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Concentration Gradients in Nitroethane + 3-Methylpentane near the Liquid-Liquid Critical Solution Point*

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Precise measurements of density profiles in the system nitroethane + 3-methylpentane near the critical solution point demonstrate that concentration gradients form rapidly, but true equilibrium is not achieved even after long times. The data are in qualitative agreement with computer calculations of the behavior of a critical mixture in a gravitational field which show that the initial gradients form by sedimentation. Thus, effects due to gravity may affect careful experiments in critical mixtures.

It is well known that large density gradients due to gravity exist in substances in the vicinity of the gas-liquid critical point and that these gradients can result in systematic errors in the determination of the properties of critical systems.¹ Thermodynamic considerations lead to the conclusion that density (or concentration) gradients of the same shape and magnitude should likewise be present in mixtures in the vicinity of a critical solution point.² Near T_c the equilibrium concentration profile is expected to be sigmoid in shape, with the largest gradient near the midpoint of the sample.

It has been suggested that such concentration gradients are of little significance to the experimenter because they form at a negligibly slow rate. This argument is based on the assumption that the rate of gradient formation is controlled by concentration diffusion: In a mixture of critical composition the diffusion rate falls to zero as the critical temperature is neared.³ Recently, however, Dickinson *et al.*,⁴ in a discussion of the effect of high gravitational fields on critical mixtures, showed that sedimentation (pressure diffusion) plays an essential role in the dynamics

of the formation of concentration gradients. In contrast to concentration diffusion, the flux due to sedimentation *diverges* near the critical point.

Attempts by earlier workers to measure concentration gradients gave negative results⁵ or were difficult to interpret.^{6,7} We describe here precise measurements of the density profile in the system nitroethane + 3-methylpentane in the neighborhood of the upper-critical-solution temperature. Our data show that a significant gradient of the shape expected from sedimentation forms rapidly, but that the time to reach an equilibrium gradient is indeed very long. We show that the time evolution of the profile is in qualitative agreement with calculations based on the mechanism previously proposed.⁴

Nitroethane (99.95%) and 3-methylpentane (99.99%) were dried over silica gel. The mixture was prepared on a vacuum line, degassed twice by freezing and pumping, and sealed in the glass cell. The total sample was 0.086 51 mole, the mole fraction of nitroethane was 0.4990, and T_c was $26.445 \pm 0.002^\circ\text{C}$. These critical parameters are in good agreement with Wims, McIntyre, and Hynne,⁸ who reported $x_c = 0.500$

and $T_c = 26.456^\circ\text{C}$. The sample was 7.6 cm high and there was a 4.6-cm³ vapor space above it. Its temperature was measured with a quartz thermometer that was calibrated with respect to a platinum resistance thermometer on the 1968 international practical temperature scale.

The density profile was measured in a magnetic densimeter⁹ which measures fluid density by the levitation of a buoy in the fluid; the resolution of the densimeter is 2 ppm. The buoy is similar to those described by Senter¹⁰; it is a sphere approximately 1 cm in diameter with pointed projections at top and bottom; its overall height is 2.2 cm. The buoy has a density of 0.784 g cm⁻³. The buoy was calibrated by measuring the support current⁹ in four liquids of known density; the standard deviation of the calibration was 53 ppm. In order to measure the density profile, the buoy was maintained in a fixed position and the sample was moved with respect to it. Measurements of the height of the buoy in the fluid are consistent to 0.05 cm and are accurate with respect to a mark on the cell to 0.10 cm. The densimeter technique has the disadvantages that the density measured is an average over the height of the buoy and that the movement of the sample past the buoy stirs the fluid to some extent.

Figure 1 shows the measurements of density and mole fraction versus height of the center of the buoy at 0.785 K above T_c . Conversion of densities to mole fractions has been made using 72.661 cm³/mole and 130.86 cm³/mole for the

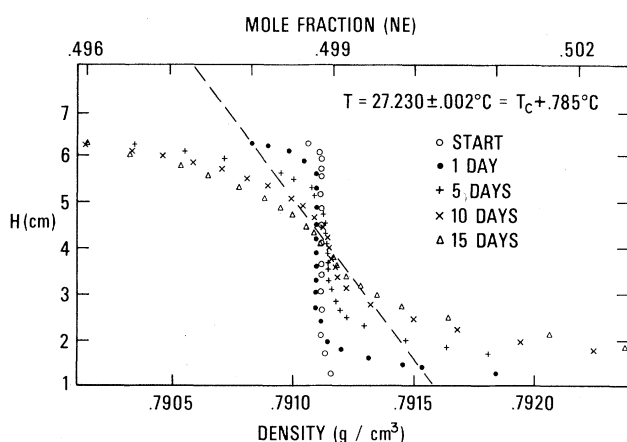


FIG. 1. Density profiles in nitroethane + 3-methylpentane at $T_c + 0.785$ K. The ordinate is the height in the fluid of the midpoint of the buoy. The dashed line represents an independent calculation of the equilibrium gradient.

molar volumes of nitroethane and 3-methylpentane, respectively, and assuming ideal mixing. An attempt was made at the start of the experiment to produce a homogeneous sample by stirring the sample with the buoy, but the stirring was not very efficient and there is a small initial gradient in the cell. Gradients are seen to form rapidly at the top and bottom of the cell; significant density changes at the center occur only much later, and equilibrium was not achieved even after 15 days. At temperatures closer to T_c , similar time development of profiles has been observed; the gradients form more rapidly, however, and are less susceptible to disturbance by stirring.

At this temperature the equilibrium gradient should be very nearly linear (as opposed to the sigmoid curve expected² closer to T_c). The equilibrium gradient can be calculated exactly² if expressions for the volume of mixing and for the derivative of the chemical potential with respect to mole fraction, $(\partial \mu_1 / \partial x_1)_{T,p}$, are known. This derivative can be obtained from the parametric equation of state¹¹ using the exponents determined by Wims, McIntyre, and Hynne.⁸ The parametric equation of state is written in reduced units and hence, in order to make comparisons between theory and experiment, it is necessary to specify the reduction parameter for μ_1 ; RT_c was selected. Volumes were calculated with the assumption of no volume change on mixing. In view of the fact that parameters have not been adjusted to optimize the fit and the fact that the data are averages over the buoy height, the calculated equilibrium line shown in Fig. 1 is comparable with the experimental gradients.

For comparison with the experimental results on the time development of the gradient, we calculated the profiles shown in Fig. 2 by the numerical solution of the flux equation^{4, 12}

$$j_1 = -j_2 = -Lx_1[(\partial \mu_1 / \partial x_1)_{T,p} \nabla x_1 + (\bar{V}_1 - M_1/\rho) \nabla p], \quad (1)$$

where j_1 is the mass flux (in the direction of the field) of component 1 relative to the average mass velocity, L is the Onsager phenomenological coefficient for diffusion, μ_1 is the chemical potential of component 1, \bar{V}_1 is its partial molar volume, M_1 is its molecular weight, x_1 is its mole fraction, and ρ is the mass density. The first term $Lx_1(\partial \mu_1 / \partial x_1) \nabla x_1$ is the diffusion term, which goes to zero approximately as $[(T - T_c) / T_c]^{0.6}$. The second term is the sedimentation

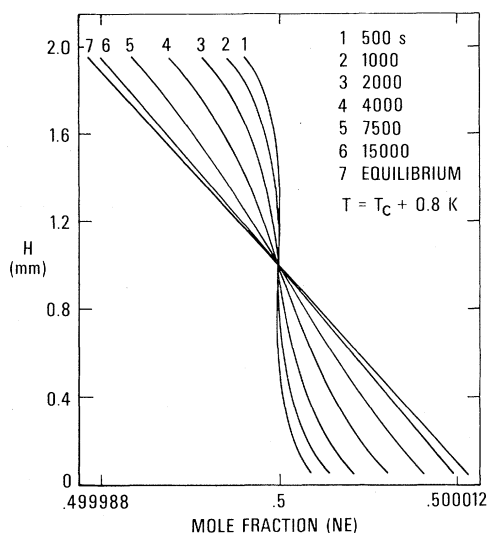


FIG. 2. Computer calculation of gradient formation near a liquid-liquid critical point in a 2-mm cell for an equal molar volume system. Other parameters have been chosen to approximate nitroethane + 3-methylpentane at $T_c + 0.8$ K.

term, which diverges approximately as $[(T - T_c)/T_c]^{-0.6}$. Because of limitations on computing time, these profiles have been obtained only for cells 2–4 mm high and for the approximation of equal molar volumes of the pure components. The parametric equation of state was employed with the same parameters used in the equilibrium-gradient calculation, and the diffusion constant, from which L is obtained, is that appropriate to nitroethane + 3-methylpentane at $T_c + 0.8$ K, 3×10^{-5} cm²/sec.¹³ The computed profiles are similar to those observed. The relaxation times τ are longest at the center of the cell and shortest at the ends; they also increase quadratically with total height of fluid. (Thus, the experimentally observed profiles would have developed about 50 times more rapidly in a cell 1–2 cm high.) In order to perform more quantitative comparisons of the time development and the magnitude of the calculated profiles with those of the observed profiles, it will be necessary to allow for nonequal molar volumes and to average the density over the height of the buoy.

Thus, we have discovered that a significant concentration gradient forms very rapidly in a binary critical mixture and that the initial concentration profile does not have the shape of the equilibrium profile. We propose that the initial profile is due to sedimentation. Our results raise serious questions about experimental stud-

ies of critical phenomena in binary mixtures. It has been shown^{1,2} that equilibrium gradients can produce significant systematic errors in studies of critical phenomena; in principle, data can be corrected for these effects. It is unlikely, however, that any experiments on binary liquid mixtures in the critical region have been performed over periods of time sufficiently long for equilibrium to be established. Sedimentation, on the other hand, is so rapid that significant gradients will form on the time scale of many experiments. Any studies of properties averaged over the height of the sample will be affected by these gradients. For example, in recent measurements¹⁴ of the thermal expansion of nitroethane + 3-methylpentane near the critical solution point by a magnetic densimeter, the expected anomaly was observed when the sample was stirred, but was not observed when the sample was not stirred. Even in the stirred sample, distortions due to gravity were found at $T < T_c + 0.1$ K. Gravity effects can be minimized by a judicious choice of mixtures, by the use of short samples,² and, to some extent, by stirring.

Our results are supported by preliminary studies of gradients by the Schlieren method¹⁵ and by a Mach-Zehnder interferometer.¹⁶

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Surface-Mode Renormalized Density-Functional Theory of the Free Surface of ${}^4\text{He}$

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We present a density-functional theory, renormalized to account self-consistently for the effects of the zero-point motion of surface modes, for the free surface of ${}^4\text{He}$ at zero temperature. Although detailed liquid-structure effects are included, no static density oscillations near the free surface are found in contrast to a theory of Regge. For the case of ${}^4\text{He}$ bounded by a single hard wall, density oscillations near the wall are obtained.

Recent years have seen the application of density-functional theory to a number of problems, principally those associated with the electron density in the vicinity of metal surfaces,¹ but also including some in the areas of liquid helium,² nuclear matter,³ and classical liquids.⁴ In this paper we present the results of a density-functional calculation of the density profile of the free planar surface of liquid ${}^4\text{He}$ at zero temperature. The theory used is a generalization of previous efforts, designed to take into account self-consistently the effects of changes in the long-wavelength (i.e., wavelengths greater than a few interatomic spacings) mode structure of the liquid when a free surface is formed in an otherwise uniform system. Specifically, we include the very important effects due to the zero-point motion of both the surface modes (ripples) and surface-altered bulk modes (phonons reflected at the surface) on the density profile and on the surface tension. Our results resolve the intriguing question, raised by previous theories of the ${}^4\text{He}$ free surface,⁵ as to whether or not there are oscillations in the density near the surface. We find no such oscillations even though we include hard-core effects (via a realistic structure factor) which might conceivably give rise to them. Further, we have applied our theory to the case where the liquid is bounded by a hard wall (ours is the first realistic calculation for this situa-

tion), and we find density oscillations similar to those found by Liu, Kalos, and Chester⁶ for a hard-sphere boson system bounded by two hard walls. This contrasting behavior shows that a free surface is simply too soft to permit static oscillations in the density. It is worthwhile to point out that the oscillations we obtain in the case of a single hard wall may reasonably be expected to persist in the situation where the helium is in contact with a real substrate, next to which one or two solid ${}^4\text{He}$ layers are formed⁷ (because of the substrate Van der Waals attraction), followed by the liquid. If so, one might expect a significant effect on the Kapitza boundary resistance in the temperature region (1–2° K) where the effective thermal-phonon wavelengths are comparable to those of the static density oscillations [recall that the phonons can strike the surface at an angle].

We begin with a description of what we term the bare density-functional (BDF) theory, "bare" in that it does not include the renormalizing effects of zero-point motion associated with the surface. Our approach is similar to that of Hohenberg and Kohn.⁸ We approximate the exact energy functional $E[n]$ in terms of a local energy density plus an expansion in powers of the difference between densities at different points in the fluid; the series is terminated in second order, and the first-order term vanishes for reasons of symmetry. Thus,

$$E[n] = \int d^3r \epsilon(n(\vec{r})) + \int d^3r d^3r' W(\vec{r}, \vec{r}') [n(\vec{r}) - n(\vec{r}')]^2. \quad (1)$$