

## Anomalies in chemical equilibria near critical points of dilute solutions

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We show that a recent prediction that the extent of reaction of a very dilute solute near the critical point of an almost pure solvent will show strong variation with temperature at fixed volume is in error. We give arguments to show that the behavior is at most weakly singular in the sense of Griffiths and Wheeler, point out the error in the earlier argument, and show that experiments adduced as evidence for the earlier argument are subject to alternative explanation. We also consider a prediction about the behavior near the critical point of a dissociating solvent.

### I. INTRODUCTION

Recently Procaccia and Gitterman<sup>1</sup> (PG) have argued that dramatic anomalies are to be expected in the extent of reaction of a very dilute solute near the critical point of an almost pure solvent. They predict (among other things) that for a dissociation reaction of the type



near the liquid-vapor critical point of an inert solvent, the extent of reaction will vary rapidly as the temperature  $T$  approaches its critical value  $T_c$  at constant density. Specifically, they predict that on the equilibrium line

$$\left. \frac{\partial \xi}{\partial T} \right|_{V, \text{equil}} \sim \left[ \frac{T - T_c}{T_c} \right]^{-\gamma}, \tag{2}$$

as  $T$  approaches  $T_c$  along the critical isochore, so long as the mole fractions of the impurities are small compared to  $(T/T_c - 1)^\gamma$ . Here  $\xi$  is the extent of reaction and  $\gamma \cong 1.24$ . They adduce in support of their argument the experiments of Krichevsky<sup>2</sup> on the equilibrium



in dilute solutions near the critical point of almost pure  $CO_2$ , which show an apparent rapid rise in the extent of reaction near  $T_c$ .

We believe that this prediction of PG is in error, and that the experimental results of Krichevsky can be explained far more plausibly as the result of critical scattering from the  $CO_2$ . Because the error arises from a rather subtle feature in the behavior of a solute near the critical point of an almost pure solvent, we believe that it may be worthwhile to discuss the problem in some detail. In this paper we present three separate lines of argument leading to the conclusion that only a weak singularity is to be expected in the variation of  $\xi$  with  $T$  in a closed system at fixed volume. These are presented in Secs. II–IV. In Sec. II we give thermodynamic arguments which demonstrate that a strong divergence is not to be expected. The derivative of interest is calculated within the context of a specific statistical-mechanical model in Sec. III. Far from  $T_c$  an apparent weak divergence (which may be observable) is obtained. Near  $T_c$  this crosses over to a weak, nondiver-

gent singularity. In Sec. IV we show that these results are quite general and discuss their range of validity. An error in the reasoning of PG that leads to their conclusion that a strong divergence should be observed is identified in Sec. V. An alternative interpretation of Krichevskii's results is given in Sec. VI. PG also make predictions about derivatives of  $\xi$  with respect to  $T$  at fixed pressure. One of these is also in error and is corrected in Sec. VII.

### II. THERMODYNAMIC ANALYSIS

For a system consisting of three species  $A$ ,  $B$ , and  $C$ , with species  $A$  the (inert) solvent and species  $B$  and  $C$  ( $=B_2$ ) capable of undergoing the chemical reaction



it is convenient to express the thermodynamics in terms of the composition variables  $N_A$ ,  $N_B$ , and the total number of  $B$  units

$$N_{B, \text{tot}} \equiv N_B + 2N_C. \tag{5}$$

It is also convenient to define the variable

$$\tilde{N} = N_A + N_{B, \text{tot}}, \tag{6}$$

which measures the total amount of material present. The variables  $N_A$ ,  $N_{B, \text{tot}}$ , and  $\tilde{N}$  have the convenient property that they are conserved in a system closed with respect to matter flow, i.e., they are independent of the extent of the reaction. The variable  $N_B$  then measures the extent of reaction. In terms of these variables, the differential of the internal energy can be written in the form

$$dU = T dS - p dV + \mu_A dN_A + \frac{1}{2} \mu_C dN_{B, \text{tot}} - \mathcal{A} dN_B \tag{7}$$

$$= T dS - p dV + \mu_A d\tilde{N} + \left( \frac{1}{2} \mu_C - \mu_A \right) dN_{B, \text{tot}} - \mathcal{A} dN_B, \tag{8}$$

where

$$-\mathcal{A} = \mu_B - \frac{1}{2} \mu_C \tag{9}$$

is the affinity,<sup>3</sup>  $\mathcal{A} = -\sum \nu_i \mu_i$ , for the reaction  $\frac{1}{2}C = B$ . It is also convenient to define the (intensive) density variables

$$\xi = N_B / N_{B, \text{tot}}, \quad \chi = N_{B, \text{tot}} / \tilde{N}, \quad v = V / \tilde{N}, \tag{10}$$

which measure in a convenient manner the extent of reaction, the concentration of impurities, and the volume. Note that in a closed-reaction vessel  $\chi$  always remains constant regardless of whether or not the volume or extent of reaction are constant. In terms of these variables, for a closed system at fixed volume, under chemical equilibrium, the derivative considered by PG can be written precisely as

$$\left( \frac{\partial \xi}{\partial T} \right)_{v, \chi, \mathcal{A}=0}, \quad (11)$$

or, equivalently, apart from a constant factor,

$$\left( \frac{\partial N_B}{\partial T} \right)_{V, N_A, N_{B, \text{tot}}, \mathcal{A}=0}. \quad (12)$$

The behavior near a critical point of partial derivatives like that on the right-hand side of Eq. (11) was considered some years ago by Griffiths and Wheeler<sup>4</sup> (GW). They used geometric arguments to arrive at predictions for the way in which such derivatives should behave on approach to the critical manifold in multicomponent systems. Similar conclusions were reached by Saam<sup>5</sup> on the basis of model scaling functions for the thermodynamic potential. Both of these approaches are in accord with results from numerous decorated lattice-gas model calculations.<sup>6</sup>

The approach of GW draws an important distinction between *density variables* like  $(N_A/V)$ ,  $\xi$ ,  $\chi$ , and  $v$  (ratios of extensive variables that, in general, take different values in coexisting phases), and *field variables* like  $T$ ,  $p$ ,  $\mu_A$ , and  $\mathcal{A}$  that are necessarily equal in coexisting phases. GW also distinguish between a *strong* divergence, analogous to that of the isothermal compressibility of a pure fluid, and a *weak* divergence, analogous to that of the constant-volume heat capacity of a pure fluid. According to GW a partial derivative of a density with respect to a field is expected to be strongly divergent on approach to the critical manifold if only fields are held constant in the derivative, weakly divergent if one density is held constant, and will remain bounded if two or more density variables are held constant. Exceptions to these general predictions can occur when the coexistence or critical manifolds bear special geometric relations to the coordinate axes in the space of field variables; examples are given in Ref. 4.

Now the partial derivative in Eq. (11) is the derivative of a density ( $\xi$ ) with respect to a field ( $T$ ) with one field ( $\mathcal{A}$ ) and two densities ( $v$  and  $\chi$ ) held fixed and, therefore, would be expected to remain bounded at any typical point on the critical locus in the equilibrium mixture of  $B$  and  $C$  with  $A$ . On this point we are in agreement with PG. For very small amounts of dissolved impurity,  $\chi \ll 1$ , and as  $\chi \rightarrow 0$ , the constraint  $\chi = \text{const} \approx 0$  becomes the same as the constraint  $z_c = e^{\mu_c/kT} = \text{const} \approx 0$  unless one is extremely close to the critical point. Thus, for systems with  $\chi \ll 1$ , the derivative in Eq. (11) will behave like the derivative

$$\left( \frac{\partial \xi}{\partial T} \right)_{v, \mu_c, \mathcal{A}}, \quad (13)$$

provided  $T$  is not too close to  $T_c$ . But this derivative still has one density variable held constant ( $v$ ) and, moreover,

this density variable couples to the order parameter even in the limit  $\chi \rightarrow 0$ . As a consequence, the derivative should diverge only at most weakly, even when  $\chi \rightarrow 0$ , according to GW, not strongly as argued by PG.

The precise nature of the divergence of strong and weak derivatives depends on the path of approach to the critical point, but for the case under consideration, the path corresponds to  $v, \chi \ll 1, \alpha = 0$  being held constant, or equivalently (not too close to  $T_c$ ),  $v, \exp(\mu_c/kT), \mathcal{A} = 0$  being held constant, and for this path the expected behavior is

$$\left( \frac{T - T_c}{T_c} \right)^{-\gamma} \quad (14a)$$

for a strong divergence, and

$$\left( \frac{T - T_c}{T_c} \right)^{-\alpha} \quad (14b)$$

for a weak divergence, where  $\gamma$  and  $\alpha$  are critical exponents with values  $\gamma \cong 1.24$  and  $\alpha \cong 0.12$ . Thus, the prediction of GW is that the apparent divergence, if observable at all, should be far less dramatic than that predicted by PG. [Both GW and PG agree that for any  $\chi > 0$ , the derivative in Eq. (11) ultimately approaches a finite limit as  $T$  approaches  $T_c(\chi)$  arbitrarily closely.] While we believe that the above analysis is correct, the application of the method of GW requires some care in cases of special geometries and limits, and so it is reassuring that explicit statistical-mechanical calculations (described below) yield the same conclusion.

### III. DECORATED-LATTICE MODEL

The behavior of a dilute solution near the critical point of an almost pure solvent was considered some years ago by one of us<sup>7</sup> using a decorated-lattice model. We concluded there that the activity coefficient of a very dilute solute could be expressed in the form

$$\gamma_i \equiv \frac{z_i}{\rho_i} = \frac{\Lambda_{0,i}}{1 + \Lambda_{1,i}\rho - \Lambda_{2,i}w}, \quad (15)$$

where  $z_i$  and  $\rho_i$  are the activity and number density of a solute, where  $\Lambda_{0,i}$ ,  $\Lambda_{1,i}$ , and  $\Lambda_{2,i}$  are smooth functions of temperature and the activities, and where  $\rho$  is the number density of the solvent and  $w$  is the symmetrized energy density of pure solvent. As the activities of the solutes become small, the  $\Lambda_{i,j}$  in Eq. (15) become functions of temperature alone. As a consequence, the derivative of  $\gamma_i$  with respect to  $T$  at fixed density in a very dilute solution is given by

$$\left( \frac{\partial \gamma_i}{\partial T} \right)_{v, \chi, \mathcal{A}=0} \approx \left( \frac{\partial \gamma_i}{\partial T} \right)_{\rho, z_i \approx 0} = \gamma_i^2 \frac{\Lambda_{2,i}}{\Lambda_{0,i}} \left( \frac{dw}{dT} \right)_\rho + \dots \sim \left( \frac{T - T_c}{T_c} \right)^{-\alpha}, \quad (16)$$

where the ellipsis represents the less singular terms. Note that it is precisely because the density  $\rho$  is held constant that there is no strongly divergent contribution to this

derivative.

The activity  $z_i$  in Eq. (15) is chosen in such a manner that  $\gamma_i \rightarrow 1$  for an ideal infinitely dilute gas. It is related to the chemical potential by

$$z_i = \left[ \frac{2\pi m_i kT}{h^2} \right]^{3/2} q_i e^{\mu_i/kT}, \quad (17)$$

where  $q_i$  is the internal partition function of species  $i$ , which is a function of temperature alone. The condition of chemical equilibrium,  $\mathcal{A} = 0$  [cf. Eq. (9)], requires that

$$z_B^2/z_C = K(T), \quad (18)$$

where  $K(T)$  is a function of temperature alone that is determined by the ideal-gas behavior of  $\text{NO}_2$  and  $\text{N}_2\text{O}_4$ , and therefore cannot have any singularity at the critical point of pure  $\text{CO}_2$ , nor along the critical line of the  $\text{CO}_2$ ,  $\text{NO}_2$ ,  $\text{N}_2\text{O}_4$  mixture. It follows that in nearly pure  $\text{CO}_2$  the equilibrium values of  $\rho_B$  and  $\rho_C$  are governed by

$$\frac{\rho_B^2}{\rho_C} = K(T) \frac{\gamma_C}{\gamma_B^2} = \left[ \frac{2\xi^2}{1-\xi} \right] \left[ \frac{\chi}{v} \right]. \quad (19)$$

Upon differentiation with respect to  $T$  at fixed  $\chi$  and  $v$ , this gives

$$\left[ \frac{\partial \xi}{\partial T} \right]_{v,\chi,\mathcal{A}=0} = \frac{\xi(1-\xi)}{(2-\xi)} \left[ \frac{\partial \ln[K(T)\gamma_C/\gamma_B^2]}{\partial T} \right]_{v,\chi,\mathcal{A}=0}. \quad (20)$$

For  $\chi \ll 1$ , Eq. (16) then gives

$$\left[ \frac{\partial \xi}{\partial T} \right]_{v,\chi,\mathcal{A}=0} \sim \left[ \frac{T - T_c}{T_c} \right]^{-\alpha}, \quad (21)$$

i.e., an apparent weak divergence, in agreement with our conclusions from the thermodynamic approach.

It should be noted, however, that for any fixed  $\chi$ , no matter how small, if  $T$  approaches arbitrarily close to  $T_c(\chi)$ , the fact that the derivative in Eq. (20) is at fixed  $\chi$  and not fixed  $z_C$  eventually becomes important, and the derivative in Eq. (20) remains bounded. Near the critical locus and for  $\chi$  small, the derivative on the right-hand side of Eq. (20) can be expressed in the form

$$\left[ \frac{\partial \ln[K(t)\gamma_C/\gamma_B^2]}{\partial T} \right]_{v,\chi,\mathcal{A}=0} = \frac{A + B\tau^{-\alpha}}{C + D\chi\tau^{-\alpha}}, \quad (22)$$

where  $A$ ,  $B$ ,  $C$ , and  $D$  are functions of  $T$ ,  $\mu_A$ , and  $\mu_C$  that approach finite nonzero limits on the critical curve, and where  $\tau$  is a smooth function of  $T$ ,  $\mu_A$ , and  $\mu_C$ . The variation of  $\tau$  with  $T$  along the path of interest can be expressed in the form

$$\left[ \frac{\partial \tau}{\partial T} \right]_{\chi,v,\mathcal{A}=0} = \frac{E}{C + D\chi\tau^{-\alpha}}, \quad (23)$$

where  $E$  is a function of  $T$ ,  $\mu_A$ , and  $\mu_C$  that approaches a finite nonzero limit on the critical curve, and the denominator is the same as in (22). For  $N_A/V$  constant,  $\chi \ll 1$ , and  $T$  not too close to  $T_c(\chi)$ ,  $\tau$  is a function of  $T$  that varies linearly with  $T - T_c(\chi)$ . Then the expression in

(22) varies as  $(A + B\tau^{-\alpha})/C$ , and there is an apparent weak divergence that will be visible if  $A$  is not too large compared to  $B\tau^{-\alpha}$ . As  $T$  approaches  $T_c(\chi)$  closely enough that  $D\chi\tau^{-\alpha}$  becomes comparable to and eventually large compared to  $C$ , the ratio in (22) saturates at the finite value  $B/D\chi$  with the behavior

$$\frac{B}{D\chi} \left[ 1 + \tau^\alpha \left[ \frac{A}{B} - \frac{C}{D\chi} \right] + \dots \right]. \quad (24)$$

This crossover occurs when, roughly

$$\tau \sim \chi^{1/\alpha}. \quad (25)$$

At this same crossover value of  $\tau$ , the temperature dependence of  $\tau$  changes, according to (23), so that when  $D\chi\tau^{-\alpha} \gg C$ ,  $\tau$  varies as

$$\tau \sim \{ [T - T_c(\chi)]/T_c(\chi) \}^{1/(1-\alpha)}.$$

Since  $\alpha$  is small (about 0.12), we conclude that for  $\chi \ll 1$ , the critical locus must be approached extremely closely before the rounding is observed. Thus, for  $\chi \ll 1$ , we can anticipate an apparent weak divergence in  $(\partial \xi / \partial T)_{v,\chi,\mathcal{A}=0}$  as a function of  $T$  until

$$[T - T_c(\chi)]/T_c(\chi) \sim \chi^p,$$

where  $p$  is about 7 to 8.

Equation (20) contains explicitly an interesting feature that is intrinsic to the problem considered here. If for a given fixed solvent we truly take the limit  $\chi \rightarrow 0$  at fixed  $T \neq T_c(\chi=0)$ , then, from Eq. (19), the equilibrium value of  $\xi$  will of necessity approach unity, independently of  $T$ , and  $(\partial \xi / \partial T)_{v,\chi,\mathcal{A}}$  must therefore be zero. This is guaranteed by the factor  $(1-\xi)$  in Eq. (20). However, it may well be that for an appropriate choice of chemical reaction and solvent,  $\chi$  may be much less than 1 and the activities of the solutes may be low enough that the constants  $\Lambda_{1,i}$  and  $\Lambda_{2,i}$  in Eq. (15) are functions of  $T$  alone (and not also of  $z_B$  and  $z_C$ ), while  $\xi$  is still substantially less than unity. It is presumed that this is the case under consideration. This assumption seems reasonable for the  $\text{N}_2\text{O}_4 = 2\text{NO}_2$  equilibrium. Under the conditions at the critical point of  $\text{CO}_2$ , the ideal-gas equilibrium constant for the reaction is  $K(T) \sim 5 \times 10^{-6}$  mole/cm<sup>3</sup>. For the experiments used by PG the concentrations of  $\text{NO}_2$  are in the range of  $4 \times 10^{-6} - 10^{-5}$  moles/cm<sup>3</sup> so that  $[\text{N}_2\text{O}_4] \sim [\text{NO}_2]$  and  $\xi$  is not identically one, while at the same time,  $\chi \sim 10^{-3} \ll 1$ .

The fact that  $(1-\xi)$  is proportional to  $\chi$  as  $\chi \rightarrow 0$ , while the ratio in (22) saturates at a value proportional to  $\chi^{-1}$  on the critical locus has the interesting consequence that  $(\partial \xi / \partial T)_{v,\chi,\mathcal{A}=0}$  evaluated on the critical locus remains nonzero and bounded as  $\chi \rightarrow 0$ . Of course, the value may be very large if  $K(T)$  is very small. Thus, the limiting value of  $(\partial \xi / \partial T)_{v,\chi,\mathcal{A}=0}$  at the pure-solvent critical point is *path dependent*, approaching zero along any path on which  $\chi \rightarrow 0$  first and then  $T \rightarrow T_c(\chi=0)$ , but approaching a nonzero finite constant as  $\chi \rightarrow 0$  along the critical curve. Path dependence of thermodynamic quantities is a characteristic feature of the approach to the critical point of a solvent, as discussed in Ref. 7 and in Sec. V.

It is interesting to note that the behavior of  $(\partial\xi/\partial T)_{v,\chi,\mathcal{A}=0}$  is somewhat different if the reaction  $B=C$  rather than  $2B=C$  is considered. In this case the ratio analogous to that in Eq. (22) still diverges proportionally to  $\chi^{-1}$  along the critical locus, but the prefactor is no longer proportional to  $\chi$ . As a consequence  $(\partial\xi/\partial T)_{v,\chi,\mathcal{A}=0}$  diverges proportionally to  $\chi^{-1}$  as  $\chi \rightarrow 0$  along the critical curve, but approaches a nonzero finite limit as  $\chi \rightarrow 0$  with  $T$  held constant [ $\neq T_c(\chi=0)$ ]. This limit then diverges weakly as  $T \rightarrow T_c$  with  $\chi=0$ .

#### IV. GENERAL ARGUMENT

Although the decorated-lattice model has certain somewhat artificial features, the conclusion that the activity coefficient of a dilute species should be a smooth function of *densities*, which is the crucial feature of Eq. (15), is much more general. First note that this is an automatic consequence of mean-field theories, such as the van der Waals equation for mixtures, that express the Helmholtz free energy as an analytic function of the densities of various components and temperature. Thus, these mean-field theories will predict no "strong" divergence of  $(\partial\xi/\partial T)_{v,\chi,\mathcal{A}=0}$  with exponent  $\gamma=1$ , but, rather, a completely nondivergent behavior for this derivative because these theories do not possess the weak singularity of non-classical theories. If, indeed,  $(\partial\xi/\partial T)_{v,\chi,\mathcal{A}=0}$  were to possess the apparently strongly divergent character predicted by PG, it would be expected to be derivable from these classical theories, and it is not.

Secondly, we note that the potential distribution formulation<sup>8</sup> of statistical mechanics expresses the activity coefficient  $\gamma_i$  in terms of an average of the potential energy felt by a test particle of type  $i$  through what has come to be called the Widom relation<sup>9</sup>

$$\gamma_i = \frac{z_i}{\rho_i} = (\langle e^{-\psi_i/kT} \rangle_{N-1})^{-1}, \quad (26)$$

where  $\psi_i$  is the potential energy felt by a test particle of species  $i$  due to the other  $N-1$  particles, and the average is over a canonical ensemble of  $N-1$  particles in which the Hamiltonian does not contain any interactions with the test particle. Now if we make the definition of densities sufficiently general that the short-ranged structure of the liquid is described by them, then it seems very reasonable to suppose that the average  $\langle e^{-\psi/kT} \rangle_{N-1}$  can be expressed as a weighted sum of their average values with weights that are smooth functions of the field variables. This is the essence of the result for the decorated-lattice model. In that model the symmetrized energy density  $w$  measures the number of empty-filled nearest-neighbor pairs of cells and gives the essential short-ranged structure necessary to specify  $\gamma_i$  once  $\rho$  is given. For a more general model we might expect to have to specify the averages of other operators as well. In general, one would expect to be able to write the average in Eq. (26) in terms of the averages of one operator that plays the role of order parameter (and can be taken to be the solvent density), the fluctuations in which are strongly divergent as the critical point is approached, a second operator whose fluctuations diverge only weakly as the critical point is approached,

and some number of additional operators whose fluctuations remains bounded near the critical point. The argument would then proceed precisely as for the decorated-lattice-model case: no strong divergence in  $(\partial\xi/\partial T)_{v,\chi,\mathcal{A}=0}$  because the constraint  $v = \text{const}$  for  $\chi \ll 1$  forces the order-parameter to be constant and thereby suppresses the strong fluctuations.

The argument above, of course, depends very much on the fact that the potential  $\psi$  is in some sense short ranged so that the operators in  $\exp(-\psi_i/kT)$  are local operators. If  $\psi$  varies on length scales large compared to the correlation length, the average in Eq. (26) will, in general, involve such operators as the square of the integral of the order parameter over regions larger than the correlation length. Such averages vary rapidly with the correlation length. Once the correlation length is larger than the effective range of the potential, however, these correlation functions cease to vary rapidly and, in particular, the most rapidly varying are those described in the general argument above. For small molecules such as  $\text{NO}_2$  and  $\text{N}_2\text{O}_4$  we expect the operators to be local in this sense throughout the range in which critical divergences are observed.

#### V. PATH-DEPENDENT LIMIT

If the above arguments are accepted as convincing, then what is wrong with the argument of PG? The error lies in a subtle interchange of limits and the rather bizarre and path-dependent behavior of certain thermodynamic derivatives at the critical point of a pure solvent. PG argue, quite correctly, that the behavior of the derivative of interest depends upon the derivative of the internal energy with respect to the extent of reaction at constant volume. In the notation adopted here their Eq. (7) reads

$$\left[ \frac{\partial\xi}{\partial T} \right]_{v,\chi,\mathcal{A}=0} = \frac{-\chi^{-1} \left[ \frac{\partial e}{\partial\xi} \right]_{T,v,\chi}}{T \left[ \frac{\partial\mathcal{A}}{\partial\xi} \right]_{T,v,\chi}}, \quad (27)$$

where

$$e = E/\tilde{N}, \quad (28)$$

and  $E$  is the internal energy of the system. They then observe that  $(\partial e/\partial\xi)_{T,v,\chi}$  can be written in terms of the derivative of the enthalpy and volume at fixed  $T, P, \chi$ ; in our notation

$$\left[ \frac{\partial e}{\partial\xi} \right]_{T,v,\chi} = \left[ \frac{\partial h}{\partial\xi} \right]_{T,p,\chi} - T \left[ \frac{\partial p}{\partial T} \right]_{v,\xi,\chi} \left[ \frac{\partial v}{\partial\xi} \right]_{T,p,\chi}, \quad (29)$$

where

$$h = H/\tilde{N}, \quad (30)$$

and  $H$  is the extensive enthalpy. They argue (correctly) that each term on the right-hand side is strongly divergent and (incorrectly) that a cancellation between them is unlikely. This might seem a strange way to proceed, since it is somewhat analogous to arguing that  $C_v$  for a pure fluid must diverge strongly because it can be written as the

difference

$$C_v = C_p - T \left[ \frac{\partial p}{\partial T} \right]_v \left[ \frac{\partial v}{\partial -p} \right]_T \quad (31)$$

between two strongly divergent quantities. Indeed, the derivative  $(\partial e/\partial \xi)_{T,v,\chi}$  is precisely the sort of derivative that would be expected to diverge only weakly by the arguments given earlier, and can be seen explicitly to diverge only weakly using the decorated-lattice-model approach. However, the argument of PG (although not stated in detail) continues in a seemingly plausible manner. Equation (29) can be rewritten

$$\chi^{-1} \left[ \frac{\partial e}{\partial \xi} \right]_{T,v,\chi} = (h_B - \frac{1}{2}h_C) - T \left[ \frac{\partial p}{\partial T} \right]_{v,\xi,\chi} (v_B - \frac{1}{2}v_C), \quad (32)$$

where  $h_B$ ,  $h_C$ ,  $v_B$ , and  $v_C$  are the partial molar enthalpies and volumes of  $B$  and  $C$ :

$$h_B = \left[ \frac{\partial H}{\partial N_B} \right]_{T,p,N_A,N_C}, \quad v_B = \left[ \frac{\partial V}{\partial N_B} \right]_{T,p,N_A,N_C} \quad (33)$$

Now as  $\chi \rightarrow 0$ , with  $T$ ,  $v$  fixed at noncritical values,  $(\partial p/\partial T)_{v,\xi,\chi}$  approaches  $(\partial p/\partial T)_v$  for the pure fluid, and this, in turn, approaches the slope of the pure-fluid coexistence curve (CC) in the  $P, T$  plane as the pure-fluid critical point is approached. On the other hand, it can be shown<sup>4</sup> that as the critical point (CP) of a pure solvent is approached along the critical line (CL) of the mixture, the ratio  $h_2/Tv_2$  for a dilute solute approaches the initial slope of the critical curve projected into the  $P, T$  plane. [Similarly, PG's Eq. (9) holds on the critical line.] Thus, if we rewrite Eq. (32) in the form,

$$\chi^{-1} \left[ \frac{\partial e}{\partial \xi} \right]_{T,v,\chi} = T(v_B - \frac{1}{2}v_C) \left[ \frac{h_B - \frac{1}{2}h_C}{T(v_B - \frac{1}{2}v_C)} - \left[ \frac{\partial p}{\partial T} \right]_{v,\xi,\chi} \right], \quad (34)$$

it is tempting to argue that, as the critical point of the pure solvent is approached,  $(v_B - \frac{1}{2}v_C)$  diverges strongly (it does), and the term in square brackets approaches

$$\left. \frac{dp}{dT} \right|_{CL} - \left. \frac{dp}{dT} \right|_{CC} \quad (35)$$

Since the slope of these two curves is not, in general, identical, a strong divergence in  $(\partial e/\partial \xi)_{T,v,\chi}$  is suggested.

The argument above would be correct if the ratio  $h_2/Tv_2$  approached a single limiting value independent of the path of approach to the pure-fluid critical point. This is not, in fact, the case. This ratio of two diverging quantities approached different limiting values depending upon the path of approach to the critical point. In fact, it is fairly easy to show that if one first lets  $\chi \rightarrow 0$  and then approaches the critical point, the limiting value of both  $h_B/Tv_B$  and  $h_C/Tv_C$  is just the slope of the coexistence curve for the pure solvent. That is, while

$$\lim_{\chi \rightarrow 0} \lim_{CL} (h_B/Tv_B) = \left. \frac{dp}{dT} \right|_{CL, \chi=0}, \quad (36)$$

nevertheless

$$\lim_{CP} \lim_{\chi \rightarrow 0} (h_B/Tv_B) = \left. \frac{dp}{dT} \right|_{CC, \chi=0}, \quad (37)$$

and similarly for component  $C$ . Now if we wish to examine the behavior of  $(\partial e/\partial \xi)_{T,v,\chi}$  for  $\chi \ll 1$  and not too close to  $T_c$ , as stated explicitly by PG, then clearly the second of these limits is a more appropriate estimate of the behavior of  $h_B/Tv_B$ . That is, one should examine the behavior of the quantity of interest in the limit  $\chi \rightarrow 0$  as a function of  $T$  and *not* the behavior of the quantity on the critical line as a function of  $\chi$ . In this case the quantity in brackets in Eq. (34) is tending to zero while  $(v_B - \frac{1}{2}v_C)$  is diverging, and no simple conclusion can be reached concerning the product. Of course, this argument does not establish the actual behavior of  $\chi^{-1}(\partial e/\partial \xi)_{T,v,\chi}$ . It does, however, show that it cannot be strongly divergent since it is the product of strongly divergent and vanishing terms.

The argument concerning the second limit, Eq. (37), proceeds as follows:

$$\begin{aligned} \frac{h_B}{Tv_B} &= \frac{\left[ \frac{\partial \mu_B/T}{\partial 1/T} \right]_{\xi,\chi,p}}{T^2 \left[ \frac{\partial \mu_B/T}{\partial p} \right]_{\xi,\chi,T}} = \left[ \frac{\partial p}{\partial T} \right]_{\xi,\chi,\mu_B/T} \\ &= \left[ \frac{\partial p}{\partial T} \right]_{\xi,\chi,v} + \left[ \frac{\partial p}{\partial v} \right]_{\xi,\chi,T} \left[ \frac{\partial v}{\partial T} \right]_{\xi,\chi,\mu_B/T}. \end{aligned} \quad (38)$$

Now, as  $\chi \rightarrow 0$  first and then the critical point of the pure fluid is approached, the limit of  $(\partial p/\partial T)_{\xi,\chi,v}$  is the desired quantity while  $(\partial p/\partial v)_{\xi,\chi,T}$  becomes  $(\partial p/\partial v)_T$  for the pure fluid which, in turn, is the reciprocal of a strongly diverging derivative. Thus, if it can be shown that the limit of  $(\partial v/\partial T)_{\xi,\chi,\mu_B,T}$  is, at most, weakly divergent, Eq. (37) will be established. We recall<sup>7</sup> that, near  $\chi=0$ ,  $\mu_B$  can be expressed as

$$\frac{\mu_B}{T} = \frac{\mu_B^*}{T} + \ln \left[ \frac{N_B}{V} \right] + \ln \gamma_B^*, \quad (39)$$

where  $\mu_B^*/T$  is a smooth function of  $T$  alone, and  $\gamma_B^*$ , as a function of temperature and density, has the property that the derivative  $(\partial \gamma_B^*/\partial T)_v$  is, at worst, weakly divergent, while  $(\partial \gamma_B^*/\partial v)_T$  is finite. Thus,  $(\partial v/\partial T)_{\xi,\chi,\mu_B/T}$  has, at most, a weak divergence, and the desired result is established. The first limit, Eq. (36), may also be obtained from Eq. (38) by noting that the ratio of interest is the derivative of  $p$  with respect to  $T$  with two densities held fixed and, therefore, by the arguments of Ref. 4, will be equal to the slope  $dp/dT$  of the critical line all along the critical line, and therefore, in particular, as  $\chi \rightarrow 0$ .

It should not be entirely unexpected that certain thermodynamic derivatives might approach finite but path-

dependent values at the critical point of a pure solvent. It has been noted both experimentally<sup>10</sup> and theoretically<sup>7</sup> that the partial molar enthalpy and volume of the *solvent* are dependent upon the path of approach to the critical point. If this limit is taken in the order  $\chi \rightarrow 0$  first, they approach the enthalpy and volume per mole of solvent at the critical point. If the limit is taken along the critical locus, however, quite different values are obtained and the limiting partial molar volume of the solvent can even be negative. As noted in Sec. III, similar behavior is observed for the derivative  $(\partial\xi/\partial T)_{v,\chi,\mathcal{A}=0}$ . The error of PG illustrates the care that must be taken in analyzing the behavior of dilute solutions near a critical point.

## VI. EXPERIMENT

The experiment of Krichevskii<sup>2</sup> is in apparent contradiction to our theoretical analysis and in apparent agreement with that of PG. In this experiment the color of a dilute solution of  $N_2O_4$  and  $NO_2$  in  $CO_2$  was measured by transmitted light. It is known that  $N_2O_4$  is transparent in the visible and that  $NO_2$  absorbs blue light, giving a red color to  $NO_2, N_2O_4$  solutions. A color change in the transmitted light within 0.1 K of the critical point, with a shift toward the red as  $T_c$  was approached from above, was interpreted by Krichevsky as an increase in the  $NO_2$  concentration as  $T \rightarrow T_c$ . His quoted values of  $NO_2$  concentration were used by PG to conclude that  $(\partial\xi/\partial T)_{v,\chi,\mathcal{A}=0}$  diverges strongly.

However, the effect of scattering from the critical fluctuations also yields an effective attenuation which is strongest in the blue and which leads to a pronounced change in color of the transmitted light near  $T_c$ , shifting it toward the red. This shift toward the red of the transmitted light and the corresponding blue color of the scattering light is readily seen by the eye when observing pure fluids near the critical point.

The relative importance of these contributions to the attenuation can be estimated from the results of Hall *et al.*<sup>11</sup> for  $N_2O$  and those of White *et al.*<sup>12</sup> and Lunacek *et al.*<sup>13</sup> for pure  $CO_2$ . From the results of Hall *et al.*<sup>13</sup> we readily compute that the attenuation coefficient of  $NO_2$  gas in the blue is approximately  $2 \times 10^5 [C_{NO_2}/(\text{mole cm}^{-3})] \text{ cm}^{-1}$  where  $C_{NO_2}$  is the concentration of  $NO_2$ . The effective attenuation coefficient of a near-critical mixture due to scattering is<sup>13</sup>

$$\begin{aligned} \tau = & \pi^2 k_B T K_T \lambda_0^{-4} [(n^2 - 1)(n^2 + 2)/3]^2 \\ & \times [(2\bar{\alpha}^{-1} + 2\bar{\alpha}^{-2} + \bar{\alpha}^{-3}) \\ & \times \ln(1 + 2\bar{\alpha}) - 2(\bar{\alpha}^{-2} - \bar{\alpha}^{-1})], \end{aligned} \quad (40)$$

where  $K_T$  is the isothermal compressibility,  $\lambda_0$  is the wavelength of the light *in vacuo*,  $n$  is the index of refraction,  $k_B$  is the Boltzmann's constant, and  $\bar{\alpha} = 8\pi^2 \bar{\xi}^2 \lambda_0^{-2}$  where  $\bar{\xi}$  is the correlation length in the critical mixture. For the purposes of the crude estimate below we assume that  $\bar{\alpha} \ll 1$ , i.e., that the correlation length is not too long, and that the index of refraction is the value for the red light used in Ref. 12, 1.106. Each of these approximations means that we will overestimate the attenuation by a

factor. In particular the  $\bar{\alpha}$ -dependent factor in square brackets in Eq. (40) decreases as  $\bar{\xi}$  gets large near the critical point. However, use of measured values of  $\bar{\xi}$  for the pure fluid has little effect. Similarly, the index of refraction is somewhat smaller in the blue. Use of realistic values again does not substantially change the result. Substituting experimentally measured values we find

$$\begin{aligned} \tau \sim & (0.1 \text{ cm}^{-1}) [ |T - T_c| / (1 \text{ K}) ]^{-1.24} \\ & \times [\lambda_0 / (4500 \text{ \AA})]^{-4}. \end{aligned} \quad (41)$$

Thus, there are wavelength-dependent contributions to the optical density from the critical scattering that imply changes in the color of the transmitted light of the right sign and order of magnitude to account for the apparent changes in  $NO_2$  concentration given by Krichevskii *et al.* This conclusion has been confirmed by Morrison<sup>14</sup> of the National Bureau of Standards who has made a careful study of Krichevskii's data using a traveling microscope and has found that both the magnitude and apparent exponent are in good agreement with critical scattering.

## VII. PREDICTIONS AT CONSTANT PRESSURE

PG also make predictions about the behavior at constant pressure of the extent of the reaction  $B_2 \rightleftharpoons 2B$  near the liquid-vapor critical point of an equilibrium mixture of pure  $B$  and  $B_2$ . They predict that on the equilibrium line the derivative  $(\partial\xi/\partial T)_{p,\mathcal{A}=0}$  should generally exhibit a strong divergence at the critical point, varying as

$$\left[ \frac{\partial\xi}{\partial T} \right]_{p,\text{equil}} \sim \left| \frac{T - T_c}{T_c} \right|^{-\gamma}. \quad (42)$$

We agree with the conclusion that this derivative should diverge strongly. We note however, that the exponent  $\gamma$  is appropriate only if the derivative is examined as the critical point is approached along a path with one density held fixed, e.g., along the path  $v = v_c = \text{const}$ . The behavior along the critical isobar is expected to be described by an exponent related to the degree of the critical isotherm  $\delta$ :

$$\left[ \frac{\partial\xi}{\partial T} \right]_{p,\mathcal{A}=0} \sim \left| \frac{T - T_c}{T_c} \right|^{-(\delta-1)/\delta} \quad (P = \text{const}) \quad (43)$$

where  $\delta$  is about 4.9. The resulting exponent is less than unity, as is required for the derivative to be integrable through the transition along the path  $P = P_c, \mathcal{A} = 0$ .

PG then consider the special limiting case in which the equilibrium concentration of the dissociation product is very small. They argue that in this case the divergence becomes that of a *product* of two strongly diverging quantities and the appropriate exponent is  $2\gamma$ . We believe that this prediction is in error. We first note that if this conclusion were correct, then the appropriate behavior along the line  $P = P_c, \mathcal{A} = 0$  would be given by

$$\left[ \frac{\partial\xi}{\partial T} \right]_{p,\mathcal{A}=0} \sim \left| \frac{T - T_c}{T_c} \right|^{-2(\delta-1)/\delta}, \quad (44)$$

which is no longer integrable. This leads to the physically unreasonable conclusion that when  $\xi$  is extremely small,  $\xi/\xi_c$  must necessarily change by many orders of magni-

tude as the critical point is approached, where  $\xi_c$  is the value of  $\xi$  at the critical point. The problem again lies in the subtle behavior of thermodynamic derivatives near the critical point of an almost pure solvent. The derivative of interest can be expressed as

$$\left[ \frac{\partial \xi}{\partial T} \right]_{P, \mathcal{A}=0} = - \frac{(\partial h / \partial \xi)_{T,P}}{T(\partial \mathcal{A} / \partial \xi)_{T,P}}. \quad (45)$$

PG argue (correctly) that in the limit of nearly pure *C* the numerator becomes a strongly divergent quantity near (but not too near) the critical point. What they fail to notice is that in the same limit the denominator, which is ordinarily strongly vanishing, becomes nonvanishing. This comes about because of the dilute-solution limit the chemical potential is dominated by a logarithmic dependence on concentration. As a result, the denominator in Eq. (45) is dominated by a term  $RT/\xi$  until strongly divergent quantities become comparable to this term; i.e., precisely over the range in which the numerator is apparently strongly divergent. As a consequence, even in the dilute-solution limit  $(\partial \xi / \partial T)_{P, \mathcal{A}}$  will exhibit only a simple strong divergence, and this will be scaled by an amplitude  $\xi$  coming from the denominator of Eq. (45). Equation (19) can be adapted to the present case by setting  $\chi=1$  and differentiating with respect to  $T$  at fixed  $P$  and  $\mathcal{A}=0$ . The result

is

$$\left[ \frac{\partial \xi}{\partial T} \right]_{P, \mathcal{A}=0} = \frac{\xi(1-\xi)}{2-\xi} \left[ \left[ \frac{\partial \ln(K_T \gamma_C / \gamma_B^2)}{\partial T} \right]_{P, \mathcal{A}=0} + \left[ \frac{\partial \ln v}{\partial T} \right]_{P, \mathcal{A}=0} \right]. \quad (46)$$

Both terms in square brackets will contribute simple strong divergence as the critical point is approached regardless of whether  $\xi$  is close to 0 or 1, or not.

### VIII. CONCLUSION

Interesting anomalies occur in the temperature dependence of chemical equilibria near critical points of fluid mixtures. Care is needed in the analysis of these anomalies in very dilute solution because of the competition between singularities due to the critical point and singularities due to the ideal dilute-solution behavior of the chemical potential.

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