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Thermal-conductivity enhancement near the liquid-vapor critical line of binary methane-ethane mixtures

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Measurements of the thermal conductivity of mixtures of methane and ethane reveal an enhancement in the mixture critical region apparently contradicting theoretical predictions. The anomaly is similar in size and temperature dependence to that found for pure fluids.

Recent extensive measurements of the thermal conductivity of the methane-ethane system indicate an enhancement in the extended critical region for both the pure fluids and their binary mixtures. The measurements were made with a transient hot-wire device, and they show an enhancement of up to 37% above background at $\Delta T^* = (T-T_c)/T_c = 0.02$ near the critical density. According to standard theoretical models, a divergence should be present at the pure fluid critical point,[1] but not at a mixture critical point.[2] The divergence of thermal conductivity near the pure fluid critical point is well established experimentally.[1] The present results establish an anomalous increase for an ordinary binary mixture. They reinforce the recent conclusion of Cohen, Dingus, and Meyer,[3] who observed a similar increase for the ^{3}He-^{4}He system.

The measurements were made on three gravimetrically prepared mixtures,[4] nominally denoted 70/30, 50/50, and 35/65, where the actual methane mole fractions are 0.685, 0.502, and 0.345. If the pure components methane[5] and ethane[6] are included, there are some 4200 thermal-conductivity points for temperatures between 110 and 330 K with pressures up to 70 MPa. Thus, the background conductivity was accurately determined and the enhancement, with critical temperatures ranging from 190 to 305 K and critical pressures from 4.6 to 6.8 MPa for the five fluids, was easily discernable. Accurate pressure, volume, and temperature (PVT) measurements have been made in this laboratory, and an equation of state is available for each of the fluids,[4] allowing us to eliminate pressure in favor of density.

The thermal conductivity of a fluid is normally measured only in the single phase. For mixtures the experiment is limited by the dew point and bubble point curves as shown in the P-T phase diagram, Fig. 1. For mixtures, complete isotherms of thermal conductivity can be obtained only at temperatures above the maximum condensation temperature $T_{\rm mc}$, which often lies considerably above the mixture critical temperature. An example of such a complete isotherm is shown in Fig. 2. At the mixture critical temperature, measurements are possible above the bubble line and below the dew line. However, it should be clear that a large range of densities is not available to the experiment. An example of measurements near the critical temperature is given in Fig. 3.

Plots similar to Fig. 2 were obtained for 11 single-phase-mixture isotherms and for nine pure isotherms. The critical enhancement $\Delta\lambda_c(\rho,T)$ is defined as the difference between the total conductivity and the background. Accurate estimates of the background for mixtures are available only in the single-phase regions, i.e., at temperatures above the $T_{\rm mc}$ as shown in Figs. 1 and 2. The smallest reduced temperatures ΔT^* achievable are on the order of 10^{-2} and thus include the critical region proper. In Fig. 2 the enhancement curve is slightly asymmetrical about a density, $\rho_{\rm cen}$, at which the enhancement reaches a maximum. The densities $\rho_{\rm cen}$ are nearly independent of temperature but may not quite coincide with the mixture critical density. This last point remains unresolved because the critical densities are uncertain by up to 1 mol/l, as the methane mole fraction increases, when interpolated from the data of Bloomer, Gami, and Parent.[7] The lack of coincidence between critical density and density of maximum enhancement was also seen in the ^{3}He-^{4}He system.[3]

For mixtures at temperatures below $T_{\rm mc}$ and even below the mixture critical temperature, evidence for an enhancement can be seen in both the liquid and the vapor phases; see, for example, Fig. 3. However, it is not possible to define the background accurately.

For measurements which include a critical enhancement, it is very important to verify that convection is indeed absent in the experiment. The apparatus used has been discussed elsewhere.[8] It is not specifically designed for critical region measurements. However, the transient hot-wire system is unique in that convection can be observed experi-

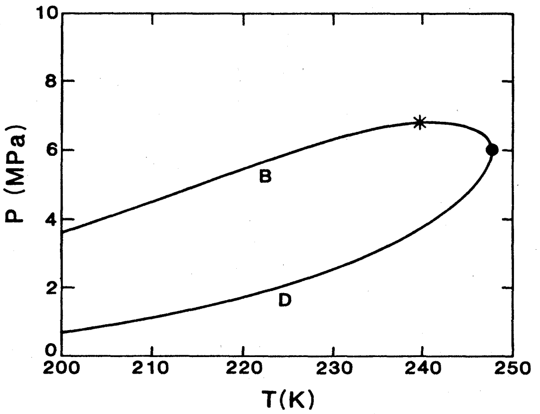

FIG. 1. The P-T phase diagram for the 70/30 methane-ethane mixture. $*$, the mixture critical point; B, bubble point line; D, dew point line; ●, the maximum condensation temperature along the two-phase liquid-vapor boundary, i.e., $T_{\rm mc}$ (Ref. 7).

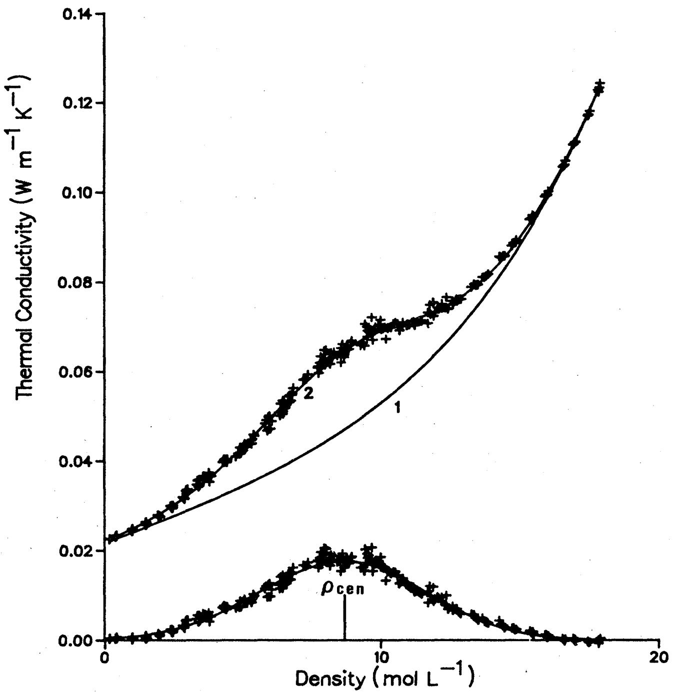

FIG. 2. A 50/50 isotherm for $T = 269.3$ K near T_{mc}; $\Delta T^* = 0.023$. Lower part: the critical enhancement. Upper part: the full isotherm. +, experimental points; 1, the background conductivity; 2, the calculated conductivity.

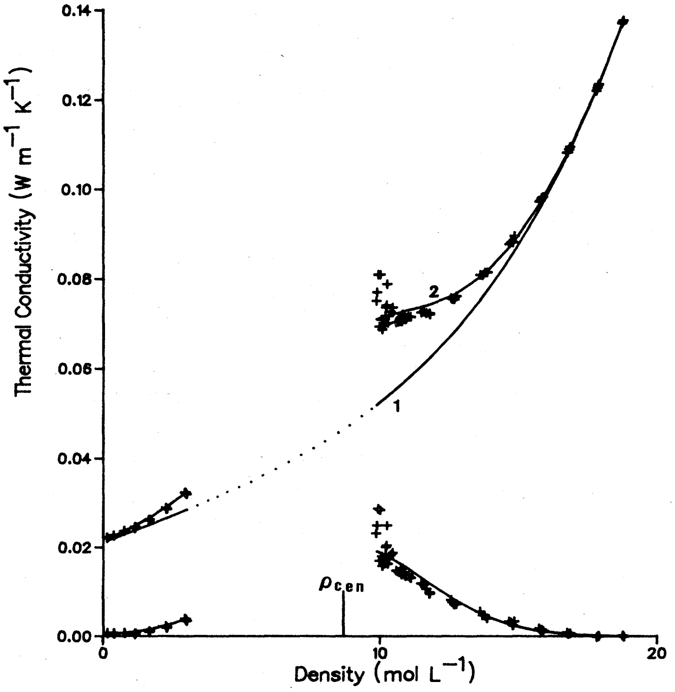

FIG. 3. A 50/50 isotherm for $T = 265.1$ K, a temperature close to the mixture T_c. Lower part: the critical enhancement for the liquid and vapor side. Upper part: the isotherm for the liquid and vapor side. +, experimental points; 1, the background conductivity; 2, the calculated conductivity.

mentally as a marked deviation from linearity of the curve showing the temperature rise of the wire versus the log of the time of heating. Such a curve is shown in Fig. 4, where it can be seen that convection, i.e., a mass movement in the cell, causes rapid cooling of the wire. Convective effects are eliminated by restricting the data analysis to sufficiently short time intervals between t_1 and t_2 (see Fig. 4). In this way, the linearity required for proper operation[9] is restored, and the absence of convection in that time interval is confirmed. The second test that is applied is the use of four different power levels at each pressure-temperature point. Each power level corresponds to a different temperature gradient and therefore to a slightly different experimental temperature and density. Independence of the measured thermal conductivity on the power implies the absence of convection. As convection is encountered in the measurements, the applied power is gradually reduced yielding smaller and smaller temperature rises. Of course, the regression error of the desired straight line increases very rapidly. In practice, the closest approach to critical conditions with this apparatus is limited to conditions where the anomalous part of the measured conductivity is no more than 50% of the background.

The values of the maximum of $\Delta\lambda_c(\rho,T)$ along isotherms are plotted against the reduced temperature ΔT^* for the three mixtures, for the pure components methane and ethane and for other fluids measured at this laboratory in Fig. 5. The behavior of pures and mixtures is seen to be quantitatively similar, but the asymptotic values of the slopes may differ. For the pures the value is -0.56, and for the mixtures the values vary between -0.82 for 70/30 and -0.32 for 35/65, considering only the temperatures closest to critical. Cohen and co-workers[3] find a slope ψ of -0.58 for the ^{3}He-^{4}He systems, which implies that $\Delta\lambda_c \sim \Delta T^{*-0.58}$.

In a mixture, both temperature gradients and their associated concentration gradients contribute to the steady-state heat flux. The relevant hydrodynamic equations, using the

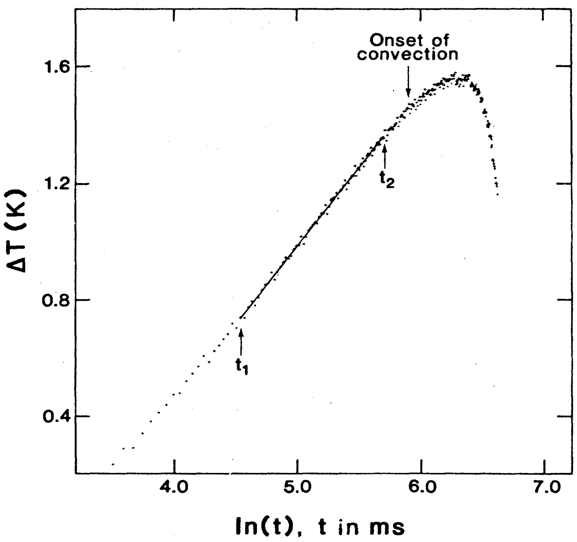

FIG. 4. Temperature rise of the hot wire vs the logarithm of time with convection present in the experiment. t_1 and t_2: initial and final times of the regression analysis.

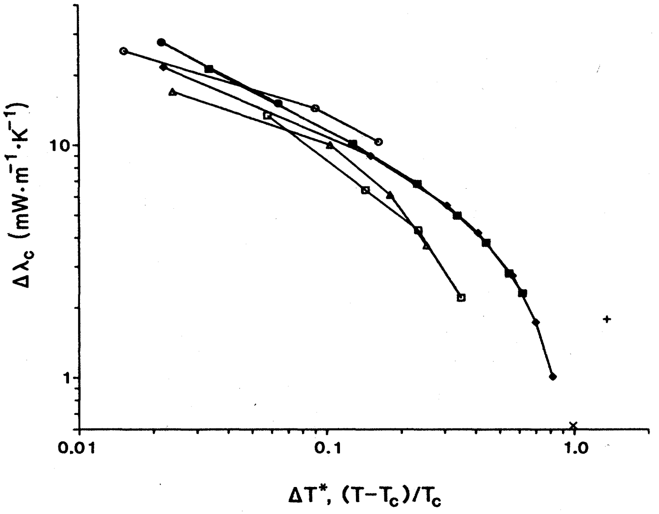

FIG. 5. The maximum enhancement $\Delta\lambda_c$ at ρ_c for the pure components, and at ρ_{cen} for the mixtures vs the reduced temperature ΔT^*. Pure components: ■, methane (Ref. 5); ●, ethane (Ref. 6). Mixtures: □, 70/30; Δ, 50/50; ○, 35/65. Other fluids: ◆, oxygen (Ref. 15); ×, argon (Ref. 18); +, *n* hydrogen (Ref. 19).

notation of Mistura,[2] are

$$\mathbf{J}_d = -\alpha\nabla\mu - \beta\nabla T \ , \tag{1}$$

$$\mathbf{J}_q = -\delta\nabla\mu - \gamma\nabla T + \mu\mathbf{J}_d \ , \tag{2}$$

where $\mathbf{J}_d$ and $\mathbf{J}_q$ are the diffusional and heat fluxes, respectively; $\mu = \mu_1/m_1 - \mu_2/m_2$ is the chemical potential, T is the temperature, and α, β, γ, and δ are the Onsager transport relations, with $\delta = \beta T$ by reciprocity. Khalifa, Kestin, and Wakeham[10] have shown that for the transient hot-wire system the appropriate boundary conditions require that the diffusional flux J_d vanishes at the wire. They indicate that for temperature gradients less than 5 K for both low densities and liquid densities, the diffusional flux produces no more than a 0.1% error to the measured thermal conductivity. Under these conditions, then, the measured quantity λ is defined by

$$\mathbf{J}_q = -\lambda\nabla T \ , \tag{3}$$

and is related to the basic coefficients by

$$\lambda = (\gamma - \beta^2 T/\alpha) \ . \tag{4}$$

Thus, in both the steady-state methods[3] and in the transient hot-wire device used for the present experiments, the measured thermal conductivity has the same relation to the basic coefficients. Kravchun and Pyasta[11] use an ac method to measure γ directly. For several liquid mixtures they have shown experimentally that the contribution of mass diffusion is less than one percent for their particular experimental conditions.

Mistura's[2] theoretical work is based on a mode-coupling model and uses the universality arguments of Griffiths and Wheeler[12] to conclude that $\Delta\lambda_c(\rho,T) = 0$ as a binary mixture critical point is approached. Specifically, Eq. (20) of Ref. 2 reads

$$\Delta\lambda_c(\rho,T) = \frac{\kappa_B T\langle\rho\rangle}{6\pi\eta\xi} C_{p,x} \ , \tag{5}$$

where η is the shear viscosity, ξ is the correlation length, and $C_{p,x}$ is the isobaric heat capacity at fixed composition. The last, according to Griffiths and Wheeler,[12] is, at most, weakly divergent except near an azeotrope. Mistura implies that $\psi > 0$, so that the term $\Delta\lambda_c$ is predicted to vanish as the critical temperature is approached. The only exception mentioned is for an azeotrope. The measurements of Gerts and Filippov[13] near liquid-liquid critical points are interpreted by Mistura to confirm the prediction of $\Delta\lambda_c \rightarrow 0$ as $T \rightarrow T_c$. Clearly, the present results differ from those of Gerts and Filippov. This suggests a difference in derivation or interpretation of Eq. (5) for liquid-vapor critical points on the one hand and liquid-liquid critical points on the other. Cohen and co-workers[3] suggest that β in Eq. (1) is nearly zero, resulting in a divergence of $\Delta\lambda_c$. This possibility can be achieved if the four distinct correlation lengths introduced by Mistura are assumed to have different critical properties, rather than being identical as assumed by Mistura. The difference in order parameters for the two types of criticality could then relate to different relative sizes of the correlation lengths and the different behavior of $\Delta\lambda_c$. Alternatively, the asymptotic approach to the critical region may be different for the two types of critical behavior, which could lead to differences in the observed, or perhaps observable, critical behavior. Cross terms in the bare kinetic coefficients arising in the mode-coupling theory may explain the enhancement. This question has been explored for a nearly azeotropic mixture in a recent study by Onuki.[14]

The measurements on binary methane-ethane mixtures present strong experimental evidence that an enhancement of thermal conductivity is present near the liquid-vapor critical point of binary mixtures. In addition, the enhancement is seen to extend quite far into the single-phase region, similar to the pure fluids methane[5] and oxygen.[15] The agreement with the work of Cohen and co-workers[3] would seem to exclude purely quantum or isotopic effects as a cause for the contradiction between experiment and theoretical predictions. Additional details concerning the measurements of the methane-ethane thermal-conductivity surface will be published in the near future.[6,16,17]

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