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Transport Properties of Fluid Mixtures in the Critical Region[1]

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Transport properties of fluid mixtures exhibit anomalous behavior near the vapor–liquid critical line. These anomalies are a result of long-range fluctuations in the system in the vicinity of a critical point. We use mode-coupling theory to describe the critical enhancements of the thermal conductivity, the viscosity, the mutual diffusivity, and the thermal-diffusion coefficients of binary mixtures. The resulting expressions not only are valid in the asymptotic critical region but also describe the crossover to regular behavior far away from a critical point. The crossover functions depend on the thermodynamic properties of the mixtures, background values of all transport coefficients, and two concentration-dependent cutoff wave numbers. We compare the proposed crossover model with experimental thermal-conductivity data for mixtures of carbon dioxide and ethane in the critical region and find good agreement between theory and experiment.

KEY WORDS: binary fluid mixtures; critical phenomena; crossover model; mutual diffusivity; plait point; transport properties; thermal conductivity; thermal diffusion coefficient; viscosity.

1. INTRODUCTION

Many transport properties of fluids exhibit singular behavior near a critical point. The thermal conductivity in a one-component fluid, for example, diverges near the vapor–liquid critical point, while the mutual

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diffusivity vanishes near a critical point of a binary mixture [1, 2]. Far away from a critical point, on the other hand, transport coefficients are generally slowly varying functions of the temperature and density. When this regular behavior is extrapolated into the critical region, one arrives at a separation of the transport coefficients into so-called background contributions and critical enhancements [1]. The critical enhancements are a result of long-range fluctuations in the system in the vicinity of the critical point and can be understood as resulting from nonlinear coupling between the hydrodynamic modes of the system. Asymptotically close to the critical point, the enhancements satisfy power laws with universal critical exponents [3]. The asymptotic critical region, though, is usually much smaller than the region in which critical enhancements are observed experimentally [4]. The range of temperatures and densities in which the transport coefficients are described neither by their background values nor by asymptotic power laws is the so-called crossover region. For the transport properties of one-component fluids, Olchowy and Sengers [5] developed a crossover model based on mode-coupling theory [6, 7]. It describes the critical enhancements of the thermal conductivity and the viscosity with the aid of crossover functions which depend on the thermodynamic properties, the background values of the transport coefficients, and one adjustable parameter, namely, a wave-number cutoff for the order-parameter fluctuations. The crossover functions incorporate the predicted asymptotic behavior of the critical enhancements and provide a smooth transition to the classical region where the order-parameter fluctuations are no longer important.

In this paper we present an extension of the theory to the transport properties of compressible binary fluid mixtures near the critical line. We calculate mode-coupling contributions to the decay rates of the relevant hydrodynamic modes and derive crossover functions that describe the critical enhancements from the asymptotic critical region to the classical region. The resulting expressions for the enhancements of the viscosity, the thermal conductivity, the mutual diffusivity, and the thermal-diffusion ratio depend on the thermodynamic properties of the mixture, the background values of the transport coefficients and two adjustable, concentration-dependent cutoff wave numbers.

2. ASYMPTOTIC PREDICTIONS

The transport properties of interest in the critical region are the viscosity η, the thermal conductivity λ, the mutual diffusivity $D = L/\chi_c$, where L is a "mass conductivity" and χ_c is the osmotic susceptibility, and the thermal-diffusion coefficient $k_T D$, where k_T is the thermal-diffusion ratio. The background contributions η^b, λ^b, L^b, and $(k_T D)^b$ are, in general, slowly varying functions of the temperature, density, and composition of the mixture, whereas the critical enhancements are predicted [8–10] to satisfy power laws in the asymptotic critical region in terms of the correlation length ξ of the order-parameter fluctuations. More specifically, the viscosity η exhibits a weak singulrity $\eta \sim \xi^{z_\eta}$, where $z_\eta = 0.063$ is the critical exponent of the viscosity. The thermal conductivity reaches a finite value at the critical point $\Delta\lambda \sim \xi^0$, whereas the critical enhancement ΔL of the mass transfer coefficient diverges like $\xi^{-1-z_\eta+\gamma/\nu} \approx \xi$, where $\gamma = 1.239$ and $\nu = 0.63$ are static critical exponents. Finally, the critical enhancement of the thermal diffusion coefficient vanishes at the critical point $\Delta(k_T D) \sim 0$. These asymptotic predictions are valid only in an extremely small region around the vapor–liquid critical line. Measurements on ^{3}He + ^{4}He [11], methane + ethane [12, 13], and CO_2 + ethane [14] seem to indicate that the thermal conductivity exhibits a diverging critical enhancement, just like in a pure fluid, rather than approach a constant value as predicted by theory. We return to this point when we compare our crossover model with experimental data.

3. THEORETICAL BASIS OF THE CROSSOVER MODEL

A compressible binary fluid mixture near the critical line has four relevant hydrodynamic modes, namely, two viscous modes, a heat mode, and a concentration mode [6]. The viscous modes correspond to fluctuations of the transverse components of the velocity $u_{\mathbf{q}}^{T,\alpha}$ with

$$\langle |u_q^{T,\alpha}|^2 \rangle = k_B T V/\rho, \qquad \alpha = 1,2 \tag{1}$$

where $\mathbf{q}$ is the wave vector of the mode, k_B is Boltzmann's constant, T is the temperature, V the volume, and ρ the mass density of the mixture. The heat mode represents fluctuations of the entropy at constant pressure and constant composition $S_{\mathbf{q}}$ with

$$\langle |S_{\mathbf{q}}|^2 \rangle = k_B V \rho c_{P,c}(q) \tag{2}$$

where $c_{P,c}$ is the isobaric specific heat capacity at constant composition. The concentration mode represents fluctuations of the mass fraction c at constant pressure and temperature $c_{\mathbf{q}}$ with

$$\langle |c_{\mathbf{q}}|^2 \rangle = k_B T V \chi_c(q)/\rho \tag{3}$$

The osmotic susceptibility $\chi_c = (\partial c/\partial \mu)_{P,T}$ is the derivative of the mass fraction c of component 2 with respect to the chemical potential of the mixture $\mu = \mu_2/m_2 - \mu_1/m_1$, where μ_i is the chemical potential of component i and m_i its mass per molecule.

The kinetic equations for these modes were derived by Kawasaki [6] under the assumption that one mode couples to at most two others. Neglecting less important terms in the critical region, we obtain

$$\frac{\partial}{\partial t} u_{\mathbf{q}}^{\mathrm{T},\alpha} = -q^2 \frac{\eta^{\mathrm{b}}}{\rho} u_{\mathbf{q}}^{\mathrm{T},\alpha} + f_{\mathbf{q}}^{\mathrm{T},\alpha} + \frac{i}{2} \sum_{k} V(u_{\mathbf{q}}^{\mathrm{T},\alpha}; S_{\mathbf{k}}, S_{\mathbf{q}-\mathbf{k}}) S_{\mathbf{k}} S_{\mathbf{q}-\mathbf{k}} + \frac{i}{2} \sum_{\mathbf{k}} V(u_{\mathbf{q}}^{\mathrm{T},\alpha}; c_{\mathbf{k}}, c_{\mathbf{q}-\mathbf{k}}) c_{\mathbf{k}} c_{\mathbf{q}-\mathbf{k}} \tag{4}$$

$$\frac{\partial}{\partial t} S_{\mathbf{q}} = -q^2 D_{\mathrm{SS}}^{\mathrm{b}}(q) S_{\mathbf{q}} - q^2 D_{\mathrm{Sc}}^{\mathrm{b}}(q) c_{\mathbf{q}} + f_{\mathbf{q}}^{S} + \sum_{\mathbf{k},\alpha} V(S_{\mathbf{q}}; S_{\mathbf{k}}, u_{\mathbf{q}-\mathbf{k}}^{\mathrm{T},\alpha}) S_{\mathbf{k}} u_{\mathbf{q}-\mathbf{k}}^{\mathrm{T},\alpha} \tag{5}$$

$$\frac{\partial}{\partial t} c_{\mathbf{q}} = -q^2 D_{\mathrm{cc}}^{\mathrm{b}}(q) c_{\mathbf{q}} - q^2 D_{\mathrm{cS}}^{\mathrm{b}}(q) S_{\mathbf{q}} + f_{\mathbf{q}}^{c} + \sum_{\mathbf{k},\alpha} V(c_{\mathbf{q}}; c_{\mathbf{k}}, u_{\mathbf{q}-\mathbf{k}}^{\mathrm{T},\alpha}) c_{\mathbf{k}} u_{\mathbf{q}-\mathbf{k}}^{\mathrm{T},\alpha} \tag{6}$$

where the coefficients $V(i; j, l)$ denote the strength of the nonlinear coupling between the modes and where f^i represents the noise in the variable i. $D_{\mathrm{SS}}^{\mathrm{b}}$ and $D_{\mathrm{cc}}^{\mathrm{b}}$ are background values of the diffusion coefficients associated with the heat mode and the concentration mode, respectively, while $D_{\mathrm{cS}}^{\mathrm{b}}$ and $D_{\mathrm{Sc}}^{\mathrm{b}}$ are background values of the coefficients associated with the cross processes.

With the aid of Green's functions techniques we derive mode-coupling integrals from these equations which we solve by the iterative procedure employed by Olchowy and Sengers [5] for the crossover model of the transport properties of one-component fluids. This leads to a crossover description for the critical enhancements of the transport coefficients in Eqs. (4)–(6) in the form

$$\Delta\eta = \eta^{\mathrm{b}}(e^{z_\eta H} - 1) \quad \text{with} \quad \lim_{\xi \to \infty} H = \ln \xi + \text{const} \tag{7}$$

$$\Delta D_{\mathrm{cc}} = \frac{k_{\mathrm{B}} T}{6\pi\eta\xi} \Omega_{\mathrm{cc}} \quad \text{with} \quad \lim_{\xi \to \infty} \Omega_{\mathrm{cc}} = 1 \tag{8}$$

$$\Delta D_{\mathrm{cS}} = \frac{k_{\mathrm{B}} T}{6\pi\eta\xi} \Omega_{\mathrm{cS}} \quad \text{with} \quad \lim_{\xi \to \infty} \Omega_{\mathrm{cS}} = 0 \tag{9}$$

$$\Delta D_{\mathrm{SS}} = \frac{k_{\mathrm{B}} T}{6\pi\eta\xi} \Omega_{\mathrm{SS}} \quad \text{with} \quad \lim_{\xi \to \infty} \Omega_{\mathrm{SS}} = 1 \tag{10}$$

where we have indicated the asymptotic critical behavior of the crossover functions H and Ω_{ij}. Explicit expressions for the crossover functions are provided elsewhere [15, 16]; here we just state that they vanish in the classical limit and depend on the thermodynamic properties $c_{p,c}$ and χ_c, the correlation length ξ, which can be estimated from $\xi \propto (\partial P/\partial \rho)_{\mu,T}$, the background values of the transport coefficients λ^b, η^b, $D^b = L^b/\chi_c$, and $(k_T D)^b$, and two cutoff wave numbers q_{DA} and q_{DB} in the mode-coupling integrals.

The physical transport coefficients η, D, $k_T D$, and λ can now be calculated as

$$\eta = \eta^b e^{z_\eta H} \tag{11}$$

$$D = D_{cc} = D^b_{cc} + \Delta D_{cc} \tag{12}$$

$$k_T D = \rho c_{p,c} D_{cS} = \rho c_{p,c}(D^b_{cS} + \Delta D_{cS}) \tag{13}$$

$$\lambda = \lambda^b + \rho c_{p,c} \Delta D_{SS} + \frac{\rho}{T}\frac{((k_T D)^b)^2}{\chi_c D^b} - \frac{\rho}{T}\frac{(k_T D)^2}{\chi_c D} \tag{14}$$

The equations for the crossover behavior of the transport properties obtained by us differ from and improve upon those proposed by Kiselev and Kulikov [17].

4. COMPARISON WITH EXPERIMENTAL DATA

We have applied the crossover model presented in the previous section to mixtures of carbon dioxide and ethane near the vapor–liquid critical line. The thermodynamic properties were calculated with the aid of the crossover model for thermodynamic properties recently proposed by Jin et al. and reviewed elsewhere [4]. Values for the backgrounds λ^b of the thermal conductivity and η^b of the viscosity were provided by Vesovic and Wakeham [18]. Since there was no information available about the mutual diffusivity and the thermal-diffusion coefficient,we represented the corresponding background coefficients as

$$D^b = \frac{\alpha^b}{\rho\chi_c} \tag{15}$$

$$(k_T D)^b = \frac{T}{\rho}\left[\alpha^b \left(\frac{\partial\mu}{\partial T}\right)_{p,c} + \beta^b\right] \tag{16}$$

and treated as adjustable parameters the background values α^b and β^b of the transport coefficients α and β introduced by Landau and Lifshitz [19]. One of the cutoff wave numbers mentioned in the previous section can be related to the corresponding cutoff wave numbers q_{D1} and q_{D2} of the pure components. Thus we write

$$q_{DA}^{1} = x q_{D2}^{1} + (1-x)\, q_{D1}^{1} \tag{17}$$

where x is the mole fraction of carbon dioxide.

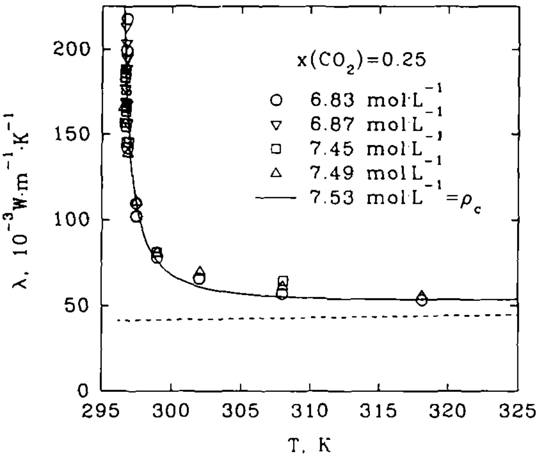

Fig. 1. Thermal conductivity of a mixture of 25% carbon dioxide and 75% ethane along the critical isochore. The symbols indicate experimental data obtained by Mostert et al. [14, 20], the solid line is calculated from our crossover model, and the dashed line indicates the background provided by Vesovic and Wakeham [18].

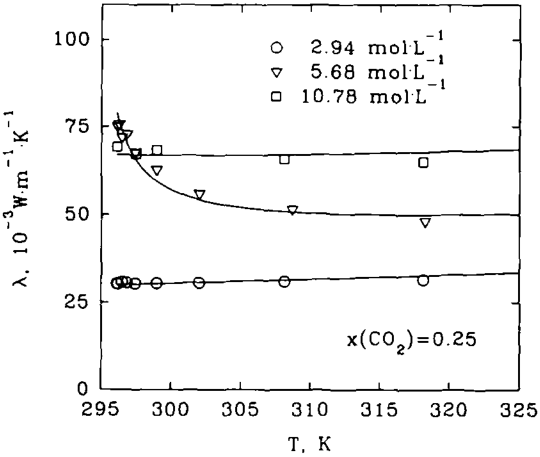

Fig. 2. Thermal conductivity of a mixture of 25% carbon dioxide and 75% ethane along three off-critical isochores. The symbols indicate experimental data obtained by Mostert et al. [14, 20]; the solid lines are calculated from our crossover model.

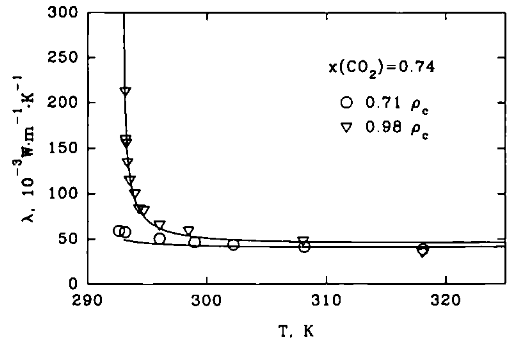

Fig. 3. Thermal conductivity of a mixture of 74% carbon dioxide and 26% ethane along two isochores. The symbols indicate experimental data obtained by Mostert et al. [14, 20]; the solid lines are calculated from our crossover model.

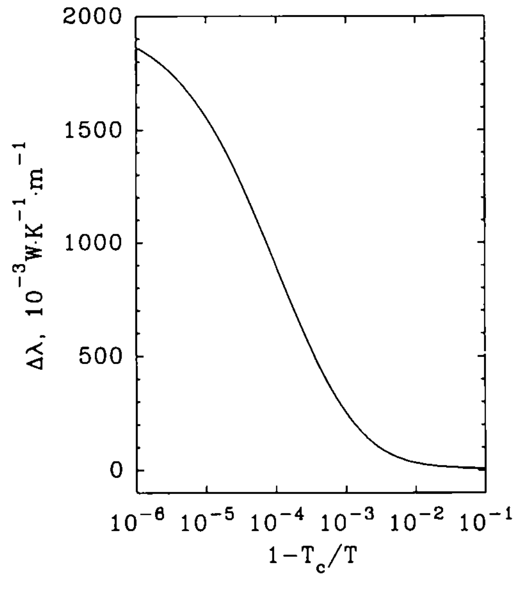

Fig. 4. The critical enhancement of the thermal conductivity of a mixture of 25% carbon dioxide and 75% ethane along the critical isochore as calculated from our crossover model.

We have determined the remaining cutoff wave-number $q_{DB}(x)$ and the background parameters α^b and β^b from a comparison with the experimental thermal-conductivity data obtained by Mostert et al. [14, 20]. As it turned out, for the temperature and density ranges considered here, the background α^b can be represented by a single constant for all concentrations. The background β^b, on the other hand, depends strongly on concentration and density but can be considered independent of temperature in the range of temperatures that is covered by the thermal-conductivity data. In Figs. 1–3 we present a comparison of our model with experimental thermal-conductivity data for two mixtures of carbon dioxide and ethane, namely, for mole fractions of 25% CO_2 and 74% CO_2. As can be seen from the figures, the crossover model provides a representation of the experimental data that is indeed quite satisfactory. Furthermore, the thermal conductivity rises strongly as the critical point is approached for the range of temperatures where experimental data are available. In Fig. 4 we present a graph of the calculated thermal conductivity as a function of the reduced temperature for near-critical temperatures. This graphs elucidates why there is no direct experimental evidence for the theoretical prediction that the thermal conductivity reaches a finite value at the critical point. The crossover from one-component-like (divergent) behavior to mixture-like (constant) behavior of the thermal conductivity occurs so close to the critical point that it is not observed in practice for a simple binary mixture such as $CO_2 + C_2H_6$.

5. CONCLUSIONS

We have presented a crossover model for the transport properties of a binary mixture in the critical region which, with only few adjustable parameters, gives a good description of experimental thermal-conductivity data near the vapor–liquid critical line. If, for a particular mixture, all background transport properties are known, only the cutoff wave numbers are adjustable parameters. If, on the other hand, only little information about transport properties is available, then the model can be used to predict unknown transport properties. For the system investigated in this work, for example, values for the mutual diffusivity and the thermal-diffusion ratio can be calculated from Eqs. (12) and (13) [15, 16]. Finally, the model explains why the observed thermal conductivity of simple binary fluid mixtures whose components have similar critical temperatures, such as $CO_2 + C_2H_6$ or $^3He + ^4He$ [11, 21], behaves like that of a one-component fluid in an appreciable range of temperatures and densities. However, one may expect to observe deviations from one-component-like thermal-conductivity behavior for mixtures of sufficiently dissimilar components [22].

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