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Two-exponential decay of dynamic light scattering in near-critical fluid mixtures

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Two hydrodynamic relaxation modes associated with mass diffusion and thermal diffusion are present in binary fluids. In near-critical binary fluids a coupling between the two modes results in two characteristic relaxation times, neither of which is associated with pure mass diffusion or pure thermal diffusion. Instead, the relaxation times are inversely proportional to two effective diffusivities D_1 and D_2, which can be detected experimentally by dynamic light scattering. The physical meaning of D_1 and D_2 changes as one considers states in the vicinity of different points on the critical locus: in the infinite-dilution limit the diffusivity D_1 of the slow mode is associated with the thermal diffusivity and the diffusivity D_2 of the fast mode with the mutual mass diffusion coefficient, while in the ''incompressible'' liquid-mixture limit D_1 is associated with the mass diffusion coefficient and D_2 with the thermal diffusivity. In addition we have determined the intensities (amplitudes) of these relaxation modes, which can also be measured with light scattering. We discuss the conditions at which a two-exponential decay of the dynamic correlation function can be measured. As an example we consider mixtures of methane and ethane near the vapor-liquid critical line where the two exponential decays indeed have been observed. [S1063-651X(98)05402-6]

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I. INTRODUCTION

Dynamic light scattering is a popular method for investigating the critical behavior of transport properties of fluids and fluid mixtures [1–3]. The critical slowing down of the fluctuations of the order parameter can be detected by measuring the time-dependent correlation function of the scattered photons. In one-component fluids the critical slowing down is caused by a dramatic decrease in the thermal diffusivity, while in binary mixtures it is associated with a similar behavior of the mutual diffusion. The theoretical description of the critical slowing down is based on dynamic scaling theory [4] and on mode-coupling theory [5], which has been confirmed experimentally by many investigators [6–14]. However, there is an important feature in dynamic critical phenomena that has not yet been adequately discussed in the literature.

In binary fluids one can in principle detect with dynamic light scattering two diffusive modes [15,16]. Specifically, the two effective diffusivities D_1 and D_2 that determine the decay rates of the two modes can be derived from the hydrodynamic theory of fluctuations [15,17]:

$$D_{1,2}=\frac{1}{2}(a+\mathcal{D})\mp\frac{1}{2}[(a+\mathcal{D})^2-4aD]^{1/2} \tag{1.1}$$

with

$$\mathcal{D}=D\left[1+\frac{k_T^2}{TC_{P,c}}\left(\frac{\partial\mu'}{\partial c}\right)_{P,T}\right], \tag{1.2}$$

where $a=\lambda/\rho' C_{P,c}$ is the thermal diffusivity, λ the thermal conductivity, ρ' the mass density, $C_{P,c}$ the isobaric specific heat capacity, D the mass diffusion coefficient, μ' the difference between the chemical potentials of the solute and of the solvent per unit mass, c the mass concentration of the solute, and $k_T=D_T/D$ the thermal-diffusion ratio with D_T being the thermodiffusion coefficient [18]. If the coupling between mass and thermal diffusion is absent ($k_T=0$), D_1 and D_2 are associated with either the pure thermal diffusivity a or the pure mutual mass diffusion coefficient D. The coupling between these two modes also vanishes in the infinite-dilution limit.

At the critical point of a binary fluid mixture the mass diffusion coefficient D vanishes and asymptotically close to the critical point the mass-diffusion mode is responsible for the critical slowing down of the order-parameter fluctuations [19]. The thermal diffusivity a should not exhibit a significant change in the immediate vicinity of the critical point of a mixture as λ remains finite and $C_{P,c}$ is either constant (in the mean-field theory) or weakly divergent (in the scaling theory) [20,21]. Therefore, asymptotically close to the critical point the coupling between the two hydrodynamic modes again becomes unimportant and the mode with diffusivity D_1 represents a *slow* (critical) diffusion mode as D_1 tends to the diffusion coefficient D, while the mode with the diffusivity D_2 represents a relatively *fast* diffusion mode as D_2 tends to the thermal diffusivity a. This is why all experiments performed on binary fluids have been interpreted until the present time in such a way that the diffusivity associated with the critical diffusion mode in mixtures was identified with the mass diffusion, whereas in pure fluids it was identified with the thermal diffusivity.

The critical decay rate has been studied extensively by dynamic light scattering in pure fluids near the vapor-liquid critical point and in binary liquid mixtures near the liquid-

liquid critical (*consolute*) *point* [6–14]. *A limited number of measurements have been carried out on binary mixtures near their vapor-liquid critical point* [10,22–24]. *Despite the fact that the theory predicts the existence of two relaxation modes near the critical points of binary fluid mixtures, there is only one experiment*, *reported by Ackerson and Hanley* [22], *in which two relaxation modes actually have been observed*: *namely, near the vapor-liquid critical point of a mixture of* 71.07 *mol* % *methane and* 28.93 *mol* % *ethane*. *The two decay rates observed were attributed to pure mass diffusion and pure thermal diffusivity*. *Miura et al.* [10] investigated ^{3}He-^{4}He mixtures of different compositions along their respective critical isochores near the vapor-liquid critical points, but were able to detect only a single decay rate corresponding to the slow relaxation mode with effective diffusivity D_1. The two decay rates, one associated with mass diffusion and another with thermal diffusivity, were also detected in a noncritical liquid mixture of carbon disulfate and acetone by Berge *et al.* [25].

In this paper we show that in binary fluid mixtures in the commonly used experimental proximity to the vapor-liquid critical point neither D_1 nor D_2 can be associated with pure mass diffusion or thermal diffusivity. While the characteristic behavior of D_1 and D_2 near the critical line is rather insensitive to the composition, the physical meaning of these effective diffusivities changes drastically from the infinite-dilution limit to the ''incompressible'' liquid-mixture limit. We will show that at infinite dilution D_1 (slow mode) becomes the thermal diffusivity a and D_2 (fast mode) becomes the mass diffusion coefficient D, while in the incompressible liquid-mixture limit D_1 is to be identified with the mass diffusion coefficient D and D_2 with the thermal diffusivity a. Generally, the apparent decay rates will obey crossover between these two limits. This fact has not yet been addressed in analyzing dynamic light-scattering experiments performed in fluid mixtures. To specify the experimental conditions for observing the two relaxation modes we calculate the relative intensities of the two modes and give a detailed comparison of the theory with experimental data for mixtures of methane and ethane.

This paper is organized as follows. Section II gives the theoretical background on light scattering from fluctuations in binary fluids. A comprehensive analysis of the two diffusive modes is presented in Secs. III and IV. In Sec. V, the theoretical results obtained are compared with experimental data for binary mixtures of methane and ethane. Detection of these two relaxation modes is a challenging task for experimentalists. We discuss the conditions for making this phenomenon experimentally observable.

II. THEORETICAL BACKGROUND

A. Thermodynamic fluctuations

The field-dependent density of the thermodynamic potential suitable for the description of near-critical binary mixtures, the pressure P, is a function of three variables, namely, the temperature T, the chemical potential of the solvent μ_1, and the solute-solvent chemical-potentials difference $\mu=\mu_2-\mu_1$, and it satisfies a differential relation of the form [20,21]:

$$dP=s\,dT+\rho\,d\mu_1+\rho x\,d\mu, \tag{2.1}$$

where ρ is the total molar density, x is the mole fraction of the solute, $s=\rho S$ is the entropy density with S being the molar entropy, and μ_1 and μ_2 are molar based chemical potentials.

In the Gaussian approximation $\langle\delta T\delta P\rangle\neq 0$, $\langle\delta S\delta x\rangle\neq 0$, and $\langle\delta T\delta\mu\rangle\neq 0$ and for either of the choices of the three thermodynamic variables (T,P,x), (S,P,x), or (T,ρ,μ), the fluctuations of these variables are not statistically independent [26]. This is why, following Refs. [15,16], we consider a variable ϕ defined as

$$\phi=T-\frac{T\alpha_T}{\rho C_{P,x}}P, \tag{2.2}$$

where $\alpha_T=-\rho^{-1}(\partial\rho/\partial T)_{P,x}$ is the thermal expansion coefficient and $C_{P,x}$ the molar heat capacity at constant pressure and composition. It can be shown that [16]

$$\delta\phi=\frac{T}{C_{P,x}}\left[\delta S+\left(\frac{\partial\mu}{\partial T}\right)_{P,x}\delta x\right]. \tag{2.3}$$

The set (T,ϕ,x) is statistically independent with

$$\langle|\delta P|^2\rangle=\frac{k_B T\rho}{V}\left(\frac{\partial P}{\partial\rho}\right)_{S,x}, \tag{2.4}$$

$$\langle|\delta\phi|^2\rangle=\frac{k_B T^2}{V\rho C_{P,x}^2}\left[C_{P,\mu}-T\left(\frac{\partial\mu}{\partial T}\right)_{P,x}^2\left(\frac{\partial x}{\partial\mu}\right)_{P,T}\right]=\frac{k_B T^2}{V\rho C_{P,x}}, \tag{2.5}$$

$$\langle|\delta x|^2\rangle=\frac{k_B T}{V\rho}\left(\frac{\partial x}{\partial\mu}\right)_{P,T}, \tag{2.6}$$

where k_B is Boltzmann's constant and V the volume in which the fluctuations are considered. We also note that the expressions for the mean squared fluctuations of the entropy S (used in calculating $\langle|\delta\phi|^2\rangle$) and of the density ρ are

$$\langle|\delta S|^2\rangle=\frac{k_B C_{P,\mu}}{V\rho}. \tag{2.7}$$

$$\langle|\delta\rho|^2\rangle=\frac{k_B T\rho}{V}\left(\frac{\partial\rho}{\partial P}\right)_{T,\mu}, \tag{2.8}$$

where $C_{P,\mu}$ is the molar heat capacity at constant pressure and constant chemical-potential difference μ.

In classical thermodynamics the derivative $(\partial S/\partial T)_{P,\mu}=C_{P,\mu}/T$ and, hence, $\langle|\delta S|^2\rangle$ are not well defined, since the zero points of chemical potentials and entropy are arbitrary [20,21]. In contrast, $C_{P,x}$ and $(\partial x/\partial\mu)_{P,T}$ and, therefore, $\langle|\delta\phi|^2\rangle$ and $\langle|\delta x|^2\rangle$ are well defined and measurable. This is why the introduction of the variable ϕ is advantageous. These expressions for the thermodynamic fluctuations will be further used in evaluating the hydrodynamic fluctuations.

B. Hydrodynamic fluctuations

The linearized hydrodynamic equations can be expressed in terms of the variables P, ϕ, and x [15]. In this paper we are interested in the entropy and concentration fluctuations at constant pressure that contribute to the central (unshifted) Rayleigh component of the spectrum of the scattered light. We, therefore, do not consider the pressure fluctuations at constant entropy responsible for Brillouin scattering.

The correlation functions as a function of the wave number q can be found from the set of the linearized hydrodynamic equations by applying a Fourier-Laplace analysis [15,16]:

$$\frac{\langle \delta\phi(\mathbf{q},t)\,\delta\phi(-\mathbf{q})\rangle}{\langle|\delta\phi(\mathbf{q})|^2\rangle}=\frac{D_1-D}{D_1-D_2}e^{-D_1q^2t}+\frac{D_2-D}{D_2-D_1}e^{-D_2q^2t}, \tag{2.9}$$

$$\frac{\langle \delta x(\mathbf{q},t)\,\delta x(-\mathbf{q})\rangle}{\langle|\delta x(\mathbf{q})|^2\rangle}=\frac{D_2-D}{D_2-D_1}e^{-D_1q^2t}+\frac{D_1-D}{D_1-D_2}e^{-D_2q^2t}, \tag{2.10}$$

$$\begin{aligned}\frac{\langle \delta x(\mathbf{q},t)\,\delta\phi(-\mathbf{q})\rangle}{\langle|\delta x(\mathbf{q})|^2\rangle}&=\frac{T}{C_{P,x}}\left(\frac{\partial\mu}{\partial x}\right)_{P,T}\frac{\langle \delta\phi(\mathbf{q},t)\,\delta x(-\mathbf{q})\rangle}{\langle|\delta\phi(\mathbf{q})|^2\rangle}\\&=\frac{(\partial\mu/\partial x)_{P,T}}{C_{P,x}}\frac{Dk_T}{D_1-D_2}\\&\quad\times\left(e^{-D_1q^2t}-e^{-D_2q^2t}\right),\end{aligned} \tag{2.11}$$

where the coefficients D_1 and D_2 are defined by Eq. (1.1), and the mean squared fluctuations of ϕ and x are determined by Eqs. (2.5) and (2.6) in the thermodynamic limit, where $|\mathbf{q}|\to 0$: $\langle|\delta\phi(|\mathbf{q}|\to 0)|^2\rangle=\langle|\delta\phi|^2\rangle$ and $\langle|\delta x(|\mathbf{q}|\to 0)|^2\rangle=\langle|\delta x|^2\rangle$.

C. Light-scattering correlation function

The time-dependent electric field $E(t)$ of the scattered light is a superposition of waves scattered from individual scattering centers. In actual dynamic light-scattering (photon-correlation) experiments, the detector of the scattered light is a photomultiplier that responds to the intensity $I(t)$ of the light that impinges on the detector. After the resulting signal has been processed by a digital correlator, the time-dependent intensity correlation function is obtained which, being normalized by the average intensity of the signal, has the form [1,2]

$$C(\mathbf{q},t)=1+\beta_0 S(\mathbf{q},t)^2, \tag{2.12}$$

where β_0 is a constant depending on experimental conditions, and $S(\mathbf{q},t)$ the dynamic structure factor proportional to the time-dependent autocorrelation function of the dielectric constant fluctuations

$$S(\mathbf{q},t)=\rho V N_{\mathrm{A}}\langle \delta\varepsilon(\mathbf{q},t)\,\delta\varepsilon(-\mathbf{q})\rangle, \tag{2.13}$$

where N_{A} is Avogadro's number. Here the dielectric constant ε is taken at the frequency of the incident light.

The dielectric constant of a binary fluid is, in general, a function of three independent variables: P, ϕ, and x. The dielectric equation of state $\varepsilon=\varepsilon(P,\phi,x)$ can be expanded in a power series in the fluctuations of these variables. In first-order approximation the local dielectric constant fluctuation $\delta\varepsilon$ reads

$$\delta\varepsilon=\left(\frac{\partial\varepsilon}{\partial P}\right)_{\phi,x}\delta P+\left(\frac{\partial\varepsilon}{\partial\phi}\right)_{P,x}\delta\phi+\left(\frac{\partial\varepsilon}{\partial x}\right)_{P,\phi}\delta x. \tag{2.14}$$

As the instantaneous fluctuations of P, ϕ, and x are statistically independent, one obtains

$$\langle\delta\varepsilon^2\rangle=\left(\frac{\partial\varepsilon}{\partial P}\right)^2_{\phi,x}\langle\delta P^2\rangle+\left(\frac{\partial\varepsilon}{\partial\phi}\right)^2_{P,x}\langle\delta\phi^2\rangle+\left(\frac{\partial\varepsilon}{\partial x}\right)^2_{P,\phi}\langle\delta x^2\rangle. \tag{2.15}$$

As we do not consider Brillouin scattering, we neglect the pressure fluctuations. The dynamic structure factor $S(\mathbf{q},t)$, which determines the light-scattering properties of the medium, is then given by

$$\begin{aligned}S(\mathbf{q},t)/\rho V N_{\mathrm{A}}&=\langle\delta\varepsilon(\mathbf{q},t)\,\delta\varepsilon(-\mathbf{q})\rangle\\&=\left(\frac{\partial\varepsilon}{\partial\phi}\right)^2_{P,x}\langle\delta\phi(\mathbf{q},t)\,\delta\phi(-\mathbf{q})\rangle+\left(\frac{\partial\varepsilon}{\partial x}\right)^2_{P,\phi}\\&\quad\times\langle\delta x(\mathbf{q},t)\,\delta x(-\mathbf{q})\rangle+\left(\frac{\partial\varepsilon}{\partial\phi}\right)_{P,\phi}\left(\frac{\partial\varepsilon}{\partial x}\right)_{P,\phi}\\&\quad\times[\langle\delta\phi(\mathbf{q},t)\,\delta x(-\mathbf{q})\rangle\\&\quad+\langle\delta x(\mathbf{q},t)\,\delta\phi(-\mathbf{q})\rangle].\end{aligned} \tag{2.16}$$

One can prove from thermodynamics, that [15]

$$\left(\frac{\partial\varepsilon}{\partial P}\right)_{\phi,x}=\left(\frac{\partial\varepsilon}{\partial P}\right)_{S,x}=\left(\frac{\partial\varepsilon}{\partial P}\right)_{T,x}+\frac{T\alpha_T}{\rho C_{P,x}}\left(\frac{\partial\varepsilon}{\partial T}\right)_{P,x}, \tag{2.17}$$

$$\left(\frac{\partial\varepsilon}{\partial\phi}\right)_{P,x}=\left(\frac{\partial\varepsilon}{\partial T}\right)_{P,x},\qquad\left(\frac{\partial\varepsilon}{\partial x}\right)_{P,\phi}=\left(\frac{\partial\varepsilon}{\partial x}\right)_{P,T}. \tag{2.18}$$

III. LIGHT SCATTERING IN BINARY FLUIDS

A. Static light scattering (thermodynamic limit)

The overall intensity of the light scattering in a binary mixture is proportional to the mean squared fluctuations of the dielectric constant given by Eq. (2.15) [and by Eq. (2.16) at $t=0$]. In the thermodynamic limit of $|\mathbf{q}|\to 0$ and $t\to 0$ we obtain

$$\langle|\delta\varepsilon|^2\rangle=\frac{k_{\mathrm{B}}T}{V\rho}\left[\left(\frac{\partial\varepsilon}{\partial T}\right)^2_{P,x}\frac{T}{C_{P,x}}+\left(\frac{\partial\varepsilon}{\partial x}\right)^2_{P,T}\left(\frac{\partial x}{\partial\mu}\right)_{P,T}\right]. \tag{3.1}$$

We modify Eq. (3.1) to separate the contributions from the density fluctuations at constant composition and the composition fluctuations at constant density [given by Eqs. (2.8) and (2.6), respectively]. To accomplish this, we use the following thermodynamic relations:

$$\left(\frac{\partial\varepsilon}{\partial x}\right)_{P,T}=\left(\frac{\partial\varepsilon}{\partial x}\right)_{\rho,T}+\left(\frac{\partial\varepsilon}{\partial\rho}\right)_{T,x}\left(\frac{\partial\rho}{\partial x}\right)_{P,T}, \tag{3.2}$$

$$\left(\frac{\partial\varepsilon}{\partial T}\right)_{P,x}=\left(\frac{\partial\varepsilon}{\partial T}\right)_{\rho,x}+\left(\frac{\partial\varepsilon}{\partial\rho}\right)_{T,x}\left(\frac{\partial\rho}{\partial T}\right)_{P,x}, \tag{3.3}$$

$$\left(\frac{\partial\rho}{\partial P}\right)_{T,x}=\left(\frac{\partial\rho}{\partial P}\right)_{T,\mu}-\rho^{-2}\left(\frac{\partial\rho}{\partial x}\right)^2_{p,T}\left(\frac{\partial x}{\partial\mu}\right)_{P,T}. \tag{3.4}$$

As the dielectric constant in practice does not depend on temperature at constant density, we neglect the derivative $(\partial\varepsilon/\partial T)_{\rho,x}$ in Eq. (3.3), so that

$$\left(\frac{1}{\alpha_T}\frac{\partial\varepsilon}{\partial T}\right)^2_{P,x}=\left(\rho\frac{\partial\varepsilon}{\partial\rho}\right)^2_{T,x} \tag{3.5}$$

and

$$\left(\frac{\partial\varepsilon}{\partial T}\right)^2_{P,x}\frac{T}{C_{P,x}}=\rho\left(\frac{1}{\alpha_T}\frac{\partial\varepsilon}{\partial T}\right)^2_{P,x}(\beta_{T,x}-\beta_{S,x}), \tag{3.6}$$

where $\beta_{S,x}=\rho^{-1}(\partial\rho/\partial P)_{S,x}$ and $\beta_{T,x}=\rho^{-1}(\partial\rho/\partial P)_{T,x}$ are the adiabatic and the isothermal compressibilities, respectively. If one adds the term

$$\frac{k_\mathrm{B}T}{V}\left(\rho\frac{\partial\varepsilon}{\partial\rho}\right)^2_{T,x}\beta_{S,x}$$

associated with the pressure fluctuations into Eq. (3.1), one obtains the general equation for the mean squared fluctuations of the dielectric constant:

$$\langle|\delta\varepsilon|^2\rangle=\frac{k_\mathrm{B}T}{V\rho}\left[\rho^2\left(\frac{\partial\varepsilon}{\partial\rho}\right)^2_{T,x}\left(\frac{\partial\rho}{\partial P}\right)_{T,\mu}+\left(\frac{\partial\varepsilon}{\partial x}\right)^2_{\rho,T}\left(\frac{\partial x}{\partial\mu}\right)_{P,T}+2\left(\frac{\partial\varepsilon}{\partial x}\right)_{\rho,T}\left(\frac{\partial\varepsilon}{\partial\rho}\right)_{T,x}\left(\frac{\partial\rho}{\partial x}\right)_{P,T}\left(\frac{\partial x}{\partial\mu}\right)_{P,T}\right], \tag{3.7}$$

which can be further transformed to

$$\langle|\delta\varepsilon|^2\rangle=\left(\frac{\partial\varepsilon}{\partial x}\right)^2_{\rho,T}\langle|\delta x|^2\rangle+\left[\left(\frac{\partial\varepsilon}{\partial\rho}\right)^2_{T,x}+2\left(\frac{\partial\varepsilon}{\partial x}\right)_{\rho,T}\left(\frac{\partial\varepsilon}{\partial\rho}\right)_{T,x}\left(\frac{\partial x}{\partial\rho}\right)_{T,\mu}\right]\langle|\delta\rho|^2\rangle \tag{3.8}$$

with

$$\left(\frac{\partial x}{\partial\rho}\right)_{T,\mu}=\left[\left(\frac{\partial\rho}{\partial x}\right)_{P,T}+\rho^2\left(\frac{\partial\rho}{\partial P}\right)_{T,x}\left(\frac{\partial\rho}{\partial x}\right)^{-1}_{P,T}\left(\frac{\partial\mu}{\partial x}\right)_{P,T}\right]^{-1}. \tag{3.9}$$

In the limit $x\to 0$ this equation takes the well-known form [27]

$$\langle|\delta\varepsilon|^2\rangle=\left(\frac{\partial\varepsilon}{\partial\rho}\right)^2_T\langle|\delta\rho|^2\rangle \tag{3.10}$$

with $\langle|\delta\rho|^2\rangle$ given by Eq. (2.8).

B. Dynamic light scattering (hydrodynamic limit)

Next we analyze the time dependence of the dynamic structure factor $S(\mathbf{q},t)$ as given by Eq. (2.16). Substituting the dynamic [Eqs. (2.9)–(2.11)] and static [Eqs. (2.5) and (2.6)] correlations into Eq. (2.16), we find that the dynamic structure factor can be written as

$$S(\mathbf{q},t)=A_1e^{-D_1q^2t}+A_2e^{-D_2q^2t}, \tag{3.11}$$

where A_1 and A_2 are the amplitudes of the two relaxation modes:

$$A_1=Z_1\frac{D_2-D}{D_2-D_1}+Z_2\frac{D-D_1}{D_2-D_1}+Z_3\frac{k_TD}{D_2-D_1}, \tag{3.12}$$

$$A_2=Z_1\frac{D-D_1}{D_2-D_1}+Z_2\frac{D_2-D}{D_2-D_1}-Z_3\frac{k_TD}{D_2-D_1} \tag{3.13}$$

with

$$Z_1=RT\left(\frac{\partial\varepsilon}{\partial x}\right)^2_{P,T}\left(\frac{\partial x}{\partial\mu}\right)_{P,T}, \tag{3.14}$$

$$Z_2=\left(\frac{\partial\varepsilon}{\partial T}\right)^2_{P,x}\frac{RT^2}{C_{P,x}}, \tag{3.15}$$

$$Z_3=-2\left(\frac{\partial\varepsilon}{\partial T}\right)_{P,x}\left(\frac{\partial\varepsilon}{\partial x}\right)_{P,T}\frac{RT}{C_{P,x}}. \tag{3.16}$$

We note that Z_1, Z_2, and Z_3 contain only thermodynamics derivatives, i.e., they are static quantities. As

$$4Z_1Z_2(D-D_1)(D_2-D)=Z_3^2D^2k_T^2, \tag{3.17}$$

the amplitudes A_1 and A_2 can be written as

$$A_1=\left[\left(Z_1\frac{D_2-D}{D_2-D_1}\right)^{1/2}+\left(Z_2\frac{D_1-D}{D_1-D_2}\right)^{1/2}\right]^2, \tag{3.18}$$

$$A_2=\left[\left(Z_1\frac{D_1-D}{D_1-D_2}\right)^{1/2}-\left(Z_2\frac{D_2-D}{D_2-D_1}\right)^{1/2}\right]^2. \tag{3.19}$$

The overall intensity of light scattered from the system is proportional to the sum $A_1+A_2=Z_1+Z_2$ that agrees with the thermodynamic relation (3.1).

C. Electromagnetic equation of state

The dielectric constant ε and the total molar density ρ are interrelated by the Clausius-Mossotti equation, which for a binary mixture takes the form [16]

$$\frac{\varepsilon-1}{\varepsilon+2}=C'\rho, \tag{3.20}$$

where C' is a function of the mole fraction x, approximated by $C'=(4\pi/3)[\alpha^{(1)}(1-x)+\alpha^{(2)}x]$, and $\alpha^{(1)}$ and $\alpha^{(2)}$ are the molar polarizabilities of the two components. Differentiating Eq. (3.20) with respect to the density and composition, we obtain

$$\left(\rho\frac{\partial\varepsilon}{\partial\rho}\right)_{T,x}=(\varepsilon-1)\frac{\varepsilon+2}{3}, \tag{3.21}$$

$$\left(\frac{\partial\varepsilon}{\partial x}\right)_{P,T}=\frac{(\varepsilon+2)^2}{3}\left[C'\left(\frac{\partial\rho}{\partial x}\right)_{P,T}+C''\rho\right], \tag{3.22}$$

where $C''=(4\pi/3)(\alpha^{(2)}-\alpha^{(1)})$ is a constant. Comparing Eq. (3.22) with Eq. (3.2), we find

$$\left(\frac{\partial\varepsilon}{\partial x}\right)_{\rho,T}=C''\frac{(\varepsilon+2)^2}{3}\rho=\frac{3\rho C''}{(1-C'\rho)^2}, \tag{3.23}$$

$$\left(\rho\frac{\partial\varepsilon}{\partial\rho}\right)_{T,x}=C'\frac{(\varepsilon+2)^2}{3}\rho=\frac{1+3\rho C''}{(1-C'\rho)^2}. \tag{3.24}$$

Equations (3.23) and (3.24) are to be used in calculating the amplitudes of the two modes observed in light scattering.

IV. TWO-EXPONENTIAL DYNAMIC CORRELATION FUNCTIONS IN NEAR-CRITICAL BINARY FLUIDS

A. Thermodynamic properties of binary mixtures near critical points

Fluids and fluid mixtures belong to the universality class of the three-dimensional Ising model (equivalent to the three-dimensional lattice gas) with two relevant scaling fields [28–30]. For mixtures the two relevant scaling fields h_1 and h_2 are linear combinations of the three physical field variables $\Delta T=T-T_c$, $\Delta\mu_1=\mu_1-\mu_{1c}$, and $\Delta\mu=\mu-\mu_c$ [20,21]:

$$h_1=a_1\Delta\mu_1+a_2\Delta T+a_3\Delta\mu, \tag{4.1}$$

$$h_2=b_1\Delta T+b_2\Delta\mu_1+b_3\Delta\mu, \tag{4.2}$$

where T_c, μ_{1c}, and μ_c are the critical values of T, μ_1, and μ, respectively. All system-dependent parameters in the relations (4.1) and (4.2), namely, the coefficients a_i and b_i as well as the critical parameters T_c, μ_{1c}, and μ_c, depend parametrically on the actual position on the critical line. This position can be specified by any of the three variables T_c, μ_{1c}, and μ_c. The scaling fields are made dimensionless by an appropriate choice of the coefficients a_i and b_i ($i=1,2,3$) in Eqs. (4.1) and (4.2).

To specify the critical behavior of binary mixtures near the critical point, the pressure is separated into a singular and a regular part [20,21]:

$$P=\Delta P(h_1,h_2)+P^r(T,\mu,\mu_1), \tag{4.3}$$

where the regular part (denoted by the superscript r) is an analytic function of the three field variables T, μ, and μ_1. A dimensionless singular part $\Delta\tilde{P}$ of the pressure satisfies a scaling law analogous to that of near-critical one-component fluids [31] and may be defined as

$$\Delta\tilde{P}=\Delta P/\rho_c RT_c=|h_2|^{2-\alpha}f(z), \tag{4.4}$$

where $f(z)=f(h_1/|h_2|^{\beta+\gamma})$ is a universal scaling function and $\alpha\simeq0.110$, $\gamma\simeq1.24$, and $\beta=(2-\alpha-\gamma)/2\simeq0.325$ are universal critical exponents [28–33]. The first scaling density φ_1 (the order parameter) conjugate to the scaling field h_1 is defined as

$$\varphi_1=\left(\frac{\partial\Delta\tilde{P}}{\partial h_1}\right)_{h_2}=|h_2|^{\beta}f'(z), \tag{4.5}$$

with $f'(z)=df/dz$. The second scaling density φ_2 conjugate to the scaling field h_2 is defined as

$$\varphi_2=\left(\frac{\partial\Delta\tilde{P}}{\partial h_2}\right)_{h_1}=|h_2|^{1-\alpha}\psi(z), \tag{4.6}$$

with

$$\psi(z)=(2-\alpha)f(z)-(\beta+\gamma)zf'(z). \tag{4.7}$$

The explicit expressions for the scaling densities φ_1 and φ_2 in terms of the physical densities ρ, ρx, and s have been obtained in an earlier publication [20]. In addition, two scaling susceptibilities may be defined as

$$\chi_1=\left(\frac{\partial\varphi_1}{\partial h_1}\right)_{h_2}=|h_2|^{-\gamma}f''(z), \tag{4.8}$$

$$\chi_2=\left(\frac{\partial\varphi_2}{\partial h_2}\right)_{h_1}=|h_2|^{-\alpha}\Psi(z), \tag{4.9}$$

where

$$\Psi(z)=(1-\alpha)\psi(z)-(\beta+\gamma)z\psi'(z), \tag{4.10}$$

with $f''(z)=d^2f/dz^2$ and $\psi'(z)=d\psi/dz$. One can also define a cross susceptibility $\chi_{12}=\chi_{21}=(\partial\varphi_1/\partial h_2)_{h_1}=(\partial\varphi_2/\partial h_1)_{h_2}$ which vanishes in zero field $h_1=0$ in the one-phase region [21]:

$$\chi_{12}=|h_2|^{\beta-1}[\beta f'(z)-(\beta+\gamma)zf''(z)]. \tag{4.11}$$

The scaling susceptibilities χ_1, χ_2, and χ_{12} as well as the scaling densities φ_1 and φ_2 are not directly measurable quantities, but one can express measurable second derivatives of the thermodynamic potential in terms of χ_1, χ_2, and χ_{12} using appropriate thermodynamic transformations [20,21]. For instance, in zero ordering field in the one-phase region the expressions for the osmotic compressibility $(\partial x/\partial\mu)_{P,T}$ and for the isothermal compressibility $(\partial\rho/\partial P)_{T,x}$, appearing in Eqs. (3.3) and (3.4), become

$$\left(\frac{\partial x}{\partial\mu}\right)_{P,T}=\left(\frac{\partial x}{\partial\mu}\right)^r_{P,T}\omega, \tag{4.12}$$

with

$$\omega=\left[\left(\frac{\partial x}{\partial\mu}\right)^r_{P,T}\right]^{-1}RT_c[(a_3-a_1x_c)^2\chi_1+(b_3-b_2x_c)^2\chi_2]+1, \tag{4.13}$$

and

$$\left(\frac{\partial\rho}{\partial P}\right)_{T,x}=(L_1\chi_1+L_2\chi_2+L_{12}\chi_1\chi_2)\,\omega^{-1}+(\partial\rho/\partial P)^r_{T,x}, \tag{4.14}$$

where

$$L_1=RT_c a_1^2\left[1+\frac{1}{\rho_c}\left(\frac{\partial\rho}{\partial x}\right)^r_{P,T}K_1\right]^2, \tag{4.15}$$

$$L_2=RT_c b_2^2\left[1+\frac{1}{\rho_c}\left(\frac{\partial\rho}{\partial x}\right)^r_{P,T}\left(K_1+\frac{K_2}{b_2}\right)\right]^2, \tag{4.16}$$

$$L_{12}=(RT_c)^2\left[\left(\frac{\partial x}{\partial\mu}\right)^r_{P,T}\right]^{-1}a_1^2K_2^2, \tag{4.17}$$

with

$$K_1=-\left(\frac{a_3}{a_1}-x_c\right), \tag{4.18}$$

$$K_2=b_2\frac{a_3}{a_1}-b_3. \tag{4.19}$$

Here $(\partial x/\partial\mu)^r_{P,T}$, $(\partial\rho/\partial P)^r_{T,x}$, and $(\partial\rho/\partial x)^r_{P,T}$ are the regular parts of $(\partial x/\partial\mu)_{P,T}$, $(\partial\rho/\partial P)_{T,x}$, and $(\partial\rho/\partial x)_{P,T}$, respectively. Asymptotically both derivatives $(\partial x/\partial\mu)_{P,T}$ and $(\partial\rho/\partial P)_{T,x}$ will diverge at the critical point: $(\partial x/\partial\mu)_{P,T}$ diverges strongly as χ_1 and $(\partial\rho/\partial P)_{T,x}$ diverges weakly as χ_2. The two characteristic parameters K_1 and K_2 determine the crossover between different types of behavior depending on the variation of the coefficients a_i and b_i along the critical line [20,21]. The parameter K_1 is responsible for strongly singular contributions associated with χ_1 and is related in the dilute-solution limit to the so-called Krichevskii parameter [34], while the parameter K_2 accounts for weakly singular contributions associated with χ_2. Specifically, the parameter K_2 determines the range of h_2 at $h_1=0$, where the so-called Fisher renormalization of the critical exponents takes place, when one makes a transformation from the theoretical scaling path $h_2\propto T-T_c$ at constant $\mu=\mu_c$ and density to the experimental path corresponding to constant concentration and density [35,36]. One should note that x_c represents the composition at the critical line (one of the critical parameters), while the densitylike variable x is generally different for the coexisting phases.

One can also deduce the corresponding expressions for the derivative $(\partial\mu/\partial T)_{P,x}=-(\partial S/\partial x)_{P,T}$ and the derivative $(\partial\mu/\partial P)_{T,x}=-\rho^{-2}(\partial\rho/\partial x)_{P,T}$, which appear in Eqs. (3.2) and (3.4). Specifically, in zero ordering field in the one-phase region one obtains [20]

$$\left(\frac{\partial\mu}{\partial T}\right)_{P,x}=\omega^{-1}\left\{\left(\frac{\partial\mu}{\partial T}\right)^r_{P,x}+RT_c[(\partial x/\partial\mu)^r_{P,T}]^{-1}\left[a_1^2K_1\left(\frac{a_2}{a_1}-S_c\right)\chi_1+b_2^2\left(K_1+\frac{K_2}{b_2}\right)\left(\frac{b_1}{b_2}-S_c\right)\chi_2\right]\right\} \tag{4.20}$$

and

$$\left(\frac{\partial\rho}{\partial x}\right)_{P,T}=\omega^{-1}\left\{\left(\frac{\partial\rho}{\partial x}\right)^r_{P,T}-\rho_cRT_c\left[\left(\frac{\partial x}{\partial\mu}\right)^r_{P,T}\right]^{-1}\times\left[a_1^2K_1\chi_1+b_2^2\left(K_1+\frac{K_2}{b_2}\right)\chi_2\right]\right\}. \tag{4.21}$$

We note that $(\partial\mu/\partial T)^r_{P,T}$ depends on the choice of zero point of entropy and, hence, contains an arbitrary constant [20,21].

To derive the equation for the isobaric molar heat capacity at constant composition $C_{P,x}=T(\partial S/\partial T)_{P,x}$, one can use the thermodynamic relation

$$\left(\frac{\partial S}{\partial T}\right)_{P,x}=\left(\frac{\partial S}{\partial T}\right)_{P,\mu}-\left(\frac{\partial\mu}{\partial T}\right)^2_{P,x}\left(\frac{\partial x}{\partial\mu}\right)_{P,T}. \tag{4.22}$$

Taking into account that

$$\left(\frac{\partial S}{\partial T}\right)_{P,\mu}=\left(\frac{\partial S}{\partial T}\right)^r_{P,\mu}+RT_c\times[(a_2-a_1S_c)^2\chi_1+(b_1-b_2S_c)^2\chi_2], \tag{4.23}$$

we find for $C_{P,x}$ in zero field in the one-phase region

$$C_{P,x}=C^r_{P,x}+T_c(\widetilde{L}_1\chi_1+\widetilde{L}_2\chi_2+\widetilde{L}_{12}\chi_1\chi_2)\,\omega^{-1}, \tag{4.24}$$

with

$$\widetilde{L}_1=RT_ca_1^2\left[S_c-\frac{a_2}{a_1}+\left(\frac{\partial\mu}{\partial T}\right)^r_{P,x}K_1\right]^2, \tag{4.25}$$

$$\widetilde{L}_2=RT_cb_2^2\left[S_c-\frac{b_1}{b_2}+\left(\frac{\partial\mu}{\partial T}\right)^r_{P,x}\left(K_1+\frac{K_2}{b_2}\right)\right]^2, \tag{4.26}$$

$$\widetilde{L}_{12}=(RT_c)^2\left[\left(\frac{\partial x}{\partial\mu}\right)^r_{P,T}\right]^{-1}\times[(a_1b_1-a_2b_2)K_1+(a_1S_c-a_2)K_2]^2, \tag{4.27}$$

where the superscript r again denotes regular parts. The isobaric molar heat capacity $C_{P,x}$ contains both a weakly divergent contribution from χ_2 and a strongly divergent contribution from χ_1. On the other hand, the derivatives $(\partial\mu/\partial T)_{P,x}$ and $(\partial\rho/\partial x)_{P,T}$, in general, do not diverge at the critical point of a mixture. Complete expressions for these thermodynamic derivatives, which are also valid for nonzero ordering field, can be found in Ref. [20]. The experimentally accessible physical properties are certain combinations of the two scaling susceptibilities χ_1 and χ_2, whose contributions are governed by the values of the coefficients a_i and b_i, which vary along the critical line. Mixing of the physical variables also exists in one-component fluids [20,21,37–39] in which the only effect of this mixing is the appearance of corrections to the asymptotic behavior related to gas-liquid asymmetry. In fluid mixtures the mixing of the field variables may also change the asymptotic critical behavior of thermodynamic properties depending on the values of the mixing coefficients a_i and b_i [20,21].

B. Transport properties of binary mixtures near critical points

The Onsager expressions for the mass diffusion current $\mathbf{j}_d$ and for the heat current $\mathbf{j}_q$ in binary mixtures read [18,40]

$$\mathbf{j}_d = -\tilde{\alpha}\nabla\mu' - \tilde{\beta}\nabla T, \tag{4.28}$$

$$\mathbf{j}_q = -\tilde{\gamma}\nabla T - T\tilde{\beta}\nabla\mu' + \mu'\mathbf{j}_d, \tag{4.29}$$

where $\tilde{\alpha}$, $\tilde{\beta}$, and $\tilde{\gamma}$ are the Onsager kinetic coefficients, $\mu' = \mu_2/M_2 - \mu_1/M_1$ the reduced chemical potential difference with M_1 and M_2 the molar masses of the pure components. Equations (4.28) and (4.29) are expressed in terms of quantities taken per unit mass, while the equations of state of fluid mixtures near critical points conventionally involve molar variables. Since this difference can cause a confusion in the interpretation of experimental data and is often ignored [20,41], we provide in the Appendix relations between specific (per unit mass) and molar thermodynamic and transport properties.

According to the theory [4,19,42–44] the kinetic coefficients $\tilde{\alpha}$, $\tilde{\beta}$, and $\tilde{\gamma}$ diverge at the critical point of a binary mixture just as the thermal conductivity diverges at the critical point of a one-component fluid [3,45,46]. Near the critical point the Onsager kinetic coefficients satisfy the following equations [47–49]:

$$\tilde{\alpha} = \tilde{\alpha}^s + \tilde{\alpha}^r = \frac{k_B T\rho'}{6\pi\tilde{\eta}\xi}\left(\frac{\partial c}{\partial\mu'}\right)_{P,T} + \tilde{\alpha}^r, \tag{4.30}$$

$$\tilde{\beta} = \tilde{\beta}^s + \tilde{\beta}^r = \frac{k_B T\rho'}{6\pi\tilde{\eta}\xi}\left(\frac{\partial c}{\partial T}\right)_{P,\mu'} + \tilde{\beta}^r, \tag{4.31}$$

$$\tilde{\gamma} = \tilde{\gamma}^s + \tilde{\gamma}^r = \frac{k_B T^2\rho'}{6\pi\tilde{\eta}\xi}\left(\frac{\partial S'}{\partial T}\right)_{P,\mu'} + \tilde{\gamma}^r, \tag{4.32}$$

where ξ is the correlation length diverging at the critical point, $\tilde{\alpha}^r$, $\tilde{\beta}^r$, $\tilde{\gamma}^r$ are regular background contributions, $\tilde{\eta}$ is the shear viscosity, $\rho' = \rho M$ is the mass density, $M = M_1(1-x) + M_2 x$ is the molar mass of the mixture, $c = (M_2/M)x$ is the mass concentration, and S' is the specific entropy.

It should be noted that the expressions for the singular parts of the Onsager coefficients $\tilde{\alpha}^s$, $\tilde{\beta}^s$, and $\tilde{\gamma}^s$ are only valid close to the critical point. Extensions of the theory to include crossover from the asymptotic critical behavior of the transport properties of mixtures to the regular behavior of these transport properties have been considered by Kiselev and Kulikov [41], by Luettmer-Strathmann and Sengers [49] and by Folk and Moser [50–53]. In this work we consider the close vicinity to the critical point where Eqs. (4.30)–(4.32) are valid. As

$$\left(\frac{\partial c}{\partial T}\right)_{P,\mu'} = -\left(\frac{\partial c}{\partial\mu'}\right)_{P,T}\left(\frac{\partial\mu'}{\partial T}\right)_{P,c}, \tag{4.33}$$

$$\left(\frac{\partial S'}{\partial T}\right)_{P,\mu'} = \left(\frac{\partial S'}{\partial T}\right)_{P,c} + \left(\frac{\partial\mu'}{\partial T}\right)^2_{P,c}\left(\frac{\partial c}{\partial\mu'}\right)_{P,T}, \tag{4.34}$$

we note from Eqs. (4.30)–(4.32) that the critical parts $\tilde{\alpha}^s$, $\tilde{\beta}^s$, and $\tilde{\gamma}^s$ of the kinetic coefficients in the asymptotic vicinity of the critical point are interrelated by [19,44]

$$\tilde{\alpha}^s = -\left(\frac{\partial\mu'}{\partial T}\right)^{-1}_{P,c}\tilde{\beta}^s = \frac{1}{T}\left(\frac{\partial\mu'}{\partial T}\right)^{-2}_{P,c}\tilde{\gamma}^s, \quad \tilde{\gamma}^s = -T\left(\frac{\partial\mu'}{\partial T}\right)_{P,c}\tilde{\beta}^s. \tag{4.35}$$

One also has (see the Appendix)

$$\left(\frac{\partial c}{\partial\mu'}\right)_{P,T} = \frac{M_1^2 M_2^2}{M^3}\left(\frac{\partial x}{\partial\mu}\right)_{P,T}, \tag{4.36}$$

$$\left(\frac{\partial\mu'}{\partial T}\right)_{P,c} = \frac{M}{M_1 M_2}\left(\frac{\partial\mu}{\partial T}\right)_{P,x} + \frac{M_2 - M_1}{M_1 M_2}S. \tag{4.37}$$

Since the response functions $(\partial c/\partial\mu')_{P,T}$, $(\partial c/\partial T)_{P,\mu'}$, and $(\partial S'/\partial T)_{P,\mu'}$ diverge asymptotically as χ_1, all three kinetic coefficients $\tilde{\alpha}$, $\tilde{\beta}$, and $\tilde{\gamma}$ diverge asymptotically as the product $\chi_1\xi^{-1}$, provided that one neglects a very weak singular critical enhancement of the shear viscosity [45], which will not be discussed here. As the correlation length is directly related to the strong scaling susceptibility χ_1, we may assume that asymptotically

$$\xi = \xi_0\left(\frac{\chi_1}{\Gamma_0}\right)^{\nu/\gamma}, \tag{4.38}$$

where ξ_0 is an amplitude of the order of a molecular size, Γ_0 is the amplitude of the strong susceptibility in zero field, and $\nu = (2-\alpha)/3 \simeq 0.63$ [54]. The amplitude ξ_0 is interrelated with the amplitude of the weak susceptibility in zero field A_0 by the universal relation $A_0\xi_0^3\rho_c N_A \simeq 0.18$ [3,31]. Therefore in zero field in the one-phase region the correlation length asymptotically behaves as $\xi = \xi_0 h_2^{-\nu}$.

The thermal conductivity λ is defined by

$$\mathbf{j}_q = -\lambda\nabla T \tag{4.39}$$

with $\mathbf{j}_d = 0$, so that λ is related to the kinetic coefficients $\tilde{\alpha}$, $\tilde{\beta}$, and $\tilde{\gamma}$ as

$$\lambda = \tilde{\gamma} - T(\tilde{\beta}^2/\tilde{\alpha}). \tag{4.40}$$

Since the singular parts of $\tilde{\alpha}$, $\tilde{\beta}$, and $\tilde{\gamma}$ are asymptotically interrelated by Eq. (4.35), their divergent contributions to λ exactly compensate each other and the thermal conductivity should remain finite at the critical point of a binary mixture [19,44,55].

The kinetic coefficients $\tilde{\alpha}$, $\tilde{\beta}$, and $\tilde{\gamma}$ are not directly measurable. To calculate the experimentally accessible transport properties of binary mixtures one should regard the chemical potential difference μ' as a function of the experimental variables, namely, P,T,c and express the mass diffusion current as [18]

$$\mathbf{j}_d = -\rho' D\left(\nabla c + \frac{k_T}{T}\nabla T + \frac{k_P}{P}\nabla P\right), \tag{4.41}$$

where D is the mutual mass-diffusion coefficient, k_T the thermal-diffusion ratio, and k_P the barodiffusion ratio. The mass-diffusion coefficient or mass diffusivity D is related to the kinetic coefficient $\tilde{\alpha}$ by

$$D = \frac{\tilde{\alpha}}{\rho'}\left(\frac{\partial\mu'}{\partial c}\right)_{P,T} = \frac{M^2}{M_1^2 M_2^2}\frac{\tilde{\alpha}}{\rho}\left(\frac{\partial\mu}{\partial x}\right)_{P,T}. \tag{4.42}$$

It follows from Eq. (4.30) that in the asymptotic vicinity of the critical point this diffusion coefficient reduces to

$$D = \frac{k_{\mathrm{B}}T_c}{6\pi\tilde{\eta}\xi} \tag{4.43}$$

and vanishes at the critical point as ξ^{-1} [7,8,14]. We note that as $(\partial\mu'/\partial T)_{P,c}$ depends on the zero point of entropy, the products $T(\partial\mu'/\partial T)_{P,c}\tilde{\alpha}/\rho'$ and $T\tilde{\beta}/\rho'$ are not well defined, whereas their sum $k_T D$ is a well defined and measurable property. The thermodiffusion coefficient D_T is defined as

$$D_T = k_T D = \frac{T}{\rho'}\left(\frac{\partial\mu'}{\partial T}\right)_{P,c}\tilde{\alpha} + \frac{T}{\rho'}\tilde{\beta} \tag{4.44}$$

and tends to a finite value at the critical point, because the singular parts of the kinetic coefficients $\tilde{\alpha}$ and $\tilde{\beta}$ compensate each other according to Eq. (4.35). The thermal-diffusion ratio is defined as

$$k_T = \frac{D_T}{D} \tag{4.45}$$

and diverges in the vicinity of the critical point as the correlation length ξ. The barodiffusion ratio

$$k_P = -\frac{P}{\rho'^2}\left(\frac{\partial\rho'}{\partial c}\right)_{P,T}\left(\frac{\partial c}{\partial\mu'}\right)_{P,T} \tag{4.46}$$

asymptotically diverges as χ_1.

The actual behavior of the transport properties observed in the experimentally studied temperature range is not asymptotic and is affected by the interplay of the regular and singular parts of the kinetic coefficients and of the thermodynamic derivatives. Therefore, the regular parts are very important and cannot be omitted even close to the critical point [20,47,48,56].

Substituting the expressions for the thermodynamic properties in terms of the universal scaling susceptibilities χ_1, χ_2, and χ_{12} into Eqs. (4.30)–(4.32), one obtains explicit expressions for the transport properties in the vicinity of the critical point [20]. The expression for the mass diffusion coefficient reads

$$D = D_0(\tilde{\xi}^{-1} + \theta\omega^{-1}), \tag{4.47}$$

where

$$D_0 = \frac{k_{\mathrm{B}}T}{6\pi\tilde{\eta}\xi_0} \tag{4.48}$$

and where we use the notation $\tilde{\xi} = \xi/\xi_0$. The parameter θ is of order unity and relates the diffusion coefficient D far away from the critical point $(\omega \simeq 1)$ to D_0: $D = \theta D_0$. Asymptotically close to the critical point Eq. (4.47) reduces to Eq. (4.43).

For the thermodiffusion coefficient we obtain [20]

$$D_T = D_0\frac{M_1M_2}{M^2}\frac{\theta x_c(1-x_c)}{R}\left[\left(\frac{\partial\mu}{\partial T}\right)_{P,x} - \left(\frac{\partial\mu}{\partial T}\right)^r_{P,x} + \tilde{k}_T^0 R\right], \tag{4.49}$$

where $(\partial\mu/\partial T)_{P,x}$ is given by Eq. (4.20) and $\tilde{k}_T^0$ is related to the Soret coefficient S_T far away from the critical point: $\tilde{k}_T^0 = -TS_T$. The thermal-diffusion ratio is given by

$$\begin{aligned} k_T = \frac{M_1M_2}{M^2}\,\frac{\theta\, x_c(1-x_c)}{\theta\omega^{-1}+\tilde{\xi}^{-1}}\Bigg\{ & \tilde{k}_T^0 + \frac{1}{R}\left(\frac{\partial\mu}{\partial T}\right)^r_{P,x}(\omega^{-1}-1) + T_c\left[\left(\frac{\partial x}{\partial\mu}\right)^r_{P,T}\right]^{-1} \\ & \times[a_1K_1(a_2-a_1S_c)\chi_1 + (b_3-b_2x_c)(b_2S_c-b_1)\chi_2]\omega^{-1}\Bigg\}. \end{aligned} \tag{4.50}$$

We note that even if $\tilde{k}_T^0 = 0$ k_T may not be zero near the critical point and Eq. (1.2) should be used to calculate D_1 and D_2 according to Eq. (1.1).

C. Critical behavior of the dynamic structure factor

Now we analyze the critical behavior of the dynamic structure factor $S(\mathbf{q},t)$ given by Eq. (3.11). Using the thermodynamic relations (3.2)–(3.4) and neglecting again the derivative $(\partial\varepsilon/\partial T)_{\rho,x}$ in Eq. (3.3), we can express the thermodynamic factors Z_1, Z_2, and Z_3 through the thermodynamic derivatives discussed in Secs. IV A and IV B:

$$Z_1 = RT\left[\zeta_2 + \zeta_1\left(\frac{\partial\rho}{\partial x}\right)_{P,T}\right]^2\left(\frac{\partial x}{\partial\mu}\right)_{P,T}, \tag{4.51}$$

$$Z_2=\zeta_1^2\left(\frac{\partial P}{\partial T}\right)^2_{\rho,x}\left(\frac{\partial \rho}{\partial P}\right)^2_{T,x}\frac{RT^2}{C_{P,x}}, \tag{4.52}$$

$$Z_3=\frac{2\zeta_1 RT}{C_{P,x}}\left(\frac{\partial P}{\partial T}\right)_{\rho,x}\left(\frac{\partial \rho}{\partial P}\right)_{T,x}\left[\zeta_2+\zeta_1\left(\frac{\partial \rho}{\partial x}\right)_{P,T}\right] \tag{4.53}$$

with

$$\zeta_1=\left(\frac{\partial \varepsilon}{\partial \rho}\right)_{T,x}, \quad \zeta_2=\left(\frac{\partial \varepsilon}{\partial x}\right)_{\rho,T} \tag{4.54}$$

determined by Eqs. (3.23) and (3.24). Neither ζ_1 nor ζ_2 diverges at the critical point.

Substituting now $(\partial x/\partial \mu)_{P,T}$ from Eq. (4.12), $(\partial \rho/\partial P)_{T,x}$ from Eq. (4.14), and $(\partial \rho/\partial x)_{P,T}$ from Eq. (4.21), we obtain the factors Z_i expressed through the susceptibilities χ_1 and χ_2. Near the critical point $\chi_1 \gg \chi_2$, so that

$$\chi_1\omega^{-1}\rightarrow\left(\frac{\partial x}{\partial \mu}\right)^{\mathrm{r}}_{P,T}[RT_c(a_3-a_1x_{\mathrm{c}})^2]^{-1}. \tag{4.55}$$

We find that asymptotically the limiting value of Z_1 is proportional to the strongly divergent susceptibility χ_1, while the limiting value of Z_2 is proportional to the weakly divergent susceptibility χ_2:

$$Z_1\rightarrow\frac{(RT_c)^2[\zeta_2(a_3-a_1x_c)^2-\rho_c\zeta_1a_1^2K_1]^2}{(a_3-a_1x_c)^2}\chi_1, \tag{4.56}$$

$$Z_2\rightarrow\zeta_1^2\left(\frac{\partial P}{\partial T}\right)^2_{\rho,x}\frac{L_{12}^2}{\widetilde{L}_{12}}\frac{(\partial x/\partial \mu)^r_{P,T}}{(a_3-a_1x_c)^2}\chi_2. \tag{4.57}$$

Asymptotically the factor Z_3 does not depend on either χ_1 or χ_2:

$$Z_3\rightarrow 2\zeta_1R\left(\frac{\partial P}{\partial T}\right)_{\rho,x}\frac{L_{12}}{\widetilde{L}_{12}}\left[\zeta_2-\zeta_1\frac{\rho_ca_1^2K_1}{(a_3-a_1x_c)^2}\right]. \tag{4.58}$$

Substituting L_{12} and $\widetilde{L}_{12}$ from Eq. (4.17) and Eq. (4.27), we obtain

$$Z_1\rightarrow(RT_c)^2a_1^2(\zeta_2K_1-\rho_c\zeta_1)^2\chi_1, \tag{4.59}$$

$$Z_2\rightarrow\zeta_1^2(RT_c)^2\left(\frac{\partial P}{\partial T}\right)^2_{\rho,x}\frac{a_1^2K_2^4}{K_1^2[(a_1b_1-a_2b_2)K_1+(a_1S_c-a_2)K_2]^2}\chi_2, \tag{4.60}$$

$$Z_3\rightarrow 2\zeta_1R\left(\frac{\partial P}{\partial T}\right)_{\rho,x}\frac{a_1^2K_2^2(\zeta_2K_1-\rho_c\zeta_1)}{K_1[(a_1b_1-a_2b_2)K_1+(a_1S_c-a_2)K_2]^2}. \tag{4.61}$$

Let us consider the one-phase region of a binary fluid near its vapor-liquid critical point in zero field, i.e., $h_1=0$ and $h_2=\tau=[T-T_{\mathrm{c}}(\mu=\mu_{\mathrm{c}})]/T_{\mathrm{c}}(\mu=\mu_{\mathrm{c}})$. There are three characteristic temperatures that determine the behavior of the transport properties in the one-phase region in zero field, defined in Ref. [20] as $\tau_1=[\Gamma_0K_1^2/x_{\mathrm{c}}(1-x_{\mathrm{c}})]^{1/\gamma}$ and $\tau_D=(\tau_1^{\gamma}/\theta)^{1/(\gamma-\nu)}$ with $\tau_D\ll\tau_1$. Far away from the critical point when $\tau\gg\tau_1$ one can neglect the susceptibilities ($\omega\simeq1$) and the singular parts of the kinetic coefficients. Close to the critical point when $\tau\ll\tau_D$ the singular parts of the kinetic coefficients dominate and they behave in accordance with the asymptotic laws. In the intermediate region $\tau_D\ll\tau\ll\tau_1$ the apparent crossover behavior of the transport properties is determined by the interplay between the singular part of the static susceptibility and the regular parts of the kinetic coefficients. Another characteristic temperature $\tau_2=[A_0K_2^2/x_{\mathrm{c}}(1-x_{\mathrm{c}})]^{1/\alpha}$ that determines the Fisher-renormalization region is usually very narrow since $\alpha\ll\gamma$ and $\tau_2\ll\tau_1$ unless special cases are considered [20,21]. The characteristic temperatures τ_1 and τ_2 find their origin in the crossover behavior of the static properties. On the other hand the parameter τ_D, first introduced by Onuki [56], is a dynamic crossover temperature. In many mixtures, even if they are not dilute, the temperature τ_D, let alone τ_2, is hardly achievable experimentally, and the intermediate crossover behavior of transport properties, rather than the asymptotic power laws, is observed.

Thus, the behavior of the dimensionless mutual mass diffusion coefficient D/D_0 exhibits three different regimes [20]:

$$\frac{D}{D_0}\simeq\begin{cases}\tau^{\nu}, & \tau\ll\tau_D\\ \theta(\tau/\tau_1)^{\gamma}, & \tau_D\ll\tau\ll\tau_1\\ \theta, & \tau\gg\tau_1.\end{cases} \tag{4.62}$$

The thermodiffusion ratio k_T also exhibits crossover behavior:

$$k_T\simeq\begin{cases}-\dfrac{1}{\rho_cR}\left(\dfrac{\partial P}{\partial T}\right)^c_{h_1=0}\theta x_{\mathrm{c}}(1-x_c)K_1^{-1}\tau^{-\nu}, & \tau\ll\tau_D\\ -\dfrac{1}{\rho_cR}\left(\dfrac{\partial P}{\partial T}\right)^c_{h_1=0}K_1\Gamma_0\tau^{-\gamma}, & \tau_D\ll\tau\ll\tau_1\\ k_T^0x_c(1-x_c), & \tau\gg\tau_1.\end{cases} \tag{4.63}$$

In addition, if experiments are conducted at constant concentration and at the critical density, a nonanalytic connection between $\tau=\tau(\mu=\text{const})$ and $\tau(x=\text{const})$ at $\tau\ll\tau_2$, that causes the Fisher renormalization [35], must be taken into account [20,21]. To show how the physical meaning of D_1 and D_2 changes along the critical line we shall consider two limiting cases: the incompressible liquid-mixture limit and the one-component limit.

D. Liquid-liquid consolute point and incompressible liquid-mixture limit

Liquid mixtures near the critical consolute points are usually weakly compressible so that the incompressible liquid-mixture model serves as a limiting case. In the close vicinity of the consolute critical point, expression (4.47) for the diffusion coefficient D reduces again to that given by Eq. (4.43). The thermodiffusion coefficient D_T tends to a finite value

$$D_T=D_0\theta x_c(1-x_c)k_T^0, \tag{4.64}$$

and the thermal-diffusion ratio $k_T=D_T/D$ near the consolute point becomes

$$k_T=x_c(1-x_c)k_T^0\tilde{\xi} \tag{4.65}$$

and, hence, diverges as the correlation length.

The diffusivity D_1 of the slow (critical) mode becomes the diffusion coefficient and the diffusivity D_2 of the fast mode the thermal diffusivity:

$$D_1\rightarrow D=\frac{k_\mathrm{B}T}{6\pi\tilde{\eta}\xi}\propto\tau^{\nu}, \tag{4.66}$$

$$D_2\rightarrow a=\frac{\lambda}{\rho C_{P,x}}\propto\tau^{\alpha} \tag{4.67}$$

with $D_1\ll D_2$ as $\tau\rightarrow 0$. In the incompressible liquid-mixture limit $dT_c/dP_c=0$ and $(\partial P/\partial T)^c_{h_1=0}\rightarrow\infty$. Therefore, the system-dependent parameter K_1 goes to infinity, while the parameter K_2 and the product K_1a_1 remain finite [20]:

$$K_1\simeq\frac{x_c(1-x_c)}{\rho_cRT_c}\left[\frac{dP_c}{dx_c}-\left(\frac{\partial P}{\partial T}\right)^c_{h_1=0}\frac{dT_c}{dx_c}\right]\rightarrow\infty, \tag{4.68}$$

$$K_2\simeq\frac{x_c(1-x_c)}{RT_c^2}\frac{dT_c}{dx_c}. \tag{4.69}$$

The amplitudes A_1 and A_2 are found from Eqs. (3.12) and (3.13) with Z_i deduced from Eqs. (4.59)–(4.61):

$$Z_1\rightarrow(RT_c)^2\zeta_2^2(K_1a_1)^2\chi_1=RT_c\left(\frac{\partial\varepsilon}{\partial x}\right)^2_T\left(\frac{\partial x}{\partial\mu}\right)_T, \tag{4.70}$$

$$Z_2\rightarrow 0,\quad Z_3\rightarrow 0, \tag{4.71}$$

$$A_1\rightarrow Z_1\propto\tau^{-\gamma}, \tag{4.72}$$

$$A_2\rightarrow Z_2\rightarrow 0. \tag{4.73}$$

Hence, in the incompressible liquid-mixture limit, the light scattered from the system is determined by the slow mass diffusion mode with $D_1=D$ and an amplitude A_1 proportional to the osmotic compressibility $(\partial x/\partial\mu)_T$.

E. Dilute solutions and one-component limit

In the experimentally accessible region $\tau_D\ll\tau\ll\tau_1$, the thermodiffusion ratio k_T vanishes as $x_c\rightarrow 0$, because $K_1\propto x_c(1-x_c)\rightarrow 0$. From Eq. (1.2) it then follows that $\mathcal{D}=D$ and the diffusivity associated with the slow (critical) mode becomes equal to the thermal diffusivity:

$$D_1=a=\frac{k_\mathrm{B}T}{6\pi\tilde{\eta}\xi}\propto\tau^{\gamma}, \tag{4.74}$$

while the diffusivity associated with the fast mode is related to the mutual mass diffusion coefficient

$$D_2=D \tag{4.75}$$

with $D_1\ll D_2$.

In the pure-solvent limit $(x_c\rightarrow 0)$ the parameter ω, defined by Eq. (4.13), becomes of order unity [20]. The system-dependent parameters K_1 and K_2 are

$$K_1=\frac{x_c}{\rho_{c1}RT_{c1}}\left[\frac{dP_c}{dx_c}-\left(\frac{\partial P}{\partial T}\right)^c_{\rho=\rho_{c1}}\frac{dT_c}{dx_c}\right]\rightarrow 0, \tag{4.76}$$

$$K_2=(1-RT_{c1}^2a_2b_2)\frac{x_c}{RT_{c1}^2}\frac{dT_c}{dx_c}\rightarrow 0, \tag{4.77}$$

where $(\partial P/\partial T)^c_{\rho=\rho_{c1}}$ represents the limiting value of $(\partial P/\partial T)_{\rho=\rho_c}$ at the critical point of the pure solvent. At infinite dilution, in the region $\tau\gg\tau_1$, the factors Z_1 and Z_2 become

$$\begin{aligned}Z_1&\simeq RT_c\left[\zeta_2+\zeta_1\left(\frac{\partial\rho}{\partial x}\right)^r_{P,T}\right]^2\left(\frac{\partial x}{\partial\mu}\right)^r_{P,T}\\&=\left[\zeta_2+\zeta_1\left(\frac{\partial\rho}{\partial x}\right)^r_{P,T}\right]^2x_c(1-x_c),\end{aligned} \tag{4.78}$$

$$Z_2\simeq\zeta_1^2R\left(\frac{\partial P}{\partial T}\right)^2_{\rho,x}\frac{L_1^2}{\tilde{L}_1}\chi_1=\rho_c^2R\left(\frac{\partial\varepsilon}{\partial\rho}\right)^2_{T,x}(\beta_{T,x}-\beta_{S,x}). \tag{4.79}$$

Thus, as $D_2\rightarrow D$, the amplitude A_1 diverges strongly

$$A_1\simeq Z_2\propto\tau^{-\gamma} \tag{4.80}$$

and the amplitude A_2 vanishes with x at $\tau\gg\tau_2$ and diverges weakly as $A_1\propto\tau^{-\alpha}$ at $\tau\ll\tau_2$:

$$A_2=Z_1\propto\begin{cases}x, & \tau\gg\tau_2\\ \tau^{-\alpha}, & \tau\ll\tau_2.\end{cases} \tag{4.81}$$

Hence, at infinite dilution, the intensity of the light scattered from the system is determined by the slow mode with D_1

being equal to the thermal diffusivity a and with an amplitude A_1 proportional to the isothermal compressibility.

F. Wave-number dependence of the static and dynamic properties

In the approach to the critical point the correlation length ξ becomes comparable with and subsequently even larger than the inverse wave number q^{-1} of the scattered light and the q dependence of the static and dynamic properties must be taken into account [54]. According to the mode-coupling theory [57] the diffusivity $D_1(q,\xi)$, that determines the critical slowing down is

$$D_1(q,\xi)=D_1(q=0,\xi)\Omega_{\mathrm{K}}(q\xi)R(q\xi), \tag{4.82}$$

where $\Omega_{\mathrm{K}}(y)$ is the so-called Kawasaki function [5]

$$\Omega_{\mathrm{K}}(y)=(3/4y^2)[1+y^2+(y^3-y^{-1})\arctan y], \tag{4.83}$$

and where $R(y)=R_0(1+b^2y^2)^{z_\eta/2}$ is a correction factor with the parameters $R_0\simeq 1.0-1.05$, $b\simeq 0.5$, and $z_\eta\simeq 0.06$ [57]. The Kawasaki function behaves as

$$\Omega_{\mathrm{K}}(y)=1+\frac{3}{5}y^2-\frac{1}{7}y^4+\cdots \tag{4.84}$$

in the regime $y=q\xi\ll 1$ and as

$$\Omega_{\mathrm{K}}(y)=\frac{3\pi}{8}y+\frac{1}{y^2}-\frac{3\pi}{8}\frac{1}{y^3}+\cdots \tag{4.85}$$

in the regime $y=q\xi\gg 1$.

Usually, the q dependence of the form (4.82) is attributed to the mass diffusion coefficient D. However, this is valid only in the limiting case that $D_1\to D$. In general, neither D nor a is equal to D_1 and the mass diffusion coefficient D as well as the thermal diffusivity a may or may not depend on q. The q dependence of the second effective diffusivity D_2 can be assumed to be negligibly small.

Thus, the two characteristic decay rates $\Gamma_1=q^2D_1(q)$ and $\Gamma_2=q^2D_2(q)$, observed with light scattering, depend on the wave number as

$$\Gamma_1(q)\propto\begin{cases} q^2, & q\xi\ll 1\\ q^{3+z_\eta}, & q\xi\gg 1,\end{cases} \tag{4.86}$$

$$\Gamma_2(q)\propto q^2. \tag{4.87}$$

The thermodynamic derivatives determining the intensity of the scattered light can be expressed through the susceptibilities χ_1, χ_2, and χ_{12}. The q dependence of the measurable thermodynamic properies results from the q dependence of the strong susceptibility χ_1 near the critical point, which for small $q\xi$ has the form [54]

$$\chi_1(\mathbf{q})=\frac{\chi_1(0)}{1+q^2\xi^2}. \tag{4.88}$$

Again, as in general neither $(\partial x/\partial\mu)_{P,T}$ nor $(\partial\rho/\partial P)_{T,x}$ is equal to χ_1, they may or may not depend on q.

V. APPLICATIONS TO MIXTURES OF METHANE AND ETHANE

To compare the predictions of the theory with experimental data [22], we have calculated thermodynamic and transport properties for mixtures of methane and ethane in the critical region with the equation of state developed by Povodyrev *et al.* [58] with the zero point of entropy assigned by Sakonidou *et al.* [59,60]. This equation incorporates the crossover from singular thermodynamic behavior near the locus of vapor-liquid critical points to regular thermodynamic behavior outside the critical region [61]. For the critical parameters of pure methane (m) and ethane (e) we adopted the following values [58]: $\rho_c^{(m)}=10.122$ mol/l, $T_c^{(m)}=190.564$ K, $P_c^{(m)}=4.5992$ MPa, and $\rho_c^{(e)}=6.8592$ mol/l, $T_c^{(e)}=305.322$ K, $P_c^{(e)}=4.8718$ MPa, respectively. The measurements of the refractive index of methane and ethane [62–65] yield for the molar polarizabilities of the pure components $\alpha^{(m)}\simeq 1.57\ \mathrm{cm^3/mol}$ and $\alpha^{(e)}\simeq 2.681\ \mathrm{cm^3/mol}$.

The viscosity $\tilde{\eta}$ as a function of the reduced temperature τ and the mole fraction x is calculated with the interpolation formula

$$\tilde{\eta}(\tau,x)=(1-2x)\tilde{\eta}(\tau,0)+2x\tilde{\eta}(\tau,0.5), \tag{5.1}$$

where $\eta(\tau,0)$ and $\eta(\tau,0.5)$ were calculated according to an equation proposed by Sakonidou *et al.* [59,60]. We have used a similar linear interpolation formula to calculate the regular part λ^r of thermal conductivity:

$$\lambda^r(\tau,x)=(1-2x)\lambda^r(\tau,0)+2x\lambda^r(\tau,0.5), \tag{5.2}$$

with $\lambda^r(\tau,0)$ and $\lambda^r(\tau,0.5)$ calculated from equation proposed by Sakonidou *et al.* [59,60].

The experimental data, shown in Fig. 1 by open circles, were obtained by Ackerson and Hanley [22] from dynamic light-scattering experiments in the mixture of 71.07 mol % methane and 28.93 mol % ethane at the critical density $\rho=\rho_c$. They observed two relaxation modes, a slow mode and a fast mode, and they attributed the two corresponding decay rates to pure thermal diffusivity and mass diffusion. As our theory shows, the two measured decay rates are to be identified with the effective diffusivities D_1 and D_2. We fitted Eq. (1.1) to the experimental data [22] simultaneously for the fast and slow modes. In this procedure the regular parts $\tilde{\alpha}^r$ and $\tilde{\beta}^r$ of the Onsager coefficients in Eqs. (4.30)–(4.32) were the only adjustable parameters. The results of the fit are shown in Fig. 1, where the solid lines represent the two effective diffusivities D_1 and D_2. The joint fit yielded $\tilde{\alpha}^r(x_0)=4.9\times 10^{-11}\ \mathrm{kg\,s\,m^{-3}}$ and $\tilde{\beta}^r(x_0)=-2.1\times 10^{-8}\ \mathrm{Pa\,s\,K^{-1}}$, where $x_0=0.2893$. The values of the Onsager coefficients found from the fit were then adopted to calculate the conventional transport properties from the crossover equation of state [58]. The dashed lines in Fig. 1 represent the thermal diffusivity $a=\lambda/\rho C_{P,x}$ and the mass diffusion coefficient D for the same mixture. Apparently, for this composition of the mixture, neither the thermal diffusivity nor the mass diffusion coefficient can be identified with the diffusivities D_1 and D_2. As the scattering angle in the measurements [22] was small (8°), the correction for any dependence on q at

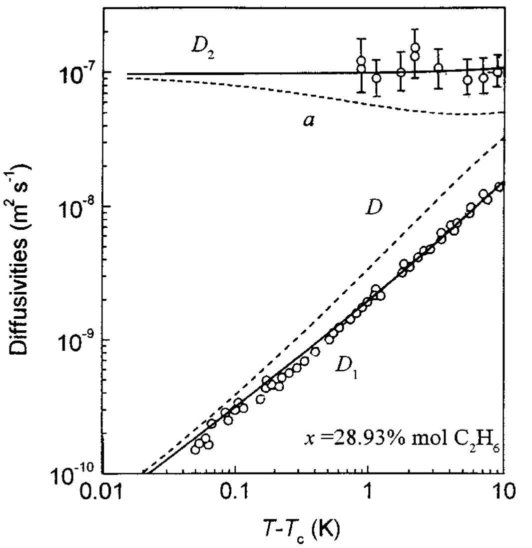

FIG. 1. Two effective diffusivities D_1 and D_2 for a near-critical mixture of methane (71.07 mol %) and ethane (28.93 mol %) at $\rho=\rho_c$ as a function of $T-T_c$. The open circles represent experimental data reported by Ackerson and Hanley [22]. The solid curves represent the values for D_1 and D_2 calculated theoretically. The dashed curves represent the values calculated for the thermal diffusivity a and the mass diffusion coefficient D.

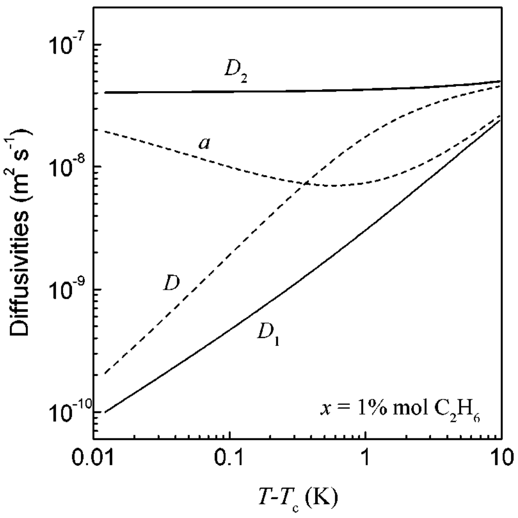

FIG. 2. Effective diffusivities D_1 and D_2, thermal diffusivity a, and mass-diffusion coefficient D calculated for a methane plus ethane mixture (1 mol % ethane) at $\rho=\rho_c$ as a function of $T-T_c$.

$T-T_c \gtrsim 10^{-2}$ K is less than 0.1% and we did not need to incorporate such a correction in calculating D_1 and D_2.

To calculate the regular parts $\tilde{\alpha}^r$ and $\tilde{\beta}^r$ of the Onsager coefficients for smaller concentrations x of ethane we assumed

$$\tilde{\alpha}^r(x)=\tilde{\alpha}^r(x_0)\frac{x}{x_0}, \quad \tilde{\beta}^r(x)=\tilde{\beta}^r(x_0)\frac{x}{x_0}. \tag{5.3}$$

We note that the values of $\tilde{\alpha}^r$ and $\tilde{\beta}^r$, quoted above for a mixture with 28.93 mol % ethane, differ considerably from the values $\tilde{\alpha}^r(0.5)=1.0\times 10^{-11}$ kg s m^{-3} and $\tilde{\beta}^r(0.5)=0.14\times 10^{-8}$ Pa s K^{-1}, deduced by Sakonidou *et al.* from their measurements of the thermal conductivity for a mixture with 50 mol % ethane [60]. However, two remarks should be made. First, it is not clear whether Eq. (5.3) adopted by us for smaller concentrations can be extrapolated to larger ethane concentrations. In addition, the actual values of both $\tilde{\beta}^r$ and $(\partial\mu'/\partial T)_{P,c}$ depend on the choice made for the zero point of entropy [20] and only the combination $\tilde{\alpha}^r(\partial\mu'/\partial T)_{P,c}+\tilde{\beta}^r$ has a physical meaning [cf. Eq. (4.44)]. As a consequence, the values found for $\tilde{\alpha}^r$ and $\tilde{\beta}^r$ are highly correlated. Kiselev and Huber have recently obtained values of the regular parts of the Onsager coefficients for the 50%-50% mixture that are much closer to our values [66]. They report $\tilde{\alpha}^r(0.5)=3.5\times 10^{-11}$ kg s m^{-3} and $\tilde{\beta}^r(0.5)=-1.94\times 10^{-8}$ Pa s K^{-1} from a joint analysis of the thermal conductivity experimental data by Sakonidou [59] and Roder and Friend [67]. Sakonidou *et al.* have shown that the variation for the asymptotic critical limit for the thermal conductivity is only 4% when the values of $\tilde{\alpha}^r(0.5)$ differ by a factor of two [60]. Moreover, the value of $\tilde{\alpha}^r$ extracted from the asymtotic thermal conductivity limit is sensitive to the choice of the critical temperature. Evidently, additional experimental data, especially for mass diffusion and thermodiffusion, are needed to resolve the concentration dependence of $\tilde{\alpha}^r$ and $\tilde{\beta}^r$ for mixtures of methane and ethane.

In Fig. 2 we show the two effective diffusivities D_1 and D_2, as well as the thermal diffusivity a and the mass diffusion coefficient D as a function of $T-T_c$ for a mixture with 1 mol % ethane at $\rho=\rho_c$ as a function of $T-T_c$. In Fig. 3 we present the same information for a mixture with 0.1 mol % ethane. On comparing Figs. 1–3 we see that the two effective diffusivities D_1 and D_2 are rather stable and do not vary strongly with concentration. However, the thermal diffusivity a and the mass diffusion D do depend strongly on the concentration. We see that for smaller and smaller ethane concentrations the mass-diffusion coefficient differs more

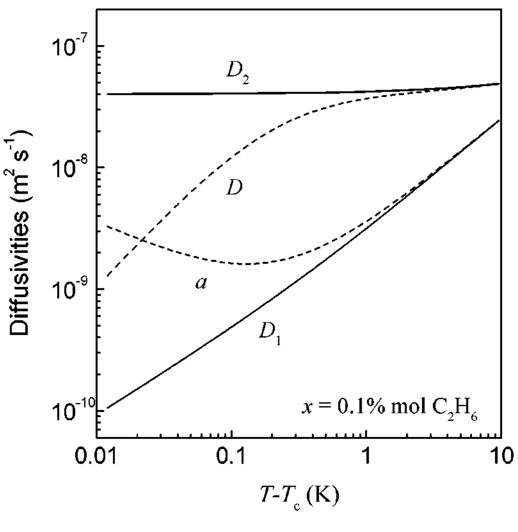

FIG. 3. Effective diffusivities D_1 and D_2, thermal diffusivity a, and mass-diffusion coefficient D calculated for a methane plus ethane mixture (0.1 mol % ethane) at $\rho=\rho_c$ as a function of $T-T_c$.

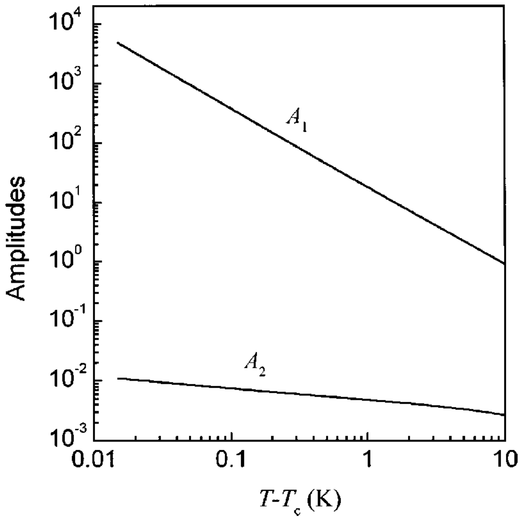

FIG. 4. Amplitudes A_1 and A_2 of the two relaxation modes calculated for a methane plus ethane mixture with 28.93 mol % ethane at $\rho=\rho_c$ as a function of $T-T_c$.

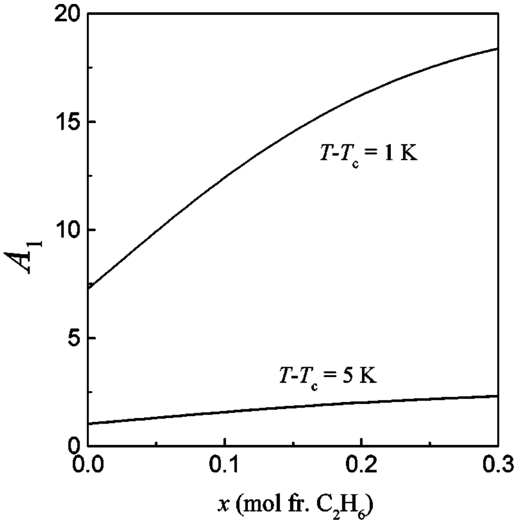

FIG. 5. Amplitude A_1 of the slow relaxation mode in methane plus ethane mixtures at $\rho=\rho_c$ and $T-T_c=1$ and 5 K as a function of the ethane concentration.

and more from the effective diffusivity D_1 of the slow mode and approaches more closely the effective diffusivity D_2. Asymptotically, the diffusion coefficient D becomes much smaller than the thermal diffusivity and approaches the effective diffusivity D_1, but this happens at temperatures too close to the critical point to be accessible experimentally.

As can be seen from Fig. 3, even for very small concentrations of ethane ($x=0.001$) the thermal diffusivity begins to deviate from the observed diffusivity D_1 already at $T-T_c \simeq 1$ K and this deviation increases rapidly upon approaching the critical temperature. This means that the interpretation of dynamic light-scattering experiments in so-called ''pure'' fluids [12], which always contain impurities, must be carried out with caution. In fact, the slow diffusion mode, being always critical, is not sensitive to impurities, whereas the actual thermal diffusivity is.

The amplitudes A_1 and A_2 of the two modes can be calculated from Eqs. (3.18) and (3.19). The calculated amplitudes A_1 and A_2 are shown in Fig. 4 for the mixture with 28.93 mol % ethane at $\rho=\rho_c$ as a function of $T-T_c$. The critical amplitude A_1 diverges strongly [as $(T-T_c)^{-\gamma}$] and the noncritical amplitude A_2 diverges weakly [as $(T-T_c)^{-\alpha}$] upon approaching the critical point. The temperature dependence of the amplitudes remains the same as we consider a more dilute solution. At infinite dilution, the noncritical amplitude A_2 vanishes. In Fig. 5 the amplitude A_1 at $\rho=\rho_c$ is shown as a function of the mole fraction x of ethane for $T-T_c=1$ K and $T-T_c=5$ K. The amplitude A_2 is shown in Fig. 6 as a function of x for $T-T_c=0.1$, 1, and 5 K. Ackerson and Hanley [22] reported some qualitative data on the ratio A_2/A_1. They considered the data reliable only far away from the critical point. At $T-T_c \simeq 10$ K they concluded A_2/A_1 to be about 0.05, whereas our calculations predict a much smaller magnitude of 0.005. This ratio appears to be very sensitive to the regular parts of the Onsager kinetic coefficients. If we use the values of $\tilde{\alpha}^r$ and $\tilde{\beta}^r$ reported by Kiselev and Huber [66] we obtain larger A_2/A_1 of about 0.03 at $T-T_c \simeq 10$ K, but the description of the fast mode is deteriorated. As we mentioned earlier, further investigation of the regular parts of the Onsager coefficients is desirable.

The parameter

$$\kappa=(\tilde{k}_T^2/TC_{P,x})(\partial\mu/\partial x)_{P,T}=(k_T^2/TC_{P,c})(\partial\mu'/\partial c)_{P,T}$$

that determines the coupling of the mass diffusion and the thermal diffusivity [cf. Eq. (1.2)] is shown in Fig. 7 as a function of temperature for three mole fractions of ethane at $\rho=\rho_c$. As we approach the critical point, κ always becomes much larger than unity. Thus the two modes are strongly coupled, until the condition $a/D \gg \kappa$ is achieved.

The measurable time-dependent correlation function of the intensity of scattered light is proportional to the structure factor $S(\mathbf{q},t)$ for heterodyne measurements, and to $[S(\mathbf{q},t)]^2$ for homodyne measurements with $S(\mathbf{q},t)$ given by Eq. (3.11). The diffusivities D_1 and D_2 and the corresponding amplitudes A_1 and A_2 can be obtained from measurements of

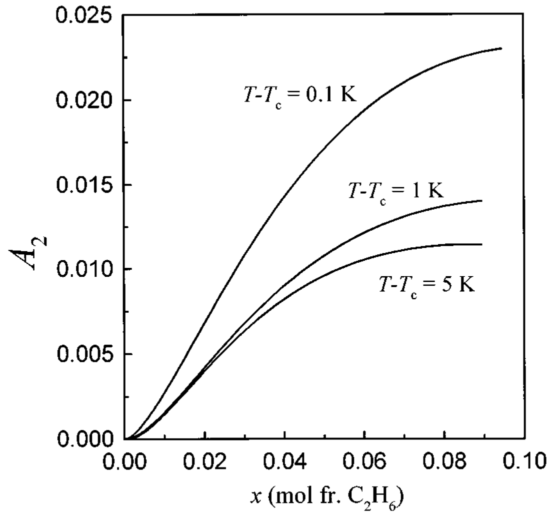

FIG. 6. Amplitude A_1 of the fast relaxation mode in methane plus ethane mixtures at $\rho=\rho_c$ and $T-T_c=0.1$, 1, and 5 K as a function of the ethane concentration.

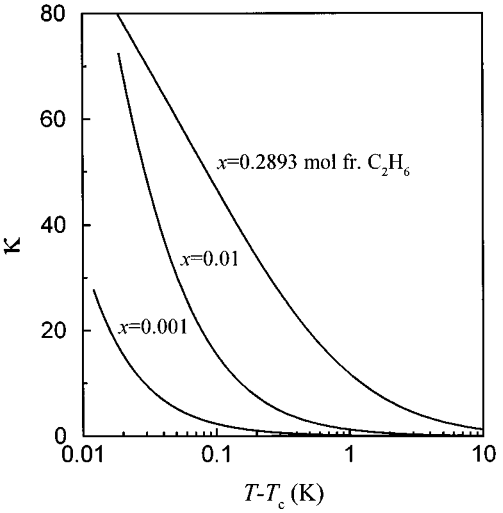

FIG. 7. Coupling parameter $\kappa=(\tilde{k}_T^2/TC_{P,x})(\partial\mu/\partial x)_{P,T}$ of methane plus ethane mixtures at $\rho=\rho_c$ as a function of $T-T_c$ for various mole fractions of ethane.

the intensity correlation function, if the amplitude A_2 is not too small compared to A_1 $(A_2/A_1 \gtrsim 10^{-3})$ and if D_1 and D_2 are significantly different. The smaller the ratio A_2/A_1, the larger difference of D_1 and D_2 is required. When the ratio A_2/A_1 is too small, a single-exponential decay corresponding to the slow (critical) mode D_1 is observed in practice. While the values of the ratio D_1/D_2 are rather similar for different fluid mixtures, one can play with the ratio A_1/A_2 by a proper choice of the components. A promising system for detecting the two modes is the mixture of nitroethane and iso-octane in the vicinity of the consolute point where, because of a very small difference in the refractive indices of the components $[(\partial\varepsilon/\partial x)_{P,T}$ is of order $10^{-3}]$, the amplitude A_1 is smaller than A_2 at $\tau \simeq 10^{-2}$ and is only 4 to 5 times larger than A_2 at $\tau \simeq 10^{-4}$ [68], whereas the ratio D_1/D_2 should behave in the same manner as in other systems. Another interesting binary fluid for which the two diffusivities have been calculated is a mixture of methane and n-hexane [69]. This system exhibits a continuous crossover between vapor-liquid critical phenomena and liquid-liquid critical phenomena along the critical line, and the order-parameter fluctuations gradually change from density fluctuations to concentration fluctuations.

VI. CONCLUSIONS

Two hydrodynamic relaxation modes are present in binary fluids. In near-critical binary fluids a coupling between these two modes results in two characteristic relaxation times: one is strongly divergent and the other is weakly divergent. Neither of these two modes can be associated with pure mass diffusion or pure thermal diffusion. Instead, the relaxation times are inversely proportional to two effective diffusivities D_1 and D_2, which can be detected experimentally by dynamic light scattering.

In special cases only (infinite dilution and incompressible limits) D_1 and D_2 are decoupled, becoming either mass diffusion or thermal diffusivity. Along the critical line the physical meaning of D_1 and D_2 changes from thermal diffusivity to mass diffusion coefficient and the physical meaning of the corresponding amplitudes A_1 and A_2 changes from compressibility to osmotic compressibility. Experimental observation of the two modes is a challenging task. However, being measured simultaneously, these two modes give a more complete picture of dynamic critical phenomena in fluid mixtures.

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APPENDIX

In this appendix we elucidate the relations between thermodynamic and transport properties of binary mixtures taken per unit mass and per mole of the mixture.

The differential of the Gibbs energy G per mole of a binary mixture is

$$dg=\rho^{-1}dP-SdT+\mu dx, \tag{A1}$$

where ρ the molar density, S is the molar entropy, $\mu=\mu_2-\mu_1$ is the chemical potential difference, μ_1 and μ_2 are the molar chemical potentials of the individual components in the mixture, and x is the mole fraction of the second component. The molar density ρ is related to the mass density ρ' by $\rho=\rho'/M$, where $M=(M_1n_1+M_2n_2)/n$ is the molar mass of the mixture, $n=n_1+n_2$ the total number of moles, M_i the molar masses and n_i the numbers of moles of the pure components with $x=n_2/n$. The mass concentration c is defined as

$$c=\frac{M_2n_2}{M_1n_1+M_2n_2}. \tag{A2}$$

Hence, the differential of the Gibbs energy G' per unit mass is

$$dG'=(\rho')^{-1}dP-S'dT+\mu'dc, \tag{A3}$$

where S' is the specific entropy and $\mu'=\mu_2/M_2-\mu_1/M_1$ the chemical-potential difference. The relations between the mole fraction x and the mass concentration c are

$$c=\frac{M_2}{M}x, \tag{A4}$$

$$c(1-c)=\frac{M_1M_2}{M^2}x(1-x), \tag{A5}$$

and

$$dc = \frac{M_1 M_2}{M^2}\, dx. \tag{A6}$$

The relation between μ and μ' is found from $\mu = (\partial G/\partial x)_{P,T}$ and $\mu' = (\partial G'/\partial c)_{P,T}$ with $G' = G/Mn$, as

$$\mu' = \frac{M}{M_1 M_2}\mu - \frac{M_2 - M_1}{M_1 M_2} G. \tag{A7}$$

One also has

$$\left(\frac{\partial c}{\partial \mu'}\right)_{P,T} = \frac{M_1^2 M_2^2}{M^3}\left(\frac{\partial x}{\partial \mu}\right)_{P,T}, \tag{A8}$$

$$\left(\frac{\partial \mu'}{\partial T}\right)_{P,c} = \frac{M}{M_1 M_2}\left(\frac{\partial \mu}{\partial T}\right)_{P,x} + \frac{M_2 - M_1}{M_1 M_2} S, \tag{A9}$$

$$\left(\frac{\partial \rho'}{\partial c}\right)_{P,T} = \frac{M^3}{M_1 M_2}\left(\frac{\partial \rho}{\partial x}\right)_{P,T} + \frac{(M_2 - M_1) M^2}{M_1 M_2}\rho. \tag{A10}$$

The linearized hydrodynamic equation of mass diffusion for a binary mixture is

$$\rho' \frac{\partial c}{\partial t} = - \ \mathrm{div}\ \mathbf{j}_d, \tag{A11}$$

where $\mathbf{j}_d$ is the linearized mass diffusion current

$$\mathbf{j}_d = -\rho' D\left[\boldsymbol{\nabla} c + \frac{k_T}{T}\boldsymbol{\nabla} T + \frac{k_P}{P}\boldsymbol{\nabla} P\right], \tag{A12}$$

D the mass-diffusion coefficient, k_T the thermal-diffusion ratio, and k_P the barodiffusion ratio. One can rewrite Eq. (A11) as

$$\frac{\partial c}{\partial t} = D\left[\nabla^2 c + \frac{k_T}{T}\nabla^2 T + \frac{k_P}{P}\nabla^2 P\right]. \tag{A13}$$

The molar diffusion current $\tilde{\mathbf{j}}_d$ is defined by $\tilde{\mathbf{j}}_d = \mathbf{j}_d / M$. Using relation (A6), one obtains

$$\tilde{\mathbf{j}}_d = -\rho\tilde{D}\left[\boldsymbol{\nabla} x + \frac{\tilde{k}_T}{T}\boldsymbol{\nabla} T + \frac{\tilde{k}_P}{P}\boldsymbol{\nabla} P\right], \tag{A14}$$

with

$$\tilde{D} = \frac{M_1 M_2}{M^2} D, \tag{A15}$$

$$\tilde{k}_T = \frac{M^2}{M_1 M_2} k_T, \tag{A16}$$

$$\tilde{k}_P = \frac{M^2}{M_1 M_2} k_P. \tag{A17}$$

Substituting $\mathbf{j}_d = \tilde{\mathbf{j}}_d M$ into Eq. (A11), one finds

$$\mathrm{div}\mathbf{j}_d = M\ \mathrm{div}\tilde{\mathbf{j}}_d + \tilde{\mathbf{j}}_d (M_2 - M_1)\boldsymbol{\nabla} x, \tag{A18}$$

and then, neglecting the second term on the right-hand side of Eq. (A18) and substituting $\tilde{\mathbf{j}}_d$, one obtains

$$\frac{\partial x}{\partial t} = \frac{M^2}{M_1 M_2}\tilde{D}\left[\nabla^2 x + \frac{\tilde{k}_T}{T}\nabla^2 T + \frac{\tilde{k}_P}{P}\nabla^2 P\right]. \tag{A19}$$

The entropy transport equation is

$$\frac{\partial T}{\partial t} - \frac{k_T}{C_{P,c}}\left(\frac{\partial \mu'}{\partial c}\right)_{P,T}\frac{\partial c}{\partial t} + \frac{T}{C_{P,c}}\left(\frac{\partial S'}{\partial P}\right)_{T,c}\frac{\partial P}{\partial t} = a\nabla^2 T, \tag{A20}$$

where $a = \lambda/\rho' C_{P,c} = \lambda/\rho C_{P,x}$ is the thermal diffusivity, and $C_{P,c} = C_{P,x}/M$ the specific heat capacity. In terms of variables per mole, this equation takes the form

$$\frac{\partial T}{\partial t} - \frac{\tilde{k}_T}{C_{P,x}}\left(\frac{\partial \mu}{\partial x}\right)_{P,T}\frac{\partial x}{\partial t} + \frac{T}{C_{P,x}}\left(\frac{\partial S}{\partial P}\right)_{T,x}\frac{\partial P}{\partial t} = a\nabla^2 T. \tag{A21}$$

Equations (A13) and (A20) [or, equivalently, Eqs. (A19) and (A21)] completely determine the spatial and temporal dependence of the temperature and concentration in the mixture.

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