New Evidence Concerning the Griffiths First Sum Rule for Tricritical Light Scattering

Anil Kumar, Richard Chamberlin, and David S. Cannell
Department of Physics, University of California, Santa Barbara, California 93106

and

Ian L. Pegg, Charles M. Knobler, and Robert L. Scott
Department of Chemistry and Biochemistry, University of California, Los Angeles, California 90024
(Received 4 March 1985)

Experimental studies of light scattering in the tricritical region of mixtures of ethane with heavier hydrocarbons show that the intensities and correlation lengths do not satisfy the asymptotic form of the Griffiths first sum rule. Both sums increase sharply rather than approaching zero as the tricritical point is approached, indicating that either (a) there is a nonclassical divergence in the sums, or (b) many terms must be retained in a power series for the coupling "constant." Similar results have been found in a reanalysis of earlier experiments.

PACS numbers: 64.60.Kw

In this Letter we report experimental studies of light scattering near an unsymmetrical tricritical point that show that the scattered intensities and correlation lengths for the three coexisting phases α, β, and γ do not satisfy the asymptotic form of the Griffiths first sum rule.[1] Rather than approaching zero, both experimental sums increase sharply as the tricritical point is approached; the intensity sum shows considerable curvature in the appropriate field variable. Similar behavior is also revealed in a reanalysis of the data of Kim and co-workers[2,3] for a quaternary system.

Theoretical analysis shows that within the context of mean-field theory neither sum should in fact approach zero, provided that care is taken to consider the effects of the proportionality factors relating the order-parameter fluctuations to the scattered intensity and the correlation length. When this is done, the experimental results are consistent with the first sum rule, but high-order terms in the proportionality factors must be retained to obtain a fit. Alternatively, the curvature could indicate that the sum is actually divergent. A third possibility is that the curvature might be due to background fluctuations that cannot be separated from the tricritical fluctuations.

According to the sum rule[1] the susceptibilities, $\chi = (\partial^2 Y/\partial\psi^2)^{-1}$, where Y is the free energy appropriate to an order parameter ψ, should satisfy the relationship

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

No statistical-mechanical model yields the "order parameter" for fluid mixtures, so that ψ must be determined empirically. The square root of the light-scattering intensity, $I^{1/2}$, and the correlation length ξ are proportional to $\chi^{1/2}$, with proportionality factors (coupling "constants") k_I and k_ξ of the form[4]

$$k = k_0 + k_1\psi + k_2\psi^2 + k_3\psi^3 + k_4\psi^4 + k_5\psi^5 + k_6\psi^6 + \dots . \tag{2}$$

As the tricritical point is approached, all the ψ's approach zero, i.e., the k's approach the k_0's. Thus, in this limit, one might expect two other sums to approach zero as well:

$$\Sigma_I = I_\alpha^{1/2} + I_\gamma^{1/2} - I_\beta^{1/2} \overset{?}{=} 0, \tag{3}$$

$$\Sigma_\xi = \xi_\alpha + \xi_\gamma - \xi_\beta \overset{?}{=} 0. \tag{4}$$

As we shall see, this is not the case, even if (1) is correct. However, if (1) is recast in the form of a dimensionless ratio,

$$R_\chi = (\chi_\alpha^{1/2} + \chi_\gamma^{1/2})/\chi_\beta^{1/2} = 1, \tag{5}$$

then, in the asymptotic limit, the corresponding experimental ratios R_I and R_ξ should also equal unity. Previous workers have reported their results exclusively in the form of ratios; we have found that trends are much more easily seen in the sums themselves.

It is well known that for tricritical phenomena the boundary between classical (mean field) behavior and nonclassical (nonanalytic) behavior occurs at a dimensionality of three, so that a classical treatment has been deemed appropriate.[5] Consequently, the first sum rule was obtained[1] from a phenomenological theory[6] that starts with a sixth-order polynomial for Y,

$$Y = a_0 + a_1\psi + a_2\psi^2 + a_3\psi^3 + a_4\psi^4 + \psi^6, \tag{6}$$

and is alleged[4] to be unaffected by the logarithmic corrections expected for tricritical points in three dimensions. In (6) the coefficients a_n, which vanish at the tricritical point, are functions of several field variables including one chosen to measure the distance from the tricritical point, perhaps $T_t - T$ or, for our quasibinary mixtures, $\Delta n = \langle n \rangle - \langle n \rangle_t$, where $\langle n \rangle$ is the average carbon number of our quasi-one-component mixture of heavier hydrocarbons. There is no coefficient a_5 in (6) because ψ is defined so that the sum of its values in the three coexisting phases, $\alpha_0 + \beta_0 + \gamma_0$, is exactly zero for all Δn. It can be shown that, *in the region of three-phase coexistence,* a_0, a_1, a_2, and a_3 scale as powers of a_4. We may conveniently take $a_4 = -6\Delta n$ and $a_3 = -4\theta(\Delta n)^{3/2}$; then a_0, a_1, and a_2 must equal $4\theta^2(\Delta n)^3$, $12\theta(\Delta n)^{5/2}$, and $9(\Delta n)^2$, respectively. Here θ is a parameter that varies across the three-phase region from -1 at one critical end point to $+1$ at the other. [In our quasibinary mixtures θ is, to a good approximation that becomes more nearly exact as one approaches the tricritical point, $(2T - T_U - T_L)/(T_U - T_L)$, where T_U and T_L are the upper and lower critical-end-point temperatures.] One can then rewrite (6) in the form

$$Y = [(\alpha_0 - \psi)(\beta_0 - \psi)(\gamma_0 - \psi)]^2 = [2\theta(\Delta n)^{3/2} + 3(\Delta n)\psi - \psi^3]^2 = 0. \quad (7)$$

Differentiation to obtain the susceptibility and substitution of ψ by its value in the appropriate phase yields each term in the sum Σ_χ, e.g., $\psi = \beta_0$ yields

$$\chi_\beta^{1/2} = [2^{1/2}(\gamma_0 - \beta_0)(\beta_0 - \alpha_0)]^{-1}. \quad (8)$$

Since α_0, β_0, and γ_0 are proportional to $(\Delta n)^{1/2}$, (8) predicts that $\chi^{1/2}$ diverges as $(\Delta n)^{-1}$, a prediction consistent with our experimental measurements of intensities and correlation lengths.

When all three susceptibilities are combined into the sum Σ_χ, one obtains the result $\Sigma_\chi = 0$. However, if one uses the proportionality factors (2) to get the intensities or the correlation lengths, the higher coefficients in the power series produce a different result:

$$\Sigma_I = [k_2 + 3k_4\Delta n + 2k_5\theta(\Delta n)^{3/2} + 9k_6(\Delta n)^2 + \dots]/2^{1/2}. \quad (9)$$

Note that the coefficients k_0, k_1, and k_3 are missing; they are multiplied by functions of α_0, β_0, and γ_0 that are exactly zero. The sum Σ_ξ will also be of the form (9), but the coefficients will be those appropriate to k_ξ rather than k_I. If the classical equation (9) is applicable, then clearly the behavior of Σ_I and Σ_ξ is determined by such high-order terms in (2) as to render hopeless any attempt to evaluate them directly, because coefficients beyond k_2 are inaccessible experimentally.

It is more natural to discuss experimental coexistence curves in terms of the directly measured experimental densities, rather than in terms of an "order parameter" constrained to make (1) and (6) exact no matter how far one is from the tricritical point. Although such an approach is unnecessary for a discussion of light scattering, the sums can be derived[7] from a free energy that is a function of several laboratory densities with the light scattering resulting from fluctuations in each. The resultant equation for Σ_I has exactly the same form as (9), although the various coefficients are now combinations of coefficients in various power series in the densities.

The discussion above, in terms of ψ, is similar to the treatment of Kaufman and Griffiths[4] who attempted to account for the experimental light-scattering results of Kim and co-workers[2,3] on the four-component system water + ethanol + benzene + ammonium sulfate. However, in attempting to evaluate k_I from experimental data, they effectively retained terms in (2) only through $k_2\psi^2$; we have found that, if both sums are to be fitted by a classical theory, one needs to keep terms up to $k_6\psi^6$.

Our light-scattering studies were carried out at the University of California at Santa Barbara on the quasibinary systems ethane + (*n*-heptadecane + *n*-octadecane) and ethane + (*n*-octadecane + *n*-nonadecane), systems whose thermodynamic properties have been studied at the University of California at Los Angeles.[8,9] Each sample is characterized by a parameter $\langle n \rangle$, the mole-fraction–average carbon number of the mixed C_{17}-C_{18} (or C_{18}-C_{19}) solute. Unlike the quaternary system, these systems allow the investigator, in a single loading of the cell, to examine the three-phase region over the entire temperature range from the lower critical end point to the upper critical end point and, by varying $\langle n \rangle$, to approach the tricritical point in a systematic manner.

Intensities of the scattered light were measured in both the forward and the backward directions, which permits calculation of ξ. Multiple scattering was significant only in the β phase of the mixture ($\langle n \rangle = 17.765$) closest to the tricritical point ($\langle n \rangle_t = 17.62$); these intensities were corrected by $\leq 10\%$ with the method of Guttinger and Cannell.[10] Details of the experimental techniques and the complete set of results will be published later.[11]

For each sample the end-point temperatures T_U and T_L were determined; for some samples the light scattering was measured at a series of temperatures between them. For a given sample (i.e., fixed $\langle n \rangle$) the experimental sums Σ_I and Σ_ξ are constant to $\pm 10\%$ (better than the experimental uncertainty) over the entire range of temperatures studied ($T_L + 10\ \mathrm{mK} \leq T \leq T_U - 10\ \mathrm{mK}$), in accord with (9) if the term $2k_5\theta(\Delta n)^{3/2}$ is negligible. Consequently many of the sets of measurements were made only at the mid-temperature $T_m \equiv (T_U + T_L)/2$.

Unlike the sums, the ratios R_I and R_ξ depend strongly upon θ, since

$$R_I - 1 = \Sigma_I / I_\beta^{1/2}. \qquad (10)$$

The intensity I_β, like the susceptibility χ_β itself, becomes infinite at the two critical end points, which makes R_I exactly equal to unity there. Between the end points $(-1 < \theta < 1)$, $R_I - 1$ has a complex dependence upon θ, and an initial proportionality to the first power of Δn, features already reported in a previous Letter.[12]

We turn now to the measurements made at the midtemperature T_m. Figures 1(a) and 1(b) show the sums Σ_I and Σ_ξ at the midtemperature T_m as a function of Δn for five samples having values of $T_U - T_L$ ranging from 38 to 1311 mK. The error bars shown result primarily from sample-dependent systematic effects, including gradient formation, slow separation of some phases after stirring, and irregular wetting of the cell windows; thus they must be considered somewhat subjective. It is apparent that as $\langle n \rangle_t$ is approached the sums increase sharply. Over the limited range of $\langle n \rangle$ for which ξ is accessible, Σ_ξ is linear in Δn and appears to approach a finite value. Over the same range, Σ_I is nearly linear, but considerable curvature is indicated by the point at $\langle n \rangle = 1.4$, which might suggest that Σ_I diverges.

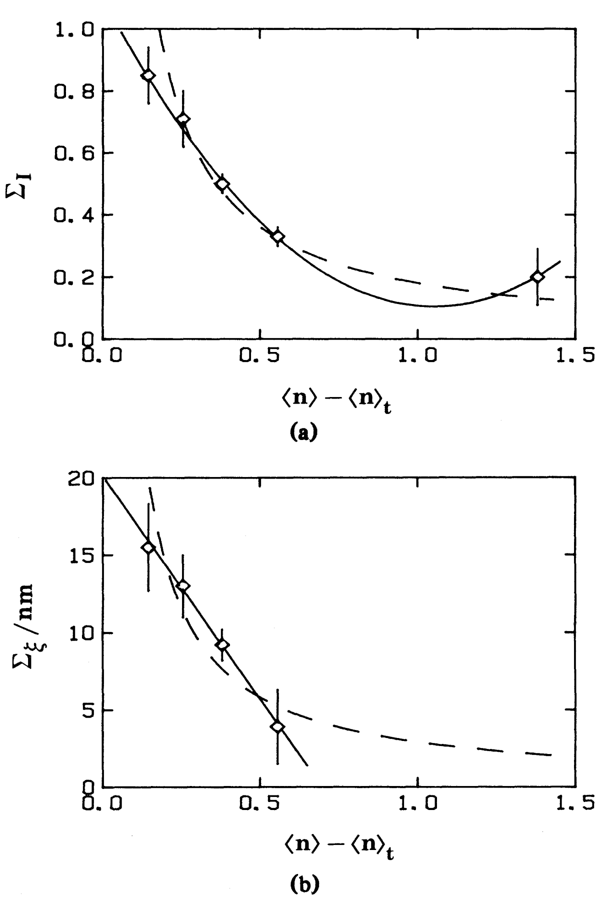

FIG. 1. (a) Intensity sums Σ_I (arbitrary units) and (b) correlation length sums Σ_ξ (nanometers) for the systems ethane + (n-heptadecane + n-octadecane) and ethane + (n-octadecane + n-nonadecane). $\langle n \rangle$ is the average carbon number of the mixture of heavier hydrocarbons and $\langle n \rangle_t = 17.62 \pm 0.02$. The fitted curves are as follows: (a) Solid line, $1.10 - 1.89\Delta n + 0.90(\Delta n)^2$, and dashed line, $0.18(\Delta n)^{-1}$; (b) solid line, $20.1 - 28.8\Delta n$, and dashed line, $2.9(\Delta n)^{-1}$.

The same trends appear in the results of Kim *et al.*[3] for two samples of fixed composition. Their measurements span the three-phase region, but do not approach either critical end point. When these sums are plotted [Figs. 2(a) and 2(b)] against $T - T_t$, the variable equivalent to our Δn, they also increase sharply as the tricritical temperature is approached. If the results

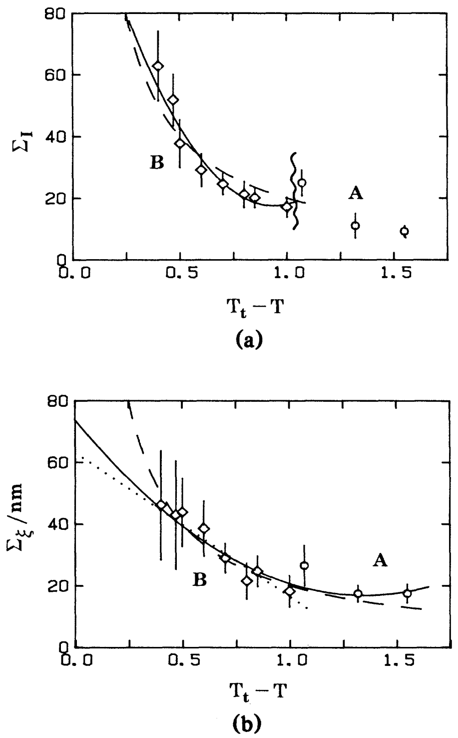

FIG. 2. (a) Intensity sums Σ_I (arbitrary units, different for samples A and B) and (b) correlation length sums Σ_ξ (nanometers) for the system water+ethanol+benzene +ammonium sulfate [Kim *et al.* (Ref. 3)]. $\Delta T = T_t - T$ is the difference between the tricritical temperature and that of the measurement. Each sample (A, denoted by circles, and B, denoted by diamonds) is a single loading (fixed composition). The fitted curves are as follows: (a) solid line, $134 - 248\Delta T + 132(\Delta T)^2$, and dashed line, $20(\Delta T)^{-1}$; (b) solid line, $74 - 84\Delta T + 31(\Delta T)^2$, dotted line, $63 - 47\Delta T$ (fitted to B points only), and dashed line $20(\Delta T)^{-1}$.

of the A and B series are combined, Σ_ξ shows marked curvature. However, it should be noted that the individual correlation lengths differ significantly between the two purportedly similar samples, so that placing the sums on the same curve may not be justified. (The intensity sums cannot be combined at all because the units are arbitrary.)

We have tried to fit each of the four sets of data by two functional forms, (9) with three parameters ($k_5=0$) and a simple divergence proportional to $(\Delta n)^{-1}$ or to $(T_t-T)^{-1}$, with the results shown in Figs. 1 and 2. The fit with a divergence is not improved substantially by addition of extra terms [e.g., terms in $(\Delta n)^0$ and $(\Delta n)^{+1}$]. The three-parameter classical fit is somewhat better than the one-parameter divergence, but the evidence is hardly conclusive.

The possibility that Σ_χ should itself be divergent has theoretical support. Fisher and Sarbach[13,14] found that amplitude ratios in a spherical model differed from their classical values; Stephen[15] reached similar conclusions for other models provided that one was not too close to the tricritical point where logarithmic corrections[16] should dominate.

These expectations have found further support in calculations by Rudnick and Jasnow[17] for an Ising model. They find that a one-loop correlation to the asymptotic classical theory shows that the sum Σ_χ diverges as $(\Delta n)^{-1}$ and, at this level of refinement, the limiting value of the ratio R_χ is greater than unity. Further renormalization-group corrections introduce logarithmic factors that slowly reduce R_χ to unity [as $(-\ln \Delta n)^{-1/2}$]; however, a weak logarithmic convergence cannot overcome a strong divergence, and so the sum Σ_χ still diverges. Unfortunately this theory does not yet give a magnitude to the proportionality factor, so that the amplitude of such a divergence is not known.

A third possibility is that background contributions to the scattered intensity, not associated with the tricritical point (i.e., due to a regular contribution to the free energy Y), become significant at large Δn, where the scattered intensity is smaller by about 2 orders of magnitude than it is for the sample with the smallest Δn. However, three of us (C.M.K., I.L.P., and R.L.S.) believe that, in an entirely classical theory,[7] all such background terms can be included in a completely general power series like (2), leading to the form (9).

The fact that the ratio Σ_I/Σ_ξ is constant for our data near the tricritical point suggests very strongly that the behavior observed in that region is actually that of Σ_χ itself and does not reflect the effects of variation of the proportionality factors k_I and k_ξ as a function of ψ. If so, then clearly Σ_χ itself does not approach zero asymptotically.

One final point: The Griffiths *second* sum rule appears to be relatively unaffected by any of these complications. The classical theory predicts that

$$\Sigma_2=\chi_\alpha^{-1/2}+\chi_\gamma^{-1/2}-\chi_\beta^{-1/2}=2^{1/2}9(\Delta n). \qquad (11)$$

Converting (11) to the second sum for experimental intensities or correlation lengths with the proportionality factors of (2) merely adds to (11) terms in $(\Delta n)^{3/2}$ and higher; there are no convenient exact cancellations as in the first sum. Our experimental measurements, like those of Kim *et al.*,[3] indicate that (11) is satisfied within reasonable experimental error.

This research was supported equally by the National Science Foundation under Grants No. DMR82-10884, No. CHE81-00125, and No. CHE82-10286. We thank M. E. Fisher, W. I. Goldburg, R. B. Griffiths, M. Kaufman, J. M. H. Levelt Sengers, and B. Widom for helpful comments on earlier drafts.

[1] M. Kaufman, K. K. Bardhan, and R. B. Griffiths, Phys. Rev. Lett. **44**, 77 (1980).

[2] M. W. Kim, W. I. Goldburg, P. Esfandiari, and J. M. H. Levelt Sengers, J. Chem. Phys. **71**, 4888 (1979).

[3] M. W. Kim, W. I. Goldburg, P. Esfandiari, J. M. H. Levelt Sengers, and E.-S. Wu, Phys. Rev. Lett. **44**, 80 (1980).

[4] M. Kaufman and R. B. Griffiths, J. Chem. Phys. **76**, 1508 (1982).

[5] F. J. Wegner and E. K. Riedel, Phys. Rev. B **7**, 248 (1973).

[6] R. B. Griffiths, J. Chem. Phys. **60**, 195 (1974).

[7] R. L. Scott, to be published.

[8] J. Specovius, M. Leiva, R. L. Scott, and C. M. Knobler, J. Phys. Chem. **85**, 2313 (1981).

[9] C. Goh, J. Specovius, C. M. Knobler, and R. L. Scott, to be published.

[10] H. Guttinger and D. S. Cannell, Phys. Rev. A **24**, 3188 (1981).

[11] A. Kumar, R. Chamberlin, D. S. Cannell, I. L. Pegg, C. M. Knobler, and R. L. Scott, to be published.

[12] R. Lindh, I. L. Pegg, C. M. Knobler, and R. L. Scott, Phys. Rev. Lett. **52**, 839 (1984).

[13] M. E. Fisher and S. Sarbach, Phys. Rev. Lett. **41**, 1127 (1978).

[14] S. Sarbach and M. E. Fisher, Phys. Rev. B **18**, 2350 (1978), and **20**, 2797 (1979).

[15] M. J. Stephen, Phys. Rev. B **12**, 1015 (1975).

[16] M. J. Stephen, J. Phys. C **13**, L83 (1980).

[17] J. Rudnick and D. Jasnow, personal communication.