Nonuniversal Dynamical Crossover in Pure and Binary Fluids near a Critical Point

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We compare the results of dynamical renormalization group theory with experiments in the nonasymptotic region at second order phase transitions in liquids and mixtures. Agreement is found with a parameter free prediction of the full temperature dependence of transport coefficients and first sound attenuation after fitting one transport coefficient (e.g., shear viscosity). Differences in the nonuniversal behavior between fluids and mixtures appear due to the flow of a dynamical parameter neglected in the mixtures so far.

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Renormalization group theory (RGT) has shown that the gas-liquid and liquid-liquid second order phase transitions in pure fluids [1] and mixtures [1,2] belong to the same universality class. The proof of universality and the calculation of universal values of exponents and amplitude ratios is considered as one of the main tasks in the field of second order phase transitions [3]. However, the experimentally accessible region is in most cases outside the asymptotic region where strict universality holds. Therefore it is necessary to take into account nonuniversal effects. So far such effects within RGT have only been taken into account by linear correction terms with transient exponents. A description analogous to the one at the superfluid transition in ^{4}He and ^{3}He-^{4}He mixtures ([4,5]; for a review see [6]) is demanded. Here we compare the recent theoretical results of such a nonasymptotic theory [7], which describes the *full* temperature dependence of the transport properties in the critical region, with experiment. Asymptotically RGT relates different time scales via the universal values of amplitude ratios. This also holds in the nonasymptotic regime, where the universal ratios are replaced by temperature dependent functions, which allow us to relate various physical quantities. Thereby we follow the strategy developed for the superfluid phase transition [6], but which is applicable quite generally.

In a pure fluid at its critical point only one time scale exists for the diverging transport coefficients (TCs), thermal conductivity κ and shear viscosity $\bar{\eta}$. This property manifests itself in the universality of the value of the Kawasaki amplitude [8] (measured relative to its mode-coupling value of $1/6\pi$) $R_{\exp}^{\text{pure}} = 6\pi\kappa_{\exp}(t)\bar{\eta}_{\exp}(t)\xi(t)/k_B T\rho C_p(t)$ in the asymptotic region, related to the asymptotic scaling law (in $d=3$) $x_\lambda + x_\eta = 1 - \eta$ [1,9], where x_λ and x_η are the critical exponents of the thermal conductivity and shear viscosity, respectively. η is the exponent, appearing in the static order parameter correlation function, ξ the correlation length, and ρC_p the specific heat per volume. At $T = T_c$ it is expected that $R_{\exp}^{\text{pure}}$ reaches the universal value R_{theor}^* [1,7,9,10]. We calculated within the model H [1] describing the critical dynamics of the pure fluid phase transition (as limiting values of the corresponding expressions for the plait point [7]) the thermal conductivity

$$\kappa_{\text{theor}}(t) = \xi^{-2}(t)\rho C_p(t)\Gamma^{(d)}(t)\left(1 - \frac{f^2(t)}{16}\right) \quad (1)$$

and the shear viscosity

$$\bar{\eta}_{\text{theor}}(t) = \frac{k_B T}{4\pi}\,\xi(t)\,\frac{1 - f^2(t)/36}{\Gamma^{(d)}(t) f^2(t)}, \quad (2)$$

using the field theoretical version of RGT in one loop order with $\eta = 0$. The dynamic parameters $f(t)$ and $\Gamma^{(d)}(t)$ are found from their flow equations (in one loop order)

$$\ell\,\frac{df}{d\ell} = -\frac{1}{2} f\left(1 - \frac{19}{24} f^2\right), \qquad \ell\,\frac{d\Gamma^{(d)}}{d\ell} = -\frac{3}{4}\,\Gamma^{(d)} f^2, \quad (3)$$

where the flow parameter ℓ is related to the temperature $t = (T - T_c)/T_c$ by $\ell = \xi_0\xi^{-1}(t)$. The nonuniversality enters the expressions via the initial conditions of the flow equations. That means two background values $\Gamma(t_0)$ and $f(t_0)$ have to be taken from experiment. Inserting the theoretical results into the definition of the Kawasaki amplitude one obtains its theoretical counterpart $R_{\text{theor}}^{\text{pure}} = 3[1 - f^2(t)/16][1 - f^2(t)/36]/2f^2(t)$. For $t = 0$, f reaches its fixed point value $f^{*2} = \frac{24}{19}$ and the Kawasaki amplitude its universal value $R_{\text{theor}}^* = 1.056$. This value for R_{theor}^* differs from the one loop value of Siggia, Halperin, and Hohenberg [1] $R_{\text{theor}}^* = 0.8$ mainly due to a different geometrical prefactor used in the field theoretical calculation ($1/4\pi$ instead of $1/2\pi^2$), but differs also in the one loop order terms [11]. Our value is near the value calculated by Paladin and Peliti [10] $R_{\text{theor}}^* = 1.038$ and the mode-coupling value $R_{\text{theor}}^* = 1$ [8]. If we calculate the vertex functions at $d = 3$ instead of performing an ϵ expansion, we obtain $R_{\text{theor}}^* = 1.063$. So our asymptotic values are within the range of the experimental values found

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so far. The dynamical critical exponents take the values $x_\lambda = 0.95$ and $x_\eta = 0.05$.

We now compare our results for the TCs with measurements in several fluids. For that purpose we insert the experimental static quantities in evaluating the theoretical expressions. The correlation length, in most cases not directly measured, is found from the two-scale factor hypothesis and the hyperscaling law [12]. We note that uncertainties of the representation of the static quantities (values of amplitudes and exponent in power laws) lead to uncertainties in the absolute values of the predicted TCs [13].

Our results for ^{3}He are presented in Fig. 1. First we fit the shear viscosity data [14] by Eq. (2) with the initial conditions $\Gamma(t = 10^{-1})$ and $f(t = 10^{-1})$ as fit parameters [see Fig. 1(a)]. Then we predict *without any further parameter* the thermal conductivity by Eq. (1) and compare with the thermal conductivity of [15] [see Fig. 1(b)]. As an additional test we also compared with the sound attenuation data of [16] [see Fig. 1(c)]. The nonasymptotic expression as a function of frequency ω and reduced temperature t has been calculated in [17] $\alpha(t,\omega) = [\omega^2/2c_1^3(t,\omega)]D_1(t,\omega)$ where $c_1(t,\omega)$ and $D_1(t,\omega)$ are determined by a complex function $y(t,\omega)$ via the relations $c_1^2(t,\omega) = \Re[y(t,\omega)]$ and $D_1(t,\omega) = -\omega^{-1}\Im[y(t,\omega)]$. The complex function is given by the expression

$$y(t,\omega) = \frac{a_q}{RT\rho}\,\frac{c^2(\ell(t,\omega))}{1 + [\gamma_q^2(\ell(t,\omega))/2]F_+(\ell(t,\omega),\omega)}\,. \tag{4}$$

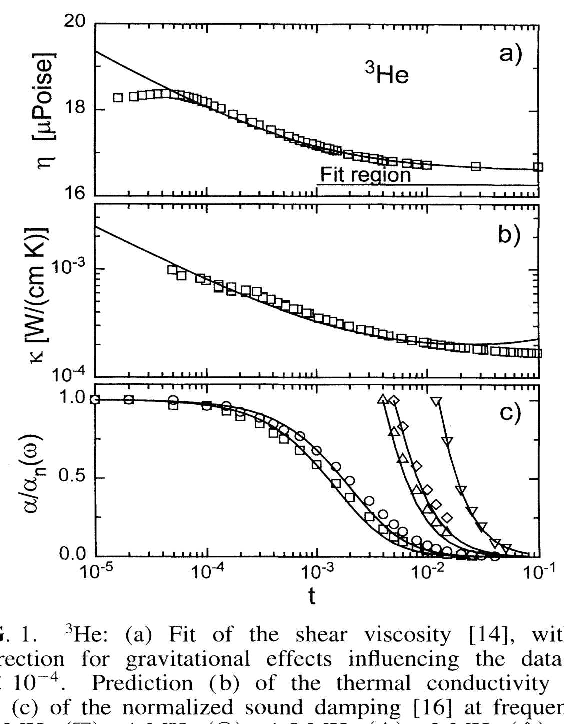

FIG. 1. ^{3}He: (a) Fit of the shear viscosity [14], without correction for gravitational effects influencing the data for $t < 10^{-4}$. Prediction (b) of the thermal conductivity [15] and (c) of the normalized sound damping [16] at frequencies 0.5 MHz (□), 1 MHz (○), 1.5 MHz (△), 3 MHz (◇), and 5 MHz (▽). The normalization $\alpha_n(\omega)$ is the value of the sound attenuation of the data point nearest to T_c for each frequency.

a_q, $\gamma_q(\ell)$, and $c^2(\ell)$ can be determined from static experimental quantities quite analogous to the λ transition in ^{4}He [18]. $F_+(\ell,\omega)$ is related to the frequency dependent specific heat, and the flow parameter ℓ is identified by the relation $|[\xi(t)^{-2}/(\xi_0^{-1}\ell)^2]^2 + 2i\omega/\Gamma^{(d)}(\ell) \times (\xi_0^{-1}\ell)^4|^2 = 1$. The same quality of agreement has been obtained with the corresponding data for ^{4}He [13]. As a second example for our comparison we chose ethane. Again from a fit of the shear viscosity [19] we calculate the thermal diffusivity, $D_T = \kappa/\rho C_p$, and compare with the data of [20] (see Fig. 2). For a recent comparison with experiment within mode-coupling theory see [21]. It is interesting to note that the value of $R^*_{\rm theor}$ adopted in their analysis agrees with our one loop value.

Let us now turn to binary mixtures. The critical behavior at the consolute point belongs to the same universality class as the gas-liquid phase transition in pure fluids. The dynamical model, however, differs (model H′ [1]) since there is now an additional equation for the entropy density besides the equation for the order parameter (concentration fluctuation). There are four TCs to be calculated: the mass diffusion, the thermal conductivity, the thermal diffusion ratio, and the shear viscosity. Universality means that the respective asymptotic critical exponents and amplitude ratios take the same values as in the pure fluid case [7].

In particular, for the mass diffusion we find

$$D_{\rm theor}(t) = \xi^{-2}(t)\Gamma^{(d)}(t)\left(1 - \frac{f^2(t)}{16}\right) \tag{5}$$

and for the shear viscosity

$$\bar\eta_{\rm theor}(t) = \frac{k_B T}{4\pi}\,\xi(t)\,\frac{1 - \frac{1}{36}f^2(t)/[1 - w^2(t)]}{\Gamma^{(d)}(t)f^2(t)}\,. \tag{6}$$

The dynamic parameter $f(t)$ and the new one $w(t)$ (see [7] for details) are found from the flow equations

$$\ell\frac{df}{d\ell} = -\frac{1}{2}f\left(1 - \frac{3}{4}f^2 - \frac{1}{24}\frac{f^2}{1 - w^2}\right),$$
$$\ell\frac{dw}{d\ell} = \frac{3}{8}wf^2, \qquad \ell\frac{d\Gamma^{(d)}}{d\ell} = -\frac{3}{4}\Gamma^{(d)}f^2. \tag{7}$$

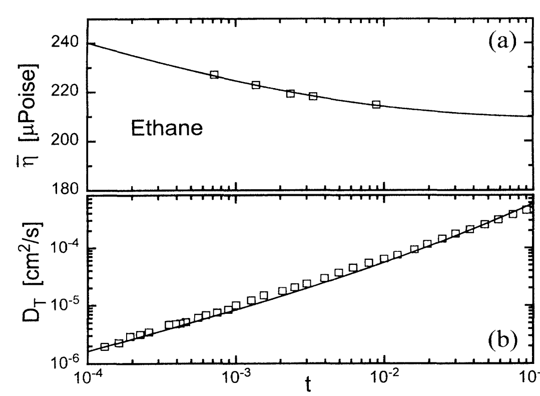

FIG. 2. Ethane: (a) Fit of the shear viscosity [19]. (b) Prediction of the thermal diffusivity [20].

The parameter w has not been considered explicitly in [1]; its fixed point value is $w^* = 0$. However, it contributes a subleading exponent $\omega_w = \frac{1}{2}x_\lambda$ [7], which is smaller than the exponents considered in the analysis of [22], and it will turn out important in the nonasymptotic analysis as is shown below. The Kawasaki amplitude reads now $R_{\rm exp}^{\rm cons} = 6\pi D_{\rm exp}(t)\bar{\eta}_{\rm exp}(t)\xi(t)/k_BT$ and inserting our theoretical expressions we get $R_{\rm theor}^{\rm cons} = 3[1 - f^2(t)/16](1 - \frac{1}{36}f^2(t)/[1 - w^2(t)])/2f^2(t)$.

Less attention has been paid to the two other TCs, the thermal conductivity κ and the thermal diffusion ratio k_T. The thermal conductivity is finite at T_c, but it has a critical enhancement. The thermal diffusion ratio diverges asymptotically like the inverse mass diffusion. For a quantitative prediction one additional time scale has to be determined from experiment [if $w(t)$ is nonzero]. This may be either the scale μ of the thermal conductivity or the time scale L of the thermal diffusion ratio. The other TC is then fixed by the flow already determined. We found [7] $D(t)k_T(t) = \rho L/R = \text{const}$ *in the whole crossover region* where both D and k_T are nonasymptotic. This temperature independence is an *exact* result within renomalization group theory in agreement with experiments in aniline-cyclohexane mixtures [23]. The thermal conductivity reads

$$\frac{\kappa_{\rm theor}(t)}{\rho T} = \frac{\mu\rho}{RT}\left(1 - \frac{w^2(t)}{1 - f^2(t)/16}\right). \tag{8}$$

We estimate the enhancement of the thermal conductivity as $\kappa_{\rm theor}(t = 0)/\kappa_{\rm theor}(t_0) \sim [1 - w^2(t_0)]^{-1}$.

We now compare $\bar{\eta}$ and D with experiments in aniline-cyclohexane mixtures. Again we fit the shear viscosity data [24] [see Fig. 3(a)] (ξ we take from [25]) and then predict the mass diffusion [26–28] [see Fig. 3(b)]. In the analysis of [26] the asymptotic Kawasaki amplitude (taking the mode-coupling value) has been used to relate the different temperature dependent physical quantities. Here we use the temperature dependence calculated by RGT for the TCs, and after fixing three parameters $[f(t_0), w(t_0), \Gamma^{(d)}(t_0)]$ we predict the temperature dependence D. It turns out that the mass diffusion behaves almost asymptotically although the shear viscosity does not. This is possible since $w(t)$ enters D only indirectly. Whereas f has almost reached its asymptotic value, w maintains to decrease from its initial value $w(t = 0.03) \sim 0.9$ to zero. The flow of $w(t)$ could be most directly checked by measuring the resulting enhancement of the thermal conductivity. From our analysis we guess roughly an enhancement of 65% in the region 10^{-2} to 10^{-4}. A more detailed study of this case and other mixtures will be given elsewhere.

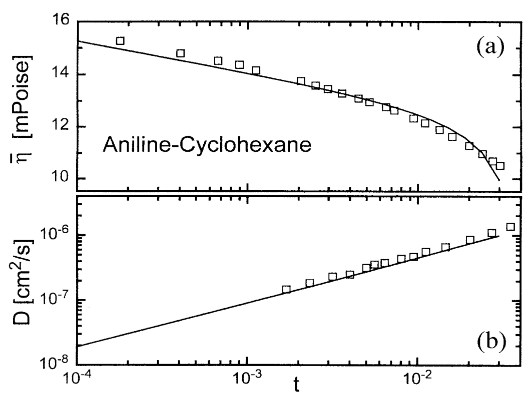

FIG. 3. Aniline-cyclohexane: (a) Fit of the shear viscosity [24]. (b) Prediction of the mass diffusion coefficient [28].

We have found surprisingly good agreement of nonasymptotic field theoretic RGT in one loop order with the critical transport properties in several fluids. This may be the basis of future more quantitative work in this field and supplements the results obtained by mode-coupling theory (for recent developments in pure liquids see [21] and in mixtures at the plait point [29], for a review [30]). More precise measurements of static quantities are needed, e.g., the correlation length should be known experimentally. Regarding the thermal conductivity at the consolute point we suggest to look for the critical enhancement in order to verify the flow of $w(t)$. On the theoretical side it would be worthwhile to include the two loop expressions. Our one loop value for x_η seems to be systematically too small. Measurements of sound attenuation are an additional test for the consistency of the nonasymptotic RGT description and are highly desirable.

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