

Thermodiffusion in the Critical Region

Jutta Luettmer-Strathmann

Department of Physics, The University of Akron, Akron, OH 44325-4001, USA

Abstract. Long range fluctuations of the order parameter affect thermodynamic as well as transport properties in the critical region. The values of transport coefficients near a critical point are typically enhanced compared to the values in the classical region far away from a critical point. Asymptotically close to a critical point, the critical enhancements obey power laws with universal critical exponents. The asymptotic critical region is surrounded by a large crossover region, where the enhancements are no longer asymptotic but still significant compared to the background values. In binary mixtures, this is also the region where differences are observed in the critical behavior of transport coefficients near liquid-liquid (consolute) and liquid-vapor (plait) critical points. In this contribution, we review the critical dynamics of binary fluid mixtures with a focus on thermodiffusion.

1 Introduction

Many transport properties of fluids exhibit singular behavior near a critical point (cf. [1,2]). The transport properties related to heat and mass transport in binary mixtures are no exception. The mutual diffusivity, for example, vanishes at a critical point while the Ludwig-Soret coefficient, describing the transport of matter in response to a temperature gradient, diverges as a critical point is approached. Since transport coefficients can have anomalous values in a large region around a critical point [1,2] a knowledge of their critical behavior is important for many technical and scientific applications. In particular, thermal diffusion in the critical region is important in such fields as supercritical-fluid chemistry, the treatment of hazardous waste, geochemistry of hydrocarbon reservoirs, and the study of the kinetics of phase separation (cf. [3-6] and references therein).

Far away from a critical point, transport coefficients are non-singular and 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 transport coefficients into the so-called background contributions and critical enhancements, see Fig. 1. The critical enhancements are due to long-range fluctuations in the fluid. Asymptotically close to the critical point, the correlation length of the fluctuations diverges leading to universal scaling laws for the critical enhancements of the transport coefficients. The asymptotic critical region, however, is usually much smaller than the region in which critical enhancements are observed experimentally (cf. [1,2]). The behavior of the transport coefficients in this so-called crossover region cannot be described in terms

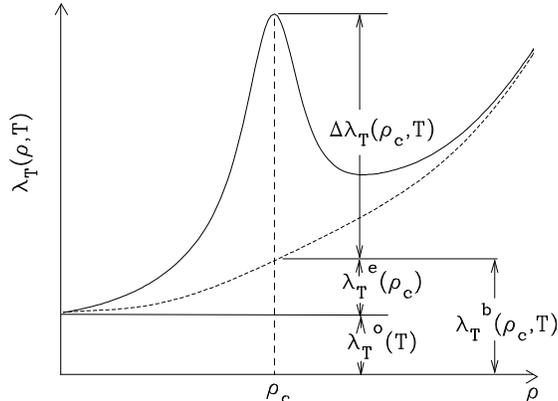


Fig. 1. Illustration of the decomposition of a transport coefficient, here the thermal conductivity of a one-component fluid, into critical enhancement $\Delta\lambda_T$ and background contributions $\lambda_T^b = \lambda_T^0(T) + \lambda_T^e(T, \rho)$, where $\lambda_T^0(T)$ is the dilute gas contribution and $\lambda_T^e(T, \rho)$ is the so-called excess term

of simple power laws and depends on details of the physical system under consideration. For binary fluid mixtures, the crossover behavior of the transport coefficients depends qualitatively on the nature of the critical point; this issue will be discussed in Section 4.

Two different theoretical approaches are widely used to investigate dynamic critical phenomena. The dynamic renormalization-group theory formulated by Halperin, Hohenberg and Ma [7] forms the theoretical basis for the concepts of dynamic scaling and universality [8]. It is an extension of the ideas of the static renormalization-group theory of Wilson and Fisher [9,10], which provides the basis for scaling and universality of thermodynamic properties in the critical region. Mode-coupling theories [11–13], on the other hand, originated from the idea of Fixman [14] that the critical enhancements of the transport coefficients are the result of non-linear coupling between the hydrodynamic modes of the system. Dynamic renormalization-group and mode-coupling theories, as well as the related decoupled-mode theory of Perl and Ferrell [15,16], have recently been extended to describe the crossover behavior of transport properties of fluids and their mixtures [17–28].

2 Thermodynamic properties in the critical region

Before we address transport properties in the critical region, we will briefly review some aspects of the thermodynamics of fluids near critical points. The critical point of a one-component fluid is characterized by its critical temperature T_c , density ρ_c and pressure P_c . When a fluid at its critical density is cooled through the critical temperature, it undergoes a continuous phase transition to a state with two coexisting phases that differ in density. The order parameter

for the phase transition can be identified with the difference between the actual and the critical density of the fluid, while the chemical potential plays the role of the ordering field [29]. Since the order parameter for the liquid-vapor phase transition is a scalar and since the interactions between molecules in a simple fluid are short ranged, simple fluids belong to the universality class of the three-dimensional Ising model [30]. Asymptotically close to the critical point, the thermodynamic properties of a fluid exhibit singular behavior and satisfy well-known power laws in the reduced temperature $\Delta\tilde{T} = (T - T_c)/T$. Of special interest in this work are the so-called generalized susceptibilities, i.e. derivatives of thermodynamic densities (e.g. the mass density ρ and the specific entropy s) with respect to thermodynamic fields (temperature T , pressure P , etc.) [31]. The specific isochoric heat capacity $c_v = T(\partial s/\partial T)_V$ and the symmetrized isothermal compressibility $\chi_T = \rho(\partial\rho/\partial P)_T$ obey the asymptotic power laws

$$c_v \sim \Delta\tilde{T}^{-\alpha}, \quad \chi_T \sim \Delta\tilde{T}^{-\gamma}, \quad \text{for } \rho = \rho_c \text{ and } T \geq T_c. \quad (1)$$

The values of these critical exponents for the universality class of the three-dimensional Ising model are given by [29,32]

$$\alpha = 0.110 \pm 0.003, \quad \gamma = 1.239 \pm 0.002. \quad (2)$$

Please note that the isochoric heat capacity diverges weakly, i.e. with exponent α , while the symmetrized isothermal compressibility diverges strongly, i.e. with exponent γ . Since the specific isobaric heat capacity $c_p = T(\partial s/\partial T)_P$ is related to c_v and χ_T through

$$\rho c_p = \rho c_v + T\rho^{-2}(\partial P/\partial T)_\rho^2 \chi_T, \quad (3)$$

and since $(\partial P/\partial T)_\rho$ remains finite at the critical point, it follows that c_p diverges strongly as the critical point is approached.

The critical behavior of the thermodynamic properties is induced by long-range order-parameter fluctuations in the critical region [33]. Denoting the local number density at position \mathbf{r} by $n(\mathbf{r})$ and its average value by $n = \langle n(\mathbf{r}) \rangle = \rho/m$, where ρ is the mass density and m is the mass of a molecule, we define the correlation function for the density fluctuations as [34,35]

$$G(|\mathbf{r}_1 - \mathbf{r}_2|) = \langle n(\mathbf{r}_1)n(\mathbf{r}_2) \rangle - n^2. \quad (4)$$

In general, the correlation function decays exponentially in space

$$G(r) \sim \exp(-r/\xi), \quad (5)$$

where ξ is the correlation length of the fluctuations [34]. The correlation length diverges as the critical point is approached and satisfies the power law [29]

$$\xi = \xi_0(\Delta\tilde{T})^{-\nu} \quad \text{for } \rho = \rho_c \text{ and } T \geq T_c, \quad (6)$$

where ξ_0 is a system-dependent amplitude and ν a critical exponent. At the critical point, the correlation function decays algebraically, $G(r) \sim r^{-d+2-\eta}$ for

$r \rightarrow \infty$ [34], where d is the spatial dimension of the system and η is another critical exponent (not to be confused with the viscosity $\tilde{\eta}$). According to the fluctuation dissipation theorem [35], the symmetrized compressibility χ_T is related to the integral over the correlation function

$$\chi_T = \frac{1}{k_B T} \int d\mathbf{r} G(r), \quad (7)$$

where k_B is Boltzmann's constant.

The divergence of the correlation length at the critical point motivates the static scaling hypothesis [33,35] “near the critical point, the correlation length ξ is the only characteristic length of the system in terms of which all other lengths must be measured” [35]. A dimensional analysis [35] then reveals that the singular behavior of the thermodynamic properties of interest can be expressed in terms of the diverging correlation length

$$c_v \sim \xi^{\alpha/\nu}, \quad \chi_T \sim \xi^{\gamma/\nu}, \quad c_p \sim \xi^{\gamma/\nu}, \quad (8)$$

where the critical exponents obey scaling relations

$$2 - \alpha = d\nu, \quad \gamma = \nu(2 - \eta). \quad (9)$$

This implies that ν and η have the values $\nu = 0.63$ and $\eta = 0.033$. The asymptotic power laws for the thermodynamic properties discussed here are valid only in a very small region around the critical point [29]. To describe fluids and fluid mixtures in the much larger region in which the critical fluctuations affect the thermodynamic properties, so-called crossover equations-of-state have to be employed (cf. [1]).

Thermodynamics of binary fluid mixtures in the asymptotic critical region are most elegantly described by the theory of Griffiths and Wheeler [31]. In this theory, thermodynamic fields are defined from combinations of the temperature, the pressure, and the chemical potentials in such a way, that the first field represents the ordering field, the second the temperature variable, and the third a non-scaling field, which is not present in one-component fluids. By keeping the non-scaling field constant, the critical behavior of binary mixtures is mapped onto that of the three-dimensional Ising model. There is some freedom in the choice of the fields. For binary mixtures near a liquid-liquid critical point (consolute point) one often takes the pressure to be the non-scaling field. This makes the concentration (fluctuating at constant pressure) the order parameter for the phase transition. For binary mixtures near a vapor-liquid critical point (plait point), on the other hand, the non-scaling field is often taken to be the difference between the chemical potentials of the two components [1] making the density (fluctuating at constant chemical potential difference) the order parameter.

According to the theory of Griffiths and Wheeler [31], a derivative of a thermodynamic density with respect to a thermodynamic field diverges strongly, i.e. like $\xi^{\gamma/\nu}$, when two thermodynamic fields are kept constant, weakly, i.e. like $\xi^{\alpha/\nu}$, when one density and one field are kept constant, and not at all, when two

densities are kept constant. For the specific heat capacities of binary mixtures, for example, this implies the following asymptotic power laws

$$c_{p,\mu} \sim \xi^{\gamma/\nu}, \quad c_{p,c} \sim \xi^{\alpha/\nu}, \quad c_{v,c} \sim \xi^0, \quad (10)$$

where c is the mass fraction of component 2 and $v = 1/\rho$, where $\rho = \rho_1 + \rho_2$ is the mass density of the mixture. The chemical potential $\mu = \mu_2/m_2 - \mu_1/m_1$, where m_i is the mass per molecule and μ_i the chemical potential of component $i \in \{1, 2\}$, is the thermodynamic quantity conjugate to c [36].

The asymptotic power laws introduced above hold near consolute as well as plait points (except at “special points” on the critical line [31]). The asymptotic critical region is (again) surrounded by a large crossover region, where the asymptotic power laws no longer describe the effect of the critical fluctuations on the thermodynamic properties. Crossover phenomena are very much in evidence for binary mixtures near plait points. In those mixtures, the thermodynamic properties suggest pure-fluid like behavior at some distance from the critical point and cross over to the asymptotic, mixture-like behavior only extremely close the critical point (cf. Fig. 16 in [25] and Fig. 15 in [37]).

3 Transport coefficients in the asymptotic critical region

According to the concept of dynamic universality [8], the critical dynamics of physical systems are determined by only a few characteristic properties. Systems within a dynamic universality class belong to the same static universality class and have the same conservation laws and Poisson-bracket relations among the order parameter and the conserved densities [8]. In the classification of Hohenberg and Halperin [8] one-component fluids and incompressible mixtures belong to model H, which Siggia *et al.* [38] extended to describe the critical dynamics of compressible fluid mixtures (model H'). The dynamic scaling hypothesis of Ferrell *et al.* [39,40] and Halperin and Hohenberg [41,42] extends scaling with the correlation length to dynamic critical phenomena. If $m(\mathbf{r}, t)$ denotes the value of the order parameter at position \mathbf{r} and time t , the correlation function (4) is generalized to

$$G(|\mathbf{r}_1 - \mathbf{r}_2|) = \langle m(\mathbf{r}_1, t_1)m(\mathbf{r}_2, t_2) \rangle - \langle m(\mathbf{r}_1, t_1) \rangle \langle m(\mathbf{r}_2, t_2) \rangle, \quad (11)$$

where the angular brackets indicate equilibrium averages. The dynamic scaling hypothesis states that the Fourier transform $\tilde{G}(q, \omega)$ of the correlation function can be expressed as

$$\tilde{G}(q, \omega) = \xi^{2-\eta} g(q\xi, \omega\xi^z), \quad (12)$$

where g is a universal scaling function, η is the static critical exponent, and z is a new dynamic critical exponent. Eq. (12) implies that a system near a critical point does not only have a characteristic length, namely ξ , but also a characteristic time τ_q , which has the scaling form $\tau_q = \xi^z f(q\xi)$, where f is

another scaling function [33]. For one-component fluids and binary mixtures, the exponent z is related to the critical exponent z_η of the viscosity $\tilde{\eta}$

$$\tilde{\eta} \sim \xi^{z_\eta}, \quad (13)$$

through $z = 3 + z_\eta$. Unfortunately, the value for the dynamic critical exponent is not as well known as the values for the static critical exponent (for a recent discussion see [43]). In this work, we will employ the renormalization-group result $z_\eta = 0.063$ by Hao [44].

In order to discuss the asymptotic scaling laws for the transport properties related to heat and mass diffusion, we start from the hydrodynamic equations of Landau and Lifshitz [45]. If the fluid as a whole is at rest then, to first order, the diffusion current \mathbf{J}_d and the heat current \mathbf{J}_q are related to the time derivatives of the mass fraction c of component 2 and the specific entropy s through [45]

$$\rho \frac{\partial c}{\partial t} = -\nabla \cdot \mathbf{J}_d, \quad (14)$$

$$\rho T \frac{\partial s}{\partial t} = -\nabla \cdot (\mathbf{J}_q - \mu \mathbf{J}_d), \quad (15)$$

where, as before, ρ is the mass density, T the temperature, and $\mu = \mu_2/m_2 - \mu_1/m_1$ the chemical potential difference. The linear laws relating the currents \mathbf{J}_d and \mathbf{J}_q to gradients of the temperature and chemical potential difference define the transport coefficients $\tilde{\alpha}$, $\tilde{\beta}$, $\tilde{\gamma}$, and $\tilde{\delta}$ [45]

$$\mathbf{J}_d = -\tilde{\alpha} \nabla \mu - \tilde{\beta} \nabla T, \quad (16)$$

$$\mathbf{J}_q - \mu \mathbf{J}_d = -\tilde{\delta} \nabla \mu - \tilde{\gamma} \nabla T, \quad (17)$$

where $\tilde{\delta} = T\tilde{\beta}$ due to Onsager reciprocal relations [46].

The transport coefficients $\tilde{\alpha}$, $\tilde{\beta}$, and $\tilde{\gamma}$ can be expressed in terms of experimentally accessible transport properties. The coefficient $\tilde{\alpha}$ plays the role of a mass conductivity and is related to the mutual diffusivity D

$$D = \frac{\tilde{\alpha}}{\rho} \left(\frac{\partial \mu}{\partial c} \right)_{T,P}. \quad (18)$$

The thermal diffusion coefficient $D_T = S_T D$, where S_T is the Soret coefficient [46], is given by

$$D_T = \frac{1}{c(1-c)\rho} \left[\tilde{\alpha} \left(\frac{\partial \mu}{\partial T} \right)_{c,P} + \tilde{\beta} \right]. \quad (19)$$

The thermal conductivity λ_T is defined by

$$\mathbf{J}_q = -\lambda_T \nabla T \quad \text{with } \mathbf{J}_d = 0, \quad (20)$$

and therefore given by

$$\lambda_T = \tilde{\gamma} - T\tilde{\beta}^2/\tilde{\alpha}. \quad (21)$$

In some experimental situations, the thermal conductivity in the absence of a concentration gradient (rather than in the absence of mass flow) is required [46,47]. This quantity corresponds to the transport coefficient L_{SS} of [25] and can be expressed as

$$L_{SS} = \lambda_T + \frac{T}{\tilde{\alpha}} \left(\tilde{\alpha} \left(\frac{\partial \mu}{\partial T} \right)_{c,P} + \tilde{\beta} \right)^2. \quad (22)$$

As customary in the critical region [1,2], each of the transport coefficients $\tilde{\alpha}$, $\tilde{\beta}$, and $\tilde{\gamma}$ is separated into a regular or background part (indicated by a superscript b) and a critical enhancement (indicated by a prefix Δ)

$$\tilde{\alpha} = \tilde{\alpha}^b + \Delta\tilde{\alpha}, \quad \tilde{\beta} = \tilde{\beta}^b + \Delta\tilde{\beta}, \quad \tilde{\gamma} = \tilde{\gamma}^b + \Delta\tilde{\gamma}. \quad (23)$$

This implies a separation of the diffusion coefficient D into background and critical enhancement, $D = D^b + \Delta D$, with

$$D^b = \frac{\tilde{\alpha}^b}{\rho} \left(\frac{\partial \mu}{\partial c} \right)_{T,P} \quad \text{and} \quad \Delta D = \frac{\Delta\tilde{\alpha}}{\rho} \left(\frac{\partial \mu}{\partial c} \right)_{T,P}. \quad (24)$$

Similarly, the thermal diffusion coefficient D_T decomposes as $D_T = D_T^b + \Delta D_T$ with

$$\begin{aligned} D_T^b &= \frac{1}{c(1-c)\rho} \left[\tilde{\alpha}^b \left(\frac{\partial \mu}{\partial T} \right)_{c,P} + \tilde{\beta}^b \right], \\ \Delta D_T &= \frac{1}{c(1-c)\rho} \left[\Delta\tilde{\alpha} \left(\frac{\partial \mu}{\partial T} \right)_{c,P} + \Delta\tilde{\beta} \right]. \end{aligned} \quad (25)$$

For the transport coefficient $L_{SS} = L_{SS}^b + \Delta L_{SS}$ we find

$$\begin{aligned} L_{SS}^b &= \tilde{\gamma}^b + T \left(\frac{\partial \mu}{\partial T} \right)_{c,P} \left[2\tilde{\beta}^b + \tilde{\alpha}^b \left(\frac{\partial \mu}{\partial T} \right)_{c,P} \right], \\ \Delta L_{SS} &= \Delta\tilde{\gamma} + T \left(\frac{\partial \mu}{\partial T} \right)_{c,P} \left[2\Delta\tilde{\beta} + \Delta\tilde{\alpha} \left(\frac{\partial \mu}{\partial T} \right)_{c,P} \right]. \end{aligned} \quad (26)$$

The thermal conductivity, finally, is written as $\lambda_T = \lambda_T^b + \Delta\lambda$ with

$$\begin{aligned} \lambda_T^b &= \tilde{\gamma}^b - T(\tilde{\beta}^b)^2/\tilde{\alpha}^b, \\ \Delta\lambda_T &= \frac{T}{\tilde{\alpha}} \left[\frac{(\tilde{\beta}^b)^2}{\tilde{\alpha}^b} \Delta\tilde{\alpha} - 2\tilde{\beta}^b \Delta\tilde{\beta} - (\Delta\tilde{\beta})^2 \right] + \Delta\tilde{\gamma}. \end{aligned} \quad (27)$$

To investigate the asymptotic critical behavior, diffusion coefficients corresponding to the transport coefficients $\tilde{\beta}$ and $\tilde{\gamma}$ are introduced [48] in analogy with equation (18)

$$\tilde{\alpha} = \rho \left(\frac{\partial c}{\partial \mu} \right)_{T,P} D_{\tilde{\alpha}}, \quad \tilde{\beta} = \rho \left(\frac{\partial c}{\partial T} \right)_{\mu,P} D_{\tilde{\beta}}, \quad \tilde{\gamma} = \rho T \left(\frac{\partial s}{\partial T} \right)_{\mu,P} D_{\tilde{\gamma}}. \quad (28)$$

From mode-coupling calculations, Kawasaki [12] showed that the mutual diffusivity D obeys a Stokes-Einstein diffusion law asymptotically close to the critical point. Mistura [48] predicted that this should be true for the critical enhancements ΔD_i of all three diffusion coefficients

$$\Delta D_i = R_D \frac{k_B T}{6\pi\tilde{\eta}\xi}, \quad i \in \{\tilde{\alpha}, \tilde{\beta}, \tilde{\gamma}\}, \quad (29)$$

where $\tilde{\eta}$ is the viscosity and where R_D is a universal amplitude. Mode-coupling calculations to first order [12,48] yield $R_D = 1$, while dynamic-renormalization group calculations yield a slightly higher value of $R_D = 1.056$ [19]. We will set $R_D = 1$ in our discussion of the asymptotic scaling laws. For the enhancements of the transport coefficients Eq. (29) yields

$$\Delta\tilde{\alpha} = \frac{k_B T \rho}{6\pi\tilde{\eta}\xi} \left(\frac{\partial c}{\partial \mu} \right)_{T,P}, \quad \Delta\tilde{\beta} = \frac{k_B T \rho}{6\pi\tilde{\eta}\xi} \left(\frac{\partial c}{\partial T} \right)_{\mu,P}, \quad \Delta\tilde{\gamma} = \frac{k_B T^2 \rho}{6\pi\tilde{\eta}\xi} \left(\frac{\partial s}{\partial T} \right)_{\mu,P}. \quad (30)$$

In order to determine the asymptotic critical behavior of the experimentally accessible transport properties, we have to take both critical enhancements and background contributions into account [1,2]. The background values $\tilde{\alpha}^b$, $\tilde{\beta}^b$, and $\tilde{\gamma}^b$ are (by definition) unaffected by critical fluctuations and therefore scale like ξ^0 . Inserting Eqs. (29) and (30) into Eqs. (25) for the mutual diffusivity D we find that D vanishes approximately like the inverse correlation length in the asymptotic critical region:

$$\left. \begin{aligned} \Delta D &= \frac{k_B T}{6\pi\tilde{\eta}\xi} \sim \xi^{1-\eta-z_\eta} \simeq \xi^{-1} \\ D^b &= \tilde{\alpha}^b \rho \left(\frac{\partial \mu}{\partial c} \right)_{T,P} \sim \xi^{\gamma/\nu} = \xi^{-2+\eta} \simeq \xi^{-2} \end{aligned} \right\} \Rightarrow D \sim \xi^{-1-z_\eta} \quad (31)$$

Because of the thermodynamic identity $(\partial c/\partial T)_{\mu,P} = -(\partial \mu/\partial T)_{c,P}(\partial c/\partial \mu)_{T,P}$ the critical enhancements of $\tilde{\alpha}$ and $\tilde{\beta}$ are related in the asymptotic critical region through $\Delta\tilde{\beta} = -(\partial \mu/\partial T)_{c,P} \Delta\tilde{\alpha}$, where the derivative $(\partial \mu/\partial T)_{c,P}$ remains finite at the critical point. Since the combination $\Delta\tilde{\beta} + (\partial \mu/\partial T)_{c,P} \Delta\tilde{\alpha}$ vanishes asymptotically close to the critical point, the critical enhancement ΔD_T in Eq. (25) vanishes, so that

$$\left. \begin{aligned} \Delta D_T &= 0 \\ D_T^b &= \frac{1}{c(1-c)\rho} \left[\tilde{\alpha}^b \left(\frac{\partial \mu}{\partial T} \right)_{c,P} + \tilde{\beta}^b \right] \sim \xi^0 \end{aligned} \right\} \Rightarrow D_T \sim \xi^0 \quad (32)$$

This implies that the Soret coefficient diverges approximately like the correlation length

$$S_T = D_T/D \sim \xi^{1+z_\eta} \simeq \xi. \quad (33)$$

The critical behavior of the transport coefficient L_{SS} is deduced with the aid of the thermodynamic identity $c_{P,c} = c_{P,\mu} - T(\partial \mu/\partial T)_{c,P}^2 (\partial c/\partial \mu)_{T,P}$. From

Eqs. (26) and (30) we conclude that the critical enhancement ΔL_{SS} vanishes in the asymptotic limit

$$\left. \begin{aligned} \Delta L_{SS} &= \frac{k_B T}{6\pi\eta\xi} \rho c_{P,c} \sim \xi^{-1-z_\eta+\alpha/\nu} \simeq \xi^{-0.9} \\ L_{SS}^b &= \tilde{\gamma}^b + T \left(\frac{\partial\mu}{\partial T} \right)_{c,P} \left[2\tilde{\beta}^b + \tilde{\alpha}^b \left(\frac{\partial\mu}{\partial T} \right)_{c,P} \right] \sim \xi^0 \end{aligned} \right\} \Rightarrow L_{SS} \sim \xi^0. \quad (34)$$

For the thermal conductivity, finally, we find from Eqs. (26) and (27) that the critical enhancement $\Delta\lambda_T$ goes to a finite constant asymptotically close to the critical point

$$\left. \begin{aligned} \Delta\lambda_T &= \frac{k_B T}{6\pi\eta\xi} \rho c_{P,c} + T(\rho c(1-c)D_T)^2/\alpha^b \sim \xi^0 \\ \lambda_T^b &= \tilde{\gamma}^b - T(\tilde{\beta}^b)^2/\tilde{\alpha}^b \sim \xi^0 \end{aligned} \right\} \Rightarrow \lambda_T \sim \xi^0. \quad (35)$$

4 Thermodiffusion near consolute and plait points

From the asymptotic analysis presented in the previous section, we expect the mutual diffusion coefficient D to vanish, $D \sim \xi^{-1-z_\eta}$, we expect the thermal diffusion coefficient D_T to approach a constant, $D_T \sim \xi^0$, and we expect the Soret coefficient to diverge, $S_T \sim \xi^{1+z_\eta}$, as the critical point is approached. The thermal diffusion ratio k_T is defined as

$$k_T = c(1-c)TS_T, \quad (36)$$

and behaves like the Soret coefficient $k_T \sim \xi^{1+z_\eta}$. Since the correlation length diverges as $\xi \sim \Delta\tilde{T}^{-\nu}$, where $\Delta\tilde{T} = (T - T_c)/T$ is the reduced temperature and $\nu = 0.63$, the asymptotic analysis predicts for the temperature dependence of these transport coefficients

$$D \sim \Delta\tilde{T}^{-(1+z_\eta)\nu} \simeq \Delta\tilde{T}^{-0.67}, \quad (37)$$

$$k_T \sim \Delta\tilde{T}^{-(1+z_\eta)\nu} \simeq \Delta\tilde{T}^{-0.67} \quad (38)$$

$$D_T \sim k_T D \sim \Delta\tilde{T}^0 \quad (39)$$

Dynamic renormalization-group (RG) calculations by Folk and Moser [21] show that the non-asymptotic critical behavior of $k_T D$ depends qualitatively on the type of critical point. The product $k_T D$ is constant throughout the critical region of a consolute point, whereas $k_T D \sim \text{const.}$ is valid only asymptotically close to a plait point.

In 1975, Giglio and Vendramini [49] performed thermal diffusion measurements near the consolute point of an aniline-cyclohexane mixture. In Fig. 2 we compare experimental data of Giglio and Vendramini [49] with the predicted asymptotic behavior. The experimental data for k_T and D agree with the asymptotic power laws close to the critical temperature but show increasing deviations

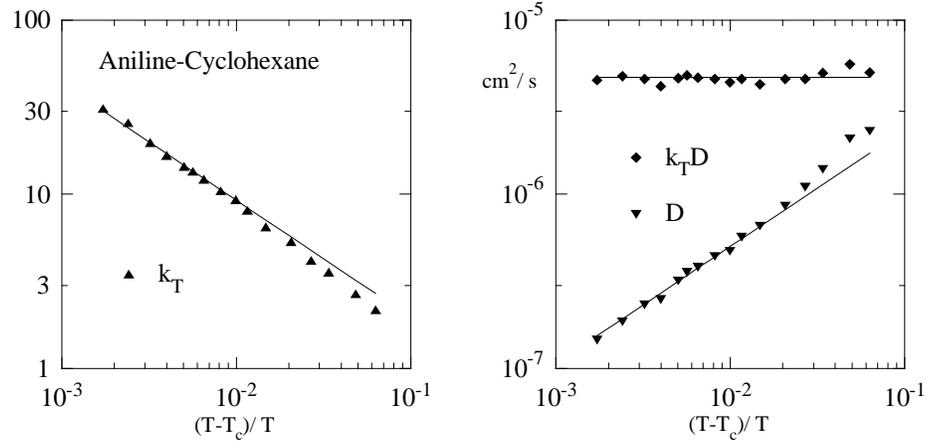


Fig. 2. Thermal diffusion data as a function of reduced temperature near the consolute point of an aniline-cyclohexane mixture. The symbols represent experimental data [49], the lines represent the (asymptotic) power laws

with increasing distance from the critical point. This is typical for the crossover behavior of binary mixtures near consolute points. Folk and Moser [21] have applied dynamic RG results to this mixture and find good agreement between their crossover theory and experimental data over the whole temperature range. Note that, as predicted by dynamic RG, the experimental values for $k_T D$ remain constant throughout the critical region.

Thermodiffusion near plait points was investigated for mixtures of ^4He - ^3He by Horst Meyer and co-workers [50,51]. In Fig. 3 we present thermal diffusion data [50,51] in the critical region of a ^4He - ^3He mixture with mole-fraction $x(^3\text{He}) = 0.8$. Also included in the figure are the asymptotic predictions of Eqs. (37)–(38). In this case, the asymptotic power laws do not describe the experimental data. Instead, the experimental values for the thermal diffusion ratio k_T seem to diverge with an exponent of 1.23 [51], almost twice as high as the asymptotic prediction of 0.67. Until recently, the situation was similar for the thermal conductivity λ_T near plait points. Experiments [51,52] suggested a pure-fluid like divergence of λ_T near a plait point, in contrast to the asymptotic prediction for mixtures that λ_T approach a finite value at the critical point, cf. Eq. (35). It was not until Sakonidou *et al.* [37,53] performed thermal conductivity measurements near the vapor-liquid critical point of a methane-ethane mixture, that the limiting finite behavior of the thermal conductivity near a plait point was observed experimentally. These data also confirmed the predicted crossover [23,25] from the pure-fluid like behavior at some distance from the critical point to the mixture-like behavior, $\lambda_T \sim \text{const.}$, very close to the critical point. In Fig. 4 we present mode-coupling predictions [25] for thermal diffusion in a CO_2 -ethane mixture of mole-fraction $x(\text{ethane}) = 0.75$. Also shown are the asymptotic power laws of Eqs. (37)–(39). Just as seen for the ^4He - ^3He mixtures, the

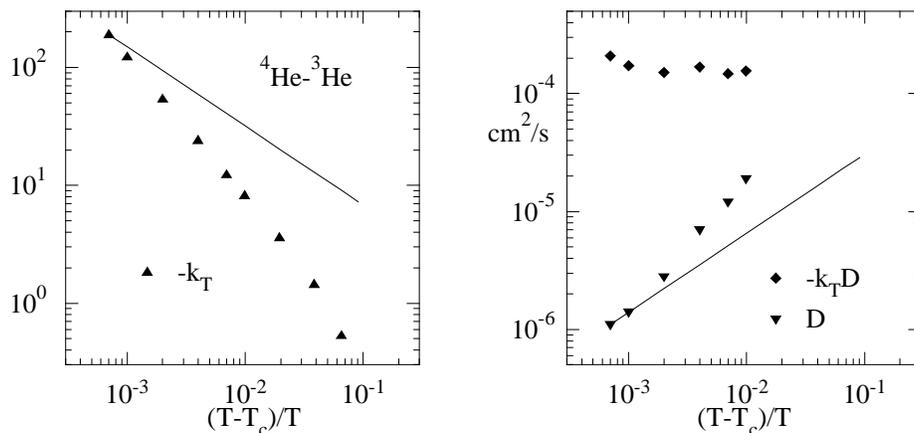


Fig. 3. Thermal diffusion data as a function of reduced temperature near the plait point of a ^4He - ^3He mixture. The symbols represent experimental data [50,51], the lines represent the asymptotic power laws

crossover thermal diffusion ratio increases much more rapidly than predicted from the asymptotic analysis for temperatures not too close to the critical point. For very small reduced temperatures, the crossover prediction [25] approaches the asymptotic power law (38), suggesting that the asymptotic critical region is extremely small and does not cover the temperature range, where experiments were performed on ^4He - ^3He mixtures. Folk and Moser [21] recently investigated

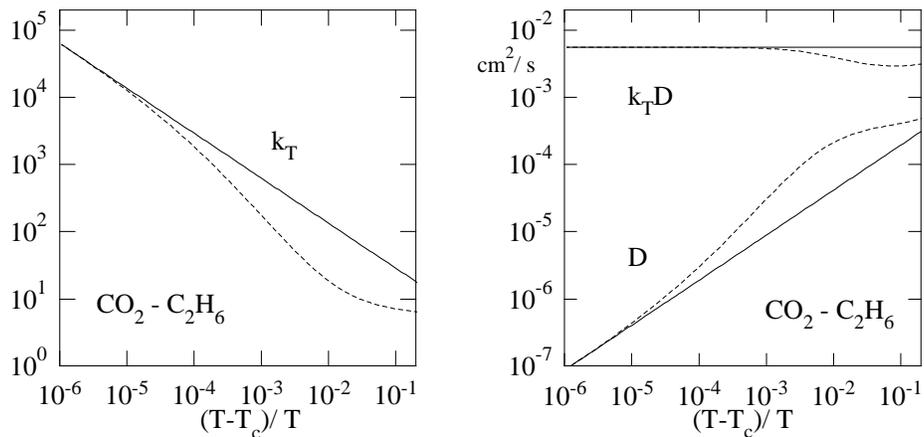


Fig. 4. Thermal diffusion near the plait point of a CO_2 -ethane mixture. The dashed lines represent predictions from a crossover model based on mode-coupling theory [25], the solid lines represent the asymptotic power laws

the critical dynamics (including sound absorption and sound attenuation) of ^4He - ^3He mixtures with the aid of dynamic renormalization-group calculations. A comparison of their results with experimental data shows generally good agreement between theory and experiment and confirms the non-asymptotic nature of the experimental data [50,51].

5 Discussion

In this contribution, we discussed scaling and universality for both static and dynamic properties of fluids mixtures. We compared experimental thermal diffusion data [49] for an aniline-cyclohexane mixture near its consolute point with the predicted asymptotic power laws and found that the experimental data confirm the asymptotic predictions as the temperature approaches the critical temperature closely. For temperatures farther away from the critical point, the data reflect the crossover [21] from the asymptotic critical to the classical region far away from the critical point. We also compared experimental thermal diffusion data for a ^4He - ^3He mixture near a plait point [50,51] with the asymptotic power laws. In this case, experiment and asymptotic prediction differ considerably over the whole temperature range where experiments were performed. By comparing this situation with experimental and theoretical results for other binary mixtures near plait points, we concluded that the asymptotic critical region in binary mixtures near plait points is smaller than in mixtures near consolute points. Furthermore, crossover models [21,25] are required to describe the critical behavior of transport properties near plait points in the whole experimentally accessible region.

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Supplementary glossary

T_c, ρ_c, P_c	critical temperature, density, pressure
$\Delta\tilde{T} = (T - T_c)/T$	reduced temperature
$\chi_T = \rho(\partial\rho/\partial P)_T$	symmetrized isothermal compressibility
ξ	correlation length
$\alpha \simeq 0.11, \gamma \simeq 1.239,$ $\eta \simeq 0.033, \nu \simeq 0.63$	static critical exponents
$z_\eta \simeq 0.063, z = 3 + z_\eta$	dynamic critical exponents
$\tilde{\eta}$	viscosity
L_{SS}	thermal conductivity in the absence of a concentration gradient
$k_T = c(1 - c)TS_T$	thermal diffusion ratio
$\tilde{\alpha}, \tilde{\beta}, \tilde{\gamma}, \tilde{\delta}$	Landau transport coefficients

Superscript

b indicates a background contribution

Prefix

Δ indicates a critical enhancement

Glossary of Symbols

c	concentration (weight fraction)
c_p	specific heat at constant pressure
c_v	specific heat at constant volume
D	mutual Diffusion coefficient
D_T	thermal diffusion coefficient
D_{th}	thermal diffusivity
F	Helmholtz free energy
k_B	Boltzmann's constant
Le	Lewis number
M	molar mass
Pr	Prandtl number
q	wave vector
t	time
Ra	Rayleigh number
Re	Reynolds number
Sc	Schmidt number
S_T	Soret coefficient (see below for sign convention): $S_T = D_T/D$
T	temperature
x	concentration (molar fraction)
u	fluid velocity
α	cubic expansion coefficient: $\alpha = -\frac{1}{\rho} \frac{\partial \rho}{\partial T}$
α_T	thermal diffusion factor: $\alpha_T = TS_T$
β	solubility expansion coefficient: $\beta = \frac{1}{\rho} \frac{\partial \rho}{\partial c}$
λ	wavelength of light
λ_T	thermal conductivity
μ	difference in chemical potential per unit mass between the two species in a binary mixture
ϕ	concentration (volume fraction)
ψ	separation ratio: $\psi = \frac{\beta}{\alpha} S_T c(1 - c)$
ρ	mass density

Sign convention for S_T and D_T

In a binary mixture of A and B, ' S_T of A' (and also D_T) is positive, if A migrates to the cold side. This implies that S_T of B must be negative, since B migrates to the hot side. Usually, one would specify S_T for the component that has been used for the definition of the concentration. Note that this definition does not depend on the densities of the two components.