm c_2|t|^\beta)\ , \qquad (4.7)$$

with $\eta_c = \eta(\tilde{x}_c)$ and the dimensionless coefficient $c_2 = c_1(\eta_{\text{ph}} - \eta_w)/\eta_c \simeq 1.6 - 1.8$. This range of values probably somewhat overestimates the strength of the temperature dependence of the background viscosity.

To proceed further we assume that b in (4.4) is a constant and take its (assumed) finite value at the critical point to be $b = b_c$. Then (4.4) and (4.7) combine to yield the conclusion that it is consistent for I to have the form (1.7) with $\theta = 1 - \beta \simeq \frac{2}{3}$, while Γ has the form (1.5) with $\tau \simeq 1$. Furthermore, the relative amplitude B in (1.5) and (3.5) would be given by $B = c_2 = 1.6 - 1.8$. The experimental fit determined $B = 0.75$, as stated in Sec. III. Recalling the order-of-magnitude estimate for $\eta(\tilde{x})$, the agreement in these determinations of B is encouraging.

One should, in general, expect the second moment b to be asymmetrical in the two-phase region; within the Ornstein–Zernike framework a perfect-fluid form analagous to (4.5) with a linear concentration dependence would not be an unreasonable choice. In that case, asymmetry in b could make some contribution to the experimentally determined relative asymmetry amplitude B in (3.5). We note here that detailed measurements of the angular dependence of scattered light could be used in principle to determine b, assuming Ornstein–Zernike form correlations; however, absolute intensity measurements would be required.

V. DISCUSSION AND SUMMARY

Both the scattered light intensity and spectral-width data near the critical point of the phenol-water system indicate asymmetry between the two coexisting phases below T_c. The spectral-width measurements for the system are much more reliable in that they cover a larger temperature range and are less susceptible to systematic errors. The asymmetry in the spectral width can be successfully characterized by the form (1.5) with $B \simeq 0.75$ and $\tau \simeq 1$. The analysis of Sec. IV shows that it is consistent with the data for the intensity to be characterized by (1.7) with $\theta = 1 - \beta$. The analysis of Sec. II indicates that this should be the case if a real two-component fluid has a most symmetric description in terms of the independent variables T, Δ, ν. One would hope that this is indeed the case, since it is a natural extension of the situation which obtains experimentally in simple one-component fluids and theoretically in lattice-gas models which have been treated. Furthermore, from a theoretical point of view the above variables (or linear combinations) are the natural choice in the usual grand canonical formulation for two-component fluids. It should be noted, however, that if real fluids do not behave so simply, other forms for the leading asymmetry exponent τ are certainly possible.

The analysis also indicates that the leading asymmetry observed in the spectral width can be due entirely to uninteresting background terms and appears to give no information relating to "intrinsic" asymmetry in the thermodynamic functions which characterize the system. Phenol and water have widely differing viscosities, which makes c_2 in (4.7) appreciable. This could be the reason that an asymmetry in Γ is easily observed in phenol water while it has not been accurately observed in other systems.

Finally we mention that impure phenol water is a three-component fluid observed at constant impurity (5.7-wt% H_3PO_2) concentration. In principle, exponent renormalization[16] is possible, but in this system has not been observed.[23]

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[15] M. Wortis and D. Saul, in *AIP Conference Proceedings No. 5—Magnetism and Magnetic Materials* (AIP, New York, 1972); and M. Wortis (private communication).

[16] Certain nonordering fields have been studied exactly in the context of symmetry-preserving decorations of the $S=\frac{1}{2}$ Ising model. See, for example, M. E. Fisher [Phys. Rev. 176, 257 (1968)] for further discussion.

[17] We note that thermodynamic arguments which use the Griffiths–Wheeler hypothesis (Ref. 7) and which generalize the one-component fluid case (Ref. 6) can be constructed. These indicate (with the same degree of strength as for the one-component fluid) that the above-mentioned derivatives have an asymmetric part diverging at least as strongly as $|t|^{-(1-\beta)}$.

[18] We do not consider here the question of a wave-number-dependent viscosity which has been suggested in recent derivations of (4.1); K. Kawasaki (unpublished).

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Odd-Parity *D* States in He

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Positions of the lowest odd-parity $^{1,3}D$ states in He have been calculated variationally. The trial wave function of Hylleraas type with four nonlinear parameters has been used. The results for the lowest $^{1,3}D$ states obtained by using 112 terms in the wave function are lower than the previous results. The mass-polarization correction has been also calculated. The transition $2\,^3P^e \rightarrow 3\,^3D^0$ is of wavelength 3014.16 Å, which agrees well with the previous calculation and the experimental result. The $^{1,3}D^0$ states of H^- were also investigated, but no states of odd parity were found in this calculation.

In a previous paper,[1] the positions of the even-parity *D* states were given. These states decay through autoionization. In this paper the positions of the lowest $^{1,3}D$ states of odd parity are presented. These states lie below the $n=2$ threshold of He^+ and decay radiatively to the lower states.