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Critical Light Scattering in Pure Liquids[1]

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Light-scattering experiments near the critical point (T_c, ρ_c) in fluid systems and, in particular, the central Rayleigh peak in the frequency spectrum are reviewed. Within a nonasymptotic renormalization-group theory, the crossover function is calculated between several regions: (i) from the background to the asymptotic region, (ii) from the hydrodynamic region (wave length $\gg$ correlation length) to the critical region (wave length $\ll$ correlation length), and (iii) from critical densities to noncritical densities. Contrary to the mode-coupling expression, the appropriate scaling function is well defined in all limits of its arguments. At T_c the crossover in the wave-vector dependence of the linewidth is also considered. Theoretical results are compared with experiments for pure liquids. Nonuniversal parameters are chosen consistent with the transport coefficients (i.e., the shear viscosity) for the same substance which can be evaluated within the same formalism.

KEY WORDS: characteristic frequency; critical point; dynamic critical phenomena; light scattering; renormalization-group theory; transport coefficients.

1. INTRODUCTION

Light scattering is a common technique to investigate the transport properties of a fluid system. Especially the characteristic frequency ω_c, defined as the half width at half height of the central Rayleigh peak in the frequency spectrum, provides useful information about the dynamical properties of the system.

Far away from the critical point in the background region, characterized by small values of the correlation length ξ or large values of the wave vector k, the behavior of the characteristic frequency is described by the van Hove theory. In the hydrodynamic region for small values of $k\xi$,

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the characteristic frequency is given by $\omega_c = D_T(T, \rho)\, k^2$ with $D_T(T, \rho)$ being the regular thermal diffusivity (the ratio of the nonsingular thermal conductivity and the specific heat at constant pressure), whereas in the "background" critical region, for large values of $k\xi$, the characteristic frequency is proportional to k^4.

In the vicinity of the critical point, characterized by large values of ξ or small values of k, fluctuations determine the form of the characteristic frequency. In the critical limit for large values of $k\xi$, the power-law behavior $\omega_c \sim k^z$ with the dynamical critical exponent $z \approx 3$ is expected. In the hydrodynamic limit for $k\xi \to 0$, the characteristic frequency is again given by $\omega_c = D_T(T, \rho)\, k^2$ but now with a singular Onsager coefficient and thus a diverging thermal conductivity.

Within the nonasymptotic renormalization-group theory we are able to describe the crossover from the asymptotic region to the background region as well as from the hydrodynamic region to the region of large wave vectors quantitatively and compare our theory to experiments in pure liquids.

2. CHARACTERISTIC FREQUENCY

The characteristic frequency ω_c can be found from the dynamic order parameter correlation function within the dynamic model H, which was briefly reviewed in Ref. 1. The dynamic correlation function is, in general, given by

$$\chi_{\mathrm{dyn}}(\xi, k, \omega) = \frac{\chi_{\mathrm{st}}(k, \xi)}{\omega_c(k, \xi)}\, F(x, y) \tag{1}$$

with $x = k\xi$ and $y = \omega/\omega_c$. Scaling theory [2] predicts a non-Lorentzian form of the shape function $F(x, y)$ in the asymptotic region close to the critical point. The non-Lorentzian shape has been calculated by mode-coupling theory [3] and the results were confirmed by experiments in liquid mixtures [4]. Within renormalization theory no such calculation is available and one-loop theory predicts a Lorentzian shape [5]. This problem is not settled so far, and so the characteristic frequency found from the dynamic order parameter vertex function is based on the Lorentzian approximation.

In one-loop perturbation theory the renormalized characteristic frequency ω_c, expressed in terms of the renormalized model parameters $\Gamma(\ell)$ and $f_t(\ell)$, is found to be of the form,

$$\omega_c(k, \xi) = \Gamma(\ell)\, k^2(\xi^{-2} + k^2) \left\{ 1 - \frac{f_t^2(\ell)}{16} \left[-5 + 6x^{-2} \ln(1 + x^2) \right] \right\} \tag{2}$$

The temperature dependence enters via the flow equations for the mode coupling $f_t(\ell)$ and the Onsager coefficient $\Gamma(\ell)$, which are given by Eqs. (7) and (8) of Ref. 1. Other than for the evaluation of the frequency-dependent shear viscosity, the connection between the flow parameter ℓ and the correlation length or the wave vector, respectively, is found from the matching condition (which arises naturally within the calculation of the vertex function),

$$(\xi_0^{-1}\ell)^2 = \xi^{-2} + k^2 \tag{3}$$

where ξ_0 is the amplitude in the power law for the correlation length $\xi = \xi_0 t^{-\nu}$. As described in Ref. 1 the correlation length may also be expressed in terms of the reduced density using the cubic model.

In order to discuss the various limits of the characteristic frequency, it is useful to rewrite Eq. (2): Extracting the critical asymptotics the characteristic frequency reads

$$\omega_c(k,x) = \Gamma_{as} k^z \left(\frac{1+x^2}{x^2}\right)^{1-x_\lambda/2} [c_{na}(k,x)]^{x_\lambda} f(k,x) \tag{4}$$

with $x = k\xi$ and $z = 4 - x_\lambda$. The critical exponent of the thermal conductivity x_λ is related to the exponent of the shear viscosity x_η by $x_\lambda + x_\eta = 1$ in one-loop order. The function $f(k, x)$ defined as (f_t^{*2} is the fixed-point value of the mode coupling)

$$f(k,x) = 1 - \frac{f_t^{*2}}{16 c_{na}(k,x)} [-5 + 6x^{-2} \ln(1+x^2)] \tag{5}$$

The nonasymptotic contributions are collected in

$$c_{na}(k,x) = \left[1 + \frac{k}{k_0}\sqrt{\frac{1+x^2}{x^2}}\right] \tag{6}$$

so that the asymptotic region is characterized by $c_{na}(k,x) = 1$ and, thus, the frequency can indeed be written in scaling form with the scaling function f depending only on the variable $x = k\xi$. And finally the asymptotic Onsager coefficient Γ_{as} and the crossover wave length k_0 are given by

$$\Gamma_{as} = \Gamma_0 \left(\frac{f_0^2 \ell_0}{f_t^{*2}\xi_0}\right)^{x_\lambda}, \qquad k_0^{-1} = \left(\frac{f_t^{*2}}{f_0^2} - 1\right)\frac{\xi_0}{\ell_0} \tag{7}$$

containing the nonuniversal initial values Γ_0, and f_0 at ℓ_0 corresponding to a temperature t_0.

3. CROSSOVER BEHAVIOR

We start this section with a discussion of the various limits of the characteristic frequency: In the *hydrodynamic* limit $x = k\xi \to 0$, we find

$$\lim_{x \to 0} \omega_c(k, \xi) = \Gamma_{as} k^2 \xi^{-2+x_\lambda} \left[1 + \frac{1}{x_0}\right]^{x_\lambda} \left\{1 - \frac{f_t^{*2}}{16}\left[1 + \frac{1}{x_0}\right]^{-1}\right\} \tag{8}$$

with $x_0 = k_0 \xi$. Here the coefficient of k^2 is the nonasymptotic expression for the temperature dependent thermal diffusion coefficient $D_T(\xi)$ discussed in Ref. 6 so that we can rewrite Eq. (8) in the well-known form $\omega_c = D_T(\xi)\, k^2$ for the hydrodynamic region. In the opposite *critical* limit $x \to \infty$ we have

$$\lim_{x \to \infty} \omega_c(k, \xi) = \omega_c(k) = \Gamma_{as} k^z \left[1 + \frac{k}{k_0}\right]^{x_\lambda} \left\{1 + \frac{5 f_t^{*2}}{16}\left[1 + \frac{k}{k_0}\right]^{-1}\right\} \tag{9}$$

which is the wave-vector dependent nonasymptotic expression of the characteristic frequency. Both nonasymptotic expressions allow consideration of the crossover from the *asymptotic* limit $\xi k_0 \to \infty$ or $k/k_0 \to 0$ to the *background* limit $\xi k_0 \to 0$ or $k/k_0 \to \infty$, respectively. In the hydrodynamic case we obtain the limits

$$\lim_{\xi k_0 \to \infty} \omega_c(k, \xi) = \Gamma_{as} k^2 \xi^{-2+x_\lambda} \left(1 - \frac{f_t^{*2}}{16}\right) \tag{10}$$

$$\lim_{\xi k_0 \to 0} \omega_c(k, \xi) = \Gamma_0 k^2 \xi^{-2} \left(1 - \frac{f_0^2}{f_t^{*2}}\right)^{x_\lambda} \tag{11}$$

where we used the expression for k_0 given in Eq. (7) for the last limit. In the background limit our expression reaches the van Hove behavior $\omega_c \propto k^2 \xi^{-2}$. In the critical region we obtain

$$\lim_{k/k_0 \to 0} \omega_c(k) = \Gamma_{as} k^z \left(1 + \frac{5 f_t^{*2}}{16}\right) \tag{12}$$

$$\lim_{k/k_0 \to \infty} \omega_c(k) = \Gamma_0 k^4 \left(1 - \frac{f_0^2}{f_t^{*2}}\right)^{x_\lambda} \tag{13}$$

where again we reach the van Hove theory for large values of the ratio k/k_0. This means that our results for the characteristic frequency describe the crossover in the correlation length (from ξ^{-2+x_λ} to ξ^{-2}) in the hydrodynamic region characterized by the limit $x \to 0$ as well as the crossover in the wave vector (from k^z to k^4) in the critical region characterized by the limit $x \to \infty$. This is shown in Fig. 1 where we have plotted the dimensionless characteristic frequency $\omega_c/\Gamma_0 k^2$ as functions of the wave

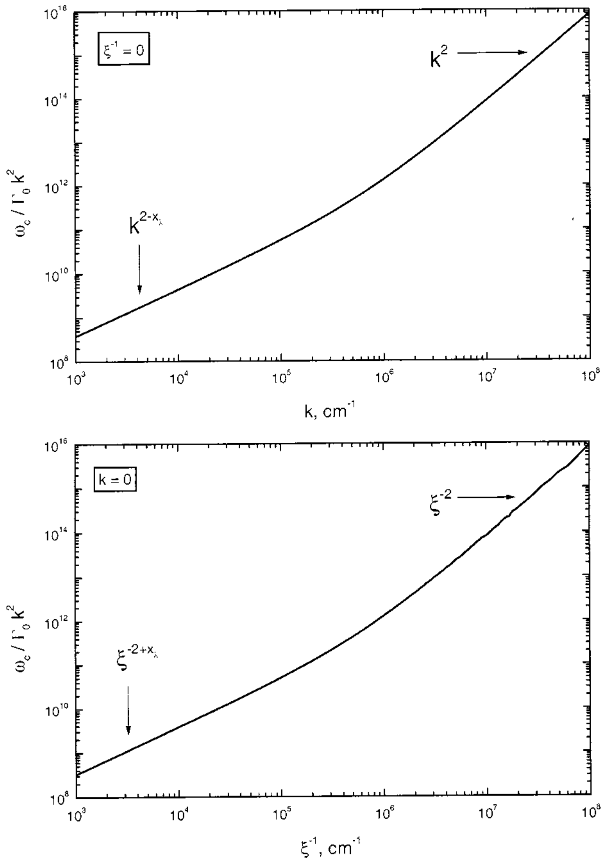

Fig. 1. Dimensionless characteristic frequency $\omega_c/\Gamma_0 k^2$ as a function of the wave vector (top) and the inverse correlation length (bottom). We can see the crossover from the asymptotics to the van Hove background.

vector and the correlation length along the critical isochore. In Fig. 2 we have plotted $\omega_c/\Gamma_0 k^2$ as a function of the reduced temperature for various values of the reduced density and the wave vector using the cubic model described in Ref. 1 (the density enters via the correlation length in the matching condition). Only at zero wave vector and along the critical isochore (that means for $\Delta\rho = 0$), we can see the asymptotic power-law behavior $\omega_c \sim \xi^{-2+x_\lambda} \sim t^{\nu(2-x_\lambda)}$ and the crossover to the van Hove theory with $\omega_c \sim t^{2\nu}$, whereas for noncritical densities or nonvanishing wave vector, the dimensionless characteristic frequency approaches a finite value for $t \to 0$.

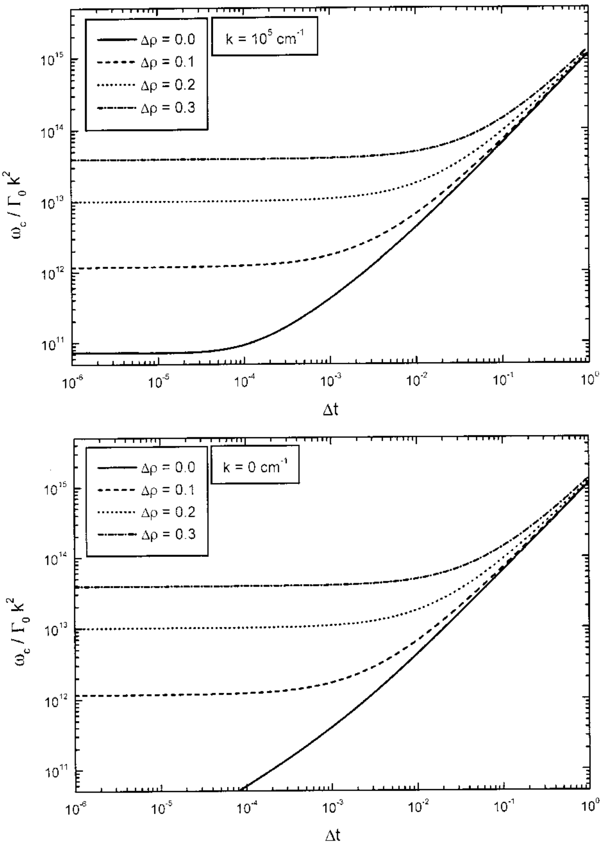

Fig. 2. Dimensionless characteristic frequency $\omega_c/\Gamma_0 k^2$ as a function of the reduced temperature t at constant wave vector (top: $k = 10^5\,\mathrm{cm}^{-1}$; bottom $k = 0\,\mathrm{cm}^{-1}$) and various values of the reduced density $\Delta\rho$.

We have seen that with our nonasymptotic theory we always reach the van Hove behavior in the nonasymptotic limit for large values of the wave vector or small values of the correlation length, respectively. This is shown very well in Ref. 7 where we have plotted the ratio of the full characteristic frequency to its van Hove expression. This behavior is different from the nonasymptotic mode coupling expression of Olchowy [8] (a recent improvement of this theory is found in Ref. 9) which does not yield the van Hove theory in the nonasymptotic region but instead becomes negative for large values of the variable x [7]. This region of unphysical negative values of the characteristic frequency is always reached at constant correlation length when the wave vector becomes larger than the nonuniversal parameter q_D. On the other hand the parameter q_D cannot be set to infinity as this limit yields an unphysical divergence in the hydrodynamic limit for $\xi \to 0$ [9].

4. COMPARISON WITH EXPERIMENTS

In Ref. 7 we have compared our asymptotic theory to the theoretical results of Kawasaki and Lo, of Paladin and Peliti, and of Burstyn et al. [10] so that we shall compare our theory only to various experiments in this paper. We start this comparison with the experimental xenon data of Swinney and Henry [11].

In Fig. 3 we compare our asymptotic (for $c_{\mathrm{na}} = 1$) and nonasymptotic (for $c_{\mathrm{na}} \neq 1$) theory for the characteristic frequency ω_{c}/k^2 with the experimental xenon data (all nonuniversal parameters are indicated in the figure). As discussed in Refs. 6 and 7 we can treat the exponent $x_\lambda = 1 - x_\eta$ as an additional free parameter in the expression for the Onsager coefficient (see Ref. 1) so that we can fit the initial value of the mode coupling f_0 and the exponent x_η from the experimental data for the characteristic frequency and, e.g., the shear viscosity (the initial value of the Onsager coefficient Γ_0 is determined by the value of the shear viscosity at t_0). Following the fitting procedure described in Ref. 1 we get the parameter f_0 from the characteristic frequency data and the exponent x_η from the microgravity shear viscosity data of Berg et al. [12]. In doing so we find good agreement for the characteristic frequency (Fig. 3) as well as for the frequency dependent shear viscosity [1].

As we can see in Fig. 3 the experimental data are not described correctly by our asymptotic expressions but only by the nonasymptotic expressions which show the crossover to the van Hove theory for large values of the reduced temperature t. Analogously any asymptotic theory [10] fails to describe the experimental data correctly. In Ref. 11 this problem was eliminated adding a regular background contribution of the form $\omega_{\mathrm{c}}^{\mathrm{B}} = (\lambda^{\mathrm{B}}/\rho c_p)\, k^2(1 + x^2)$ to the critical expression for the characteristic frequency with λ^{B} being the regular part of the thermal conductivity and c_p the full specific heat at constant pressure containing also critical contributions. The use of the full specific heat together with the term $1 + x^2$ ensures the crossover to the van Hove theory for large values of the reduced temperature as well as for large values of the wave vector (the background characteristic frequency is proportional to $k^2\xi^{-2}$ for $x \to 0$ and to k^4 for $x \to \infty$) so that the full characteristic frequency $\omega_{\mathrm{c}} = \omega_{\mathrm{c}}^{\mathrm{C}} + \omega_{\mathrm{c}}^{\mathrm{B}}$ obtained by this procedure yields basically the same curves as our nonasymptotic theory (see Fig. 6 of Ref. 11). As discussed in Ref. 7 we have to

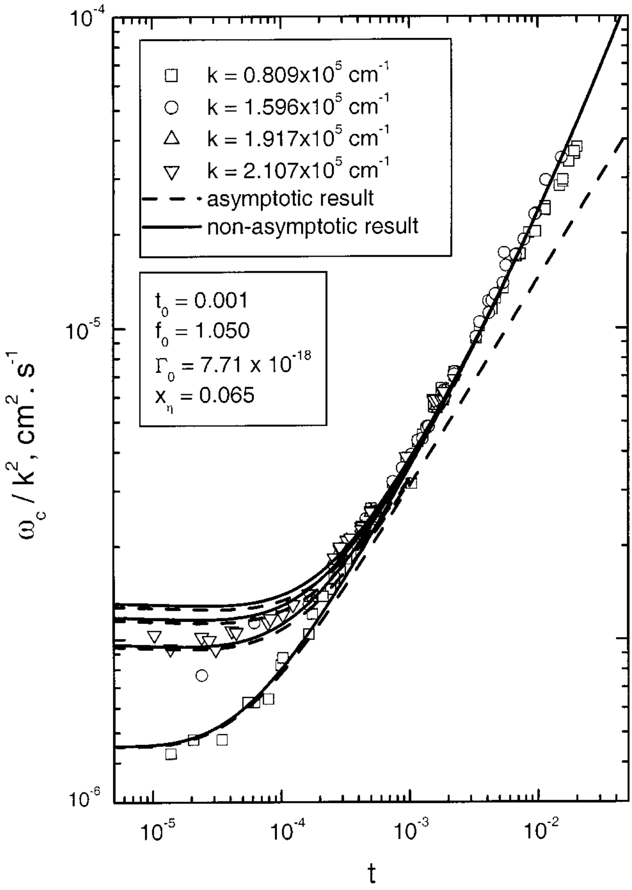

Fig. 3. Comparison of the asymptotic (dashed lines) and non-asymptotic (full lines) expressions for ω_c/k^2 with the Xe data of Ref. 11; from Ref. 7.

use a background characteristic frequency of the form $\omega^B = D_T^B(T, \rho)\, k^2 - D_T^B(T_c, \rho_c)\, k^2$, with the background thermal diffusivity given by $D_T^B = \lambda^B/\rho c_p^B$ and the background specific heat c_p^B containing only the regular temperature dependence without the critical singularity, in our theory. As this background term turns out to be negligibly small in the temperature range shown in Fig. 3, we have neglected it so that our asymptotic and nonasymptotic curves for Xe contain only the critical contributions discussed in this paper. So the main difference between our nonasymptotic theory and the results of Ref. 10 is that the crossover to the van Hove theory, which is clearly seen in experiments, is already contained in our

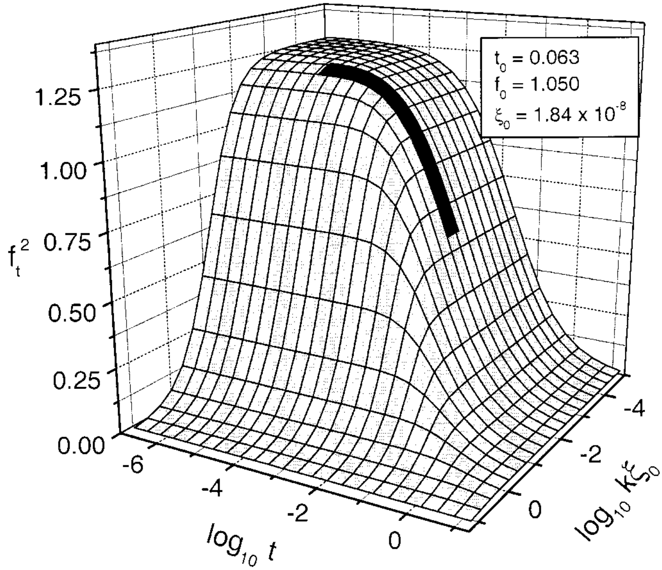

Fig. 4. Mode coupling $f_t^2(t, \omega)$ (all nonuniversal parameters for xenon) as a function of the reduced temperature t and the dimensionless wave vector $k\xi_0$ along the critical isochore. For small values of the wave vector and the reduced temperature we reach the fixed point value $f_t^{*2} = 24/19$. The dark region marks the range of experimental data for the characteristic frequency in xenon.

expressions for the characteristic frequency and not added by an appropriate form of the background contribution!

The crossover from the asymptotic to the background behavior can be seen most easily looking at the relevant values of the mode coupling which are shown in Fig. 4. Here we have plotted the mode coupling as a function of temperature and wave vector. The experimental region (dark area) for the xenon data covers the slope of the crossover from asymptotics to background.

5. CONCLUSION

We were able to show that our one-loop perturbation theory result for the characteristic frequency evaluated within the field theoretical method of the renormalization group theory does not only reproduce the correct wave vector and correlation length dependence in the hydrodynamic region as well as in the critical region but is also able to describe experimental data sufficiently well for a large range of wave vectors and reduced temperatures.

There are, however, some points which indicate the need for a two-loop analysis of the model. First, we have seen that in one-loop order the dynamic correlation function is always of Lorentzian form whereas scaling theory [2] predicts deviations for large frequencies. Second, the comparison of the frequency dependence of the shear viscosity with experimental data [1] also requires the calculation of the vertex function up to two-loop order.

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