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Dynamic scaling function for critical fluctuations in classical fluids

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A closed-form approximant is proposed for the dynamic scaling function that characterizes the behavior of the wave-number—dependent diffusion of the order-parameter fluctuations in a fluid near a critical point. The expression contains two parameters that determine the expected behavior of the diffusion coefficient in the hydrodynamic and in the nonlocal critical limits. The proposed scaling function yields an accurate representation of our recent experimental data for the 3-methylpentane and nitroethane mixture near the critical mixing point with parameter values that are in good agreement with the values predicted from theory.

I. INTRODUCTION

The state of a fluid near a critical point is characterized by large fluctuations in an order parameter s. The dependence of the order-parameter fluctuations with wave number q on the time t can be represented by an exponential decay law of the form

$$\langle s_q(t)s_{-q}(0)\rangle = \chi_q e^{-Dq^2t}\,, \tag{1.1}$$

where $\chi_q = \langle\, |s_q|^2\rangle$ is the static correlation function with correlation length ξ and where D is a diffusion coefficient. For one-component fluids near the gas-liquid critical point, D is to be identified with the thermal diffusivity and for binary liquid mixtures near the critical mixing point, with the mutual mass diffusion coefficient. The diffusion coefficient D, in the hydrodynamic limit $q \rightarrow 0$, vanishes at the critical point, a phenomenon known as the critical slowing down of the fluctuations.

The critical order-parameter fluctuations in fluids can be investigated experimentally most conveniently by the use of light scattering techniques. The wave number q of the fluctuations is related to the scattering angle θ by the Bragg condition $q = 2q_0\sin(\theta/2)$, where q_0 is the wave number of the incident light in the medium. Hence, by measuring the time-dependent scattered-intensity correlation function, as a function of temperature and scattering angle, one can determine the diffusion coefficient D as a function of temperature T and wave number q in the critical region. In Fig. 1 we show the diffusion coefficient for the binary liquid 3-methylpentane and nitroethane at the critical concentration as a function of $T - T_c$, T_c being the critical temperature, as deduced from our recent experimental decay-rate data for this system.[1] The data were obtained at three different scattering angles θ (29.8°, 89.5°, and 146.8°) corresponding to the wave numbers $q = 0.704\times10^5$, 1.92×10^5, and 2.62×10^5 cm^{-1}.

In order to interpret the observed behavior of the diffusion coefficient a distinction should be made between a hydrodynamic regime $q\xi \ll 1$, where the wavelength of the fluctuations is large compared to the correlation length ξ, and a nonlocal critical regime $q\xi \gg 1$, where the wavelength of the fluctuations is small compared to ξ. At temperatures well away from T_c the data correspond to the hydrodynamic regime $q\xi \ll 1$, and the diffusion coefficient D at wave number q may be identified with the diffusion coefficient in the hydrodynamic limit $q \rightarrow 0$. However, at temperatures closer to T_c and at a given wave number q, $q\xi$ becomes larger than unity and D depends explicitly on q. This general behavior of the diffusion coefficient associated with the critical fluctuations has been observed by many investigators. For a review of the earlier experimental work the reader is referred to a paper of Swinney and Henry.[2] Very close to the critical temperature the diffusion coefficient also becomes a function of frequency as revealed by the presence of deviations from exponential decay of the order-parameter correlation function.[3-5] However, the phenomenon is only observable in the last 10 mK from the critical temperature and the effect on the actual value deduced for the diffusion coefficient remains small.[5]

In a previous paper we demonstrated that the experimental decay-rate data are consistent with the predictions of the mode-coupling theory for dynamic critical phenomena.[1] For that purpose we solved two coupled integral

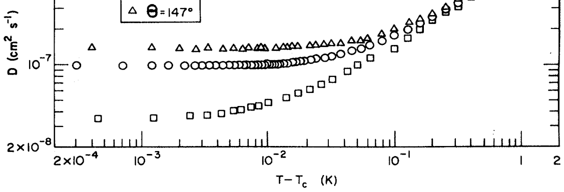

FIG. 1. Diffusion coefficient of a mixture of 3-methylpentane and nitroethane at the critical concentration as a function of $T - T_c$ deduced from light scattering measurements at three different scattering angles θ.

equations by numerical methods. It is the purpose of this paper to derive an explicit expression that describes the observed dependence of the diffusion coefficient on temperature and wave number.

The principle of dynamic scaling[6–8] implies that the critical diffusion coefficient should depend on the wave number q through the scaled variable $x = q\xi$. As we shall see, our experimental data are indeed consistent with the principle of dynamic scaling to a high degree of accuracy. In order to characterize the dynamic scaling function we derive in Sec. II theoretical estimates for the amplitudes of the dynamic scaling function in the limits of small and large values of the scaled wave number x and propose a closed-form approximant for the dynamic scaling function consistent with these limits. This dynamic scaling function is then compared with our experimental data for the mixture of 3-methylpentane and nitroethane in Sec. III. Because of some controversies in the literature concerning the precise values of the parameters for the dynamic scaling function, we include a careful study of how an experimental determination of these parameters is affected by the presence of possible background correction terms in the diffusion coefficient. Our conclusions are summarized in Sec. IV.

II. THEORY OF DYNAMIC SCALING FUNCTION

A. General formulation

According to the theory of critical phenomena the static correlation function χ_q can be represented by a scaling law of the form[9,10]

$$\chi_q = \Gamma \epsilon^{-\gamma} g(q\xi) , \tag{2.1}$$

where $\epsilon = (T - T_c)/T_c$. The correlation length diverges as

$$\xi = \xi_0 \epsilon^{-\nu} . \tag{2.2}$$

The critical exponents γ and ν and the static scaling function $g(x)$ are universal, i.e., independent of the nature of the fluid. For small values of $x = q\xi$ the correlation scaling function $g(x)$ approaches the Ornstein-Zernike form[9]

$$g(x) = \frac{1}{1+x^2} . \tag{2.3}$$

The precise behavior of $g(x)$ for larger values of x is complicated.[9–13] However, any deviations of $g(x)$ from the Ornstein-Zernike form remain small and for many applications $g(x)$ is identified with (2.3) for all values of x. This is often done in solving the mode-coupling equations for critical dynamics, and we also adopt this approximation here.

The diffusion coefficient D can be related to an Onsager coefficient L by[14]

$$D = L/\chi_q . \tag{2.4}$$

In the treatment of dynamic critical phenomena it is customary to separate the transport coefficients, such as the Onsager coefficient L and the hydrodynamic shear viscosity η_s into bare or background contributions $\bar{L}, \bar{\eta}$ and singular or anomalous contributions[15,16] $\Delta L, \Delta\eta$, so that

$$L = \Delta L + \bar{L} \tag{2.5a}$$

and

$$\eta_s = \Delta\eta + \bar{\eta} . \tag{2.5b}$$

Here $\bar{L}$ and $\bar{\eta}$ represent the transport coefficients in the absence of critical fluctuations, while ΔL and $\Delta\eta$ are meant to represent the additional contributions due to the critical fluctuations. The separation of L into a singular contribution ΔL and a background contribution $\bar{L}$ implies a similar separation for the diffusion coefficient D,

$$D = \Delta D + \bar{D} \tag{2.6}$$

with

$$\bar{D} = \bar{L}/\chi_q . \tag{2.7}$$

The diffusion coefficient D and the shear viscosity η_s satisfy asymptotically equations of the form[8]

$$D - \bar{D} = \Delta D = \frac{k_B T}{6\pi\eta_s\xi}\Omega(x) , \tag{2.8}$$

$$\eta_s = \bar{\eta}(Q_0\xi)^{z_\eta} , \tag{2.9}$$

where, as suggested by theory,[17] we assume that the background $\bar{\eta}$ in (2.5b) has become the multiplicative factor in (2.9). Here k_B is Boltzmann's constant, Q_0 a system-dependent amplitude, z_η a universal critical exponent, and $\Omega(x)$ a universal dynamic scaling function. Various authors[18–22] have reported theoretical estimates for the critical exponent z_η; we shall further discuss this exponent in Sec. III A.

The dynamic scaling function $\Omega(x)$ satisfies the boundary conditions[8]

$$\Omega(0) = R , \tag{2.10a}$$

where R is a universal dynamic amplitude ratio, and for $x \gg 1$,

$$\Omega(x) \propto x^y , \tag{2.10b}$$

where the dynamic scaling exponent y satisfies the exponent relation

$$y = 1 + z_\eta . \tag{2.11}$$

From (2.8), (2.9), and (2.10b) it follows that at the critical temperature ($\xi \to \infty$) the diffusion coefficient should vary with q as

$$\Delta D \propto q^y . \tag{2.12}$$

In zeroth order, the dynamic scaling function $\Omega(x)$ is commonly approximated by the so-called Kawasaki function $\Omega_K(x)$ defined as[16]

$$\Omega_K(x) = (3/4x^2)[1 + x^2 + (x^3 - x^{-1})\arctan x] . \tag{2.13}$$

This function behaves as

$$\Omega_K(x) = 1 + \tfrac{3}{5}x^2 - \tfrac{1}{7}x^4 + \cdots \tag{2.14}$$

in the regime $x \ll 1$, and as

$$\Omega_K(x)=\frac{3\pi}{8}x+\frac{1}{x^2}-\frac{3\pi}{8}\frac{1}{x^3}+\cdots \tag{2.15}$$

in the extreme nonlocal regime $x \gg 1$. The Kawasaki function is obtained from the mode-coupling integral for the critical diffusion coefficient when the static correlation function is approximated by the Ornstein-Zernike form (2.3) and when the shear viscosity is approximated by $\bar{\eta}$, independent of q.[23,24] In practice, however, the critical behavior of the shear viscosity is sufficiently important that its effect on the diffusion coefficient cannot be neglected, as was pointed out originally by Chang and coworkers.[25]

The Kawasaki function $\Omega_K(x)$ satisfies the boundary condition (2.10a) for $x=0$ with $R=1.0$. The actual value of the dynamic amplitude ratio R has been the subject of some controversy, since Siggia and co-workers reported the estimate $R \simeq 1.20$ from a dynamic renormalization-group theory[20]; we shall return to this subject in Secs. II C and III B.

The Kawasaki function has a deficiency for large values of x, where it varies as x rather than as x^y and thus violates condition (2.10b). In our previous paper we tried to remedy this deficiency by solving the mode-coupling equations for the shear viscosity and the decay rate of the order-parameter fluctuations numerically.[1] In this paper we prefer to exhibit the desired scaling behavior explicitly by introducing a correction factor $S(x)$, which we shall subsequently call the scaling function, and which we define by

$$\Omega(x) \equiv \Omega_K(x)[S(x)]^{z_\eta} . \tag{2.16}$$

In particular, we shall consider the two limits

$$\lim_{x \to 0} S(x) = a_0 \tag{2.17a}$$

and

$$S(x) = a_\infty x \quad \text{for } x \gg 1 . \tag{2.17b}$$

From (2.17a) it follows that the coefficient a_0 is related to the amplitude R by

$$a_0^{z_\eta} = R , \tag{2.18}$$

while (2.17b) follows from (2.10b). An important feature of $S(x)$ will be the ratio

$$b = \frac{a_\infty}{a_0} . \tag{2.19}$$

Sections II B and II C are devoted to obtaining theoretical estimates for the coefficient a_0 and a_∞ and, hence, for the ratio b. For a comparison with the experimental data the ratio b has some advantage relative to the individual coefficients a_0 and a_∞. The reason is that the latter coefficients are subject to systematic errors and uncertainties which are expected to cancel when one takes the ratio.

To calculate this ratio b we use a kind of "minimal" theoretical framework in which we adopt the point of view that the single-loop or decoupled-mode theory, in its self-consistent form, works very well.[26] This is an approximation to the more complete theory in one of its three equivalent forms: (1) higher-order mode coupling,[16] (2) equation of motion approach,[27] or (3) dynamic renormalization group.[20] The decoupled-mode approximation neglects the vertex corrections which we regard for the present purposes as an acceptable shortcoming, since their effects are expected to be small, when one considers the ratio $b = a_\infty / a_0$. (The λ transition in liquid helium is a special case, where, because of a numerical accident, the results are crucially dependent upon vertex corrections.[27])

B. Scaling function in the nonlocal limit $x \gg 1$

In the decoupled-mode approximation the critical diffusion coefficient is given by a integral of the form[26]

$$\Delta D(\xi^{-1},q)=\frac{k_B T}{(2\pi)^3}\int \frac{d\vec{k}\,\sin^2\theta}{k^2\eta(\xi^{-1},k,\omega_\Gamma)}\,\frac{g(k'\xi)}{g(q\xi)} , \tag{2.20}$$

where $\vec{k}'=\vec{q}-\vec{k}$, and θ is the angle between the wave numbers q and k. Even in this simplest approximation an unavoidable complication arises due to the presence of the viscosity function $\eta(\xi^{-1},k,\omega)$ that depends not only on the temperature via ξ^{-1}, but also on the wave number k and the frequency ω which, after averaging, becomes an effective frequency ω_Γ associated with the decay of the order-parameter fluctuations. Dynamic scaling[6,7] requires that the experimentally observed critical behavior of the hydrodynamic shear viscosity $\eta_s(\xi^{-1})$ is simply one aspect of a fully nonlocal viscosity function in space and time. Only in the $k=0$ and $\omega=0$ limit can the nonlocal viscosity be identified with its hydrodynamic value according to

$$\eta(\xi^{-1},0,0) \equiv \eta_s(\xi^{-1}) . \tag{2.21}$$

For this reason it is not permitted to ignore the k and ω dependence of η inside the integral (2.20) for ΔD. Upon comparing with (2.8) we can, however, describe the result of the averaging over $\eta(\xi^{-1},k,\omega_\Gamma)$ that is effected by the integration over the wave numbers as

$$\Delta D(\xi^{-1},q)=\frac{k_B T}{6\pi\xi}\,\frac{\Omega_K(q\xi)}{\eta_{\text{eff}}(\xi^{-1})} . \tag{2.22}$$

Here the effect is represented by an effective hydrodynamic viscosity $\eta_{\text{eff}}(\xi^{-1})$ such that

$$\eta_{\text{eff}}(\xi^{-1}) \equiv \eta_s(\xi_{\text{eff}}^{-1}) = \eta_s(\xi^{-1})\left[\frac{\xi_{\text{eff}}}{\xi}\right]^{z_\eta} , \tag{2.23}$$

where we have used (2.9) to express η_{eff} in terms of an effective correlation length ξ_{eff}.

Perl and Ferrell[26] have carried out the computation of $\Delta D(\xi^{-1},q)$ and of ξ_{eff}^{-1} in the limit $\xi^{-1}=0$ which corresponds to the critical point. Dynamic scaling requires that in this case ξ_{eff}^{-1} must be proportional to q. This result can be understood from the observation that the wave numbers that contribute most heavily to the single-loop integral (2.20) are of the order of the external wave number q. From the decoupled-mode integral for the nonlocal viscosity Perl and Ferrell found, at zero frequency,[26]

$$\eta(0,q,0)=\eta_s(a_{\text{eff}}^{\text{NL}}q) \tag{2.24}$$

with $a_{\text{eff}}^{\text{NL}}=2\exp(4\pi/9\sqrt{3}-\frac{11}{5})\simeq 0.496$, thus yielding $\xi_{\text{eff}}^{-1}=a_{\text{eff}}^{\text{NL}}q$. However, they also showed that inclusion of the frequency dependence canceled most of the effect of the nonlocality in space, leaving the net result[26]

$$\xi_{\text{eff}}^{-1}=a_{\text{eff}}^{\text{visc}}q \tag{2.25}$$

with $a_{\text{eff}}^{\text{visc}}=0.90$. This result has been confirmed subsequently by Bhattacharjee and Ferrell.[4] Substitution of (2.23) and (2.25) into (2.22) yields for $q\xi=x\gg 1$,

$$\Delta D(\xi^{-1},q)=(a_{\text{eff}}^{\text{visc}}x)^{z_\eta}\frac{k_B T\Omega_K(x)}{6\pi\xi\eta_s(\xi^{-1})} . \tag{2.26}$$

Comparison of (2.26) with (2.8), (2.16), and (2.17b) permits the identification

$$a_\infty=a_{\text{eff}}^{\text{visc}}=0.90 . \tag{2.27}$$

C. Scaling function in the hydrodynamic limit $x\ll 1$

We now turn our attention to the $x=0$ limit and calculate the coefficient a_0 as defined by (2.17a). From the single-loop integral (2.20) and the definitions (2.8) and (2.16) for the scaling functions it follows that

$$[S(x)]^{z_\eta}=\left\langle\frac{\eta_s}{\eta}\right\rangle , \tag{2.28}$$

where the average of some function Q is defined as

$$\langle Q\rangle=\frac{\int\frac{dk}{k^2}\sin^2\theta g(k'\xi)Q}{\int\frac{dk}{k^2}\sin^2\theta g(k'\xi)} . \tag{2.29}$$

The effect of the averaging which is indicated in (2.29) depends upon the precise manner in which the wave number and frequency dependence enter into the critical shear viscosity. We consider first its zero-frequency limit which we write in the form

$$\eta(\xi^{-1},k,0)=\eta_s(\xi^{-1})f_{\text{NL}}^{-z_\eta}(k\xi) . \tag{2.30}$$

The nonlocal correction factor f_{NL} has, by virtue of its definition, the value $f_{\text{NL}}(0)=1$ in the long-wavelength limit. From (2.24) it follows that in the extreme nonhydrodynamic limit $f_{\text{NL}}=a_{\text{eff}}^{\text{NL}}k\xi$ with $a_{\text{eff}}^{\text{NL}}=0.496$, which we round off to $\frac{1}{2}$. For intermediate wave numbers we then approximate the nonlocal correction factor as

$$f_{\text{NL}}(k\xi)=\left[1+\left[\frac{k\xi}{2}\right]^2\right]^{1/2} , \tag{2.31}$$

consistent with the rule of thumb[28] that in the convolution integral for the critical viscosity the wave-number scale is set by $2\xi^{-1}$.

In the hydrodynamic limit $q=0$ the integral (2.29) reduces to the isotropic form

$$\langle Q\rangle=\frac{2}{\pi}\int_0^\infty\frac{dk\,\xi}{1+k^2\xi^2}Q(\xi^{-1},k,\omega_\Gamma) . \tag{2.32}$$

Continuing for the moment to ignore the frequency dependence, we write

$$Q(\xi^{-1},k,0)=\frac{\eta_s(\xi^{-1})}{\eta(\xi^{-1},k,0)}=f_{\text{NL}}^{z_\eta}\simeq 1+z_\eta\ln f_{\text{NL}} , \tag{2.33}$$

where the linearization is permitted, since $z_\eta\ll 1$. Similarly, we can write

$$S^{z_\eta}(0)=a_0^{z_\eta}=1+z_\eta\ln a_0 . \tag{2.34}$$

If we substitute Eqs. (2.31)–(2.34) into (2.28) and identify the first-order terms, we obtain

$$\ln a_{\text{NL}}=\langle\ln f_{\text{NL}}\rangle=\tfrac{1}{2}I(\tfrac{1}{4}) \tag{2.35}$$

with

$$I(t)=\frac{1}{\pi}\int_0^\infty\frac{dp}{t^2+p^2}\ln(1+p^2) . \tag{2.36}$$

The integration can be carried out for $t=0$ to give $I(0)=1$. Furthermore, for $t\ll 1$ we find $I(t)\simeq 1-\sqrt{t}/2$, which suggests the Padé approximant

$$I(t)\simeq\frac{1}{1+\sqrt{t}/2} . \tag{2.37}$$

A check on (2.37) can be made at $t=1$ where it gives $\frac{2}{3}$, only 3% below the exact value of ln2. As we only need (2.37) for $0<t<1$, the discrepancy with the exact asymptotic behavior of $\ln t/2\sqrt{t}$, which sets in for $t\gg 1$ is of no consequence. Substitution of $t=\frac{1}{4}$ into (2.37) yields $I(\frac{1}{4})=\frac{4}{5}$, so that from (2.35) $\ln a_{\text{NL}}=\frac{2}{5}$ or

$$a_{\text{NL}}\simeq 1.49 . \tag{2.38}$$

This result is physically reasonable, because the effect of nonlocality is to decrease the viscosity compared to its hydrodynamic value.

In analogy to (2.30) the additional reduction in η due to the frequency dependence (retardation) can be written as

$$\frac{\eta(\xi^{-1},k,\omega)}{\eta(\xi^{-1},k,0)}=f_{\text{ret}}^{-z_\eta} , \tag{2.39}$$

leading to an additional factor in a_0 determined by

$$\ln a_{\text{ret}}=\langle\ln f_{\text{ret}}\rangle . \tag{2.40}$$

The evaluation of the average in (2.40) is presented in Appendix A. The result is

$$a_{\text{ret}}=1.10 , \tag{2.41}$$

so that the net correction factor for both nonlocality and retardation is

$$a_0=a_{\text{NL}}a_{\text{ret}}=1.65 . \tag{2.42}$$

We note that the retardation effect is much weaker than the nonlocal effect in the hydrodynamic regime, which contrasts with the near cancellation that occurs in the nonhydrodynamic limit.

With $z_\eta\simeq 0.06$, as discussed in Sec. III A, we obtain from (2.18) and (2.42)

$$R=1.03\ . \tag{2.43}$$

This value is substantially smaller than the value $R=1.20$ estimated by Siggia and co-workers from a calculation based on a renormalization-group treatment of critical dynamic behavior.[20] It is also slightly smaller than the value $R=1.075$ more recently obtained by Paladin and Peliti.[22]

D. Proposed approximant for the dynamic scaling function

In order to interpolate between the value of the scaling function [as defined in (2.16)] for $x=0$ and its asymptotic behavior for $x\rightarrow\infty$, we are guided by some general theoretical considerations. The first deviation of $S(x)$ from $S(0)$ has to be proportional to q^2, and hence to $x^2=q^2\xi^2$. At the other end of the scale, i.e., for $x\gg1$, the fractional change of $S(x)$ relative to its asymptotic behavior is expected to be inversely proportional to ξ^2 and hence proportional to x^{-2}. We adopt the simplest approximant that satisfies these requirements,

$$S(x)=(a_0^2+a_\infty^2x^2)^{1/2}=a_0(1+b^2x^2)^{1/2} \tag{2.44}$$

with b defined in (2.19). From (2.8), (2.16), (2.18), and (2.44) it follows that the critical diffusion coefficient is given by

$$\Delta D=\frac{Rk_BT}{6\pi\eta_s\xi}\Omega_K(x)(1+b^2x^2)^{z_\eta/2}\ . \tag{2.45}$$

From (2.27) and (2.42) we obtain for the parameter b the theoretical estimate

$$b=\frac{a_\infty}{a_0}=0.55\ . \tag{2.46}$$

We note that Paladin and Peliti[22] proposed an expression for the scaling function which is equivalent to replacing $S(x)/a_0$ in (2.44) by $(1+x^2)/\Omega_K(x)$. By virtue of the asymptotic behavior (2.15) of the Kawasaki function this corresponds to $b=8/3\pi=0.85$, a value larger than the theoretical estimate (2.46) obtained by us. We believe that our theoretical estimate for the parameter b is more accurate than our estimates for the individual amplitudes a_∞ and a_0, and hence for R, since the neglected vertex corrections are likely to cancel to some extent in taking the ratio a_∞/a_0.

III. COMPARISON WITH EXPERIMENT

A. Viscosity

As reported by several investigators the critical exponent z_η for the viscosity was originally predicted to be close to 0.054 on the basis of the mode-coupling theory of fluctuations.[16,18,23,26] Subsequently, Siggia and co-workers suggested the revised value 0.065 on the basis of a dynamic renormalization-group calculation[20]; this value appeared to be in good agreement with the experimental viscosity data for the mixture of 3-methylpentane and nitroethane.[1,29] Siggia *et al.* obtained this value from a perturbation expansion in terms of $4-d$, where d is the dimensionality, retaining terms up to $(4-d)^2$. However, Bhattacharjee and Ferrell noticed recently that inclusion of terms of order $(4-d)^3$ would modify the theoretical estimate from 0.065 to about 0.051 and argued that the actual value of z_η may be close to the value 0.054 earlier estimated from the mode-coupling theory.[30] Because of this development we reconsider here the analysis of the experimental viscosity data of 3-methylpentane and nitroethane.

The viscosity of 3-methylpentane and nitroethane near the critical mixing point was measured by Stein, Allegra, and Allen,[31] by Tsai and McIntyre,[32] and recently also by Sorensen.[33] The data of Tsai and McIntyre have the higher apparent precision, but, as argued previously,[1,29] they should be shifted by (3.1±0.7)% so as to conform to the calibration of Stein *et al.* The more recent data of Sorensen agree within error with the data of Stein *et al.*, thus giving added justification to this interpretation.[33]

The temperature dependence of the background viscosity $\bar{\eta}$ is commonly represented by an Arrhenius equation of the form

$$\bar{\eta}=A_\eta\exp(B_\eta/k_BT)\ . \tag{3.1}$$

Tsai and McIntyre also estimated $\bar{\eta}$ by extrapolating experimental data far away from the critical concentration to the critical concentration. If their values for $\bar{\eta}$ are fitted to (3.1) we obtain[1,29]

$$\begin{aligned}A_\eta&=2.431\times10^{-5}\ \mathrm{Pa\,s}=0.02431\ \mathrm{cP}\ ,\\ B_\eta&=1.333\times10^{-20}\ \mathrm{J}\ .\end{aligned} \tag{3.2}$$

Allen and co-workers adopted an alternative procedure for estimating the background viscosity using independent experimental information from tracer-diffusion measurements.[34] If their estimates for $\bar{\eta}$ are fitted to (3.1) we obtain

$$\begin{aligned}A_\eta&=1.085\times10^{-5}\ \mathrm{Pa\,s}=0.01085\ \mathrm{cP}\ ,\\ B_\eta&=1.471\times10^{-20}\ \mathrm{J}\ .\end{aligned} \tag{3.3}$$

In spite of the difference between the parameter sets quoted in (3.2) and (3.3), both parameter sets turn out to yield the same values for $\bar{\eta}$ in the experimental temperature range within about 1%. In view of the agreement between the two very different procedures for estimating $\bar{\eta}$ we can have confidence in our knowledge of the background viscosity $\bar{\eta}$ for 3-methylpentane and nitroethane at the critical concentration.

In the analysis of the experimental data we adopt for the power law $\xi=\xi_0\epsilon^{-\nu}$ the parameters[13]

$$\nu=0.630,\quad \xi_0=0.216 \tag{3.4}$$

(where ξ_0 is in nm) in agreement with the current theoretical estimate[35] for the exponent ν. If we then fit the experimental viscosity data of Tsai and McIntyre to the power law $\eta=\bar{\eta}(Q_0\xi)^{z_\eta}$ with the background viscosity $\bar{\eta}$ given by (3.1) and (3.2), we obtain

$$z_\eta=0.063\pm0.002\ , \tag{3.5a}$$

$$Q_0=1.4\pm0.9 \tag{3.5b}$$

(with Q_0 in nm^{-1}), where the quoted errors represent *two* standard deviations. In performing the least-squares analysis we adopted for the viscosity measurements the liberal error estimates suggested by Sorensen,[33] which we consider realistic. A comparison between the experimental data and the equation is shown in Fig. 2. The power law (2.9) appears to reproduce the experimental viscosity data with a standard deviation of less than 0.2%. In order to obtain some more information concerning the accuracy of the parameters quoted in (3.4) we also analyzed the data of Tsai and McIntyre with the background parameters (3.3) deduced from the data of Stein *et al.*, as well as with those background parameters free. Of course, when the background parameters are left free, we obtain an estimate for the coefficient $A_\eta Q_0^{z_\eta}$, but not for the amplitude Q_0 separately. We also repeated the analysis for the data of Stein *et al.*[31] and of Sorensen.[33] The results are presented in Table I. From the information in this table we conclude that the experimental value for the critical exponent z_η lies in a range bounded by

$$z_\eta = 0.062 \pm 0.005 \ . \tag{3.6}$$

This range is in good agreement with the experimental values for z_η reported for other binary liquids[36,37] and the values tend to be somewhat larger than the value 0.054 predicted from the mode-coupling theory.

The power law (2.9) represents the asymptotic behavior of the viscosity near the critical temperature. Far away from the critical temperature the viscosity should approach the background viscosity $\bar{\eta}$. As shown by Bhattacharjee *et al.* the crossover behavior of the viscosity from its critical behavior to its normal behavior can be represented by an equation of the form[38]

$$\eta_s = \bar{\eta} \exp(z_\eta H) \ , \tag{3.7}$$

where the function H is specified in Eq. (B11) in Appendix B. The function H depends on the temperature via the correlation length ξ and contains, in addition, two parameters q_C and q_D. The parameter q_D is a Debye-cutoff wave number in the decoupled-mode integral for the viscosity and the parameter q_C is related to the background diffusion coefficient $\bar{D}$ as elucidated in Appendix B; these parameters are related to the amplitude Q_0 in the power law (2.9) by

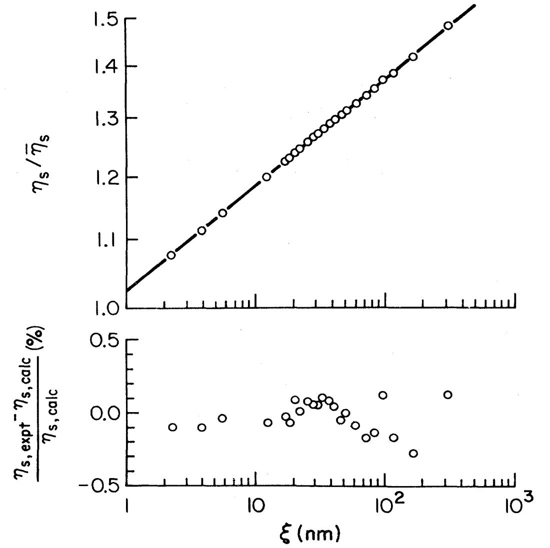

FIG. 2. Comparison between the experimental viscosity data of Tsai and McIntyre and the values calculated from (2.9) and (3.1) with parameters from (3.2) and (3.5).

$$Q_0^{-1} = \tfrac{1}{2} e^{4/3} (q_C^{-1} + q_D^{-1}) \ . \tag{3.8}$$

The experimental viscosity data satisfy the simple power law (2.9) with considerable accuracy as is evident from Fig. 2. Nevertheless, we investigated the possible effects of corrections to this asymptotic behavior by fitting the viscosity data to (3.7). However, it was found that use of (3.7) did not improve the quality of the fit, while the values obtained for the exponent z_η remained within error equal to the values quoted in Table I. On the other hand, the values obtained from the amplitude Q_0 via (3.8) were somewhat sensitive to the introduction of the crossover function (3.7). For the analysis of the diffusion coefficient data we need an estimate for the parameter q_C as discussed below. From fits of the viscosity data to (3.7) for various values of the ratio q_D/q_C we found that the possible values of q_C are in the range (in nm)

TABLE I. Analysis of viscosity data in terms of the power law (2.9).

$Q_0 \pm \sigma_{Q_0}$ (nm^{-1})	$z_\eta \pm \sigma_{z_\eta}$	Reduced χ^2	Data source	Background parameters
1.4±0.4	0.063±0.001	0.06	Reference 32	Equation (3.2)
1.4±0.4	0.060±0.001	0.3	Reference 32	Equation (3.3)
	0.063±0.002	0.05	Reference 32	Free
1.2±0.3	0.066±0.001	1.2	Reference 31	Equation (3.2)
1.2±0.3	0.063±0.001	1.6	Reference 31	Equation (3.3)
	0.067±0.001	1.2	Reference 31	Free
1.3±0.3	0.067±0.001	0.9	Reference 33	Equation (3.2)
1.8±0.06	0.057±0.001	1.4	Reference 33	Equation (3.3)
	0.066±0.003	0.9	Refernece 33	Free

$$0<q_C^{-1}<0.22\ . \tag{3.9}$$

If we impose a ratio $q_D/q_C \simeq 1.7$, which is about the average value of this ratio found from the viscosity data for some fluids near the gas-liquid critical point,[39] we obtain $q_C^{-1} \simeq 0.17$ nm with a spread of about ±0.03 nm.

B. Diffusion coefficient

In order to compare the experimental diffusion coefficient data with the theoretically predicted behavior (2.8) we need an estimate for the background diffusion coefficient $\bar{D}$. As shown in Appendix B this background contribution can be approximated by

$$\bar{D}=\frac{k_B T}{16\bar{\eta}\xi}\left[\frac{1+q^2\xi^2}{q_C\xi}\right] . \tag{3.10}$$

In the absence of direct experimental information for the background diffusion coefficient $\bar{D}$, Oxtoby and Gelbart suggested that it be estimated from the critical behavior of the viscosity.[40] In our terminology their procedure amounts to determining q_C from (3.8) with $q_D^{-1}=0$. With the value $Q_0=1.4\ \text{nm}^{-1}$ as quoted in (3.5b) we would obtain $q_C^{-1}=0.36$ nm. However, for fluids near the gas-liquid critical point, where the background contribution to the diffusion of the order-parameter fluctuations can be estimated more directly from thermal conductivity data,[15] we found earlier that the procedure of Oxtoby and Gelbart yields a background which is too large.[39] Comparison with (3.9) confirms that $q_C^{-1}=0.36$ nm is too large and we think that about half this value, i.e., $q_C^{-1}\simeq 0.18$ nm, is a more realistic estimate.

In Fig. 3 we show the relative background contribution $\bar{D}/D$ as calculated from (3.10) with $q_C^{-1}=0.18$ nm. We note that this background contribution does not vanish at the critical temperature as is often assumed,[41] but reaches the finite limit

$$\lim_{T\to T_c}\frac{\bar{D}}{D}\simeq\lim_{T\to T_c}\frac{\bar{D}}{\Delta D}=\frac{q}{q_C}\left[\frac{Q_0}{a_\infty q}\right]^{z_\eta} . \tag{3.11}$$

The background contributions are most important for the data obtained at the larger wave number q, i.e., at the larger scattering angle.

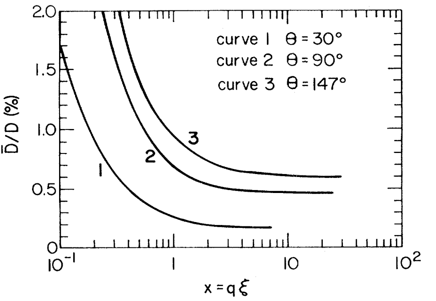

FIG. 3. Ratio $\bar{D}/D$ as a function of the $x=q\xi$ at the wave numbers corresponding to the three scattering angles.

We are unable to estimate the background contribution accurately. To prevent our background estimates from influencing the comparison between theory and experiment, we retain for further analysis only those experimental data for which the estimated background correction $\bar{D}/D$ does not exceed 1%. Thus for the experimental data obtained at the three scattering angles 30°, 90°, and 147° we retain the data corresponding to values of $x=q\xi$ larger than 0.2, 0.6, and 0.8, respectively.

From (2.8) we note that it is advantageous to introduce a reduced diffusion coefficient D^* defined as

$$D^*=\frac{6\pi\eta_s\xi}{k_B T}(D-\bar{D})=\Omega(x) . \tag{3.12}$$

The reduced diffusion coefficient D^*, deduced from the experimental data, is plotted in Fig. 4 as a function of the scaling variable $x=q\xi$. The data obtained at the three different scattering angles do collapse onto a single curve within experimental accuracy, thus confirming the validity of the hypothesis of dynamic scaling for the order-parameter fluctuations.

A value for the dynamic scaling exponent y was deduced from our experimental light scattering data previously.[1,42] In terms of the notation adopted in the present paper this was done by fitting the data at a given temperature to a power law of the form

$$D^*\propto x^{y_{\text{eff}}(T)}\propto q^{y_{\text{eff}}(T)} , \tag{3.13}$$

so that

$$y=\lim_{T\to T_c} y_{\text{eff}}(T) . \tag{3.14}$$

The values obtained for this effective exponent $y_{\text{eff}}(T)$ close to the critical temperature are shown in Fig. 5(a) as a function of $T-T_c$; this figure corresponds to Fig. 3 in Ref. 42. Extrapolating the data linear to $T-T_c=0$, we obtain

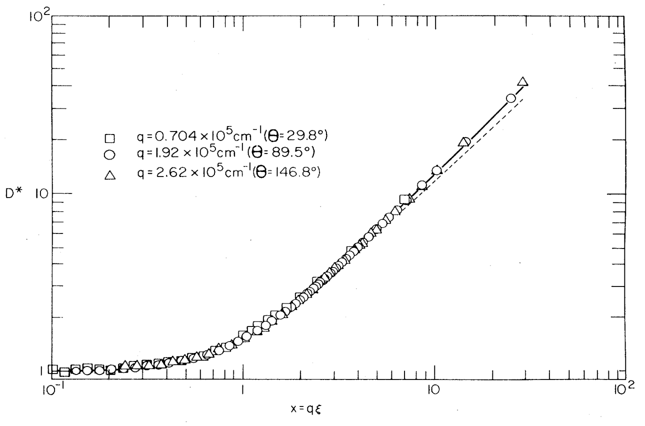

FIG. 4. Reduced diffusion coefficient $D^*=6\pi\eta_s\xi(D-\bar{D})/k_B T$ as a function of the scaling variable $x=q\xi$. Dashed curve represents the Kawasaki function $\Omega_K(x)$ and the solid curve represents the approximant for the dynamic scaling function proposed in this paper.

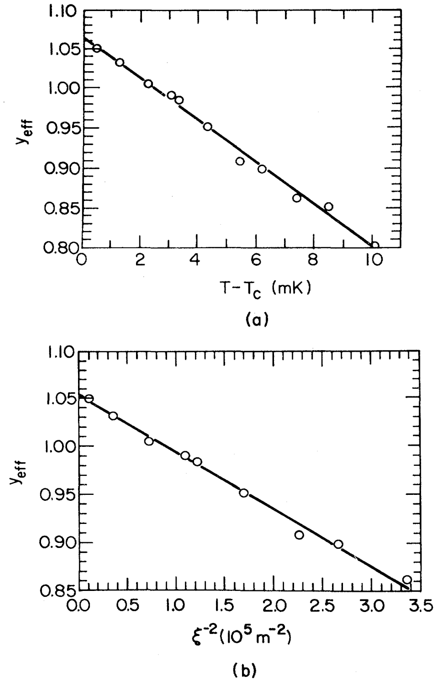

FIG. 5. Effective exponent $y_{\text{eff}}(T)$ close to the critical temperature (a) as a function of $T-T_c$ and (b) as a function of ξ^{-2}.

$$y = 1.063 \pm 0.024 , \qquad (3.15)$$

where the quoted error represents two standard deviations. However, as pointed out by Bhattacharjee and Ferrell,[30] for given wave number q, y_{eff} should approach its limiting value not as a linear function of $(T-T_c)$ but as $x^{-2} \propto \xi^{-2}$. In Fig. 5(b) we show the asymptotic behavior of y_{eff} as a function of ξ^{-2}. Extrapolating the data linearly in ξ^{-2} we obtain

$$y = 1.053 \pm 0.024 . \qquad (3.16)$$

The two limiting procedures yield the same value of the exponent y within error and confirm the validity of the dynamic exponent relation (2.11). However, we are unable on the basis of our light scattering data to discriminate between the value $y = 1.054$ suggested by the mode-coupling theory and the value $y = 1.063$ deduced via (2.11) from the experimental viscosity data.

We now return to the main topic of this paper, namely, the determination of the dynamic scaling function. Our experimental data were obtained at three different scattering angles. However, as discussed in our previous paper,[1] the data obtained at 90° have a higher accuracy than those obtained at 30° and 147°. For this reason we use the 90° scattering data to determine the dynamic scaling function.

The experimental values of the dynamic scaling function $\Omega(x)$ are determined from (3.12). In order to focus our attention more directly on the deviations of the experimental dynamic scaling function data from the Kawasaki function $\Omega_K(x)$ we consider

$$\frac{1}{x^2}\left[\frac{D^*}{\Omega_K(x)}\right]^{2/z_\eta} = \frac{S^2(x)}{x^2} = a_0^2 x^{-2} + a_\infty^2 . \qquad (3.17)$$

The values thus deduced for $S^2(x)/x^2$ from the 90° scattering data with $z_\eta = 0.063$ are plotted as a function of x^{-2} in Fig. 6. The values for $x > 1$ are also shown on a larger scale in Fig. 7. The experimental data can be represented by a straight line well within experimental accuracy and we obtain $a_0^2 = 1.53 \pm 0.06$ and $a_\infty^2 = 0.34 \pm 0.04$, where the quoted errors represent two standard deviations. The coefficient $b^2 = a_\infty^2 / a_0^2 = 0.22$ is determined by the intercept of the line with the horizontal axis as shown in Fig. 7, so that $b = 0.47$, while $R = a_0^{z_\eta} = 1.01$. The standard deviations obtained from a least-squares fit do not account for the effect of systematic errors. Specifically, the coefficient b is affected by an error in z_η. If we repeat the procedure with $z_\eta = 0.053$, found from (3.16), we obtain $a_0^2 = 1.62 \pm 0.06$ and $a_\infty^2 = 0.51 \pm 0.04$, so that $b = 0.56$ and $R = 1.01$. By considering the results of fits with different weighting procedures and including the effects of a 20% error in z_η, a 1% error in D due to uncertainties in the background correction, a 0.5° error in the scattering angle, a 0.2-mK error in T_c, a 1% error in the correlation length ξ, and a 1.5% error in the viscosity η_s, we find

$$b = 0.5 \pm 0.2 , \qquad (3.18)$$

$$R = 1.01 \pm 0.04 . \qquad (3.19)$$

In the analysis we have neglected deviations of the order-parameter correlation function from the Ornstein-Zernike form (2.3). The effect of such deviations on the diffusion coefficient can be accounted for by a factor $C(x)$ evaluated previously.[1] However, the corrections are within experimental accuracy and would affect the value of b by less than 10%.

The experimental values $b = 0.5 \pm 0.2$ and $R = 1.01 \pm 0.04$ are in good agreement with the values $b = 0.55$ and

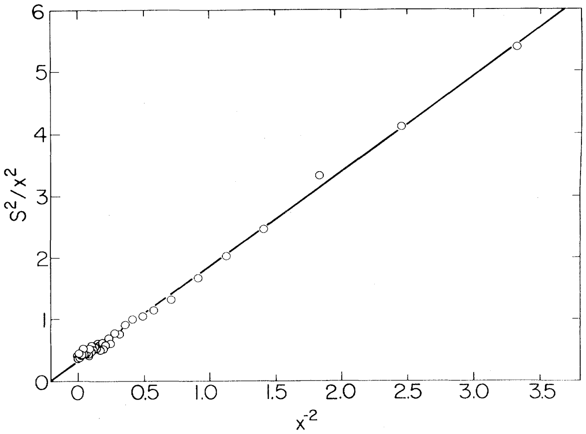

FIG. 6. Scaling function $S^2(x)/x^2$ as a function of x^{-2}. Open circles represent the values deduced from our 90° scattering data.

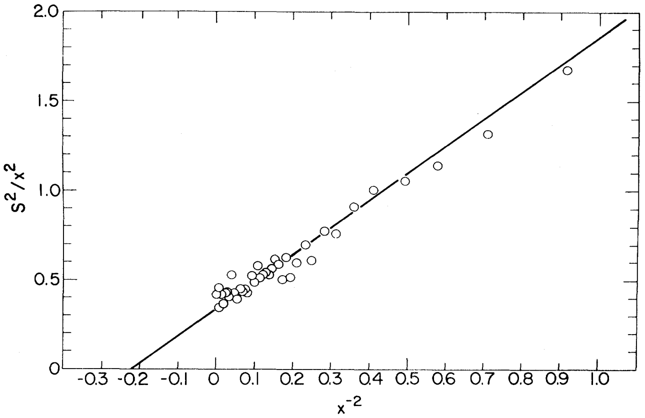

FIG. 7. Scaling function $S^2(x)/x^2$ as a function of x^{-2} for large values of x.

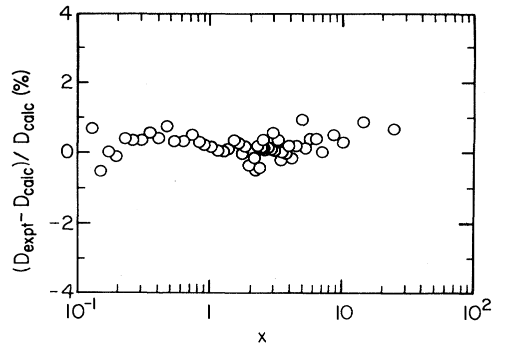

FIG. 8. Comparison of the critical diffusion coefficient calculated from Eq. (4.1) with the experimental values deduced from the 90° scattering data.

$R=1.03$ found in (2.46) and (2.43) from the decoupled-mode theory, but do not agree as well with those proposed by Paladin and Peliti.[22] The value obtained for the amplitude R also agrees with the value $R=1.02\pm0.06$ earlier deduced[29] from an asymptotic analysis of the data for small x. The smaller error estimate in (3.19) is due to the fact that the previous determination included also the less accurate scattering data obtained at 30° and 147°; furthermore, the data at small x are more strongly affected by errors in the background corrections.

Our result for the amplitude R is significantly smaller than the value $R=1.16\pm0.01$ found by Beysens from data for seven fluids.[43,44] However, values consistent with our value $R=1.01\pm0.04$ have been obtained by Güttinger and Cannell[45] for xenon, by Chang and Doiron[46] for ethane, by Hamano *et al.*[47] for polydimethylsiloxane-diethylcarbonate, and by Chen *et al.* for *n*-hexane and nitrobenzene.[41]

In addition, we have obtained an accurate experimental value for the amplitude of the dynamic scaling function in the nonhydrodynamic limit.

IV. DISCUSSION

It appears that the critical part ΔD of the diffusion coefficient can be represented by a simple generalized Stokes-Einstein diffusion law of the form

$$\Delta D=\frac{Rk_BT}{6\pi\eta_s\xi}\Omega_K(x)(1+b^2x^2)^{z_\eta/2} \tag{4.1}$$

as a function of the scaling variables $x=q\xi$ with parameter values

$$z_\eta=0.06\pm0.02,\quad R=1.01\pm0.04,\quad b=0.5\pm0.2 \tag{4.2}$$

in agreement with theoretical estimates. In Fig. 8 we show the difference between the experimental values deduced from the 90° scattering data and the values calculated from (4.1) with the parameter values (4.2). The experimental data are reproduced to well within 1%.

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APPENDIX A: RETARDATION CORRECTION

We calculate here the average $\langle \ln f_{\rm ret}\rangle$ needed in (2.40), making use of the theoretically predicted frequency dependence of the viscosity.[48]

The general correction factor $f_{\rm ret}(\xi^{-1},k,\omega)$ is difficult to calculate. In the limit $k=0$ this factor can be fit to an equation of the form[48,49]

$$\ln f_{\rm ret}(\xi^{-1},0,\omega)=\tfrac{1}{3}\ln\left[1+B\frac{-i\omega}{\xi^{-2}D(\xi^{-1},0,0)}\right]. \tag{A1}$$

In the low-frequency range $B=B_0=3\pi/32=0.294$, while in the high-frequency range the much smaller value $B=B_\infty=4e^{-4}=0.073$ is obtained. For our present purposes the value $B\simeq\frac{3}{16}$ provides a good fit over the relevant frequency range.[50]

The "conservation of energy" condition in the decoupled-mode formalism requires that the frequency in (2.20) and (A1) be identified with $\omega_\Gamma=i\Gamma$, the negative of the order-parameter mode, so that

$$\begin{aligned}-i\omega_\Gamma&=\Gamma(\xi^{-1},k',0)=\Gamma(\xi^{-1},k,0)\\&=k^2D(\xi^{-1},0,0)\,.\end{aligned} \tag{A2}$$

We thus obtain from (A1)

$$\ln f_{\rm ret}\simeq\tfrac{1}{3}\ln(1+Bk^2\xi^2) \tag{A3}$$

and the average required in (2.40) is therefore

$$\langle \ln f_{\rm ret} \rangle = \tfrac{2}{3}\sqrt{B}\, I(B) \; . \tag{A4}$$

This result is, however, an overestimate because of the fact that the small—wave-number approximation breaks down for $k \gg \xi^{-1}$. In the limit $k\xi \to \infty$, (A3) has to be replaced with[4,51]

$$\ln f_{\rm ret}(0,k,i\Gamma(0,k,0)) = \tfrac{1}{3}\ln(1+A) \; , \tag{A5}$$

where[52]

$$A = 6\ln 2 + 6 - 3\pi = 0.734 \; , \tag{A6}$$

which we round off to $\frac{3}{4}$. Comparison of (A5) with (A3) yields a "saturation" value of $k\xi$ as

$$p_s = (A/B)^{1/2} = 2 \; . \tag{A7}$$

The overestimate originates in the interval $k\xi = p > p_s$ from the excess of $\ln(1+Bp^2)$ over its saturation limit $\ln(1+Bp_s^2) = \ln(1+A)$. The range $p \geq p_s$ contributes to the average the fractional weight

$$\frac{2}{\pi}\int_{p_s}^{\infty} \frac{dp}{1+p^2} = \frac{2}{\pi}\,\mathrm{arccot}2 = 0.295 \; , \tag{A8}$$

so that the contribution of the saturation region to $3\langle \ln f_{\rm ret} \rangle$ is

$$\frac{2}{\pi}\int_{p_s}^{\infty} \frac{dp}{1+p^2}\ln(1+A) = 0.165 \; . \tag{A9}$$

The range $0 \leq p \leq p_s$ contributes, on the other hand,

$$\frac{2}{\pi}\int_{0}^{p_s} \frac{dp}{1+p^2}\ln(1+Bp^2) = 2\sqrt{B}\, I(B,\sqrt{A}\,) \; , \tag{A10}$$

where the integral

$$I(t,u) = \frac{1}{\pi}\int_{0}^{u} \frac{dp}{t+p^2}\ln(1+p^2) \tag{A11}$$

is the generalization of (2.36) with a finite upper limit. For $t=0$ we obtain

$$I(0,u) = \frac{2}{\pi}\arctan u - \frac{1}{\pi u}\ln(1+u^2) \tag{A12}$$

with the limit $I(0,\infty)=1$ as before. In the present case with $A = \frac{3}{4}$ we obtain from (A12)

$$I(0,\sqrt{A}\,) = 0.454 - 0.206 = 0.248 \; . \tag{A13}$$

The effect of finite t is given by the difference

$$I(t,u) - I(0,u) = -\frac{t}{\pi}\int_{0}^{u} \frac{dp}{t+p^2}\,\frac{\ln(1+p^2)}{p^2} \; . \tag{A14}$$

Because $u = \sqrt{A} < 1$, the Taylor series $p^{-2}\ln(1+p^2) = 1 - \frac{1}{2}p^2 + \frac{1}{3}p^4 + \cdots$ is uniformly convergent. Integration then gives a rapidly converging series, the first two terms of which yield the sufficiently accurate result

$$I(t,u) - I(0,u) \simeq -\frac{\sqrt{t}}{\pi}\arctan\frac{u}{\sqrt{t}} + \frac{t^{3/2}}{2\pi}\left[\frac{u}{\sqrt{t}} - \arctan\frac{u}{\sqrt{t}}\right] . \tag{A15}$$

With $u = \sqrt{A} = \frac{1}{2}\sqrt{3}$ and $t = B = \frac{3}{16}$, we obtain from (A10), (A13), and (A15)

$$\frac{2}{\pi}\int_{0}^{p_s} \frac{dp}{1+p^2}\ln(1+Bp^2) = 0.093 \; . \tag{A16}$$

On adding (A9) to (A16) we arrive at a total retardation correction of

$$\ln a_{\rm ret} = \langle \ln f_{\rm ret} \rangle = \tfrac{1}{3}(0.165 + 0.093) = 0.086 \; , \tag{A17}$$

so that

$$a_{\rm ret} = 1.10 \; , \tag{A18}$$

which is used in (2.42) in Sec. II C.

APPENDIX B: BACKGROUND CONTRIBUTION TO DIFFUSION COEFFICIENT

In Sec. II A we made a distinction between the anomalous contributions ΔL and $\Delta\eta$ to the transport coefficients due to long-range critical fluctuations and background contributions $\bar{L}$ and $\bar{\eta}$ due to noncritical short-range fluctuations. For the gas-liquid critical-point phase transition it has been clearly demonstrated that incorporation of background corrections is necessary to obtain quantitative agreement between theory and experiment.[2,15] For the critical mixing transition in binary liquids one must expect the presence of similar correction terms. In practice, however, such correction terms are usually not considered in the interpretation of the experimental data for binary liquid mixtures.[2] Part of the problem arises from the fact that it is more difficult to estimate the background contributions to the decay rate of the order-parameter fluctuations for binary liquids than for gases. For gases the background contribution $\bar{L}$ can be deduced from available experimental data of the thermal conductivity coefficients.[53] For binary liquids similar experimental information for the coefficients $\bar{L}$ is usually not available. Nevertheless, for an accurate comparison between theory and experiment we need an estimate for the background correction terms.[25]

As in earlier work of Bhattacharjee *et al.*[38] we write the background contribution $\bar{D}$ to the diffusion coefficient in the form

$$\bar{D} = \frac{k_B T}{16\bar{\eta}\xi}\left[\frac{1+q^2\xi^2}{\tilde{q}_C\xi}\right] . \tag{B1}$$

Since $\bar{\eta}$ and T are slowly varying functions of temperature, it can be readily verified that (B1) is consistent with (2.7) in the Ornstein-Zernike approximation.

The critical diffusion coefficients ΔD is given by the decoupled-mode integral (2.20). In order to derive the scaled asymptotic expression (2.8) for ΔD one needs to carry out the integration over the entire range of wave numbers k. However, physically the mode-coupling contributions must disappear at a large but finite cutoff wave number q_D as originally pointed out by Perl and Ferrell.[26] We thus expect

$$\Delta D = \frac{k_B T}{(2\pi)^3}\int_0^{q_D} dk \int_0^{\pi} d\theta\,\sin^3\theta \int_0^{2\pi} d\phi\,\frac{g(k'\xi)}{\eta(k)g(q\xi)} \; , \tag{B2}$$

where θ and ϕ are the polar and azimuthal angles of $\vec{k}$ with respect to $\vec{q}$. As a consequence ΔD is related to the asymptotic behavior of

$$\Delta D=\frac{k_B T}{6\pi\eta_s\xi}\Omega(q\xi)-\frac{k_B T}{3\pi^2}\int_{q_D}^{\infty}\frac{dk\,g(k\xi)}{\eta(k)g(q\xi)}\;, \tag{B3}$$

which is a more correct version of (2.8). Here we have made use of the approximation that $k\simeq k'\gg q$ in the correction term in (B3). In the limit $k\xi\gg 1$ we have $q(k\xi)=1/k^2\xi^2$ and $\eta(k)=\bar{\eta}(Q_0/a_{\text{eff}}^{\text{visc}}k)^{z_\eta}$, so that the correction term becomes

$$\frac{k_B T}{3\pi^2}\int_{q_D}^{\infty}\frac{dk\,g(k\xi)}{\eta(k)g(q\xi)}\simeq C\frac{k_B T}{16\bar{\eta}\xi}\left[\frac{1+q^2\xi^2}{2q_D\xi}\right] \tag{B4}$$

with

$$C=\frac{32}{3(1-z_\eta)\pi^2}\left[\frac{a_{\text{eff}}^{\text{vis}}q_D}{Q}\right]^{z_\eta}\simeq\frac{32}{3\pi^2}\;, \tag{B5}$$

because $z_\eta\ll 1$. The constant C is close to unity. It follows from (B1), (B3), and (B4) that in this approximation

$$D=\frac{k_B T}{6\pi\eta_s\xi}\Omega(q\xi)-\frac{k_B T}{16\bar{\eta}\xi}\left[\frac{1+q^2\xi^2}{2q_D\xi}\right]+\frac{k_B T}{16\bar{\eta}\xi}\left[\frac{1+q^2\xi^2}{\tilde{q}_C\xi}\right]. \tag{B6}$$

In our previous paper[1] we compared the experimental data with the finite cutoff integral (B2). For that purpose we introduced a background correction of the form given by (B1). In this paper we want to compare the experimental data with the fully scaled asymptotic behavior (2.8). From (B6) it follows that this goal can be accomplished by redefining the background correction as

$$\bar{D}=\frac{k_B T}{16\bar{\eta}\xi}\left[\frac{1+q^2\xi^2}{q_C\xi}\right], \tag{B7}$$

where the wave numbers q_D, q_C, and $\tilde{q}_C$ are related by[38]

$$\frac{1}{\tilde{q}_C}=\frac{1}{q_C}+\frac{1}{2q_D}\;. \tag{B8}$$

The critical viscosity in the hydrodynamic limit $q\rightarrow 0$ is given by the integral

$$\Delta\eta=\frac{k_B T}{(2\pi)^3}\int_0^{q_D}dk\int_0^{\pi}d\theta\sin^3\theta\cos^2\theta\int_0^{2\pi}d\phi\left[\frac{k^2\xi^2}{1+k^2\xi^2}\right]^2\frac{1}{D(k)}\;, \tag{B9}$$

where we have assumed that the cutoff wave number q_D is the same as in the integral (B2) for the diffusion coefficient. If one substitutes (B6) and (B8) into (B9), one arrives at an equation for the viscosity which we write in the form

$$\eta_s=\bar{\eta}\exp(z_\eta H)\;. \tag{B10}$$

The function H depends on the parameters q_C and q_D and can be approximated by[38]

$$H=\tfrac{1}{12}\sin(3\psi_D)-\frac{1}{4q_C}\xi\sin(2\psi_D)+\frac{1}{(q_C\xi)^2}[1-\tfrac{5}{4}(q_C\xi)^2]\sin\psi_D-\frac{1}{(q_C\xi)^3}\{[1-\tfrac{3}{2}(q_C\xi)^2]\psi_D-|(q_C\xi)^2-1|^{3/2}L(w)\}\;, \tag{B11}$$

where

$$\psi_D=\arccos(1+q_D^2\xi^2)^{-1/2}\;, \tag{B12}$$

$$w=\left|\frac{q_C\xi-1}{q_C\xi+1}\right|^{1/2}\tan\frac{\psi_D}{2}\;, \tag{B13}$$

$$L(w)=\begin{cases}\ln\dfrac{1+w}{1-w} & \text{if } q_C\xi>1\\ 2\arctan|w| & \text{if } q_C\xi\le 1\;.\end{cases} \tag{B14}$$

For large values of ξ, i.e., close to the critical point, (B7) reduces to the power law $\eta_s=\bar{\eta}(Q_0\xi)^{z_\eta}$ with

$$\frac{1}{Q_0}=\tfrac{1}{2}e^{4/3}\left[\frac{1}{q_C}+\frac{1}{q_D}\right]. \tag{B15}$$

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