

Finite thermal conductivity at the vapor-liquid critical line of a binary fluid mixture

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Experimental thermal-conductivity measurements, obtained for an equimolar mixture of methane and ethane very close to the critical point, confirm that the thermal conductivity of a mixture does not diverge at the vapor-liquid critical point but crosses over to a finite limiting behavior at the critical point. A recently developed extension of the mode-coupling theory for dynamic critical phenomena in mixtures gives a good quantitative description of the experimental thermal-conductivity data. [S1063-651X(97)51611-4]

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It has been well established that the thermal conductivity of one-component fluids exhibits a strong enhancement near the critical point and ultimately becomes infinite at the critical point [1,2]. This phenomenon has been confirmed by many experiments [3] and is in agreement with the theory for the effects of critical fluctuations on the transport properties [4].

The first theoretical predictions for the asymptotic critical behavior of the transport properties of fluid mixtures near vapor-liquid critical points were already made in the early 1970's [5,6]. It was concluded that the thermal conductivity of a fluid mixture should remain finite at the critical point, in contrast to the divergent critical behavior of the thermal conductivity of one-component fluids. More recently, this prediction has been confirmed by the dynamic renormalization-group theory [7]. Measurements of the thermal conductivity of mixtures in the critical region have been reported for mixtures of ³He and ⁴He [8,9], for mixtures of methane and ethane [10,11] and more recently, for mixtures of carbon dioxide and ethane [12,13]. All these measurements showed the presence of a pronounced thermal-conductivity enhancement in the critical region comparable to that observed for one-component fluids and the expected finite asymptotic critical enhancement of the thermal conductivity was not observed experimentally.

To interpret the experimental data it is necessary to consider nonasymptotic contributions to the critical behavior of the thermal conductivity [14–16]. A theory of the critical behavior of the thermal conductivity of fluid mixtures, that includes the crossover to the regular behavior of the thermal conductivity far away from the critical point, has been developed recently [16–18]. When the nonasymptotic critical contributions to the thermal conductivity are incorporated, the theory predicts that for mixtures of carbon dioxide and ethane a crossover to a finite limiting thermal-conductivity value does not occur unless the critical temperature is approached to well within 10^{-5} , a range not readily accessible experimentally for measuring the thermal conductivity [17].

In an attempt to further investigate the critical behavior of the thermal conductivity of fluid mixtures we have measured the thermal conductivity of an equimolar mixture of methane and ethane in the vicinity of the critical point. Unlike carbon dioxide and ethane, methane and ethane have appreciably

different critical temperatures, namely, 190.56 and 305.32 K, so that differences between one-component-like behavior and mixture-like behavior are expected to be more pronounced. Moreover, an accurate equation of state for calculating the thermodynamic properties of mixtures of methane and ethane has recently become available [19].

We have measured the thermal conductivity with a guarded parallel-plate apparatus especially designed for measurements in the critical region of fluids and fluid mixtures. We have further improved the experimental apparatus previously employed for measuring the thermal conductivity of mixtures of carbon dioxide and ethane in the critical region [20] and have recently used it to determine the thermal conductivity of methane in the close vicinity of the critical point [21]. The thermal conductivity of mixtures of methane and ethane in the critical region has been investigated previously by Roder and Friend [10,11], but they were unable to approach the critical temperature closer than 2 K, due to the limitations of their transient hot-wire method. With our improved guarded parallel-plate apparatus we have been able to approach the critical temperature to within 20 mK and our measurements do reveal a crossover of the apparent divergent behavior of the thermal conductivity to a finite limiting value at the critical point. Moreover, the observed crossover behavior of the thermal conductivity is well represented by the theoretical equation recently developed by Luettmmer-Strathmann and Sengers [17].

The methane-ethane mixture used for the thermal-conductivity measurements was supplied by Praxair; the mole fraction of either component was 50% with a stated accuracy of $\pm 0.02\%$. The thermal conductivity was measured as a function of temperature along five isochores covering a density range from $\rho = 6.2$ to $\rho = 10.5$ mol L⁻¹ and a temperature range from $T = 310.9$ K down to $T = 257.4$ K, which is below the critical temperature. The density corresponding to each isochore was determined by measuring the filling pressure at the initial temperature of 310.9 K, which is far above the critical temperature and then calculating the density from the equation of state of Povodyrev *et al.* [19]. The critical temperature $T_c = 263.62$ K, as determined *in situ*, is 0.07 K higher than the value implied by the equation of state mentioned above but well within the accuracy the critical temperature of methane-ethane mixtures is known

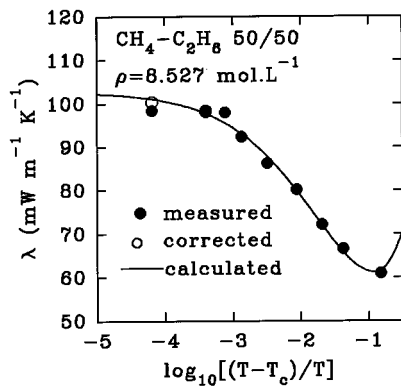


FIG. 1. Thermal conductivity of an equimolar mixture of methane and ethane at the critical density $\rho_c = 8.527 \text{ mol L}^{-1}$ as a function of temperature.

[19]. For the critical density we continued to adopt the value $\rho_c = 8.527 \text{ mol L}^{-1}$ implied by the equation of Povodyrev *et al.* [19]. The measurements at each isochore were carried out in descending order of temperature, while after completion of the isochoric measurements the thermal conductivity was remeasured at the reference temperature as a check of the reproducibility of the measurements.

In Fig. 1 we show the thermal conductivity λ of the methane-ethane mixture at $\rho = \rho_c = 8.527 \text{ mol L}^{-1}$ as a function of the reduced temperature difference $(T - T_c)/T$. The solid circles indicate the experimental data and the curve represents values calculated from the theoretical equation of Luetzmer-Strathmann and Sengers, as further discussed below. In our parallel-plate method the thermal conductivity is determined by measuring the heat flow needed to maintain a temperature difference ΔT across a horizontal fluid layer with a height of about $140 \mu\text{m}$ and a cross-sectional area of 11.5 cm^2 [20]. The temperature difference ΔT in the experiments varied from $\Delta T = 6 \text{ mK}$ at $T = 310.9 \text{ K}$ down to about 1 mK at temperatures within 1 K from the critical temperature. This temperature difference could be determined with an accuracy of about $4 \mu\text{K}$. Further details will be published elsewhere. While the thermal conductivity of the methane-ethane mixture initially increases upon approaching the critical temperature, from Fig. 1 we note that at $(T - T_c)/T \approx 10^{-3}$ a crossover to a finite limiting critical behavior is observed. Near the critical point experimental measurements are in principle affected by gravitationally induced density and concentration gradients which can be estimated from the known equation of state [22]. The resulting corrections on our measurements of the thermal conductivity are very small leading to a maximum possible correction of 2% at the datum point closest to T_c (indicated by the open circle in Fig. 1). Hence, our experiments reveal for the first time that the thermal conductivity indeed crosses over to a finite asymptotic limit. We have found a similar crossover phenomenon at two off-critical densities very close to the transition temperature.

In order to analyze the critical behavior of the transport properties it is advantageous to consider three “diffusion” coefficients D_{cc} , D_{cs} , and D_{ss} associated with the fluctuations in the concentration c and the specific entropy s [17]. The coefficient D_{cc} is to be identified with the mass diffusion coefficient D , while D_{ss} reduces in the one-component limit

to the thermal diffusivity. The coefficient D_{cs} is not a diffusion coefficient itself but is related to the thermal diffusion coefficient $k_T D$ by $k_T D = \rho c_{p,c} D_{cs}$, where ρ is the density and $c_{p,c}$ the isobaric specific heat capacity. These diffusion coefficients are decomposed as $D_{ij} = \bar{D}_{ij} + \Delta D_{ij}$ where \bar{D}_{ij} is a regular background contribution, while ΔD_{ij} represents the contribution from critical fluctuations. Asymptotically close to critical point ΔD_{cc} and ΔD_{ss} satisfy a Stokes-Einstein diffusion law of the form $k_B T / 6\pi\eta\xi$ where k_B is Boltzmann’s constant, η the shear viscosity, and ξ the correlation length, while any contribution from ΔD_{cs} can be neglected in first approximation [17]. If one includes nonasymptotic critical contributions, one obtains more general expressions for ΔD_{ij} in terms of so-called crossover functions $\Omega_{cc}(\xi, q_{DA}, q_{DB})$, $\Omega_{cs}(\xi, q_{DA}, q_{DB})$, and $\Omega_{ss}(\xi, q_{DA}, q_{DB})$. These crossover functions depend on various thermodynamic properties, on background contributions to the transport coefficients, on the correlation length ξ , and on two cutoff wave numbers q_{DA} and q_{DB} . Detailed expressions for the diffusion coefficients ΔD_{ij} and the corresponding crossover function Ω_{ij} have been presented elsewhere [17].

The thermal conductivity λ can be represented as a sum of three terms [17]

$$\lambda = \bar{\lambda} + \Delta\lambda_c^{(1)} + \Delta\lambda_c^{(2)}, \quad (1)$$

where $\bar{\lambda}$ is the background contribution to the thermal conductivity, while $\Delta\lambda_c^{(1)}$ and $\Delta\lambda_c^{(2)}$ are given by

$$\Delta\lambda_c^{(1)} = \rho c_{p,c} \Delta D_{ss}, \quad (2)$$

$$\Delta\lambda_c^{(2)} = \frac{\rho^3 c_{p,c}^2}{T(\partial c / \partial \mu)_{P,T}} \left\{ \frac{\bar{D}_{cs}^2}{\bar{D}_{cc}} - \frac{D_{cs}^2}{D_{cc}} \right\}, \quad (3)$$

where μ is the difference between the specific chemical potentials of the two components, which is the thermodynamic field conjugate to the concentration c . The background contributions \bar{D}_{cc} and \bar{D}_{cs} to D_{cc} and D_{cs} are related to the background contributions $\bar{\alpha}$ and $\bar{\beta}$ to two Onsager kinetic coefficients as

$$\bar{D}_{cc} = \frac{\bar{\alpha}}{\rho} \left(\frac{\partial \mu}{\partial c} \right)_{P,T}, \quad (4)$$

$$\bar{D}_{cs} = \frac{T}{\rho^2 c_{p,c}} \left\{ \bar{\alpha} \left(\frac{\partial \mu}{\partial T} \right)_{P,c} + \bar{\beta} \right\}. \quad (5)$$

The viscosity η is expected to diverge as

$$\eta = \bar{\eta} \exp(c_{\eta} z H), \quad (6)$$

where $\bar{\eta}$ is the background contribution to the viscosity, $c_{\eta} = 1.076$ and $z = 0.063$ are universal constants [4], while $H(\xi, q_{DA}, q_{DB})$ is an additional crossover function [17]. For mixtures of methane and ethane the background contributions $\bar{\lambda}$ and $\bar{\eta}$ have been calculated by Vesovic and Wakeham [23].

To compare our experimental thermal-conductivity data with the theoretical expression (1) we have calculated the correlation length ξ from the equation of state [19] by relat-

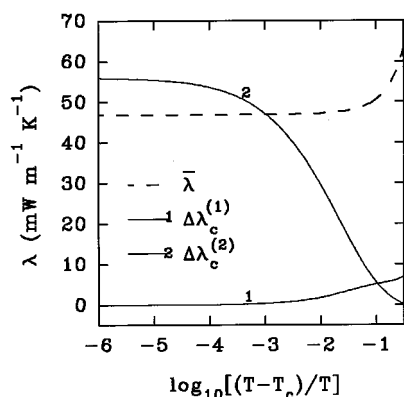


FIG. 2. Individual contributions $\bar{\lambda}$, $\Delta\lambda_c^{(1)}$, and $\Delta\lambda_c^{(2)}$ to the total thermal conductivity λ as a function of temperature.

ing it to the appropriate isomorphous susceptibility [17]. We note that q_{DA} may be estimated from the cutoff wave numbers of the pure components by $q_{DA}^{-1} = xq_D^{-1}(\text{CH}_4) + (1-x)q_D^{-1}(\text{C}_2\text{H}_6)$, where x is the mole fraction of methane [17]. With the values $q_D^{-1} = 0.217 \text{ nm}$ and $q_D^{-1} = 0.167 \text{ nm}$ found for methane [21] and for ethane [17] we obtain $q_{DA}^{-1} = 0.192 \text{ nm}$ for a 50%-50% methane+ethane mixture, leaving, in principle, q_{DB} as the only adjustable parameter. In practice we have also used the background contributions $\bar{\alpha}$ and $\bar{\beta}$ in Eqs. (4) and (5) as adjustable parameters due to the lack of adequate experimental information for \bar{D}_{cc} and \bar{D}_{cs} , just as was done by Luettemer-Strathmann and Sengers [17] for mixtures of carbon dioxide and ethane. The solid curve in Fig. 1 represents the values calculated from Eq. (1) with $q_{DB}^{-1} = 0.9 \text{ nm}$, $\bar{\alpha} = 1.0 \times 10^{-11} \text{ kg s m}^{-3}$, and $\bar{\beta} = 0.1415 \times 10^{-8} \text{ Pa s K}^{-1}$. The actual value of $\bar{\beta}$ depends on the equation of state adopted for μ [17]. Equations (1)–(6) reproduce our experimental thermal-conductivity data with a standard deviation of 1.8%.

To further elucidate the behavior of the thermal conductivity of the mixture we have plotted the individual contributions $\bar{\lambda}$, $\Delta\lambda_c^{(1)}$, and $\Delta\lambda_c^{(2)}$ to the total thermal conductivity in Fig. 2 as a function of temperature. In the original work of Mistura [6] the critical enhancement $\Delta\lambda_c$ was identified with $\Delta\lambda_c^{(1)}$, which led to the conclusion that the critical enhancement would vanish at the vapor-liquid critical point of a mixture. However, near the critical point the contribution $\Delta\lambda_c^{(2)}$ becomes important which crosses over to a limiting plateau value of $T_c[\bar{\alpha}(\partial\mu/\partial T)_{P,c} + \bar{\beta}]^2/\bar{\alpha}$ [14,15,17].

In Fig. 3 we present a comparison of our thermal-conductivity data of the methane+ethane mixture along the

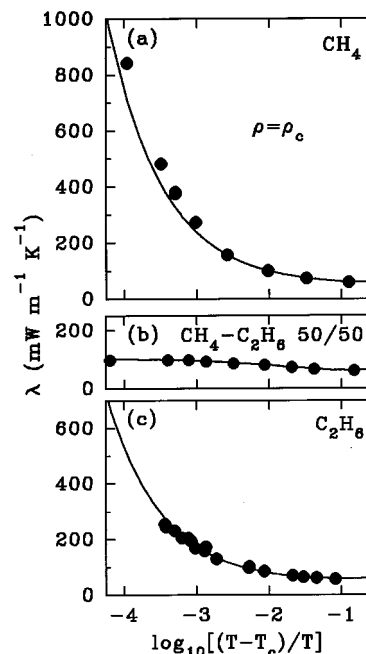


FIG. 3. Thermal conductivity at the critical density as a function of temperature for (a) pure methane, (b) an equimolar mixture of methane and ethane, and (c) for pure ethane. The symbols indicate experimental data and the curves represent values calculated from the crossover theory.

critical isochore with the thermal-conductivity data obtained in our laboratory for pure ethane [4,12] and pure methane [21]. At $\tau = (T - T_c)/T \geq 10^{-2}$ the thermal conductivity increases upon approaching the critical temperature for the mixture as well as for the pure fluids. This led some previous authors to the conclusion that the behavior of mixtures in the critical region would appear to be similar as that of one-component fluids [10]. However, while for pure fluids at $\tau < 10^{-2}$ the thermal conductivity continues to increase upon approach of the critical temperature, our experiments clearly show that in the case of the mixture the thermal conductivity crosses over to a finite limiting value at the critical point.

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