# Thermal Diffusion Measurements near the Liquid-Vapor Critical Point

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The authors report measurements of the density and temperature gradients in $^3$He-$^4$He mixtures near their liquid-vapor critical point, as induced by a heat flux. From these they deduce the thermal diffusion ratio $k_T$ and the conductivity $\kappa$. They find that $k_T$ and $\kappa$ diverge with respective effective exponents $\varphi \approx 1.2$ and $\psi \approx 0.6$. Both of these results are in contradiction with the asymptotic predictions for binary mixtures and are discussed in the light of the hydrodynamic transport equations.

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The transport properties in binary liquid mixtures near their consolute critical point ($T_c$, $c_{\rm crit}$) at saturated vapor pressure have been investigated for a number of years. Here $T_c$ and $c_{\rm crit}$ are the critical temperature and mass concentration. For instance, the thermal conductivity $\kappa$ in the homogeneous phase for several systems such as nitrobenzene-hexane has been measured for various compositions, including the critical one $c_{\rm crit}$.[1] No anomalous behavior, such as divergence, was detected. The thermal diffusion ratio $k_T$ was measured for the aniline-cyclohexane system by Giglio and Vendramini,[2] and a divergence of the form $k_T \propto t^{-\varphi}$ was obtained, where $t=(T-T_c)/T_c$ is the reduced temperature and $\varphi = 0.73$. This exponent is close to that for the correlation length divergence, $\nu \simeq 0.63$.

The analogy between a liquid binary mixture near the *consolute point* and a pure fluid near the liquid-vapor critical point for both the static and the dynamic critical behavior has been brought out on a number of occasions.[3] In the first case, the order parameter is the deviation from the critical composition, $c - c_{\rm crit}$, while in the second it is the deviation from the critical number density, $\rho - \rho_c$. However, for the important category of binary mixtures near the *liquid-vapor critical point,* or plait point, the situation is more complicated because it is not clear what the correct order parameter is, except of course as the concentration of one component vanishes. The static critical properties of such mixtures have been investigated both experimentally[4-6] and theoretically.[7,8] However, in spite of the obvious relevance in technological separation processes, little research has been done on the critical dynamics of such mixtures.[9] Only in the last few years did systematic investigations on critical transport properties start, where optical,[10,11] acoustic,[12] and thermodynamic methods[13] were used. From the critical dynamics theories,[2,14] it has been inferred that the singularities in $\kappa$ and $k_T$ should be the same for binary liquids near their consolute point and for binary mixtures near their plait point, but as we shall see, this is in strong disagreement with experiment over the accessible temperature range.

In this paper, we report measurements on the critical behavior of both $\kappa$ and $k_T$ for two representative mixtures, $^3\text{He}_{0.80}$-$^4\text{He}_{0.20}$ and $^3\text{He}_{0.66}$-$^4\text{He}_{0.34}$, near their plait point, where the subscripts represent the respective mole fractions, $X_i$. The method involved creating a vertical temperature and density gradient in a flat horizontal cell by means of a heat flux $q$. These gradients were measured by means of matched germanium thermometers and perforated capacitors. The latter registered the dielectric-constant gradients which were then converted into density gradients by means of the Clausius-Mossotti relation. In Fig. 1, we schematically show the arrangement. The diameter of the cell was 1.9 cm, its height was 0.17 cm, and the distance between the capacitor centers was 0.11 cm. Because the thermal expansion coefficient at constant pressure and composition, $-\rho^{-1}(\partial\rho/\partial T)_{c,P}$, is positive, the heat flux was directed downward to reduce the possibility of convection. The temperature of the cell bottom, $T$(bot), was kept constant within about 0.5 $\mu$K and $T$(top) − $T$(bot) was taken between 1 mK far above $T_c$ and about 50 $\mu$K at $t = 8\times10^{-4}$. It was difficult to approach $T_c$ closer than this temperature because of the very long relaxation times (> 5 h) needed to reach steady state. However, with a cell of 0.03-cm height, where only conductivity measurements could be performed,[13] the relaxation times were much shorter and $T_c$ could be located more accurately.

From measured static properties for these

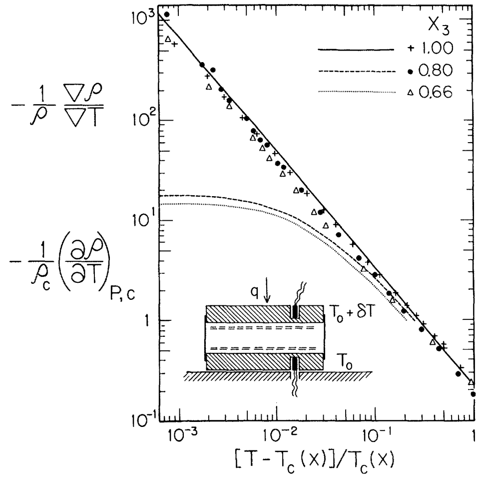

FIG. 1. The measured $-\rho_c{}^{-1}\nabla\rho/\nabla T$ (symbols) vs the reduced temperature for $^3$He and two mixtures. The lines (solid, dashed, and dotted) are the calculated thermal expansion coefficients $-\rho_c{}^{-1}(\partial\rho/\partial T)_{P,c}$ for these same fluids. Inset: Schematic presentation of the experimental cell. The dashed horizontal lines represent the perforated capacitor plates, and the rectangles with leads the thermometers.

mixtures, we have deduced $k_T$ in the steady state with zero mass current, where[15]

$$k_T = -T\nabla c/\nabla T, \tag{1a}$$

where $c$ is the mass concentration of $^3$He.

The concentration change throughout the cell, $\delta c$, is expressed as a function of the changes in temperature, density, and pressure. But the only stable pressure gradient results from gravity and it can be subtracted out by measuring $\delta c$ and $\delta\rho$ in the absence of a heat flow. We then obtain

$$\frac{\nabla c}{\nabla T} = \left[\frac{\nabla\rho}{\nabla T} - \left(\frac{\partial\rho}{\partial T}\right)_{c,P}\right]\left(\frac{\partial c}{\partial\rho}\right)_{T,P}. \tag{1b}$$

For $^3$He-$^4$He mixtures well above the plait point, $k_T$ is always negative,[16] which means that the lighter isotope $^3$He becomes enriched at the warmer end of the cell. For the gaseous mixtures, this background value $k_{T,\,\mathrm{reg}}$ is found to be[16]

$$k_{T,\,\mathrm{reg}} \approx -0.08X_3(1-X_3). \tag{2}$$

As we shall see below, the $k_T$ deduced from our measurements near the plait point is always much larger than $k_{T,\,\mathrm{reg}}$ and has the same sign.

Before presenting the mixture results, we will briefly discuss the "control" experiment for pure $^3$He near $T_c$. Here $q$ produces density and temperature gradients at constant average density and constant pressure through the cell. (We neglect the small pressure gradient produced by gravity, which can be subtracted in our experiment.) Then we expect $\mathrm{grad}\rho/\mathrm{grad}T = (\partial\rho/\partial T)_P$ since there is no concentration gradient. From published data[17,18] and the relation $(\partial\rho/\partial T)_P = -(\partial\rho/\partial P)_T(\partial P/\partial T)_\rho$ we obtain the expansion coefficient, a quantity that has the same strong divergence as the isothermal compressibility (critical exponent $\simeq 1.2$), since $(\partial P/\partial T)_\rho$ remains nearly constant. As shown in Fig. 1, our expectations are verified and we obtain agreement within ~5% of previous data.

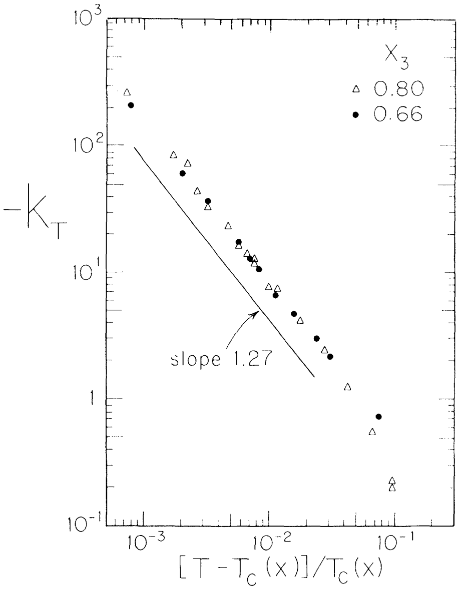

FIG. 2. The thermal diffusion ratio $k_T$ for two mixtures along the critical isochore.

Similar results are obtained in the two mixtures for $\mathrm{grad}\rho/\mathrm{grad}T$ versus $t$ along near-critical isochores, as shown in Fig. 1. Here, however, the limiting behavior of $(\partial\rho/\partial T)_{P,c}$ near $T_c$ indicates a weak divergence as expected from theory.[7] Calculations using published data[4,5] show that as a result $\mathrm{grad}\rho/\mathrm{grad}T \gg (\partial\rho/\partial T)_{c,P}$ for $t \lesssim 10^{-1}$. Using the relation

$$\left(\frac{\partial\rho}{\partial c}\right)_{T,P} \approx \frac{d\rho_c}{dc} - \left(\frac{\partial\rho}{\partial T}\right)_{c,P}\frac{dT_c}{dc} - \left(\frac{\partial\rho}{\partial P}\right)_{T,c}\frac{dP_c}{dc} \tag{3}$$

with data from Ref. 4 along the critical line, we determine $k_T$ via Eq. (1). Here the total derivatives refer to differentiation along the critical line. The results are shown in Fig. 2 indicating a strong divergence of $k_T$ with an exponent of approximately 1.2 and with a very large amplitude.

In Fig. 3, we show the singular part of $\kappa$ for the two mixtures, $\kappa_{\text{sing}} = \kappa - \kappa_{\text{reg}}$, as compared with that for pure $^3$He. The divergence in the three situations is very nearly the same.

The mode-coupling theory[14] has provided predictions on the behavior of binary mixtures, namely $k_{T,\text{sing}} = 0$, $k_T = k_{T,\text{reg}} \propto \xi \propto t^{-\nu}$ and $\kappa_{\text{sing}} = 0$, $\kappa = \kappa_{\text{reg}}$. These appear to be consistent with observations on binary liquids near the consolute point.[1,2] More recent renormalization-group calculations[19] predict a small cusp for $\kappa$. However, these predictions are in strong disagreement with the data on mixtures near the plait point, where we find $k_T \propto t^{-\varphi}$ with $\varphi \simeq 1.2$ and $\kappa_{\text{sing}} \propto t^{-\psi}$ with $\psi \sim 0.58$.

It is conceivable that the predictions are valid for a temperature range so close to $T_c$ that it is inaccessible to the present experiments. It is well known that for static properties of the binary mixtures near the plait point, the asymptotic predicted behavior cannot be observed.[7] Far above $T_c$, the properties are similar to those for a pure fluid. There is a crossover region in the vicinity of $t = t_{\text{cross}}$, where departures from such a behavior take place, with a tendency towards a mixturelike behavior as $T_c$ is approached. For the compressibility in $^3$He-$^4$He mixtures, $t_{\text{cross}}$ is clearly observable,[4,5] being of the order of $10^{-2}$, $0.1 \lesssim c \lesssim 0.9$. Hence we expected this crossover region to be equally observable in transport properties, in disagreement with our experiment. It is striking that there is no difference between the divergences in $\kappa$ and in $\text{grad}p/\text{grad}T$ for the pure fluid and the binary mixture. Except for the critical parameters such as $T_c$, $\rho_c$, and critical amplitudes that vary smoothly with composition, the critical divergences apparently do not depend on concentration fluctuations, but only on number-density fluctuations.

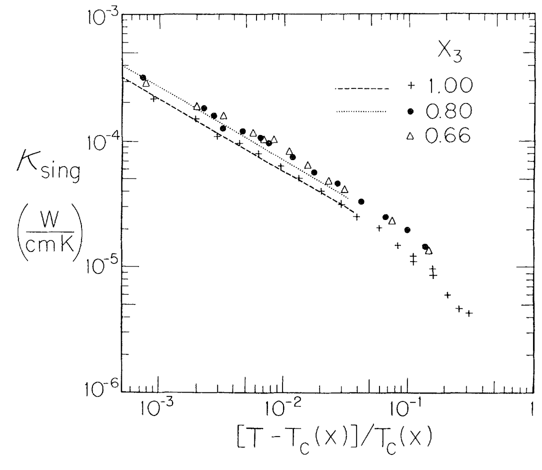

FIG. 3. The singular part of the thermal conductivity, $\kappa_{\text{sing}}$, for pure $^3$He and two mixtures, as measured in the experimental cell shown in Fig. 1. The dashed and dotted lines show the results for $X = 1.00$ and 0.80 obtained in this laboratory with use of a cell with a height of 0.3 mm (Ref. 13), permitting closer approach to the critical point because of smaller relaxation times.

In order to discuss the consequences of our observations, we now write down the hydrodynamic transport equations[15]:

$$\vec{\mathrm{i}} = -\alpha\,\text{grad}\,\mu - \beta\,\text{grad}\,T, \tag{4a}$$

$$\vec{\mathrm{q}} = -\beta T\,\text{grad}\,\mu - \gamma\,\text{grad}\,T + \mu\vec{\mathrm{i}}, \tag{4b}$$

where $\mu$ is the chemical potential difference and $\alpha$, $\beta$, and $\gamma$ are transport coefficients. One obtains

$$\vec{\mathrm{q}} = (\mu + \beta T/\alpha)\vec{\mathrm{i}} - \kappa\,\text{grad}\,T, \tag{5a}$$

where

$$\kappa = \gamma - \beta^2 T/\alpha. \tag{5b}$$

The thermal conductivity $\kappa$ is measured in the steady state where $\vec{\mathrm{i}} = 0$. The definitions for the mass diffusion $D$ and for the thermal diffusion coefficient $k_T D$ are[15]

$$D = \frac{\alpha}{\rho}\left(\frac{\partial\mu}{\partial c}\right)_{T,P}, \quad \rho k_T D/T = \alpha\left(\frac{\partial\mu}{\partial T}\right)_{c,P} + \beta \tag{6}$$

which lead[15] to our Eq. (1a) for $\vec{\mathrm{i}} = 0$ [c.f. Eq. (58.11) of Ref. 15]. If we make the *ad hoc* assumption of $\beta \approx 0$, it follows that for $\vec{\mathrm{i}} = 0$

$$\alpha\,\text{grad}\,\mu \cong 0, \quad \kappa = \gamma, \tag{7a}$$

and

$$k_T \simeq T\left(\frac{\partial\mu}{\partial T}\right)_{c,P}\left(\frac{\partial c}{\partial\mu}\right)_{T,P}. \tag{7b}$$

Since $(\partial\mu/\partial T)_{c,P}$ does not diverge, while $(\partial c/\partial\mu)_{T,P}$ diverges like $\xi^2$, it follows that $k_T \propto \xi^2$, in agreement with our experiment. It is interesting that under these conditions $k_T$ can be calculated from static properties alone. For $^3$He-$^4$He mixtures these can be obtained from the theory of Ref. 7. Furthermore, according to the mode-coupling prediction,[14] $\gamma_{\text{sing}} \propto (\eta\xi)^{-1} C_{p,\mu}$, where $C_{p,\mu}$ diverges like $\xi^2$. (The divergence of the shear viscosity $\eta$ is weak and can be neglected here.) As a result, one finds $\kappa_{\text{sing}} \propto \xi$, again in agreement with experiment. In the mode-coupling predictions,[14] however, $\beta$ is not negligible. The strong divergence of $\gamma$ in Eq. (5b) is then cancelled out by the second term, leading to a vanishing of $\kappa_{\text{sing}}$ as $T_c$ is approached, in contradiction with the experiment.

It remains to be understood why $\beta$ might be so small in the binary mixtures near the plait point, while this is obviously not so for binary liquids near the consolute point. It is important therefore to find the correct order parameter that determines transport properties in these systems of which $^3$He-$^4$He mixtures are representative examples. Calculations of the crossover functions between scaling and noncritical behavior in these mixtures, as they have been carried out for $^3$He-$^4$He mixtures near the superfluid transitions,[20] might well provide the correct picture to this interesting problem.

A more complete paper on these measurements, which includes also the relaxation times required to reach steady state, will be published in the near future.

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[1] L. P. Filippov, Int. J. Heat Mass Transfer 11, 331 (1968), and references therein.

[2] M. Giglio and A. Vendramini, Phys. Rev. Lett. 34, 561 (1975).

[3] See, for instance, P. C. Hohenberg and B. Halperin, Rev. Mod. Phys. 49, 435 (1977).

[4] B. A. Wallace and H. Meyer, Phys. Rev. A 5, 953 (1972).

[5] T. Doiron, R. P. Behringer, and H. Meyer, J. Low Temp. Phys. 24, 345 (1976).

[6] J. V. Sengers and J. M. H. Sengers, in *Progress in Liquid Physics*, edited by C. A. Croxton (Wiley, New York, 1978), p. 103.

[7] S. S. Leung and R. B. Griffiths, Phys. Rev. A 8, 2670 (1973).

[8] G. R. Anderson and J. C. Wheeler, J. Chem. Phys. 70, 1326 (1979).

[9] An early experiment was performed by M. Giglio and A. Vendramini, Opt. Commun. 9, 80 (1973).

[10] R. F. Chang and T. Doiron, in *Proceedings of the Eighth Symposium on Thermophysical Properties*, edited by J. V. Sengers (American Society of Mechanical Engineers, New York, 1982), Vol. 1, p. 458.

[11] Y. Miura, H. Meyer, and A. Ikushima, Phys. Lett. A 91, 309 (1982).

[12] T. Doiron, D. Gestrich, and H. Meyer, Phys. Rev. B 22, 3202 (1980).

[13] L. H. Cohen, M. L. Dingus, and H. Meyer, J. Low Temp. Phys. 49, 545 (1982).

[14] L. Mistura, Nuovo Cimento B 12, 35 (1972), and J. Chem. Phys. 62, 4572 (1975).

[15] L. D. Landau and I. M. Lifshitz, *Fluid Mechanics* (Pergamon, New York, 1959), Chap. 6.

[16] W. L. Taylor, in *Low Temperature Physics, LT-13*, edited by K. D. Timmerhaus, W. J. O'Sullivan, and E. F. Hammel (Plenum, New York, 1974), Vol. 1, p. 631, and references therein.

[17] R. P. Behringer, T. Doiron, and H. Meyer, J. Low Temp. Phys. 24, 315 (1976).

[18] C. E. Pittman, T. Doiron, and H. Meyer, Phys. Rev. B 20, 3678 (1979).

[19] E. D. Siggia, B. I. Halperin, and P. C. Hohenberg, Phys. Rev. B 13, 2110 (1976).

[20] V. Dohm, R. Folk, and J. Bhattacharjee, to be published; J. Bhattacharjee, to be published.