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Critical transport and critical scattering in fluids

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We consider the critical properties of fluids induced by the critical fluctuations in the order parameter. The theory describes the crossover from the analytic background behaviour to the universal asymptotic behaviour of several dynamic quantities.

Key words: *gas-liquid phase transition, critical dynamics, light scattering, transport coefficients*

PACS: *05.70.Jk, 64.60.Ht, 64.70.Fx, 64.70.Ja*

1. Introduction

Collective effects dominate near the phase transition while there arises a critical behaviour quite different from the behaviour further away from the critical point. These critical phenomena are seen in the experiments in a more or less wide region round the critical point. E.g., the thermal conductivity of a pure liquid diverges strongly, with an exponent of $\mathcal{O}(1)$, whereas the shear viscosity diverges weakly, with an exponent of $\mathcal{O}(0.1)$, as a function of the relative temperature distance from the critical point with some power law in the region asymptotically near the critical temperature T_{c}. Outside this region, a normal analytic behaviour is observed. A delicate point is the strength of the critical behaviour compared to the noncritical or background behaviour and determining the background values of the transport properties. Depending on this strength, both types of behaviour can be separated with more or less accuracy. In a series of papers, the crossover behaviour from criticality to the background behaviour has been studied [1,2] and extended to mixtures [3]. The goal of these studies was the description of all dynamical quantities within the formalism of the field theoretic formulation of renormalization group (RG) theory [4]. One advantage of the nonasymptotic RG-theory is that the calculations lead directly to the complete value (without the analytic temperature dependence) of the transport coefficients in the background and no separation of the fluctuation contribution as in the mode coupling theory has to be performed [5].

An important issue in the description of the critical behaviour is the appropriate choice of the collective variables [7] connected to the so-called order parameter (OP).

In statics near the liquid-gas critical point in pure liquids these are the deviations of the density from the critical density, in dynamics according to model H [8] it is the entropy density fluctuation $\Delta\sigma$, and we introduce the order parameter field ϕ_0 given by

$$\phi_0(x) = \sqrt{N_{\mathrm{A}}}(\triangle\sigma(x) - \langle\triangle\sigma(x)\rangle) \ . \tag{1}$$

In addition, one has to consider the tranverse momentum current $\boldsymbol{j}_t$ which is dynamically coupled to the OP. The Hamiltonian describing thermodynamic equilibrium is

$$H = \int \mathrm{d}^d x \ \Big\{ \frac{1}{2} \overset{o}{\tau} \phi_0^2(x) + \frac{1}{2}(\boldsymbol{\nabla}\phi_0(x))^2 + \frac{\overset{o}{\tilde{u}}}{4!}\phi_0^4(x) + \frac{1}{2}a_j \boldsymbol{j}_t^2(x) \Big\} \ , \tag{2}$$

and the dynamic equations are

$$\begin{aligned} \frac{\partial\phi_0}{\partial t} &= \overset{o}{\Gamma} \nabla^2 \frac{\delta H}{\delta\phi_0} - \overset{o}{g} (\boldsymbol{\nabla}\phi_0) \frac{\delta H}{\delta \boldsymbol{j}} + \Theta_\phi \ , & (3) \\ \frac{\partial \boldsymbol{j}_t}{\partial t} &= \overset{o}{\lambda}_t \nabla^2 \frac{\delta H}{\delta \boldsymbol{j}_t} + \overset{o}{g} \mathcal{T} \left\{ (\boldsymbol{\nabla}\phi_0) \frac{\delta H}{\delta\phi_0} \right\} \\ &\quad - \overset{o}{g} \mathcal{T} \left\{ \sum_k \left[j_k \boldsymbol{\nabla} \frac{\delta H}{\delta j_k} + \nabla_k \boldsymbol{j} \frac{\delta H}{\delta j_k} \right] \right\} + \boldsymbol{\Theta}_t \ . & (4) \end{aligned}$$

$\mathcal{T}$ is the projector to the direction of the transverse momentum density, which corresponds to a projection orthogonal to the wave vector in Fourier space. In the fast fluctuating forces $\Theta_i(x,t)$ $(i = \phi, t)$ memory effects are irrelevant and their Gaussian spectrum fulfils the Einstein relations

$$\langle \Theta_i(x,t) \ \Theta_j(x',t') \rangle = 2L_{ij}(x)\delta(t-t')\delta(x-x'), \tag{5}$$

where the matrix $[L_{ij}]$ of the diffusive modes is given by

$$[L_{ij}] = \begin{pmatrix} -\overset{o}{\Gamma} \nabla^2 & \\ 0 & -\overset{o}{\lambda}_t \nabla^2 \end{pmatrix} . \tag{6}$$

The nonrenormalized mode coupling is defined as $\overset{o}{g} = RT/\sqrt{N_{\mathrm{A}}}$ with the gas constant R and the Avogadro number N_{A}.

Within this model all static and dynamic critical properties can be calculated. One obtains especially the correlation functions, and from their half width the characteristic frequencies. In the hydrodynamic region the transport coefficients as functions of temperature result from these frequencies [1]. Our theory yields all these dynamical quantities as functions of the measurable correlation length ξ and the dynamical parameters entering the model equations (3) and (4). The most important is the renormalized mode coupling f_t (its nonrenormalized counterpart is $\overset{o}{g} / \sqrt{\overset{o}{\Gamma}\overset{o}{\lambda}_t}$). It's value for a certain temperature, wave vector or frequency, is determined by the solution (see equation (9) below) of a renormalization group equation and an appropriate matching condition.

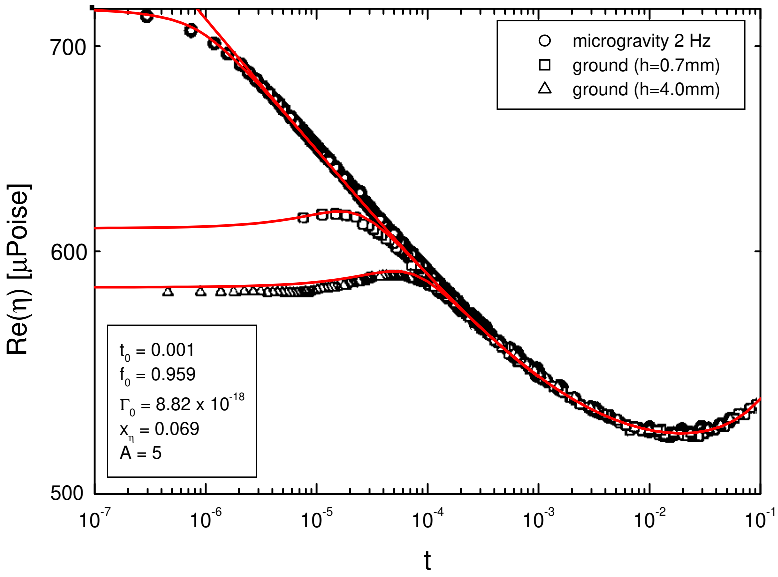

Figure 1. Shear viscosity of xenon [9] with and without gravity compared with RG theory.

2. Shear viscosity

The temperature and density dependent shear viscosity at zero frequency calculated within model H reads [2]

$$\bar{\eta}(t,\Delta\rho) = \bar{\eta}_0 \frac{1 - f_t^2(t,\Delta\rho)/36}{1 - f_0^2/36} \left(\frac{f_0^2 \xi(t,\Delta\rho)}{f_t^2(t,\Delta\rho)\xi(t_0)} \right)^{x_\eta} \equiv \bar{\eta}_0 \exp(x_\eta H(t,\Delta\rho)) \,, \tag{7}$$

with the amplitude

$$\bar{\eta}_0 = \frac{k_{\mathrm{B}}T}{4\pi} \frac{\xi(t_0)}{f_0^2 \Gamma_0} \left(1 - \frac{f_0^2}{36} \right) \,, \tag{8}$$

and the mode coupling

$$f_t^2(t,\Delta\rho) = \frac{24}{19} \left[1 + \frac{\xi(t_0)}{\xi(t,\Delta\rho)} \left(\frac{24}{19 f_0^2} - 1 \right) \right]^{-1} . \tag{9}$$

The dependence on the relative temperature distance from the critical temperature T_{c} and the relative density distance from the critical density ρ_{c} enters via the correlation length $\xi(t,\Delta\rho)$ which is obtained from the equations

$$t = \frac{T - T_{\mathrm{c}}}{T_{\mathrm{c}}} = (1 - b^2\theta^2)\, r \,, \tag{10}$$

$$\Delta\rho = \frac{\rho - \rho_{\mathrm{c}}}{\rho_{\mathrm{c}}} = k\,(\theta + c\,\theta^3)\, r^{\beta} \,, \tag{11}$$

$$\xi(t,\Delta\rho) = \xi_0\,(1 + 0.16\theta^2)\, r^{-\nu} = \xi_0\, t^{-\nu}\,(1 + 0.16\theta^2)(1 - b^2\theta^2)^{\nu} \,, \tag{12}$$

of the cubic model [6].

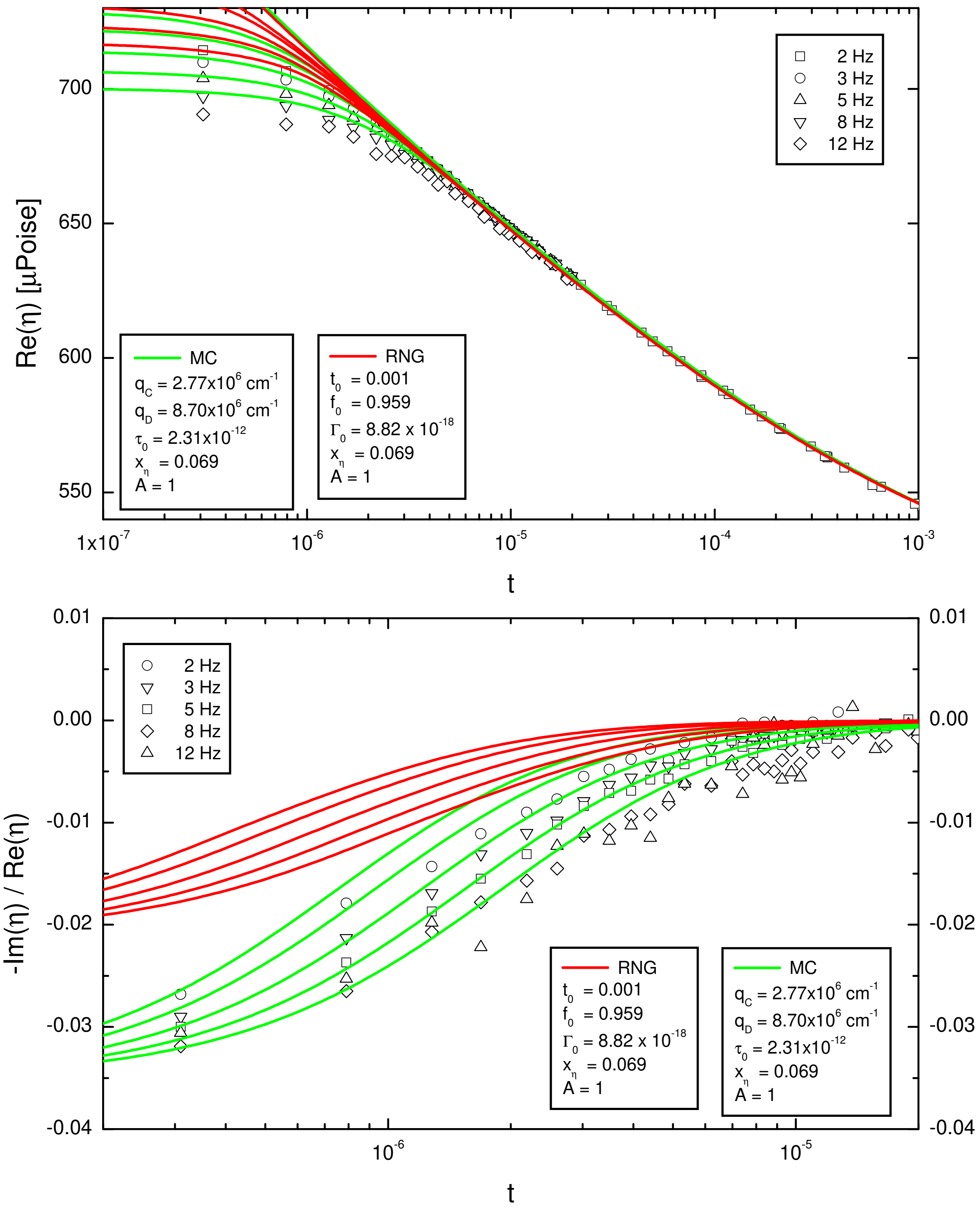

Figure 2. Comparison of the mode coupling theory [10] (light gray) and the RG theory (dark). Data from [9].

It is necessary to know the density dependence to calculate the gravity effects on the shear viscosity measurements on earth. Because of the finite height of the cell, a density gradient over the cell height is caused by gravity and depending on the positions of the oscillating disks by which the shear viscosity is measured a mean value of shear viscosities at different densities is measured. Since the gravity field is conjugated to the order parameter, the gradient over the cell increases when one approaches the critical temperature and this drives the shear viscosity away from the critical point at $t = \Delta\rho = 0$. Therefore it reaches a finite value instead of diverging near the critical point. This is demonstrated in figure 1 where two measurements on earth in different cells and the measurements on board the "Discovery" [9] are shown together with our calculations.

In the low gravity experiment, the frequency dependence of the shear viscosity can be observed. This is not possible on earth since the gravity effects already cover up the frequency effects. The frequency dependence of the shear viscosity was also calculated in one loop order [1,2] and we compare our result with the low gravity experiments [9] and mode coupling theory [10] in figure 2. No agreement is found in both theories. Introducing a phenomenological parameter into the frequency scale [9] agreement can be achieved in mode coupling theory for both the real part and the ratio of the real part to the imaginary part of the viscosity. This also holds for the RG-result for the real part of the viscosity (with a value different [11] from the mode coupling theory). The ratio of the real part to the imaginary part of the viscosity cannot be improved by this procedure since its limiting value at $T_{\rm c}$ is given by the universal one loop order result [11] ($f_t^{*2} = 24/19$)

$$\lim_{T\to T_{\rm c}} \frac{\Im(\eta)}{\Re(\eta)} = \frac{f_t^{*2}}{96}\frac{\pi}{2}\left[1 - \frac{f_t^{*2}}{96}\{3\ln(1/4) - 1/3\}\right]^{-1} \simeq 0.0195. \tag{13}$$

Within the mode coupling theory of [10,9] the value

$$\lim_{T\to T_{\rm c}} \frac{\Im(\eta)}{\Re(\eta)} = \tan\frac{\pi x_\eta}{2(3 + x_\eta)} \simeq 0.0353 \tag{14}$$

is obtained (the experimental value $x_\eta = 0.069$ of the shear viscosity exponent is used) and seems to be in agreement with the data. As a result, one might conclude that the one loop theory is not sufficient to describe the critical frequency dependence of the shear viscosity. A complete two loop calculation is in preparation [12].

3. Thermal diffusivity

For a complete description of the dynamic critical behaviour it is also necessary to consider the thermal conductivity or thermal diffusivity. Once the values of the nondynamical universal parameters such as Γ_0 and f_0 are determined, all quantities can be calculated from one theory. E.g., the thermal diffusivity reads

$$D_T(t,\Delta\rho) = D_0\frac{\xi^2(t_0)}{\xi^2(t,\Delta\rho)}\frac{\left(1 - \frac{f_t^2(t,\Delta\rho)}{16}\right)}{\left(1 - \frac{f_0^2}{16}\right)}\left(\frac{f_0^2\xi(t.\Delta\rho)}{f_t^2(t,\Delta\rho)\xi(t_0)}\right)^{x_\kappa}, \tag{15}$$

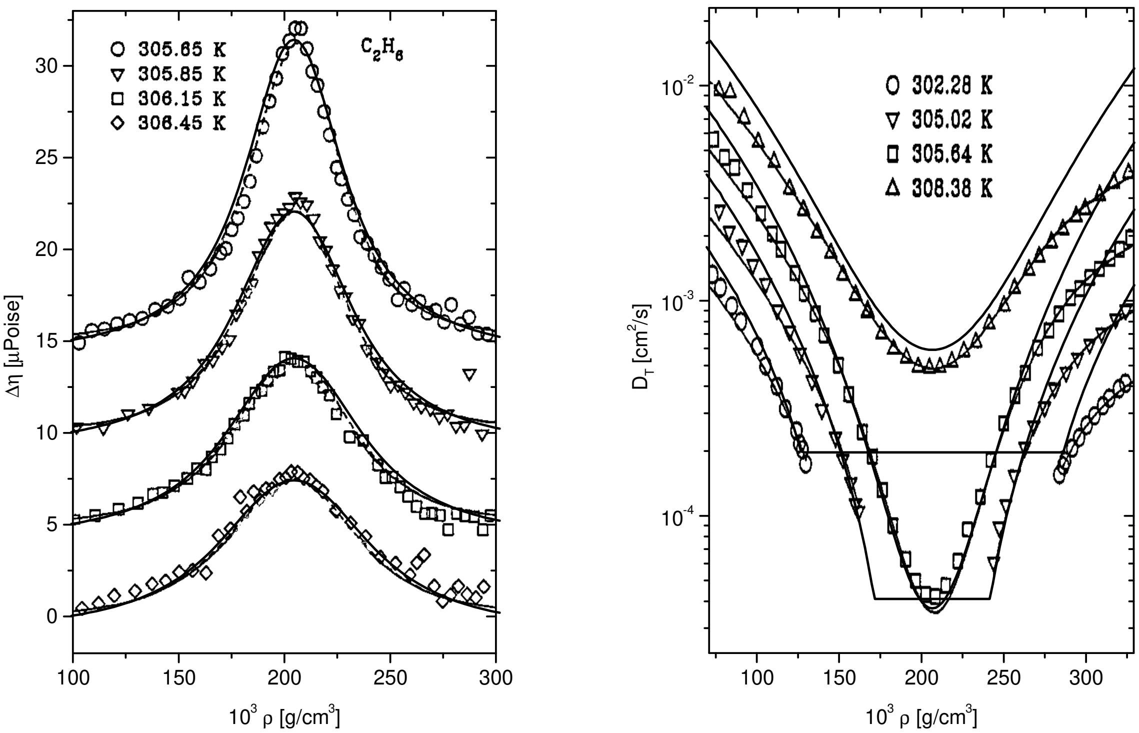

Figure 3. (a) Shear viscosity in C_2H_6 along various isotherms. The plot contains our results (thick curves) as well as experimental data [15] and theoretical results of the mode coupling theory (thin dashed curves) [14]. The curves were shifted by 5, 10 or 15 μPoise respectively for better clearness. (b) Thermal diffusivity in C_2H_6 along various isotherms. The plot contains our results (thick curves) as well as experimental data [16] and theoretical results of the mode coupling theory (thin curves) [14]. We have used the analytic background expressions of [17] (from [2]).

As an example the comparison of a calculation of the shear viscosity and the thermal diffusivity is shown in figure 3. Only the shear viscosity data at $\Delta\rho = 0$ are used to determine the nonuniversal parameters. It should be mentioned that an extension of such calculations to sound propagation is possible and it has also been considered for pure fluids in [1] and for mixtures in [3].

4. Scaling for pure fluids

The dynamic scaling assumption states that the dynamic correlation function $\chi_{\rm dyn}$ of the OP in the asymptotic region is a homogeneous function of its variables and can be written in the form (see [13])

$$\chi_{\rm dyn}(\xi, k, \omega) = \frac{\chi_{\rm st}(\xi, k)}{\omega_{\rm c}(\xi, k)} F\left(\frac{\omega}{\omega_{\rm c}(\xi, k)}, k\xi\right). \tag{16}$$

The characteristic frequency ω_c (we define the half width at half height) is also a homogeneous function

$$\omega_c(\xi, k) = k^z f(k\xi), \tag{17}$$

where the frequency is measured in an appropriate time scale. The static correlation function χ_{st} also scales as

$$\chi_{st}(\xi, k) = k^{-2+\eta} g(k\xi)\,, \tag{18}$$

and the shape function $F(y, x)$ ($y = \omega/\omega_c(\xi, k)$ and $x = k\xi$) fulfils the relations

$$\int \mathrm{d}y F(y, x) = 2\pi, \quad F(1, x) = \frac{1}{2}F(0, x). \tag{19}$$

Since the OP is conserved for the cases considered here, the correlation function has to be proportional to k^2 in the limit $k \to 0$. Neglecting static and dynamic interactions of fluctuations, conventional theory leads to the exponents $\eta = 0$ and $z = 4$ (for a nonconserved OP the exponent would be $z = 2$). Moreover, the shape function $F(y, x)$ is independent of x. RGT calculates the values of the exponents as $\eta \sim 0.04$ and $z = 4 - \eta - x_\lambda \sim 3$ since $x_\lambda \sim 0.916$ [8].

In addition to this considerable change of the exponent's values, the shape function $F(y, x)$ will depend on x. Let us now consider several regions in the (ξ^{-1}, k, ω)-space.

In the hydrodynamic region $k\xi \ll 1$ in fluids and mixtures the dynamic behaviour is described by diffusive modes, e.g. $\omega = Dk^2$ for the thermal diffusion, that means for the temperature dependence of the OP diffusion D

$$D(\xi) = \Gamma(\xi)/\chi_{st}(\xi) \sim \xi^{2-z}, \qquad \Gamma(\xi) \sim \xi^{2-z+\gamma/\nu} \tag{20}$$

with Γ the OP Onsager coefficient. In the conventional theory Γ is noncritical, whereas RGT predicts $\Gamma \sim \xi^{x_\lambda}$ (we have used the static scaling law $\gamma = \nu(2 - \eta)$). In the background both Γ, χ and D are temperature independent (apart from a weak analytic temperature dependence outside the scope of our considerations). Throughout the hydrodynamic regime, the shape of the correlation function is of Lorentzian form

$$\chi_{dyn}(\xi, k, \omega) = \chi_{st}(\xi, k) 2\,\Re \frac{1}{-\mathrm{i}\omega + D(\xi)k^2} \tag{21}$$

thus

$$F(y, x << 1) = 2\,\Re \frac{1}{\mathrm{i}y + 1}. \tag{22}$$

In order to consider the scaling laws in the critical region $k\xi \gg 1$ we may directly go to T_c. At T_c ($\xi = \infty$), the correlation function can be written as

$$\chi_{dyn}(k, \omega) \sim k^{-z-2+\eta} F(y, \infty) \tag{23}$$

since $\omega_c \sim k^z$ and $\chi_{st} \sim k^{-2+\eta}$. Because of the conservation property of the correlation function in the limit $k \to 0$ mentioned above and because its value is finite in

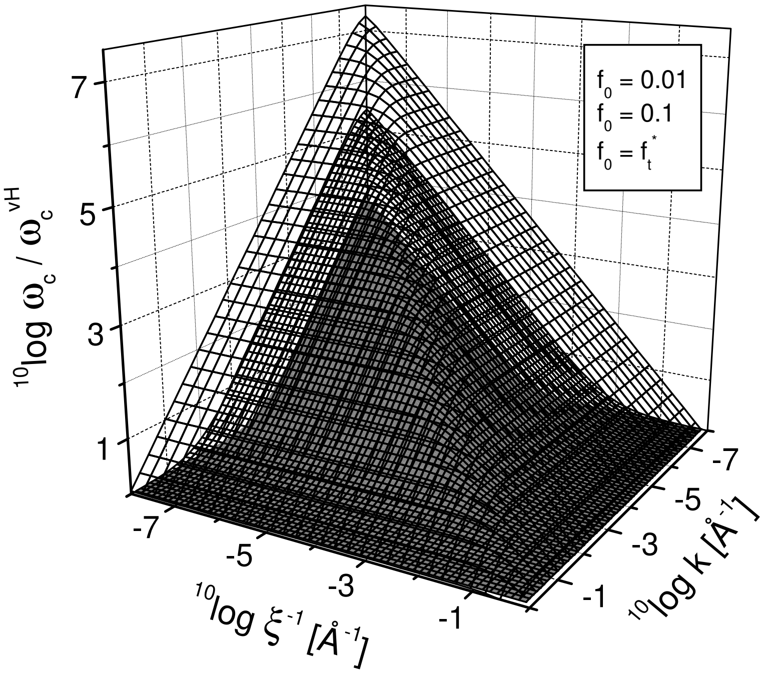

Figure 4. Ratio of the nonasymptotic characteristic frequency of the RG calculation to the characteristic frequency of the van Hove theory for different background values of the mode coupling f_0. Upper wide mash $f_0 = f^*$, next lower mash $f_0 = 0.1$, inner 'pyramid' $f_0 = 0.01$. For $f_0 = 0$ one obtains for the ratio the bottom plane. The smaller the value of the mode coupling the smaller is the region around the critical point $k = \xi^{-1} = 0$ where the asymptotic power laws are seen.

the limit $\omega \to 0$, the shape function behaves as

$$F(y, \infty) \sim \text{const}, \quad y \to 0; \tag{24}$$

$$F(y, \infty) \sim y^{-(z+4-\eta)/z}, \quad y \to \infty. \tag{25}$$

This shows that RGT predicts a non-Lorentzian shape at T_c since it decays faster in the scaled frequency, namely roughly as $y^{-2.3}$ instead of y^{-2}. In other words this demonstrates the non Markovian property of the OP time correlations.

5. Characteristic frequency

A complete calculation of the shape function and width in RG-theory is lacking. A one loop calculation gives no frequency dependent perturbational contribution to the order parameter vertex functions, which seems to be in contradiction to the scaling arguments of the preceding section. In the following we remain within the Lorentzian approximation for the correlation function, then the result of a nonasymptotic RG calculation of the characteristic frequency yields

$$\omega_c(k, x) = \Gamma_{as}\, k^z \left(\frac{1 + x^2}{x^2}\right)^{1 - x_\lambda/2} c_{na}^{x_\lambda}(k, x) f(k, x) \tag{26}$$

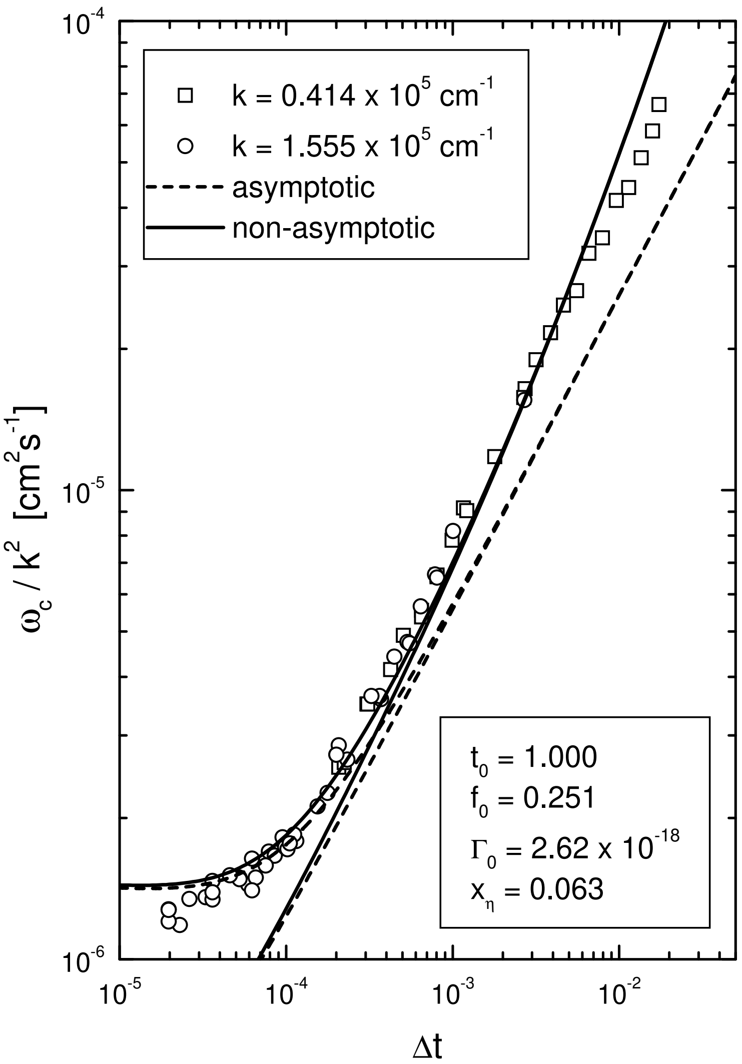

Figure 5. Nonasymptotic and asymptotic characteristic frequency ω_{c} as function of temeperature for diffenrent wave vectors k calculated in ε-expansion. Data for CO_2 from [18].

with

$$c_{\mathrm{na}}(k,x)=\left[1+\frac{k}{k_0}\sqrt{\frac{1+x^2}{x^2}}\right] \tag{27}$$

and

$$f(k,x)=1-\frac{3}{38\,c_{\mathrm{na}}(k,x)}\left[-5+6\,x^{-2}\,\ln(1+x^2)\right], \tag{28}$$

where

$$x=k\xi(t), \qquad \Gamma_{\mathrm{as}}=\Gamma_0\left(\frac{19}{24}\,\frac{f_0^2\ell_0}{\xi_0}\right)^{x_\lambda}, \qquad k_0^{-1}=\left(\frac{24}{19f_0^2}-1\right)\frac{\xi_0}{\ell_0}. \tag{29}$$

There are two dynamic non universal parameters. One of them, Γ_0, sets the scale of the frequency and the other one, the dimensionless mode coupling f_0, achieves the crossover from the van Hove theory ($f_0 = 0$, and $z = 4$)

$$\omega_{\mathrm{c,vH}} = \Gamma_0\, k^4 \left(\frac{1+x^2}{x^2}\right) \tag{30}$$

to the asymptotic theory ($f_0 = f^*$, $z \sim 3$)

$$\omega_{\mathrm{c,as}} = \Gamma_0 \left(\frac{\ell_0}{\xi_0}\right)^{x_\lambda} k^z \left(\frac{1+x^2}{x^2}\right)^{1-x_\lambda/2} \left(1 - \frac{3}{38}\left[-5 + 6\,x^{-2}\,\ln(1+x^2)\right]\right). \tag{31}$$

For any finite f_0, a crossover from the van Hove theory in the background to the asymptotics results near the critical point, $\xi \to \infty$ and $k \to 0$. In this case the asymptotic amplitude, Γ_{as} (29), of the characteristic frequency depends on the mode coupling f_0.

We rewrite the nonasymptotic expression for the characteristic frequency in the following form

$$\omega_{\mathrm{c}}(k,\xi) = \omega_{\mathrm{c,vH}}(k,\xi)\,(k\xi_0)^{-x_\lambda} \left(\frac{19}{24}\,f_0^2\ell_0\right)^{x_\lambda} \left(\frac{1+x^2}{x^2}\right)^{-x_\lambda/2} c_{\mathrm{na}}(k,x)^{x_\lambda} f(k,x). \tag{32}$$

The crossover behaviour for finite mode coupling f_0 can be seen in figure 4. Near T_{c} the asymptotic expression (31) applies whereas in the background van Hove behaviour is reached. Taking the nonuniversal value for Γ_0 from the shear viscosity the value of f_0 is adjusted to fit the characteristic frequency data. This leads to a value definitive different from the fixed point value as can be seen from figure 5. Similar results are obtained for xenon [11].

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Критичний перенос і критичне розсіяння у плинах

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Розглядаються критичні властивості плинів, що індуковані критичними флюктуаціями параметра порядку. Теорія описує кросовер від аналітичної фонової поведінки до асимптотичної поведінки для кількох динамічних величин.

Ключові слова: *фазовий перехід газ-рідина, критична динаміка, розсіяння світла, коефіцієнти переносу*

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