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Universality Versus Nonuniversality of Critical Transport Properties in Liquid Mixtures

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The critical behavior near consolute points and plait points in mixtures and along lines connecting such points in the phase diagram belongs to the universality class of gas–liquid transitions in pure liquids. We give a survey of the results for the temperature dependence of transport coefficients, thermal conductivity, mass diffusion, and thermal–diffusion ratio, in mixtures within a non-asymptotic renormalization-group theory of critical dynamics. The observable critical behavior in some cases is nonuniversal and may be strongly concentration dependent. This is explained by different crossover temperatures in the singular Onsager coefficient of the order parameter and in the hydrodynamic transport coefficients. At the plait point the value of $(\partial c/\partial \sigma)_{P\Delta}$ determines the crossover to the asymptotic behavior in the transport coefficients, and its smallness explains the situation in ^{3}He–^{4}He mixtures. We also consider ionic solutions, where long-range forces may be present. The dynamical universality class in this case is different from that of mixtures with short-range interaction. As well as the "classical" static behavior for sufficient long-range interaction potentials, the dynamical critical behavior depends on the exponent of the power law for the spatial decrease in this interaction. This offers an additional possibility to determine this exponent by measuring the temperature dependence of the hydrodynamic transport coefficients.

KEY WORDS: dynamic critical phenomena; ^{3}He–^{4}He mixtures; ionic solutions; mixture critical points; renormalization-group theory; transport properties.

1. INTRODUCTION

Mixtures of liquids show a large variety of different phase diagrams [1] containing lines of critical points connecting liquid–vapor critical points

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(called plait points in the mixture), critical lines of consolute points ending in a pure liquid critical point, or lines leading from consolute points to plait points. All these phase transitions are expected to be in the same static and dynamic universality class [2, 3], namely, the universality class of the pure fluid [4]. That means in statics Ising model-like critical properties (a scalar order parameter) and in dynamics model H-like behavior (two nonlinearily coupled equations for the order parameter and the transverse momentum density [4]).

These expectations have been verified by a large amount of measurements in statics and dynamics; for a recent review see Refs. 5 and 6 and, especially, for the dynamics see Ref. 7. However, there have been prominent and striking exceptions: the dynamical critical behavior in ^{3}He–^{4}He mixtures at the plait point [8] and the static as well as dynamic critical behavior in ionic solutions [9].

The nonuniversal behavior of physical systems near a phase transition may have several reasons: (i) the systems are in fact not in the same universality class, and (ii) the experimental region is outside the asymptotic critical region. In the second case one may observe either a crossover between the asymptotic behavior belonging to two different fixed points or a crossover from the background to the asymptotics. The crossover may lie in the experimental region if there is a slow transient. A prominent example of this case is realized in the critical dynamics at the superfluid transition in ^{4}He [10], where one dynamical transient exponent is almost zero. For fluids no such small transient exponents appear [11] and one expects to observe the asymptotics in the region of $t \simeq 10^{-3}$. But even in absence of a slow transient, background terms may be dominant in physical quantities, since besides the development of the singular behavior governed by the flow of the dynamical parameters of the model, it is important how the singular part enters the quantity under consideration. This explaines the situation in the dynamics near the plait point of ^{3}He–^{4}He mixtures [12]. Although the singular Onsager coefficients (OCs) behave according to the asymptotic power law, the transport coefficients (TCs) do not show the asymptotic behavior, because the singular OC has a small amplitude compared to the noncritical OCs appearing in the TCs [13].

For the ionic fluids it seems to be the long-range Coulomb force which leads to a different (classical critical) behavior compared to nonionic fluids, but at the moment the situation is unclear and under discussion (for a recent review see Ref. 14). It is possible that either true asymptotic behavior or just a crossover to the pure fluid behavior with short-range interaction is observed. It may be that an effective interaction of strength $1/r^{3+\sigma}$ dominates. This leads to classical exponents in statics [15] for $\sigma < \frac{3}{2}$ and to nonclassical behavior in the dynamics for $\sigma > 1$ [16]. For the $1/r^4$

interaction the power law behavior of the OCs is replaced by powers of logarithms because one is at the dynamical borderline dimension $d_c = 2 + \sigma$ in $d = 3$. Near that border line dimension a small dynamical transient exponent appears.

2. MIXTURES WITH SHORT-RANGE INTERACTION

Transport properties at the liquid–vapor critical point in pure liquids are well understood within the renormalization-group theory (RNG) [4, 11] and mode-coupling theory (MCT) [17]. Two OCs behave singularly, leading to a thermal conductivity diverging like $t^{-x_\lambda \nu}$, $t = (T - T_c)/T_c$ and a shear viscosity diverging like $t^{-x_\eta \nu}$. Nonuniversal effects are weak but observable [5, 7]. In mixtures, however, the situation is less uniform. One expects at the phase transition a finite thermal conductivity (measured at zero mass flow), a mass diffusion which goes to zero like $t^{\gamma - x_\lambda \nu}$, a thermal-diffusion ratio diverging like $t^{-\gamma + x_\lambda \nu}$, and a shear viscosity diverging like $t^{-x_\eta \nu}$. At the consolute point [5, 7] this has been observed (again, nonuniversal effects are weak but observable), but at the plait point the behavior depends on the chemical composition of the mixtures and the concentration. Recent calculations within RNG [12, 13] have resolved this problem and are asymptotically in agreement with the mode-coupling theoretical ansatz. The disagreement with experiments on the thermal conductivity for ^{3}He–^{4}He mixtures [8] with the theoretical predictions of [18, 19] is due to the use of the static theoretical expression for $(dP/dT)_{v,c}$ in disagreement with experiment and not due to a disagreement of the dynamical theoretical part [20]. See also the recent mode-coupling calculations of Luettmer-Strathmann and Sengers [21].

The main points of the theoretical calculation of the TCs are (i) identification of the order parameter, (ii) identification of the singular OCs, (iii) separation of genuine dynamic and static quantities, (iv) calculation of the TCs as functions of static quantities and the OCs, and (v) calculation of the critical dynamics within a nonasymptotic RNG procedure [10].

Our starting point is the hydrodynamics of a mixture, which is described by the densities (per volume) of the conserved quantities such as entropy per volume s, mass density ρ of the mixture, mass density ρ_3 of the second liquid, and momentum current density $\mathbf{j}$. From hydrodynamics one has, for a mixture at rest ($\mathbf{j} = 0$) [22],

$$T \frac{\partial s}{\partial t} = -\nabla(\mathbf{q} - \Delta \mathbf{i}), \qquad \frac{\partial \rho_3}{\partial t} = -\nabla \mathbf{i} \tag{1}$$

The mass current $\mathbf{i}$ and the total heat current $\mathbf{q}-\Delta\mathbf{i}$ are linear functions of the gradient of the temperature T and the chemical-potential difference Δ. In lowest order, one has

$$\mathbf{i}=-\beta\,\nabla T-\alpha\,\nabla\Delta, \qquad \mathbf{q}-\Delta\mathbf{i}=-\gamma\,\nabla T-\delta\,\nabla\Delta \tag{2}$$

From Onsager symmetry one has $\beta=\delta/T$. With Eq. (2), the hydrodynamic equations, Eq. (1), are

$$\frac{\partial s}{\partial t}=\frac{\gamma}{T}\nabla^2 T+\beta\,\nabla^2\Delta, \qquad \frac{\partial \rho_3}{\partial t}=\beta\,\nabla^2 T+\alpha\,\nabla^2\Delta \tag{3}$$

The time development of the momentum density is determined by the linearized equation

$$\frac{\partial \mathbf{j}}{\partial t}=\left(\zeta+\frac{\eta}{3}\right)\nabla(\nabla\mathbf{v})+\eta\,\nabla^2\mathbf{v} \tag{4}$$

where η is the shear viscosity and ζ the bulk viscosity.

Equations (3) and (4) are the starting point of the mode-coupling theory, which assumes a similar behavior of the OCs α, β, γ according to a Stokes–Einstein diffusion law [23]. The TCs read

$$\begin{aligned} D&=\frac{\alpha}{\rho}\left(\frac{\partial\Delta}{\partial c}\right)_{PT}\\ \kappa&=\gamma-\frac{\beta^2 T}{\alpha}\\ k_T&=\left[\alpha\left(\frac{\partial\Delta}{\partial T}\right)_{Pc}+\beta\right]\frac{T}{\rho D}\end{aligned} \tag{5}$$

According to the assumptions about the singular behavior of the OCs and inclusion of background values of the OCs [24], one gets the critical behavior of the TCs.

We follow renormalization-group theory in order to calculate the singular contributions in the OCs and the TCs. We shall see that the singularities enter differently depending on the choice of the order parameter. For generality we take the order parameter as linear combination of the entropy per mass $\sigma=s/\rho$ and mass concentration $c=\rho_3/\rho$ fluctuations with coefficients depending on the form of the critical line in the phase diagram.

$$N_A^{1/2}\frac{\sigma}{R}=a_{11}\,y_1+a_{12}\,y_2, \qquad N_A^{1/2}c=a_{21}\,y_1+a_{22}\,y_2 \tag{6}$$

The a_{ij} are considered as functions of the thermodynamic fields temperature, pressure, and mean concentration [25]. They have to be taken from experiment, namely, the phase diagram of the mixture considered. The factor $N_A^{1/2}$, with N_A Avogadro's number, is chosen for convenience to transform the Boltzmann constant to the general gas constant in the thermodynamic expressions. The limiting case of the plait point $a_{11} = a_{22} = 1$, $a_{12} = a_{21} = 0$, and the consolute point $a_{11} = a_{22} = 0$, $a_{12} = a_{21} = 1$, have been treated in Ref. 12, and we shall frequently refer to these cases. To obtain a Hamiltonian which is invariant under order parameter inversion (no third-order term), and in which the order parameter is decoupled in quadratic order from the secondary density, we define the order parameter ϕ_0 and the second conserved density q_0 as

$$\phi_0 = y_1 - b_1, \qquad q_0 = y_2 - Q_1 \phi_0 \tag{7}$$

in which b_1 is a suitable static constant and

$$Q_1 = \frac{1}{W} \left\{ R \left(\frac{\partial c}{\partial \sigma} \right)_{P\Delta} \left[a_{11} a_{22} + a_{12} a_{21} + a_{11} a_{12} R \left(\frac{\partial T}{\partial \Delta} \right)_{Pc} \right] - a_{22} a_{21} \right\} \tag{8}$$

with

$$W = a_{22}^2 - a_{12} R \left(\frac{\partial c}{\partial \sigma} \right)_{P\Delta} \left[a_{12} R \left(\frac{\partial T}{\partial \Delta} \right)_{Pc} + 2a_{22} \right] \tag{9}$$

Neglecting the sound degrees of freedom [26], we restrict the expansion of the Landau–Ginzburg–Wilson Hamiltonian $\mathscr{H}$ to relevant terms only and include and the transverse part of the momentum density **j**. Then the Hamiltonian reads

$$\mathscr{H} = \int d^d x \left\{ \frac{1}{2} \mathring{\tau} \phi_0^2 + \frac{1}{2} (\nabla \phi_0)^2 + \frac{\mathring{u}}{4!} \phi_0^4 + \frac{1}{2} a_q q_0^2 + \frac{1}{2} \mathring{\gamma} q_0 \phi_0^2 + \frac{1}{2} a_j \mathbf{j}^2 \right\} \tag{10}$$

Standard calculations lead to the strong ($t^{-\gamma}$) and weak diverging ($t^{-\alpha}$) susceptibilities, which expressed by thermodynamic derivatives are

$$\langle \phi_0 \phi_0 \rangle_c = \frac{WT}{Y^2 R \rho} \left(\frac{\partial \sigma}{\partial T} \right)_{P\Delta}, \qquad \langle q_0 q_0 \rangle_c = \frac{RT}{W\rho} \left(\frac{\partial c}{\partial \Delta} \right)_{P\sigma} \tag{11}$$

with $Y = a_{11} a_{22} - a_{12} a_{21}$. The subscript c denotes the cummulant $\langle AB \rangle_c = \langle AB \rangle - \langle A \rangle \langle B \rangle$. With Eq. (10) the critical behavior of Eq. (11) can be calculated within a perturbation expansion. Since in the following the static parts are taken directly from experiment, rather than from a theoretical calculation (see e.g., Ref. 27), we do not further treat the static model given by Eq. (10).

2.1. Dynamic Equations and Transport Coefficients

Let us now turn to the dynamics, which is our main concern. Proceeding in the standard way we derive the dynamical equations by considering the Poisson brackets between the variables above and including irreversible terms compatible with the statics and the hydrodynamic equations Eqs. (3) and (4). We recover model H' in the notation of Ref. 4 for *any* linear combination of the entropy density and concentration fluctuation, Eq. (7).

$$\frac{\partial \phi_0}{\partial t} = \mathring{L}_{11} \nabla^2 \frac{\delta \mathcal{H}}{\delta \phi_0} + \mathring{L}_{12} \nabla^2 \frac{\delta \mathcal{H}}{\delta q_0} - \mathring{g}(\nabla \phi_0) \frac{\delta \mathcal{H}}{\delta \mathbf{j}} + \Theta_\phi \tag{12}$$

$$\frac{\partial q_0}{\partial t} = \mathring{L}_{12} \nabla^2 \frac{\delta \mathcal{H}}{\delta \phi_0} + \mathring{L}_{22} \nabla^2 \frac{\delta \mathcal{H}}{\delta q_0} - \mathring{g}(\nabla q_0) \frac{\delta \mathcal{H}}{\delta \mathbf{j}} + \Theta_q \tag{13}$$

$$\frac{\partial \mathbf{j}}{\partial t} = \mathring{L}_j \nabla^2 \frac{\delta \mathcal{H}}{\delta \mathbf{j}} + \mathring{g} \mathcal{T} \left((\nabla \phi_0) \frac{\delta \mathcal{H}}{\delta \phi_0} + (\nabla q_0) \frac{\delta \mathcal{H}}{\delta q_0} \right) + \mathbf{\Theta}_j \tag{14}$$

The Onsager coefficients $\mathring{L}_{11}$, $\mathring{L}_{12}$, $\mathring{L}_{22}$, and $\mathring{L}_j$ are related to the fluctuating forces Θ_i $(i = \phi, q, j)$ via Einstein relations. The mode-coupling is $\mathring{g} = RT/N_A^{1/2}$ and $\mathcal{T}$ is the projector transversal to the direction of the wave-vector $\mathbf{k}$.

The limiting cases treated so far were the dynamics at the plait point, where σ was taken as order parameter, and the dynamics at the consolute point, where c has been taken as order parameter. The independence of the model equations on the choice of the order parameter reflects the fact that all phase transitions on the critical line are in the same universality class and the OCs contain the same singularities.

With Eqs. (12)–(14) in this model we have calculated the nonasymptotic expressions for the TCs D, κ, and k_T, which are valid in the crossover region from background behavior to the asymptotic critical behavior and which can be compared with the experimental data. The theoretical approach is in the same spirit as in the case of the superfluid transition in ^{4}He [10] and ^{3}He–^{4}He mixtures [28], although the reason for the non-asymptotic behavior is different as we see below. The renormalization is performed by absorbing the dimensional singularities in Z-factors [11] leading to renormalized parameters L_{11}, L_{12}, L_{22}, L_j, and g.

To proceed we introduce dynamical parameters for the model by the diffusion time ratio w and the mode-coupling f,

$$w = \frac{L_{12}}{\sqrt{L_{11} L_{12}}}, \qquad f = \frac{g}{\sqrt{L_{11} L_j}} \tag{15}$$

The variation of the renormalized parameters under renormalization is described by the flow equations, which are in one loop-order,

$$l\frac{dw}{dl}=\frac{3}{8}wf^2, \qquad l\frac{df}{dl}=-\frac{1}{2}f\left(\varepsilon-\frac{3}{4}f^2-\frac{1}{24}\frac{f^2}{1-w^2}\right) \tag{16}$$

where $\varepsilon=4-d$ is the distance from the upper critical dimension above which the behavior is classical, which means the OCs are uncritical. The flow parameter l is related to the inverse correlation length, and in this way it is a measure for the distance to T_c. In the asymptotic region the parameters reach their fixed-point values which determine the critical exponents; they are found as $f^*=f^*_{\text{fluid}}$, the fixed-point value for the pure liquid [4], and $w^*=0$.

The OCs are then calculated as a function of the model parameters. We define renormalized OCs as (note that no static parts appear in these definitions)

$$\tilde{L}_{11}(l)=L_{11}(l)\exp\int_1^l\frac{-3}{4}f^2(l')\frac{dl'}{l'} \tag{17}$$

$$\tilde{L}_j(l)=L_j(l)\exp\int_1^l\frac{-1}{24}\frac{f^2(l')}{1-w^2(l')}\frac{dl'}{l'} \tag{18}$$

with the amplitudes in one-loop order,

$$L_{11}(l)=L_{11}\left(1-\frac{1}{16}f^2(l)\right), \qquad L_j(l)=L_j\left(1-\frac{1}{36}\frac{f^2(l)}{1-w^2(l)}\right) \tag{19}$$

The coefficients L_{12} and L_{22} remain constant. The temperature dependence of the OCs follows from the flow equations, Eqs. (16), together with two nonuniversal initial conditions in the background. There is no slow transient (the dynamical transient exponents ω_f and ω_w are of $O(1)$ [11], and therefore it is sufficient to parameterize the OCs as (see Fig. 1)

$$\begin{aligned}\tilde{L}_{11}(t)&=\hat{L}_{11}t^{-x_\lambda\nu}+L_{11}, &\qquad \tilde{L}_{12}&=L_{12}\\ \tilde{L}_j(t)&=\hat{L}_jt^{-x_\eta\nu}+L_j, &\qquad \tilde{L}_{22}&=L_{22}\end{aligned} \tag{20}$$

with the exponent $x_\lambda=\frac{3}{4}f^{*2}$ and $x_\eta=\frac{1}{24}f^{*2}$ in one-loop order (one may include the two-loop terms of the pure fluid [4]). In this way crossover temperatures for the OCs $t_{L_{11}}^{x_\lambda\nu}=\hat{L}_{11}/L_{11}$ and $t_{L_j}^{x_\eta\nu}=\hat{L}_j/L_j$ may be defined. They are expected to be within the order of 10^{-2}. All other OCs are unrenormalized and enter the expressions of the TCs as background parameters.

The next step is to identify the TCs by comparing the model equations with the hydrodynamic equations, Eqs. (3). This identification depends on

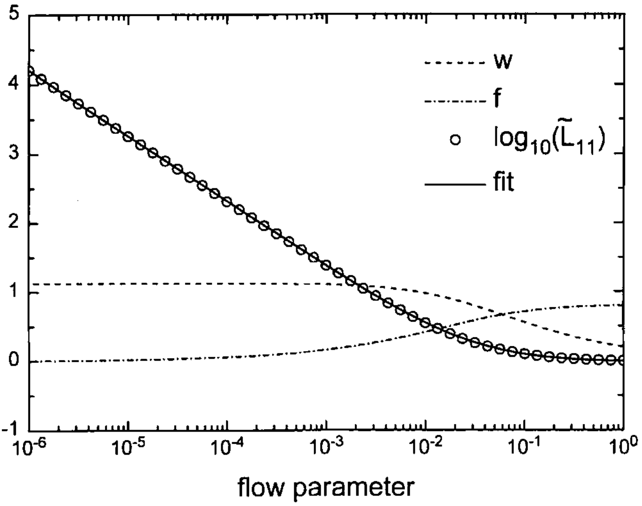

Fig. 1. Solutions of the flow equations, Eqs. (16), and resulting model OC $\tilde{L}$ of Eq. (17) (open circles). The dependence of $\tilde{L}$ is fitted by the simple form corresponding to Eqs. (20).

the choice of the order parameter. The isothermal diffusion constant D, the thermal conductivity in the absence of mass flow κ, the thermal diffusion ratio k_T, and the shear viscosity η are

$$\begin{aligned} D(t) = \frac{\rho}{RTY\chi_c} \Bigg\{ & Y^2 \frac{a}{W}\left[a_{11} + \frac{a_{12}}{b}\right] [a_{11}\tilde{L}_{12} - (a_{21} - a_{11}Q_1)\,\tilde{L}_{11}(t)] \\ & + W\left(\frac{\partial\sigma}{\partial T}\right)_{P\Delta}\left(\frac{\partial T}{\partial\sigma}\right)_{Pc} [(a_{22} - a_{12}Q_1) + (a_{21} - a_{11}Q_1)\,b] \\ & \times [a_{11}\tilde{L}_{22} - (a_{21} - a_{11}Q_1)\,\tilde{L}_{12}]\Bigg\} \end{aligned} \tag{21}$$

$$\frac{\kappa(t)}{\rho T} = \frac{Y^2\rho^2}{T^2\chi_c D(t)}(\tilde{L}_{11}(t)\,\tilde{L}_{22} - \tilde{L}_{12}^2) \tag{22}$$

$$\begin{aligned} \frac{k_T(t)}{T} = \frac{1}{a_{11} + (a_{12}/b)} \Bigg\{ & \frac{\rho}{T}\frac{W}{aD(t)}[(a_{21} - a_{11}Q_1)\,\tilde{L}_{12} \\ & - a_{11}\tilde{L}_{22}] - a_{11}\left(\frac{\partial c}{\partial T}\right)_{P\sigma}\Bigg\} \end{aligned} \tag{23}$$

$$\eta(t) = \frac{\tilde{L}_j(t)}{RT} \tag{24}$$

with the static functions $\chi_c = (\partial c/\partial \Delta)_{PT}$, $a = R(\partial c/\partial \sigma)_{P\Delta}$, and $b = (1/R)(\partial \sigma/\partial c)_{PT}$. Asymptotically we recover the temperature behavior of the TCs known from the consolute point and plait point $D = D_a t^{\gamma - x_\lambda \nu}$, $\kappa = \kappa_c$, $k_T = k_{Ta} t^{-\gamma + x_\lambda \nu}$, and $\eta = \eta_a t^{-x_\eta \nu}$, where the a_{ij} have to fulfill the condition

$$\frac{a_{21} - a_{11} Q_1}{a_{22} - a_{12} Q_1} = -a \qquad \text{or} \qquad \frac{a_{22} - a_{12} Q_1}{a_{21} - a_{11} Q_1} = -b \tag{25}$$

depending on the sign of the determinant of the coefficient matrix.

At the plait point, where one has $a_{11} = a_{22} = 1$, $a_{12} = a_{21} = 0$, $Y = 1$, $Q_1 = a$, Eqs. (21)–(23) reduce to

$$D(t) = \frac{\rho}{RT\chi_c} (\tilde{L}_{22} + a^2 \tilde{L}_{11}(t) + 2a\tilde{L}_{12}) \tag{26}$$

$$\frac{\kappa(t)}{\rho T} = \frac{\rho^2}{T^2 \chi_c D(t)} (\tilde{L}_{11}(t)\, \tilde{L}_{22} - \tilde{L}_{12}^2) \tag{27}$$

$$\frac{k_T(t)}{T} = -\frac{\rho}{TaD(t)} (\tilde{L}_{22} + a\tilde{L}_{12}) \dot{-} \left(\frac{\partial c}{\partial T}\right)_{P\sigma} \tag{28}$$

while at the consolute point, with $a_{11} = a_{22} = 0$, $a_{12} = a_{21} = 1$, $Y = -1$, $Q_1 = b$, Eqs. (21)–(23) reduce to

$$D(t) = \frac{\rho \tilde{L}_{11}(t)}{RT\chi_c}, \quad \frac{\kappa(t)}{\rho T} = \frac{R\rho}{T} \left(\tilde{L}_{22} - \frac{\tilde{L}_{12}^2}{\tilde{L}_{11}(t)} \right), \quad \frac{k_T(t)}{T} = R\chi_c \frac{\tilde{L}_{12}}{\tilde{L}_{11}(t)} \tag{29}$$

It must be remarked that in Refs. 12 and 16 rescaled OCs L_{ij} were used (κ should be replaced by $\kappa/\rho T$ there) and we use here a dimensionless entropy density σ/R. Comparing Eqs. (26)–(28) with Eq. (29) makes clear why the observable behavior of the TCs at the consolute point is so much different from the plait point. At the consolute point the mass diffusion is directly proportional to the critical OC and therefore its critical behavior is not masked by other noncritical OCs. A nonasymptotic behavior would be purely the result of the flow equations, which may not have reached the fixed point values (small $t_{L_{11}}$). However the mass diffusion at the plait point contains the singular OC, multiplied by $(\partial c/\partial \sigma)_{P\Delta}^2$, *besides* the nonsingular OCs. Even if the flow has reached the fixed point values of the dynamical parameters and the OCs behave according to the asymptotic power law, one may not observe the true asymptotic behavior of the TCs depending on the relative strength of the singularity with respect to the nonsingular OCs.

2.2. Crossover Temperatures

A straightforward application of the theory, using the flow equations for the comparison with experiment at the plait point, is not convenient at this stage for several reasons: (i) we have the theoretical uncertainties because of using the one-loop expressions only; (ii) apart from experimental uncertainties in static quantities, the coefficient $a=R(\partial c/\partial\sigma)_{P\Delta}$ is not completely defined, because of the freedom in the definition of the entropy at the phase transition line (see also Ref. 20) (we do not need the explicit value of a but only its concentration dependence, however, going back to the model OCs the value of a has to be known); (iii) the dynamic background values [as initial parameters of the flow equations, Eqs. (16)] remain parameters of the theory anyway; and (iv) we do not want to use the viscosity data for the analysis of the TCs in Eqs. (21)–(23), because we did not introduce the "Kawasaki amplitude" for the plait point (see Ref. 13) and because we want to use a minimal number of experimental TCs (often only the thermal conductivity is the only available TC). Therefore, we take the nonasymptotic expressions for the OCs given by Eq. (20). In this way we may introduce amplitudes and crossover temperatures instead of the four adjustable dynamic parameters $\hat{L}_{11}$, L_{11}, L_{12}, and L_{22} in the TCs. We may write for the strongly diverging static susceptibility

$$\chi_c=\chi_0(1+(t/t_\chi)^{-\gamma}) \tag{30}$$

and we assume that the static parameters χ_0 and t_χ are known from experiment [8].

The new independent parameters are t_D, t_κ, D_0, κ_0.

$$D=D_0\frac{1+(t/t_D)^{-x_\lambda\nu}}{1+(t/t_\chi)^{-\gamma}} \tag{31}$$

The thermal conductivity

$$\kappa=\kappa_0\frac{1+(t/t_\kappa)^{-x_\lambda\nu}}{1+(t/t_D)^{-x_\lambda\nu}} \tag{32}$$

and the thermal-diffusion ratio

$$k_T/T=\bar{k}_T/T\frac{1+(t/t_\chi)^{-\gamma}}{1+(t/t_D)^{-x_\lambda\nu}}+A(1+(t/t_{\mathrm{cp}})^{-\alpha}) \tag{33}$$

where $\bar{k}_T$ can be expressed by the parameters in D and κ and a weak diverging static susceptibility enters. No new dynamical crossover temperature is defined for k_T. The introduced amplitudes and crossover temperatures are found by comparing Eqs. (31)–(33) with Eqs. (21–(23). We discuss only the two limiting cases of the plait point and consolute point (t_κ is the same in all cases). At the plait point we have

$$t_D^{x_\lambda \nu} = \frac{a^2 \hat{L}_{11}}{L_{22} + a^2 L_{11} + 2aL_{12}} < t_{L_{11}}^{x_\lambda \nu} \tag{34}$$

$$t_\kappa^{x_\lambda \nu} = \frac{\hat{L}_{11} L_{22}}{L_{11} L_{22} - L_{12}^2} > t_{L_{11}}^{x_\lambda \nu} \tag{35}$$

Since the matrix of the OCs is positive definite, one can prove that in any case $t_D < t_\kappa$.

At the consolute point we have

$$t_D^{x_\lambda \nu} = t_{L_{11}}^{x_\lambda \nu} \tag{36}$$

$$t_\kappa^{x_\lambda \nu} = \frac{\hat{L}_{11} L_{22}}{L_{11} L_{22} - L_{12}^2} > t_{L_{11}}^{x_\lambda \nu} \tag{37}$$

We see that the small crossover temperature in the case of the plait point is caused by the smallness of the static amplitude a and therefore is not related to the usual correction terms in the OCs. Even when the singular OC $\tilde{L}_{11}$ behaves according to the asymptotic power law, this would not be seen in the experimental accessible region if a is sufficiently small (small t_D).

The vanishing of a is expected to govern the crossover from the plait-point behavior to the pure-fluid behavior in the mass diffusion and, more importantly, in the thermal conductivity. In this limit $X \to 0$ (X is the mean molar concentration; corresponding behavior holds in the limit $X \to 1$), the values of the involved quantities are

$$\chi_c \sim X, \qquad t_\chi^\gamma \sim X, \qquad a \sim X, \qquad L_{22} \sim X, \qquad L_{12} \sim X \tag{38}$$

Then the parameters have the limiting values

$$t_D \to 0, \qquad t_\kappa \to \frac{\hat{L}_{11}}{L_{11}}, \qquad D_0 \to \frac{L_{22}}{\chi_0}, \qquad \kappa_0 \to L_{11} \rho T \tag{39}$$

and κ diverges at T_c as

$$\kappa = \hat{\kappa} t^{-x_\lambda \nu}, \qquad \hat{\kappa} = \hat{L}_{11} \rho T \tag{40}$$

The surprising fact is that even in mixtures near 50% ^{3}He, in ^{4}He where a should be largest, t_D is so small that it lies outside the experimental accessible region and one observes pure liquid-like behavior in the thermal

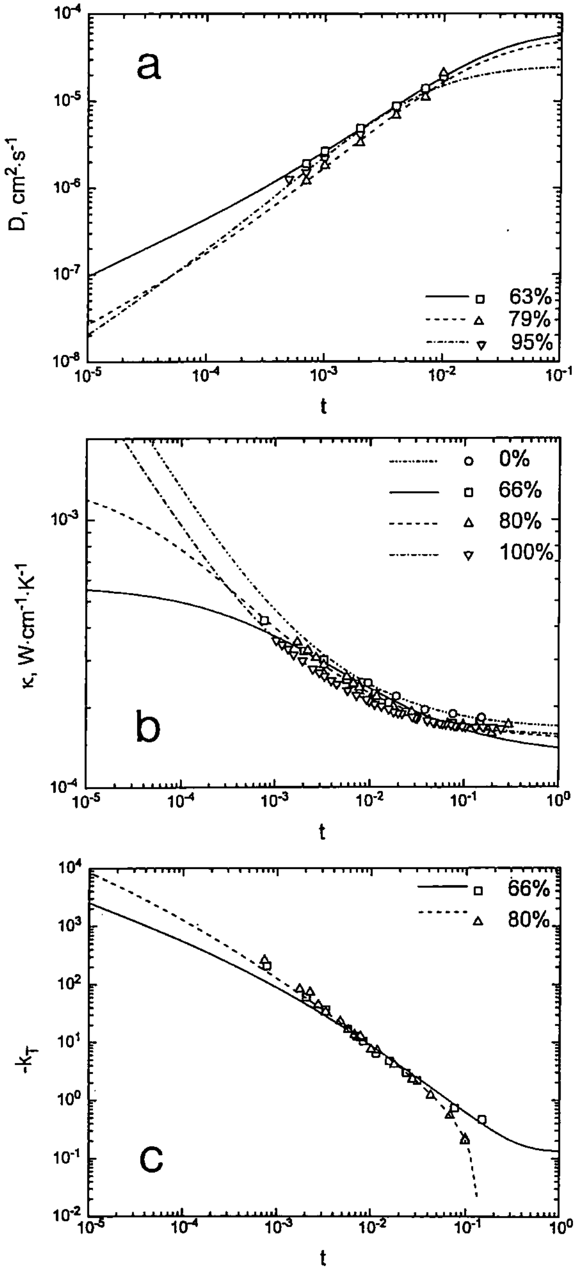

Fig. 2. (a) Mass diffusion as a function of temperature for different molar concentrations of ^{3}He in ^{4}He. Data from Ref. 30; lines are fits with Eq. (31). (b) Thermal conductivity as a function of temperature for different molar concentrations. Data from Ref. 31 for mixtures and Ref. 32 for pure fluids; lines are fits with Eq. (32). (c) Thermal diffusion ratio as a function of temperature for different molar concentrations. Data from Ref. 29; lines are fits with Eq. (33) (from Ref. 12).

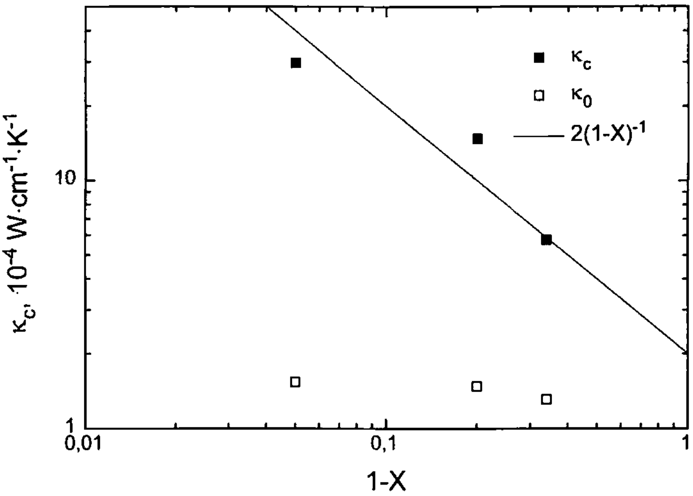

Fig. 3. Thermal conductivity in the background κ_0 and at $T_c\kappa_c$ in the mixtures according to Eq. (41) with the values obtained from the fits shown in Fig. 2. For the concentration $X=0.95$ we have taken t_κ and κ_0 from $X=1$.

conductivity [29]. This is seen from a fit of the experimental data (Fig. 2), where the extrapolation of κ demonstrates the crossover to a finite value at T_c for the mixtures. The value of κ at T_c can be expressed by the fit parameters

$$\kappa_c = \frac{Rp^2 L_{22}}{a^2} = \kappa_0 \left(\frac{t_\kappa}{t_D}\right)^{x_\lambda \nu} \tag{41}$$

and, according to the concentration dependence from above, should diverge as X^{-1} for $X \to 0$. This is compatible with our fits (see Fig. 3).

3. FLUIDS WITH LONG-RANGE INTERACTION

Measurements of *statics* in ionic solutions near the consolute point or near the critical point in metallic fluids showed classical critical behavior [33–37]. It is suspected that the Coulomb interaction (to some extent screened) or other molecular multipol interactions lead to an effective interaction of long range of the type $r^{-3-\sigma}$ with $0<\sigma<2$ (the exponent σ may not be confused with the entropy density), but the specific type of the effective interaction remains unclear. Recently, light-scattering measurements of dynamical quantities such as the mass diffusion at the consolute point have been performed [35–37]. Therefore it is of interest to study the dynamics for such systems [16]. We shall see that even if the statics is classical, the dynamics may be nonclassical. Because of the interaction the critical behavior belongs to a new universality class.

We consider now, instead of Eq. (10), the Hamiltonian (in Fourier space) [15]

$$\mathscr{H} = \int d^d k \frac{1}{2} \{ (\tau + k^\sigma) \phi_k \phi_{-k} + a_q q_k q_{-k} + a_j \mathbf{j}_k \mathbf{j}_{-k} \}$$

$$+ \frac{u}{4!} \int d^d k \int d^d k_1 \int d^d k_2 \phi_k \phi_{k_1} \phi_{k_2} \phi_{-k-k_1-k_2} \tag{42}$$

where the long-range interaction leads to the k^σ instead of a k^2 term for the short-range interaction. It has been shown in Ref. 15 that in the case of $0 < \sigma < 1.5$, the static exponents are "classical," $\gamma = 1$, $\beta = \frac{1}{2}$, $\alpha = 0$, but $\nu = 1/\sigma$ and $\eta = 2 - \sigma$, fulfilling the usual scaling laws. Therefore measurements of ν or η can give information about the parameter σ governing the range of the effective interaction.

Let us now turn to the dynamics, which is our main concern. The model equations are the same as Eqs. (12)–(14) if we consider the mixture. For the pure fluid Eq. (13) for q_0 and the respective terms in the other equations would be absent.

A dimensional analysis shows that the dynamical critical dimension above which the mode-coupling terms are irrelevant is given by

$$d_c^{\text{dynamic}} = 2 + \sigma \tag{43}$$

This may be compared with $d_c^{\text{static}} = 2\sigma$, which is always below the dynamical critical dimension. Therefore in the region $1 < \sigma < 1.5$ the statics are "classical," whereas the dynamics show nonclassical critical behavior. For $0 < \sigma < 1$ the OCs remain noncritical.

Proceeding as in Section 2, the flow equations in one-loop order at $d = 3$ are

$$l \frac{dw}{dl} = a(\sigma) w f^2 \qquad l \frac{df}{dl} = -\frac{1}{2} f \left(\sigma - 1 - b(\sigma) f^2 - c(\sigma) \frac{f^2}{1 - w^2} \right) \tag{44}$$

with $a(\sigma)$, $b(\sigma)$, $c(\sigma)$ found in Ref. 16. The fixed-point values are $w^* = 0$ and $f^{*2} \sim (\sigma - 1)$. The OCs follow, then, again in one-loop order,

$$L_{11}(l) = L_{11} \left(1 - \left(\frac{1}{2 + \sigma} \right)^2 f^2(l) \right) \tag{45}$$

$$L_j(l) = L_j \left(1 - \frac{\sigma(24 + 46\sigma + 17\sigma^2 + \sigma^3)}{24(2 + \sigma)^2 (4 + \sigma)^2} \frac{f^2(l)}{1 - w^2(l)} \right) \tag{46}$$

The temperature dependence of the OCs is given by the flow equations, Eqs. (16), together with suitable initial conditions in the background. A slow transient may appear near $\sigma = 1$ [the dynamical transient exponents ω_f and ω_w are now $O(\sigma - 1)$], nevertheless, we may simply parameterize the OCs as in Eq. (20). The corresponding exponents in one-loop order are found to be (remember $\varepsilon = 2 + \sigma - d$; thus for $d = 3$ we have simply $\varepsilon = \sigma - 1$)

$$x_\lambda = \frac{12(4+\sigma)}{48 + 12\sigma + \sigma^2}(\sigma - 1), \qquad x_\eta = \frac{\sigma^2}{48 + 12\sigma + \sigma^2}(\sigma - 1) \tag{47}$$

They fulfill in $d = 3$ the exact relation

$$x_\lambda + x_\eta = \sigma - 1 \tag{48}$$

However, the crossover temperatures for the OCs $t_{L_{11}}^{x_\lambda \nu} = \hat{L}_{11}/L_{11}$ and $t_{L_j}^{x_\eta \nu} = \hat{L}_j/L_j$ may now become smaller than 10^{-2}. In fact for $\sigma = 1$ the temperature dependence of the TCs is given by powers of logarithms. For $\sigma = 1$ the fixed point value for the mode-coupling is zero but is reached only logarithmically. For $w(1) = 0$ Eq. (44) for $f(l)$ reduces to

$$l\frac{df}{dl} = \frac{31}{90} f(l)^3 \tag{49}$$

with the solution

$$f(l) = \left(\frac{1}{f^2(1)} - \frac{31}{45}\ln(l)\right)^{-1/2} \tag{50}$$

Therefore from

$$\begin{aligned} \tilde{L}_{11}(l) &= L_{11}(l) \exp \int_1^l \frac{-2}{3} f^2(l')\frac{dl'}{l'} \\ \tilde{L}_j(l) &= L_j(l) \exp \int_1^l \frac{-1}{90} f^2(l')\frac{dl'}{l'} \end{aligned} \tag{51}$$

with the amplitudes given in Eqs. (45) and (46) we arrive at

$$\tilde{L}_{11}(t) \sim |\ln t|^{2/3}, \qquad \tilde{L}_j(t) \sim |\ln t|^{1/90} \tag{52}$$

An important quantity in light-scattering experiments is the Kawasaki amplitude [38] in $d = 3$, which is defined by the following ratio involving

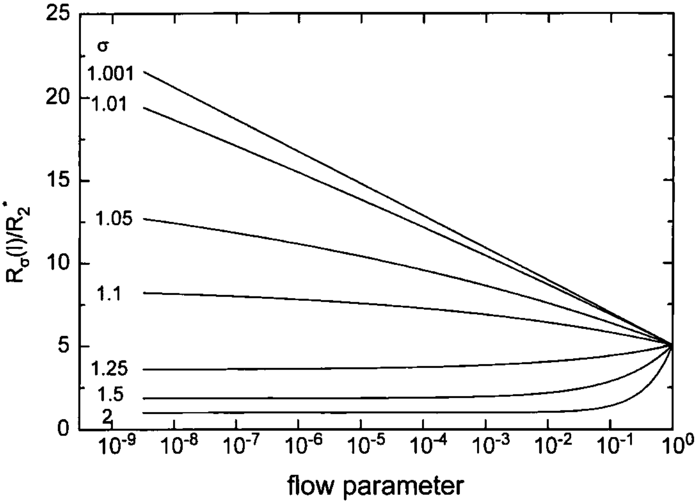

Fig. 4. The ratio of the nonasymptotic Kawasaki amplitude for the long-range interacting liquid to the asymptotic value of this amplitude for the short-range interacting liquid as a function of the flow parameter l for different values of σ (from Ref. 16).

the thermal diffusion $D_R = D_T = \kappa/\chi$ for the pure fluid or the mass diffusion $D_R = D$ for the mixture at the consolute point and the shear viscosity

$$\mathcal{R}_\sigma(t) = \frac{D_R(t)\,\bar{\eta}(t)\,\xi(t)}{k_B T} \tag{53}$$

It reaches a universal value for $T \to T_c$, whose value relative to the value in liquids with short-range interaction reads

$$\frac{\mathcal{R}_\sigma^*}{\mathcal{R}_2^*} = \frac{1}{\sigma - 1}\,r(\sigma) \tag{54}$$

In the range $2 \geqslant \sigma \geqslant 1$ $r(\sigma)$ decreases from $r(2) = 1$ only by 4% and therefore one can use $r(\sigma) = 1$. The amplitude is formally divergent when one approaches the dynamical critical dimension. This is an artifact of the asymptotic expression one has to consider in the case of a small fixed-point value of f and, because of small slow transients, the nonasymptotic expression of the amplitude [10]. The dependence of this nonasymptotic amplitude on σ and on the flow parameter l is shown in Fig. 2 for the pure liquid [$w(l) \equiv 0$ in Eq. (18)] in the lowest approximation

$$\frac{\mathcal{R}_\sigma(l)}{\mathcal{R}_2^*} = \frac{24}{19 f(l)^2} \tag{55}$$

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