Resistance anomaly in a weak acid near the critical point[*]

David Jasnow,[†] W. I. Goldburg, and J. S. Semura[‡]

Physics Department, University of Pittsburgh, Pittsburgh, Pennsylvania 15260

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Recently published data on the resistance anomaly in a critical isobutyric acid-water mixture near the phase-separation critical point are analyzed. It is shown that the data below a value of $t \equiv (T - T_c)/T_c \simeq 5 \times 10^{-5}$ may be influenced by gravitational effects which were not accounted for in the original analysis. In the temperature range above this value of t, a fit of the form $(R_c - R)/R_c \approx At^{1-\alpha} + Bt$ (with α the specific-heat exponent) is shown to be satisfactory, and a semiquantitative theory which yields this result is presented.

I. INTRODUCTION

In a recent publication[1] an anomaly in the electrical conductivity of a critical mixture of isobutyric acid and water near the phase-separation critical point was reported. In Fig. 1 the quantity $(R_c - R)/R_c$ vs $t = (T - T_c)/T_c$ is plotted with R the resistance and R_c its (finite) value[2] at the critical point. Measurements on two different samples are shown in the figure along with a plot of the function

$$(R_c - R)/R_c = 4.1t^{1-\alpha} - 1.6t \qquad (1.1)$$

with $\alpha = 0.12$, which is approximately the specific-heat exponent for three-dimensional Ising systems.[3] The above quoted value of α is the specific-heat exponent for this binary liquid mixture as deduced from scaling.[4] The fit is quite acceptable over the range $2 \times 10^{-5} \lesssim t \lesssim 10^{-2}$, the range of most previous critical-point experiments on mixtures of this type.

The coefficients on the right-hand side of (1.1) are particularly sensitive to specific choices of the exponent α: in a least-squares fit the amplitude of the singular term can change by as much as a factor of 2 if a change of 0.04 is made in $1 - \alpha$. Hence we do not take the specific amplitudes in (1.1) too seriously. Below we shall indicate our reasons to expect an energy-density singularity in (1.1), and we shall show that the over-all numerical variation of $(R_c - R)/R_c$ is roughly in accord with our estimates.

In Sec. II we comment briefly on the fact that gravitational effects may be influencing the data in the temperature range $t \lesssim 5 \times 10^{-5}$. In Sec. III the mechanism which we believe produces the energy singularity in (1.1) is discussed. Section IV is devoted to summary and further comments.

II. GRAVITATIONAL EFFECTS

It has been appreciated that experiments on one-component fluids are susceptible to gravitational

effects, and it has been argued[5] that in binary mixtures *concentration* gradients could be induced which are of the same order as density gradients in one-component fluids. Gravity does indeed separate the A-rich and B-rich phases in a typical binary mixture below the critical point.

As can be seen in Fig. 1, below $t \simeq 2 \times 10^{-5}$, the two sets of measurements break away, and the function (1.1) is no longer adequate. An order-of-magnitude estimate indicates that below that temperature, gravitational effects can be influencing the data.

One can make an order-of-magnitude estimate which is based on thermodynamics and which is similar in spirit to the initial estimates of Hohenberg and Barmatz[6] for one-component fluids. If we use[7] the number fraction $x = N_A/N$ and the chemical potential Δ which couples to the number difference $N_A - N_B = N(2x - 1)$, we find the following equation for the spatial (z direction) variation of the concentration at constant temperature:

$$\chi^{-1}[1 + ax]\left(\frac{dx}{dz}\right) + \tfrac{1}{2}g[m_A - m_B(1 + a)] = 0. \qquad (2.1)$$

Here m_A and m_B are the molecular masses of the two species; χ is the susceptibility-measuring order-parameter fluctuations and is given by

$$\chi \equiv (\partial x/\partial \Delta)_{T,P}$$
$$\approx (\tilde{A}/k_B T_c) t^{-\gamma}, \quad t \to 0+. \qquad (2.2)$$

The dimensionless parameter a is given by

$$a = (\partial v/\partial x)_{T,P}[v - x(\partial v/\partial x)_{T,P}]^{-1}, \qquad (2.3)$$

with $v = V/N$ the mean molecular volume of the system. Equation (2.1) results from expressing the chemical potentials μ_A and μ_B of the two species as $\mu_i = \mu_i^0(T, P, x) + m_i gz$ ($i = A, B$), where P and x depend on position z, and requiring that the μ_i are independent of z. To obtain an order-of-magnitude estimate the equation is linearized by
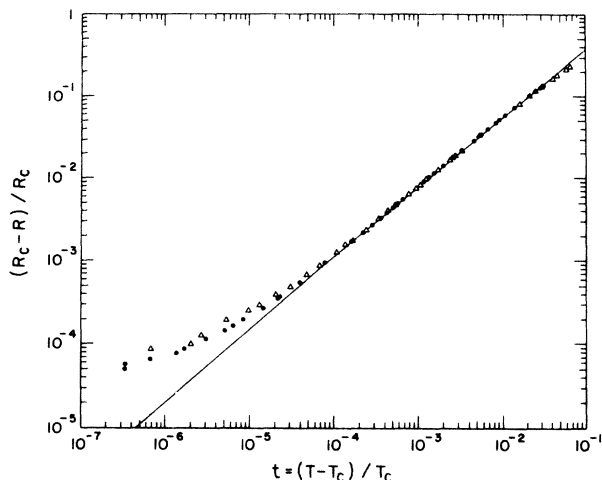
FIG. 1. Resistance of a critical mixture of isobutyric acid and water near the critical point. $(R_c - R)/R_c$ vs t for two runs using the data of Ref. 1. The solid line is a plot of Eq. (1.1).

treating χ and a as independent of z; then for a given sample height h, we find a top-to-bottom concentration difference $\delta x(t)$ which depends on temperature principally through χ. At some temperature $t_0 > 0$, δx is equal to the concentration difference between the two coexisting phases at temperature $-t_0$. Hence an estimate of the temperature regime where gravitational effects should become apparent is given by the identification

$$\delta x(t_0) = 2x_c \bar{B} |t_0|^\beta , \tag{2.4}$$

where the shape of the coexistence curve is specified by

$$|x - x_c|/x_c \simeq \bar{B}|t|^\beta , \quad t < 0 . \tag{2.5}$$

Carrying out the above prescription we find

$$t_0 \simeq \left[\frac{\bar{A}}{4\bar{B}} \frac{m'gh}{x_c k_B T_c} \right]^{1/(\beta+\gamma)}_{x=x_c} , \tag{2.6}$$

with

$$m' = \frac{m_A - m_B(1+a)}{1+ax_c}$$

$$= \frac{m_A \bar{v}_B - m_B \bar{v}_A}{v} , \tag{2.7}$$

where $\bar{v}_A$ and $\bar{v}_B$ are the partial molecular volumes. The form of this result is identical to that used in the order-of-magnitude estimate of Hohenberg and Barmatz[6] for a one-component fluid [see their Eq. (3.4)]. Note that it is not the mass difference alone which determines the relative importance of the gravitational effects in a given temperature range.

We estimate a (and hence m') using an ideal-solution approximation: $v = xv_A + (1 - x)v_B$ where

v_A and v_B are the molecular volumes of the pure individual species. In the isobutyric-acid–water system, $x_c \simeq 0.11$ (38 wt% acid), $T_c \simeq 26.23$ °C; the acid has molecular weight 88, and the acid density $\simeq 0.95$ g/cm^3. Approximately, then, $a \simeq 4$ from which we find $t_0 \simeq 5 \times 10^{-5}$, where we have used $h = 1$ cm^{1,8} and $\bar{B} \simeq \bar{A} \simeq 1$. We have also used the Ising exponent values[3] $\gamma = \frac{5}{4}$ and $\beta = \frac{5}{16}$, which are in good agreement with experimental values for this material[4] and sufficient for estimation purposes. The value for $\bar{B}$ seems quite reasonable for many binary mixtures and single-component fluids. However, direct measurements of the amplitude $\bar{A}$ are not generally available; three-dimensional Ising models, which are frequently used to represent such systems, have $\bar{A} \simeq 1$. Since the acid-water mixture does not have a critical concentration $x_c = \frac{1}{2}$, and since specific amplitudes are not in general universal, it is possible that $\bar{A}$ might be as small as, say, 0.1–0.2, as we have roughly estimated. This reduction would lower our estimate of t_0 by about a factor of 2. In any event we feel that one can be suspicious of the interpretation of the data below perhaps $t_0 = 2 \times 10^{-5}$; the original data and analysis[1] extend as low as $t = 3 \times 10^{-7}$.

III. CONDUCTIVITY ANOMALY

There are several mechanisms which contribute to the conductivity of a weakly dissociated acid which we denote symbolically as HA. In an aqueous solution of a strong or weak acid one finds that the dominant conduction mechanism is the rapid diffusion or "hopping" of the H$^+$ from water molecule to water molecule, temporarily forming H$_3$O$^+$ ions. For example in a dilute isobutyric-acid–water solution, the H$^+$ mobility is more than 10 times that of the basically diffusive A$^-$ mobility. A small fraction of the H$^+$ mobility (on the order of 10%) is due to diffusion from the random motion of H$_3$O$^+$ ions as contiguous units.[9] In a first crude picture of the conductivity of isobutyric (and similar) acid-water mixtures, we focus on the H$^+$ hopping mechanism and ignore for the moment all other contributions. We are in effect assuming that (i) the same mechanisms which prevail in very dilute solutions continue to dominate in these more concentrated systems $(x_c \simeq 0.11)$ and (ii) contributions from diffusive mechanisms are either less singular or small in magnitude in the temperature range considered. As to (i), our reading of related measurements indicates that hopping continues to dominate, although perhaps not as strongly as in dilute solutions. We shall comment further on diffusive contributions in Sec. IV.

Although the system is in reality a multicomponent system with chemical dissociation taking

place, the phase transition is basically of the binary liquid type: below T_c the liquid separates into acid-rich and acid-poor coexisting phases. The degree of dissociation is small, due to the weakness of the acid. Defining the volume per H^+ ion as $\frac{4}{3}\pi r_0^3$, we estimate $r_0 \sim 50$ Å in this system. As far as the phase separation is concerned, the positive and negative ions may be treated as "impurities" perhaps inducing constraints (see below). But viewed alternatively, the strong concentration correlations in the medium can have an important effect on the ion system and can induce ancillary critical phenomena such as conductivity anomalies. In fact, over cells large compared to r_0 one might expect large ion-number fluctuations, since in a given region the ion numbers will depend on the acid concentration, a strongly fluctuating quantity near T_c.[10] Near the critical point $T \lesssim T_c$ the ions are preferentially in the acid-rich phase even though the degree of dissociation is lower. This last fact allows us to proceed with our semiquantitative theory of the resistive anomaly.

Basically, the idea is to reduce the multicomponent system to two components which can be represented in Ising lattice-gas language. To a good approximation the phase separation can be described by considering the two "components," water molecules and "acids." The second component consists predominantly of HA molecules with a very small fraction (due to weak dissociation) of A^- and H_3O^+ (we neglect water dissociation). The phase separation is into water-rich and "acid"-rich phases. Consider a given H_3O^+ ion slightly above T_c. The hopping mobility of the proton will surely depend on the H_3O^+-H_2O correlation function at short range (nearest neighbors in a lattice-gas sense). Given an H_3O^+-H_2O nearest-neighbor pair, the intrinsic hopping rate depends on a rotation time for the two molecules to orient properly.[9] In general, the rate is modified by the nearest-neighbor correlation function or a conditional probability that the proper jump site is available. This fact alone gives an indication that the energy-density singularity appropriate to the acid-water phase separation should appear in the mobility, hence in the resistive anomaly given in (1.1).

To be slightly more quantitative, we note that the above correlation is simply the nearest-neighbor "acid"-water correlation [treating the H_3O^+ as an "acid" (A) since the ions tend to phase separate from the water (W)]. In Ising lattice-gas language this is

$$\langle n_W(\vec{r})n_A(\vec{r}+\delta)\rangle = \langle \tfrac{1}{2}[1+\sigma(\vec{r})]\tfrac{1}{2}[1-\sigma(\vec{r}+\vec{\delta})]\rangle , \quad (3.1)$$

where $\sigma(\vec{r}) = \pm 1$, the upper (lower) sign correspond-

ing to the presence of a water ("acid") molecule in the cell at $\vec{r}$. From this analogy we conclude that the proton hopping mobility $\mu(t)$, which is determined in standard kinetic theory arguments by the effective hopping rate, is related to the ordinary Ising nearest-neighbor correlation function according to

$$\mu(t) \propto 1 - \Gamma(\vec{\delta}; t) \quad (3.2)$$

with

$$\Gamma(\vec{\delta}) = \langle \sigma(\vec{r})\sigma(\vec{r}+\vec{\delta})\rangle . \quad (3.3)$$

In three-dimensional Ising systems we believe that

$$\Gamma(\vec{\delta}) = \Gamma_c - Et^{1-\alpha} + Ft, \quad t \to 0+ \quad (3.4)$$

where numerical estimates of the constants Γ_c, E, and F, and $\alpha = \frac{1}{8}$ have been made[3] using the method of high-temperature series expansions. For example, for the fcc and sc lattices a specific-heat analysis[3,11] allows one to deduce

$$\Gamma_c \simeq 0.248, \quad E \simeq 2.03, \quad F \simeq 2.02 \quad \text{(fcc)}$$
$$\Gamma_c \simeq 0.328, \quad E \simeq 1.94, \quad \cdots \quad \text{(sc)}. \quad (3.5)$$

The value of F for the sc lattice cannot be obtained from Ref. 11 but seems to be fairly lattice independent when deduced from values for two-dimensional lattices which are quoted. Focussing on the fcc values[12] (there not being a great difference among the three-dimensional lattices), one would expect a mobility decrease (or a resistance increase assuming for the moment a fixed number of carriers) as the critical point is approached according to

$$\left(1 - \frac{R}{R_c}\right)_{\text{calc}} = 1 - \frac{\mu_c}{\mu} \approx \frac{Et^{1-\alpha} - Ft}{1 - \Gamma_c}$$

$$\approx 2.70t^{1-\alpha} - 2.69t, \quad t \to 0+ \quad (3.6)$$

which can be compared with (1.1).

While we do not take the specific amplitudes seriously as a measure of the resistance, they compare favorably with the fit to the data quoted in (1.1). We have commented earlier that the amplitudes in (1.1) are very sensitive to the exact choice of $1 - \alpha$, analogously to the difficulties one experiences in evaluating amplitudes in the series-expansion method.[12] Nonetheless, the order-of-magnitude agreement of the coefficient of the singular term in (1.1) with that of (3.6) is extremely encouraging.

Since slight changes in the choice of $1 - \alpha$ have a strong effect on the specific coefficients in (1.1), the over-all fit to the data remaining unaffected, it makes sense to compare numerically the over-all measured variation of resistance to our estimates based on Ising values. One finds from the

data approximately a 30% fall in resistance from $t = 0$ to $t = 0.1$, whereas the Ising prediction based on (3.6) would be around 10%. In light of the crudeness of the approximations, this agreement is again encouraging.

IV. DISCUSSION

We have shown that in the temperature range above about $t = 2 \times 10^{-5}$ the resistance of a critical isobutyric-acid–water mixture is fit well by the form $(R_c - R)/R_c \approx At^{1-\alpha} + Bt$, using a deduced value of α which is approximately equal to the Ising value $\alpha = \frac{1}{8}$. We have also argued that the data below this temperature may require corrections for the effects of gravity in order to obtain a proper interpretation. While this may be possible in principle, the scarcity of accurate equation-of-state (and hence critical-amplitude) data for binary mixtures limits the quantitative study that can be made.

We then argued that the proton-hopping contribution to the conductivity is determined by short-range correlations in the system, the hopping distance being much less than the correlation length ξ near T_c. This fact provides evidence for the energy-density singularity[13] which has been found to provide a fit to the data. Furthermore, it has been shown that sensible numerical estimates are obtained simply by considering the numerical behavior of the Ising-model nearest-neighbor correlation function.

In fact the arguments of Sec. III can be put on a somewhat more microscopic basis by mapping the system onto a quantum lattice-gas Hamiltonian. In that way the linear-response equation for the hopping conductivity (ignoring complications due to Coulomb forces[14]) is mapped onto the *kinetic coefficient L* for spin diffusion in a uniaxial (Ising-like) magnet with short-range exchange. As has been shown by Kawasaki,[15] in such systems L remains finite at the critical point (corresponding to finite conductivity); further analysis[16] of Kawasaki's equations indicates that $L \approx L_c + L_1 t^{1-\alpha}$, which is consistent with the present phenomenological result for the behavior of the mobility.

Up to this point we have assumed a constant charge-carrier density which is determined by the over-all acid concentration. The chemical reaction, namely dissociation, imposes a constraint equation on the chemical potentials of the various species involved. Considered from the point of view of critical exponent renormalization,[17] the ion density itself may have an energy-density singularity or a finite (renormalized) temperature derivative[5] depending on experimental conditions. This latter possibility may prove to be experimentally unobservable, however. Since dissociation is a phenomenon which samples energy and entropy densities in a medium experiencing concentration fluctuations, it seems reasonable to expect some sort of energy-density singularity in the ion concentration. Specifically, the dissociation of an acid molecule depends conditionally on the presence of a water molecule in its neighborhood. It would seem that arguments similar to those used in Sec. III should apply, thereby indicating that short-range correlations determine the resulting anomaly. These are posed here as possibilities which are receiving further attention. Suffice it to say that an energy singularity in the ion density does not disturb our over-all conclusions but may affect numerical estimates.

Finally, we can comment on alternative contributions to the total conductivity. The divergence of the kinetic coefficient for diffusion in an ordinary binary liquid is pictured qualitatively as due to fluctuating spheres of A-rich region of linear dimension ξ diffusing through the B medium according to Stokes law.[18] Such events probably do not account for electrical-current fluctuations, as we suppose the concentration fluctuations are slow and electroneutrality is preserved in these regions. In other words, a region of concentration fluctuation may have a greater ion number on the average, but always maintains ion balance. Fluctuations involving motion of one ion species relative to the other would not seem to involve the long-range velocity-field correlations that yield a strong anomaly in ordinary diffusion.[18] Dilute electrolyte theory (which is probably not directly applicable) produces a specific conductivity or mobility which depends on the Debye length (which in turn depends on the ion density) and the viscosity. We have already commented on the ion density. The whole question of a viscosity anomaly in binary fluids is not settled; in any event the singularity observed in the temperature range considered is far different than what could be accounted for by the cusplike behavior sometimes seen in the viscosity of simple fluids and binary mixtures.[19] A serious consideration of diffusive contributions to the conductivity would require further attention.

Finally we mention that experiments are underway to study the resistive anomaly in a critical phenol-water solution. Phenol is also a weak acid.

in solution. One of us (D.J.) has had many conversations which have helped crystallize the ideas presented here. Thanks go to Professor J. S. Langer, Professor R. B. Griffiths, Professor B. Widom, and Professor M. E. Fisher for their interest and suggestions. We wish to thank Professor H. L. Friedman for detailed comments and suggestions.

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‡Present address: Department of Physics, Portland State University, Portland, Oregon 97207.

†Alfred P. Sloan Foundation Fellow.

[1]A. Stein and G. F. Allen, Phys. Rev. Lett. 29, 1236 (1972) (unpublished); and A. Stein and G. F. Allen, J. Chem. Phys. (to be published). We wish to thank Professor Allen for making the data available to us and for informing us of the dimensions of the conductance cells.

[2]We have used the values of R_c quoted in Ref. 1. Our estimates of R_c which exclude data below $t = 10^{-4}$ differ from these by less than 0.01%. Differences of this order do not materially affect the plot above $t \simeq 5 \times 10^{-5}$.

[3]See, for example, M. E. Fisher, Rep. Prog. Phys. 30, 615 (1967).

[4]To estimate α we have used $\gamma \simeq 2\nu$ and $\alpha + 2\beta + \gamma = 2$. For values of the critical exponents see B. Chu, S. P. Lee, and W. Tscharnuter, Phys. Rev. A 7, 353 (1973); B. Chu, F. J. Schones, and W. P. Kao, J. Am. Chem. Soc. 90, 3042 (1968).

[5]R. B. Griffiths (private communications).

[6]P. C. Hohenberg and M. Barmatz, Phys. Rev. A 6, 289 (1972).

[7]See, for example, D. Jasnow and W. I. Goldburg, Phys. Rev. A 6, 2492 (1972).

[8]We use here the electrode height which is about 1 cm. The actual cell is somewhat higher. Hence with the value of h chosen we are slightly underestimating t_0.

[9]The authors are indebted to Professor H. Frank for several discussions on these points. For a clear presentation with numerical tables, see, for example, J. O'M. Bockris and A. K. N. Reddy, *Modern Electrochemistry* (Plenum, New York, 1970), Vol. 1; R. A. Robinson and R. H. Stokes, *Electrolyte Solutions* (Butterworths, London, 1959).

[10]For reference purposes the Debye length is on the order of r_0. We expect the system to adjust itself rapidly to maintain charge neutrality over distances the order of r_0. Mass action would indicate the ion concentration in cells large compared to r_0^3 varies with the square root of the acid concentration. While this precise form may not hold near T_c the general dependence on acid concentration is still expected.

[11]M. F. Sykes, J. L. Martin, and D. L. Hunter, Proc. Phys. Soc. 91, 671 (1967).

[12]We should point out that earlier work which assumed a $t|\ln t|$ dependence in (3.4) yields nearly the same values for Γ_c but differs by as much as a factor of 5 in the amplitude E when compared with an analysis using the more recently accepted $t^{1-\alpha}$.

[13]The mechanism by which the resistive anomaly carries the energy singularity in a ferromagnetic metal has been discussed by M. E. Fisher and J. S. Langer, Phys. Rev. Lett. 20, 665 (1968).

[14]P. C. Martin, Phys. Rev. 161, 143 (1967).

[15]K. Kawasaki, Progr. Theoret. Phys. 39, 285 (1968); K. Kawasaki, Ann. Phys. (N.Y.) 61, 1 (1970).

[16]J. S. Semura and D. Jasnow (unpublished).

[17]M. E. Fisher, Phys. Rev. 176, 257 (1968).

[18]See, for example, R. A. Ferrell, Phys. Rev. Lett. 24, 1169 (1970), and references quoted therein.

[19]J. V. Sengers, in *Proceedings of the International School of Physics "Enrico Fermi"*, Course 51, Varenna, Italy, edited by M. S. Green (Academic, New York, 1971); J. C. Allegra, A. Stein and G. F. Allen, J. Chem. Phys. 55, 1716 (1971). See also P. M. Gammell and C. A. Angell [Phys. Lett. A 40, 49 (1972)] who also measured the conductivity but observed no anomaly down to $t \simeq 2 \times 10^{-5}$. In our view the conductivity measurements are not sufficiently complete for a critical-point analysis.