

## **Decay Rate of Critical Fluctuations in Ethane + Carbon Dioxide Mixtures Near the Critical Line Including the Critical Azeotrope<sup>1</sup>**

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Using the technique of photon correlation spectroscopy we have measured the decay rate of critical fluctuations in mixtures of ethane and carbon dioxide of various compositions including a near-azeotropic mixture. Our experimental data indicate that there is only one dominant mode of fluctuations and the decay rate is well described by the predictions of the mode-coupling theory with the exponent  $\nu = 0.63$  for all compositions. The decay rate, its background contributions, the shear viscosity, and the correlation length for the mixtures appear to interpolate simply between those of ethane and carbon dioxide.

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**KEY WORDS:** azeotrope; carbon dioxide; critical fluctuation; ethane; mixtures; plait point; transport properties.

### **1. INTRODUCTION**

The decay rate of critical fluctuations has been studied extensively in the past by means of light scattering in pure fluids near the vapor-liquid critical point and in binary liquid mixtures near the consolute point. The measurements of the Rayleigh linewidth of simple fluids and liquid mixtures have been compared to theory in several reviews [1, 2]. However,

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studies of binary fluid mixtures near a vapor-liquid critical point (also known as a plait point) have been few [3-5] and only recently have systematic investigations been started on the  $^3\text{He} + ^4\text{He}$  system [6] and the  $\text{CO}_2 + \text{C}_2\text{H}_6$  system [7]. Such measurements are desirable not only for scientific reasons but also for their technological applications. For instance, it is important to know the transport properties of mixtures for the design and efficient operation of supercritical extraction processes.

It is known that for pure fluids near a vapor-liquid critical point the order parameter of critical fluctuations is density, whereas for binary liquid mixtures near a consolute point it is concentration [2]. But what is the order parameter in the case of binary fluid mixtures near a plait point where both concentration and density fluctuate? How does the behavior near a plait point compare with that near a consolute point? An attempt to answer such questions is one of the motivations behind this investigation.

One of the reasons we have chosen the carbon dioxide + ethane system is that many of the mixtures' properties as well as those of pure  $\text{CO}_2$  and  $\text{C}_2\text{H}_6$  are sufficiently well known that a Leung-Griffiths-type equation of state has been formulated [8]. Furthermore, the presence of the critical azeotrope where concentration fluctuations are expected to be suppressed might provide an opportunity for a mixture to mimic a pure fluid.

In this report, we present measurements of the decay rate of three  $\text{CO}_2 + \text{C}_2\text{H}_6$  mixtures near their plait points obtained with the technique of photon correlation spectroscopy. The compositions are 5.4, 35.8, and 68.0 (a near-azeotropic mixture) mol% of carbon dioxide. The decay rate was measured along the critical isochore at constant composition. We also measured the decay rate of pure carbon dioxide and ethane along the critical isochore and we are therefore able to compare the mixtures with the pure fluids.

## 2. REVIEW OF THEORY

In general, for a binary fluid mixture there are two modes of fluctuations associated with the Rayleigh line in a light-scattering experiment: heat and mutual diffusion. The decay rates associated with the two modes are related, respectively, to the thermal diffusivity and diffusion coefficient.

In a light-scattering experiment, the electromagnetic field correlation function of scattered light is proportional to that of the dielectric constant,  $\epsilon$ , of the medium, which in turn is proportional to the Fourier transform of the structure factor,  $S(k, \omega)$ . For the Rayleigh line alone,  $S(k, \omega)$  may be obtained from the linearized hydrodynamic equations and its time Fourier transform has the following form [9, 10]:

$$\begin{aligned}
S(k, \tau) &= \int_{-\infty}^{\infty} S(k, \omega) \exp(-i\omega\tau) d\omega/2\pi \\
&= \left(\frac{\partial\varepsilon}{\partial T}\right)_{pc}^2 (k_B T/C_{pc}) [Z \exp(-z_1\tau) + (1-Z) \exp(-z_2\tau)] \\
&\quad + \left(\frac{\partial\varepsilon}{\partial c}\right)_{pT}^2 k_B T \left(\frac{\partial c}{\partial\mu}\right)_{pT} [(1-Z) \exp(-z_1\tau) + Z \exp(-z_2\tau)] \\
&\quad + \left(\frac{\partial\varepsilon}{\partial T}\right)_{pc} \left(\frac{\partial\varepsilon}{\partial c}\right)_{pT} (k_B T/C_{pc}) k_T \left(\frac{2Dk^2}{z_1 - z_2}\right) \\
&\quad \times [\exp(-z_1\tau) - \exp(-z_2\tau)] \tag{1a}
\end{aligned}$$

where

$$Z = (z_1 - Dk^2)/(z_1 - z_2) \tag{1b}$$

$$z_1 = (k^2/2)(\chi + (1+A)D) + \{[\chi + (1+A)D]^2 - 4\chi D\}^{1/2} \tag{1c}$$

$$z_2 = (k^2/2)(\chi + (1+A)D) - \{[\chi + (1+A)D]^2 - 4\chi D\}^{1/2} \tag{1d}$$

with  $A = [(k_T)^2/(TC_{pc})](\partial\mu/\partial c)_{pT}$ . Here  $k_B$  is Boltzmann's constant,  $T$  the temperature,  $p$  the pressure,  $c$  the mass fraction of one component,  $\mu$  the difference in the chemical potential per unit mass of the two components,  $k_T$  the thermal diffusion ratio,  $\chi$  the thermal diffusivity,  $D$  the diffusion coefficient,  $k$  the scattering vector, and  $C_{pc}$  the heat capacity per unit mass at constant  $p$  and  $c$ . Equation (1) predicts that the correlation function of the scattered light field consists of two exponentially decaying functions and the associated time constants are, in general, neither  $\chi$  nor  $D$  due to the coupling of the two modes as represented by the constant  $A$ . If the two modes are decoupled, ( $A = 0$ ), then  $z_1 = \chi k^2$  and  $z_2 = Dk^2$ .

### 3. EXPERIMENTAL RESULTS AND DISCUSSION

In photon correlation spectroscopy, we measure the correlation function of the scattered light intensity  $\langle I(\tau) I(0) \rangle$ , which in turn is related to that of the scattered electromagnetic field  $\langle E(\tau) E(0) \rangle$  in the following way:

$$\langle I(\tau) I(0) \rangle = B[1 + b |g^{(1)}(\tau)|^2] \tag{2}$$

where

$$g^{(1)}(\tau) = \langle E(\tau) E(0) \rangle / \langle I \rangle \tag{3}$$

Here the angular brackets denote a statistical average,  $B = \langle I^2 \rangle$ , and  $b$  is a constant related to the spatial coherence of the detected light. The experimental details concerning the apparatus and sample preparation have been published elsewhere [7].

We have measured  $g^{(1)}(\tau)$  as a function of temperature along the critical isochore for three mixtures ( $x=0.054$ ,  $0.358$ , and  $0.680$ , where  $x$  is the mole fraction of  $\text{CO}_2$ ) as well as pure carbon dioxide and ethane. In order to detect the presence of two exponential functions in  $g^{(1)}(\tau)$ , we applied a cumulant analysis [11]. The square root of  $[\langle I(\tau) I(0) \rangle / B - 1] / b$  is analyzed to the second cumulant (and sometimes third when necessary). Single exponential decay was indicated by a statistically insignificant second cumulant. The first cumulant of the analysis is defined as the decay rate. The cumulant analysis showed that for carbon dioxide and ethane, the measured correlation functions were well described by one exponential function, as one would expect except at temperatures very close to or very far from the critical temperature,  $T_c$ . The correlation functions deviate from single exponential form in the temperature range  $(T - T_c) / T_c < 7 \times 10^{-5}$  because of the onset of multiple scattering, whereas in the temperature range  $(T - T_c) / T_c > 3 \times 10^{-3}$  the scattering intensity is so low that heterodyning with the stray light may no longer be negligible. In the intermediate temperature range where the pure fluids showed single exponential correlation functions, the cumulant analysis showed that the correlation functions for the mixtures could be described likewise. The same conclusion has also been reached by other researchers [3, 5].

The decay rate thus determined for all three mixtures and two pure components is plotted as a function of  $t \equiv (T - T_c) / T_c$  in Fig. 1. A striking feature of this plot is that the mixture data strongly resemble the pure fluid data; they seem simply to interpolate between those of  $\text{CO}_2$  and  $\text{C}_2\text{H}_6$  according to the compositions. One is inclined to believe that the critical fluctuations in mixtures may be dominated by the mutual diffusion mode and the decay rate should reflect the diffusion coefficient  $D$ . The fact that the decay rate of the mixtures seems to reflect, instead, the thermal diffusivity of pure fluids is puzzling.

For the  $^3\text{He} + ^4\text{He}$  system Miura et al. [6] have found that the measured decay rate of mixtures was actually  $z_2$  in Eq. (1). Not only is  $z_1$  much larger than  $z_2$ , but the amplitude of the  $z_1$  term is also much smaller than that of the  $z_2$  term. Moreover, it was also found that  $z_2$  was approximately equal to  $Dk^2$  of the mixtures and  $D$  of the mixtures was close to  $\chi$  of  $^3\text{He}$ . A similar analysis for the  $\text{CO}_2 + \text{C}_2\text{H}_6$  system is not yet possible because the required thermal diffusion ratio data are not known.

Recently, Onuki has put forth a crossover theory for near-azeotropic binary fluid mixtures [12]. He defines a dimensionless degree of azeotropy,  $\alpha_2$ , by

$$\alpha_2 = -\rho^{-1}(\partial p / \partial \Delta)_{T, cxs} \quad (4)$$

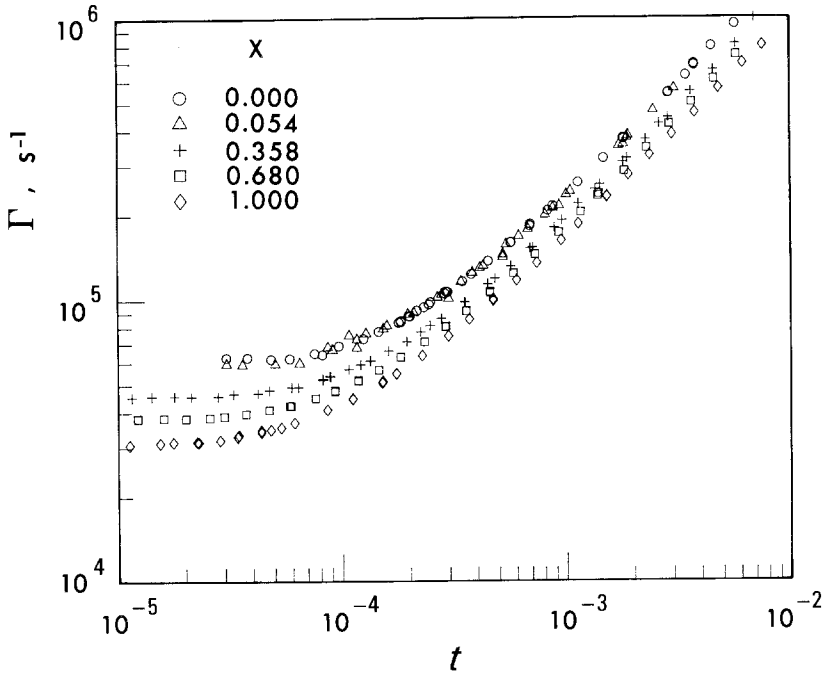


Fig. 1. Decay rate of ethane, carbon dioxide, and three mixtures along the critical isochore as a function of  $t = (T - T_c)/T_c$ . The compositions are indicated by the mole fraction,  $x$ , of carbon dioxide.

where  $\rho$  is the molar density,  $\Delta$  is the difference of the chemical potentials per mole of the two components, and  $cx_s$  denotes coexistence surface. The azeotropic line is the locus of points on the coexistence surface along which  $\alpha_2 = 0$ . The theory introduces crossover temperatures for the critical behavior of near-azeotropic mixtures which are characterized by  $|\alpha_2| \ll 1$ . Sufficiently close to  $T_c$  the thermodynamic properties of such systems are characteristic of a binary mixture. However, farther from  $T_c$  beyond the crossover temperature, pure-fluid behavior should prevail. Static properties share one crossover temperature,  $t_{s1}$ , whereas dynamic properties share another,  $t_D$ . Both of these temperatures are expressed in the same reduced form as  $t = (T - T_c)/T_c$ . According to Onuki's estimate,  $t_D \simeq (t_{s1})^2$ .

To demonstrate the crossover phenomena in mixtures, we have calculated the osmotic susceptibility,  $(\partial x/\partial \Delta)_{pT}$ , and the isothermal compressibility at constant composition,  $K_{Tx}$ , for the mixtures of carbon dioxide and ethane using a Leung-Griffiths-type equation of state developed for these mixtures [8]. In Fig. 2 we show  $(\partial x/\partial \Delta)_{pT}$  and  $K_{Tx}$ , in

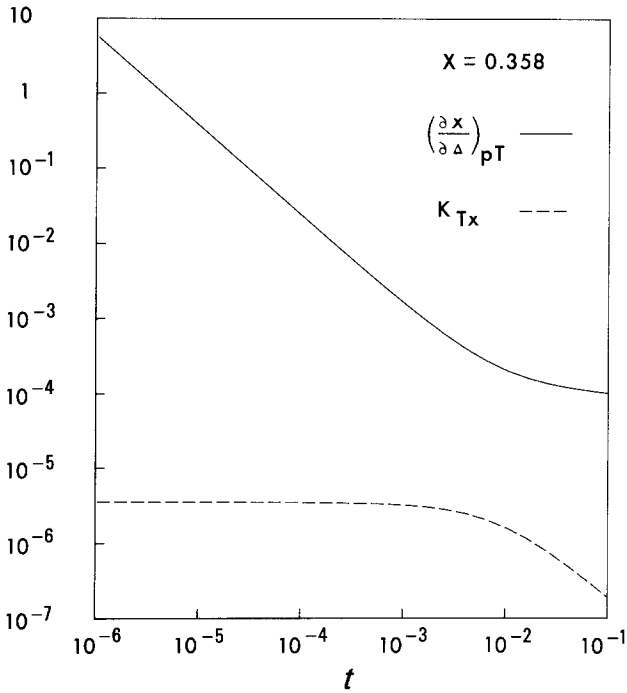


Fig. 2. The osmotic susceptibility in units of  $\text{mol} \cdot \text{J}^{-1}$  and the isothermal compressibility in units of  $\text{m}^2 \cdot \text{N}^{-1}$  along the critical isochore-isopleth calculated as a function of  $t = (T - T_c)/T_c$  using a Leung-Griffiths-type equation of state for  $x = 0.358$  (mole fraction of carbon dioxide). Note that the crossover occurs at  $t \approx 10^{-2}$ .

units of  $\text{mol} \cdot \text{J}^{-1}$  and  $\text{m}^2 \cdot \text{N}^{-1}$ , respectively, calculated for  $x = 0.358$ . The crossover temperature in the reduced form,  $t_{s1}$ , and the degree of azeotropy,  $\alpha_2$ , have nearly their largest values at this composition and they are, respectively, 0.01 and 0.07. Then  $t_D$ , being approximately the square of  $t_{s1}$ , is of the order of  $10^{-4}$ . This implies that all three mixtures behave like pure fluids for most of the temperature range of the experiment. Therefore it is not surprising that at least for the range  $t > 10^{-4}$ , the decay-rate data of mixtures seem to interpolate between those of the two pure components.

Onuki further states that the linearized hydrodynamic equations lead to two modes of fluctuations but only one of these undergoes the critical slowing-down governed by the mode-coupling theory [12]. The asymptotic form for the critical part,  $\Gamma_c$ , of the decay rate of the critical fluctuations is then given by [13]

$$\Gamma_c = k^2 (k_B T / 6\pi\eta\xi) \Omega(x) \quad (5a)$$

with

$$\Omega(x) = R\Omega_K(x)[1 + (x/2)^2]^{z/2} \quad (5b)$$

and

$$\Omega_K(x) = (3/4x^2)[1 + x^2 + (x^3 - x^{-1}) \arctan(x)] \quad (5c)$$

where  $\eta$  is the shear viscosity,  $\xi$  is the correlation length,  $R$  is a dynamic amplitude ratio,  $z \simeq 8/(15\pi^2)$ , and  $x = k\xi$  ( $x$  should not be confused with the mole fraction of carbon dioxide). There are only two system-dependent quantities in Eq. (5), namely,  $\eta$  and  $\xi$ . The correlation length  $\xi$  diverges as [14]

$$\xi = \xi_0 t^{-\nu} \quad (6a)$$

and the viscosity as [2]

$$\eta = \eta_0 t^{-z\nu} \quad (6b)$$

The two main points of the discussion can now be summarized as follows. First, the order parameter of the critical fluctuations crosses over from pure fluid-like (density) to mixture-like (concentration) as  $T \rightarrow T_c$ . Second, the decay rate of the fluctuations, regardless of the nature of the order parameter, is still prescribed by Eq. (5). Consequently, our decay-rate data of the mixtures interpolate between those of the two pure components according to the compositions.

#### 4. DATA ANALYSIS

It is commonly acknowledged that the measured decay rate consists of two parts: the critical part,  $\Gamma_c$ , and the background part,  $\Gamma_B$ , which is given by [2]

$$\Gamma_B = \beta_0 k^2 t^\gamma (1 + x^2) \quad (7)$$

where  $\beta_0$  is the background decay-rate coefficient and is virtually a constant in the temperature range of our experiment and  $\gamma$  is a critical exponent. When the decay rate is analyzed with

$$\Gamma = \Gamma_c + \Gamma_B \quad (8)$$

there are only three system-dependent parameters, namely, the amplitudes  $\eta_0$ ,  $\beta_0$ , and  $\xi_0$ . The theoretical estimates for the dynamic amplitude ratio  $R$  in Eq. (5b) range from 1.03 to 1.2 [2]. Because of the high degree of inter-

dependence among  $\eta_0$ ,  $\beta_0$ ,  $\xi_0$ , and  $R$ , the value of  $R$  can be determined experimentally only if the values of the other three are known. That is the case for carbon dioxide. For the temperature range of our experiment it is determined that  $\eta_0 = 2.92 \times 10^{-5} \text{ Pa} \cdot \text{s}$ ,  $\beta_0 = 6.16 \times 10^{-7} \text{ m}^2 \cdot \text{s}^{-1}$  [15], and  $\xi_0 = 0.150 \text{ nm}$  [14]. However, the appropriate values for the exponents in Eqs. (6b) and (7) are then 0.0253 and 1.23 instead of the asymptotic values of 0.0340 and 1.24, reflecting the fact that the temperature range of our experiment is not in the asymptotic region for  $\eta$  and  $\Gamma_B$ .

Using the values of  $\eta_0$  and  $\beta_0$  along with  $\nu = 0.63$ ,  $k = 1.555 \times 10^7 \text{ m}^{-1}$ , and  $T_c = 304.1783 \text{ K}$ , a least-squares procedure for fitting the data of  $\text{CO}_2$  to Eq. (8) with  $R$  as the only free parameter yielded the best value,  $R = 1.02 \pm 0.01$ . This result is in good agreement with the prediction of mode-coupling theory and experimental values of binary liquid mixtures [2, 16, 17] and pure fluids [7, 18]. The comparison between the theory and the data is shown in Fig. 3, where open circles represent the data points and the curve the best-fit function of Eq. (8). The rms deviation of the fit is 1.81%. It should be mentioned that data points at  $t > 5 \times 10^{-3}$  and  $t < 4 \times 10^{-5}$  are assigned weights of zero in the fitting procedure to

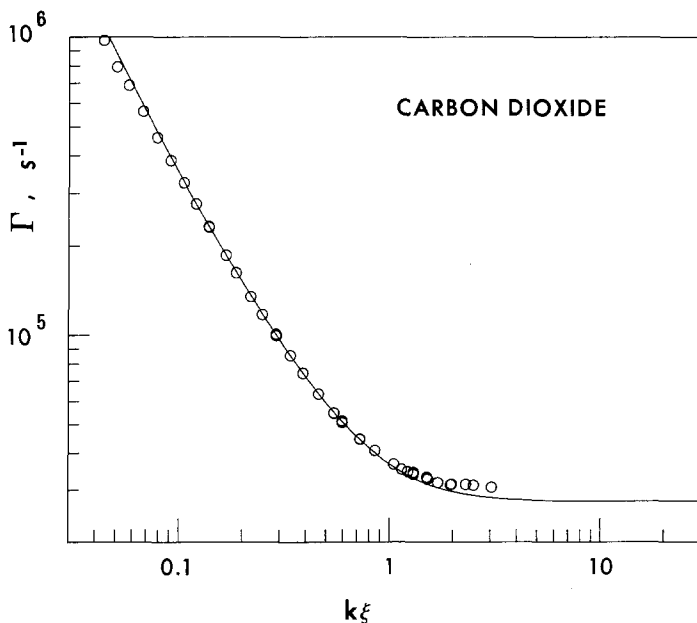


Fig. 3. Comparison between the decay rate of carbon dioxide and Eq. (8) using  $R$  as the only free parameter. The best-fit value obtained for  $R$  is 1.02. The rms deviation of the fit is 1.81%.



**Table I.** Best-Fit Values of the Amplitudes of Viscosity,  $\eta_0$ , Correlation Length,  $\xi_0$ , and Background Contributions,  $\beta_0$ , for Mixtures of Various Compositions,  $x$ , Given in Terms of Mole Fractions of Carbon Dioxide

$x$	$\eta_0$ ( $10^{-6}$ Pa·s)	$\xi_0$ (nm)	$\beta_0$ ( $10^{-7}$ m <sup>2</sup> ·s <sup>-1</sup> )	rms dev. of fit (%)
1.000	28.1	0.157	5.8	0.84
0.680	22.5	0.179	7.1	0.46
0.358	19.4	0.199	8.0	0.68
0.054	16.0	0.216	9.4	3.06
0.000	16.4	0.216	10.3	1.41

minimize the effects of distortions in the data caused by multiple scattering and stray light.

The data for mixtures can not be treated in the same way as the CO<sub>2</sub> data because of lack of information on  $\eta_0$ ,  $\beta_0$ , and  $\xi_0$ . But for the purpose of intercomparison, we have used the fixed value  $R = 1.02$  and let  $\eta_0$ ,  $\beta_0$ , and  $\xi_0$  be the free parameters in the least-squares fit for all five sets of data. Data points at  $t$  greater than  $5 \times 10^{-3}$  or less than  $4 \times 10^{-5}$  are again assigned weights of zero. The best-fit values are listed in Table I. Although this procedure does not reproduce the known parameters for CO<sub>2</sub> exactly, the agreement is still satisfactory. The best-fit values of  $\eta_0$ ,  $\beta_0$ , and  $\xi_0$  of the mixtures appear to interpolate between those of the two pure fluids just as the decay-rate data themselves.

## 5. CONCLUSIONS

We have measured the decay rate of critical fluctuations in mixtures of carbon dioxide and ethane along with that of pure carbon dioxide and ethane. This system of mixtures has a critical azeotrope near  $x = 0.7$  (mole fraction of CO<sub>2</sub>). As a consequence it can be characterized as "near-azeotropic" for all compositions. Near-azeotropic mixtures exhibit crossover behavior from pure fluid-like to mixture-like as  $T \rightarrow T_c$ . Our data show that even though the order parameter of fluctuations may cross over from one to the other, there is only one diffusive mode of critical fluctuations which is governed by the mode-coupling theory. Consequently, our data are well described by the predictions of mode-coupling theory. Henry et al. [3] and Saad and Gulari [5] also reported that they detected only one mode of fluctuations, whereas Ackerson and Hanley [4] reported that they detected two distinct modes.

Moreover, using known values of viscosity, background contributions, and correlation length for carbon dioxide, we have also determined experimentally the value of 1.02 for the dynamic amplitude ratio  $R$ , in good agreement with mode-coupling theory.

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