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Thermal-Diffusion Measurements near a Consolute Critical Point*

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Using a classical Soret cell and the beam-deflection technique, we have, for the first time, accurately determined the nature of the divergence of the thermal-diffusion ratio k_T near the consolute critical point of the aniline-cyclohexane mixture. Furthermore, having measured with the same technique the diffusion coefficient D, we have also determined the behavior of the thermal-diffusion coefficient $D_T = k_T D$. The thermal-diffusion ratio diverges as a function of $T - T_c$ with a critical exponent close to that of the long-range correlation length ξ, while D_T is practically constant at 4.5×10^{-6} cm^2/sec.

Although diffusion processes in multicomponent liquid systems are primarily due to concentration gradients, appreciable diffusion flows can also be induced by temperature gradients (the so-called "Soret" or "thermal-diffusion" cross effect[1,2]). As a consequence, when a temperature gradient is applied to a previously homogeneous mixture, a concentration gradient is observed at steady state, the two opposing flows due to ordinary diffusion and thermal diffusion exactly balancing out. In order to describe the magnitude of this effect, one usually introduces[1,2] the thermal-diffusion ratio $k_T = -T\,\mathrm{grad}c/\mathrm{grad}T$, where c is the mass-fraction concentration of the heavier component. While the Soret effect is rather unconspicuous in ordinary mixtures,[2] large effects are expected near a consolute critical point, where k_T is predicted to diverge. So far contradictory theoretical predictions have been formulated,[3-5] and the experimental data available[6,7] on the subject do not allow one to draw any firm conclusion.

In this Letter we present, for the first time, accurate measurements of the thermal-diffusion ratio k_T in the neighborhood of the consolute critical point of the mixture aniline-cyclohexane. These measurements have been performed, as a function of temperature, on a classical Soret cell, by utilizing the steady-state beam-deflection technique.[2] Furthermore, by studying the time evolution of the beam deflection, we have also redetermined the temperature dependence of the (isothermal) diffusion coefficient D. From our measurements of k_T and D, we have then determined the behavior of the thermal-diffusion coefficient $D_T = k_T D$.

The optical setup we have used consists of a He-Ne laser, a focusing system, and a slit-photomultiplier assembly mounted on a vertical driving stage. The beam is strongly attenuated (to avoid self-heating problems), carefully spatially filtered, and mildly focused in front of the Soret cell, the beam diameter (at the $1/e^2$ points) inside the sample being $\approx$0.4 mm. The transmitted beam is intercepted at a distance $L = 82$ cm away from the cell by the slit-photomultiplier assembly. Vertical scans of the intensity distribution can thus be performed, and the beam-center position $Z(t)$ can be followed as a function of time.

The Soret cell is made up of two metal plates and a thick-wall cylindrical glass window. The window, whose inner diameter is 20 mm, has been ground and polished from a solid piece of optical glass. To avoid beam deformation, the outer surface has been polished flat on the two small areas traversed by the beam, the residual astigmatism associated with the inner cylindrical surface being reasonably low because of the fair index matching between the glass and the mixture. Aluminum alloy was chosen for the plates, since it provides little contamination when used with aniline mixtures. A recessed hole has been drilled in each plate in order to house two quartz thermometer probes. An additional hole was also drilled in the top plate, so that a tight-fit housing was provided for a carbon resistor. The plates have circular expansions which slide into the glass window, sealing being provided by indium gaskets. The sample is a fluid slab of thickness $a = 1.02$ mm confined in the gap between the expansions. Variations in a due to plate misalignment are less than ±0.01 mm.

The mixture was prepared at the critical concentration by using aniline and cyclohexane of analytic-reagent-grade quality, and no attempt was made to purify the components. Separate tests performed on the two compounds, however, indicated that no appreciable thermodiffusion process due to the presence of impurities could be detected.

After the filling operations, the cell was placed inside a massive aluminum box, the lower plate only being in mechanical contact with the box itself. The temperature of the box was controlled to better than ±0.0002 °C over a period of a few hours by means of a two-stage temperature controller. The critical temperature T_c was determined by performing absolute measurements of the turbidity before and after the thermal-diffusion measurements. No appreciable drift was observed over a period of 15 days, and T_c was located to better than ±0.002 °C.

Thermal-diffusion measurements are performed as follows. The system is allowed to thermalize at a given temperature; then a small dc current is injected into the resistor located inside the top plate, so that, at steady state, a constant heat flow traverses the fluid slab, and consequently a stable temperature difference is maintained across it. To avoid the rather long transient associated with the warming up of the top plate, a current pulse is also applied at the beginning, so that the top-plate temperature is rapidly brought close to its steady-state value. After a few minutes, the temperature difference $T_1 - T_2$ read by the probes reaches a stable value, drifts over a few hours being comparable with the resolution of the probes (±0.0001°C). Typical temperature differences applied to the plates are $T_1 - T_2 = 28.7$ mdeg at $T - T_c = 0.524$°C and $T_1 - T_2 = 190.0$ mdeg at $T - T_c = 19.921$°C (T is the average temperature between T_1 and T_2). As a consequence of the temperature difference, a gradient in the refractive index gradually builds up in the fluid, and, consequently, the beam is deflected downward and its position on the slit plane changes as a function of time. If we assume that the positive z axis points upwards, and take into account that the beam is located in the midplane of the cell, the time evolution of the beam displacement $Z(t) - Z(0)$ is given by[8]

$$Z(t)-Z(0)=nLl\,\frac{T_1-T_2}{a}\left\{\left(\frac{dn}{dT}\right)_{p,c}-\frac{k_T}{T}\left(\frac{dn}{dc}\right)_{p,T}\left[1-\frac{4}{\pi}\exp\left(\frac{t}{\theta}\right)\right]\right\} \tag{1}$$

for $t/\theta \geqslant \frac{1}{3}$, where

$$\theta = a^2/\pi^2 D\,, \tag{2}$$

n is the index of refraction, and l is the length of the fluid sample. The first term in curly brackets in Eq. (1) accounts for the noninteresting thermal-expansion contribution which sets in almost instantaneously, and whose explicit time dependence has been omitted. Plots of $\Delta Z(t) = Z(t) - Z(\infty)$ for various temperatures are shown in Fig. 1 (the time origin is arbitrarily chosen at a time at which $T_1 - T_2$ readings have assumed a stable value). In agreement with Eq. (1) the data accurately follow a pure exponential decay, and therefore allow a precise determination of θ, and therefore of D. The values of D are reported as a function of the reduced temperature $T - T_c$ in Fig. 2, together with the best-fit line to the light-scattering data of Bergê *et al.*[9] The two sets of data are in very good numerical agreement, and this can be taken as an indication that no spurious effects, such as convective remixing, play an important role in our cell. The numerical values for k_T are derived, with use of Eq. (1), from the steady-state beam-deflection data $Z(\infty) - Z(0)$. The values for n and $(dn/dc)_{p,T}$ have been taken from the literature,[10] while $(dn/dT)_{c,p}$ has been evaluated as an average between the two pure-component data.[11] It should be pointed out that,

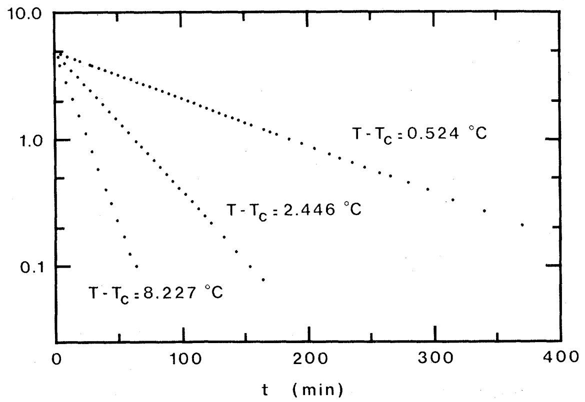

FIG. 1. Typical time evolution of the beam deflection $\Delta Z(t) = Z(t) - Z(\infty)$ for various values of $T - T_c$.

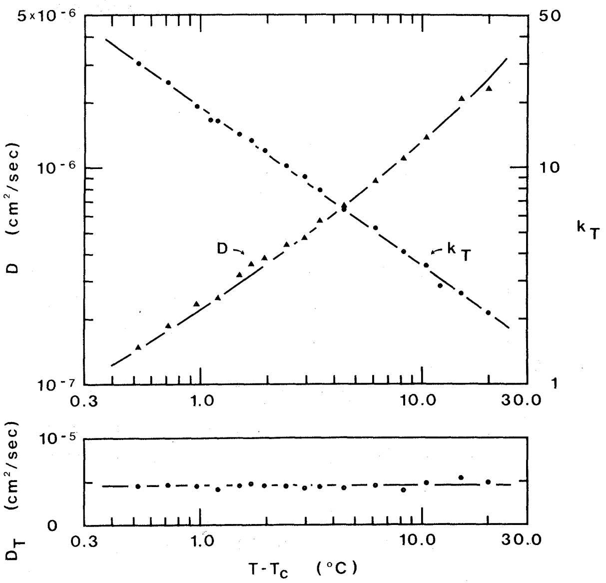

FIG. 2. Plots of the thermal-diffusion ratio k_T, of the diffusion coefficient D, and of the thermal-diffusion coefficient D_T as a function of $T - T_c$. The line through the D data is the best fit to the light-scattering data of Bergé *et al.* (see Ref. 9). The k_T data have been fitted with a simple power law $k_T \propto (T - T_c)^{-\varphi}$ with $\varphi = 0.73$.

because of the large values of k_T, most of the beam deflection is actually due to the concentration gradient, the thermal-expansion contribution becoming appreciable only far from T_c. The data are shown in Fig. 2 as a function of $T - T_c$. The best fit with a power law of the type $k_T \propto (T - T_c)^{-\varphi}$ gives $\varphi = 0.73 \pm 0.02$. Such a simple fit, however, is rather misleading. In fact, when the data for $D_T = k_T D$ are reported as a function of $T - T_c$ (see lower part of Fig. 2), one notices that D_T is practically constant at 4.5×10^{-6} cm^2/sec. Furthermore, the temperature dependence of the diffusion coefficient D is given by[4]

$$D = (\alpha/\rho)(\partial\mu/\partial c)_{p,T}, \qquad (3)$$

where $(\partial\mu/\partial c)_{p,T} \propto \xi^{-2}$ (ξ is the long-range correlation length and μ is the chemical potential) and the Onsager coefficient α is given by[4,12] $\alpha = \alpha_0 + \alpha_{\text{crit}}$ with α_0 the background contribution and α_{crit} the critical part which diverges like ξ. Consequently, since the data show that $k_T \propto D^{-1}$, we conclude that the divergence of k_T is asymptotically described by the same divergence of ξ ($\varphi \approx 0.63$). Not too close to T_c, however, a somewhat steeper temperature dependence is expected, and this explains the rather large value of φ we have found in the region we have investigated.

Our results are in contradiction with the rather qualitative data of Thomaes[6] on the system nitrobenzene-n-hexane ($\varphi \approx 1.3$), and those of Tichacek and Drickamer[7] on the system isooctane-perfluoroheptane ($\varphi < 0.4$).[13] Our results are also in disagreement with the prediction of Papoular,[5] who predicts $\varphi = 1.2$, but are in agreement with the results of Swift[3] and those of Giterman and Gorodetskii[4] who predict a ξ-type divergence for k_T. In concluding we would like to point out how this prediction is nonintuitive, the prediction $\varphi = 1.2$ seeming instead maliciously obvious. The three kinetic coefficients α, β, and γ entering the two coupled heat and diffusion flow equations can be related to experimentally determinable quantities by Eq. (3) and by the following relations[4,5]:

$$\rho(k_T/T)D = \alpha(\partial\mu/\partial T)_{c,p} + \beta, \qquad (4)$$

$$k = \gamma - (\beta^2/\alpha)T, \qquad (5)$$

where k is the steady-state thermal conductivity. Since k is known to be well behaved,[14] Eq. (5) strongly suggests that both β and γ are finite or, at most, β should diverge like $\xi^{1/2}$. Consequently, since $(\partial\mu/\partial T)_{c,p}$ is finite, the prediction that $k_T D$ should diverge like ξ (and therefore $k_T \propto \xi^2$) seems rather tempting. Giterman and Gorodetskii[4] have shown instead that all four terms appearing on the right-hand side of Eqs. (4) and (5) diverge. However, because of an unexpected cancelation of the strong divergences both in Eq. (4) and in Eq. (5), k remains finite and $k_T D$ is at most weakly divergent. According to Swift,[3] the divergence of D_T is characterized by an exponent $(\gamma + \alpha - 2\nu)/2 \approx 0.03$ (here γ, α, and ν are the critical exponents). Such a weak divergence, however, cannot be confirmed on the basis of our experimental results.

As a final comment we would like to point out that thermal-diffusion processes are commonly used for materials-separation programs. Since the exact nature of the divergence of k_T near a critical point is now established, it would be interesting to investigate whether thermal diffusion could be more advantageously exploited by operating near critical points of multicomponent systems.

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Unusual Magnetic Relaxation in Superfluid ^{3}He

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Pulsed-NMR measurements of the longitudinal spin-relaxation time T_1 in superfluid ^{3}He are reported which indicate that new and very unconventional relaxation mechanisms exist below T_c. In A-^{3}He, T_1 decreases very rapidly below T_c and the magnetization recovery from saturation is *linear* in time. In B-^{3}He, the magnetization recovery is exponential in time, but the relaxation rate $1/T_1$ is linear in applied field *gradient.* Possible explanations of these phenomena are discussed.

Several experimental results suggest that the low-temperature phases of ^{3}He are superfluids.[1-4] Calculations based on the magnetic nature of these superfluids have predicted that transport of nuclear magnetization through magnetic supercurrents might exist in these phases.[5] In this Letter, we report measurements, using pulsed-NMR techniques, of very fast[6] and unusual longitudinal spin relaxation in both A-^{3}He and B-^{3}He which appear to result either from such magnetic supercurrents or from new and unknown bulk relaxation mechanisms. We describe our apparatus, present our results, and discuss possible explanations for the behavior we observe.

Longitudinal spin relaxation was measured by applying a short burst of an ~1-Oe radio-frequency magnetic field, $\vec{H}_1$, at the Larmor resonance frequency (γH_0) normal to the static external field $\vec{H}_0$ to tip the net nuclear magnetism (M_z) away from $\vec{H}_0$ by some angle Φ. In general, the recovery of M_z is expected to be governed by the Bloch equation, $dM_z/dt = [\chi H_0 - M_z(t)]/T_1$, where $\chi H_0 = M_z(\infty)$ and T_1 is the characteristic recovery time. This has the solution $M_z(t) = \chi H_0[1 - \exp(-t/T_1)]$. In the following we will use T_1 as a general reference to the recovery time for M_z. In A-^{3}He,