Decay Rate of Critical Fluctuations in Steam and in Dilute Steam–NaCl Mixtures[1]

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The decay rate of critical fluctuations in steam and in a steam–NaCl mixture has been investigated experimentally with the aid of photon correlation spectroscopy. For pure steam, the measurements have been performed along seven isochores $[(|\rho - \rho_c|)/\rho_c < 0.09]$ as a function of the temperature T for $(T - T_t) < 1$ K. The results have been compared with the values predicted by the renormalization-group theory written as a modification of the classical mode coupling theory. The agreement between experiment and theory is satisfactory along the critical isochore, but larger deviations are noted for $\rho \neq \rho_c$ when approching the transition temperature T_t. The decay rate of a 0.1% (molar) dilute mixture of NaCl in H_2O has been measured along some near-critical isochores as a function of temperature. Its behavior, which is very different from that observed for pure steam, is dicussed.

KEY WORDS: critical fluctuations; diffusivity; light scattering; mixtures; sodium–chloride solutions; steam.

1. INTRODUCTION

Near a critical point, a system exhibits large fluctuations in its order parameter. The measurement of the decay rate of these fluctuations allows a better understanding of the dynamical behavior of the system. We have investigated the decay rate of the density fluctuations in steam, in the density range $\rho^* = [(\rho - \rho_c)/\rho_c] < 0.1$ (ρ_c is the critical density) and in the temperature range $0.02 < (T - T_t) < 1$ K (T_t is the temperature of the one phase–two phase transition). To our knowledge, the results presented here

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are the first which have been obtained for steam. This is probably due to experimental difficulties related to the high values of the critical temperature and pressure and to the corrosive properties of supercritical steam. The experimental results are compared with the predictions of the dynamic theories of critical phenomena. The characteristic time of the critical fluctuations in a dilute $NaCl-H_2O$ solution has been also studied. We present preliminary results that we discuss in comparison with the behavior of pure steam.

2. EXPERIMENTAL DEVICE

We used the conventional technique of photon correlation spectroscopy to measure the decay rate of the critical fluctuations. The cylindrical high-pressure optical cell is made of refractory nickel-base alloy. Its axis is colinear to the incident laser beam. The cell is closed at each end by two parallel sapphire windows whose tightness is ensured by gold seals. The third saphire window is at an angle of 90° to the longitudinal axis of the cell. The cell is filled at room temperature under vacuum. The amount of water is measured by weighing the empty and filled cell. The accuracy of the fluid density in the cell is estimated to be better than 0.5%.

The cell is enclosed in a two-stage thermostat. The outer stage is an air circulating thermostat whose temperature is set at $(80 \pm 0.1)°C$. The inner stage is a three-part electrically heated copper furnace which maintains a constant temperature at the level of the cell within 3 mK. A nisil–nicrosil thermocouple located in the furnace is the sensitive element used to control the temperature. The two copper blocks located at each end of the main part of the furnace allow the cancellation of the longitudinal temperature gradients. The temperature of the cell is measured with a calibrated chromel–alumel thermocouple. The reproducibility of the transition temperature at a fixed density at the beginning and the end of a run (i.e., over 36 h) is a test of keeping water free of contamination.

The light source is a He–Ne laser (wavelength $\lambda_L = 632.8$ nm). The light scattered at 90° is received by a photomultiplier. The dynamic analysis is made by the homodyne method using a 50-ns-250-channel digital correlator. The analysis of the autocorrelation of the photopulses yields the decay time $\tau = 1/\Gamma$ (Γ is the decay rate) of the critical fluctuations. The experimental uncertainty in the determination of τ increases from 3% for $\tau > 10$ μs up to 5% for $\tau \sim 2$ μs. The distance to the temperature T_t of the transition is determined with a 5-mK uncertainty.

3. DECAY RATE OF CRITICAL FLUCTUATIONS IN PURE STEAM

3.1. Experimental Results

We define a generalized thermal diffusivity D_T^* by

$$D_T^* = \frac{\Gamma}{q^2} = \frac{1}{\tau q^2} \tag{1}$$

where $q = (4\pi n/\lambda_L) \sin \theta/2$ is the wave number of the scattered light, n being the refractive index of steam ($n = 1.093$ at critical density ρ_c), λ_L the wavelength of light, and θ the scattering angle.

For $\rho \neq \rho_c$, the refractive index n has been calculated from the Lorentz–Lorenz relation:

$$\frac{n^2 - 1}{n^2 + 2} \frac{1}{\rho} = \text{const} \tag{2}$$

The experimental values of D_T^* obtained for seven densities including the critical density are shown in Fig. 1.

At the critical density, the transition temperature has been obtained at $T_c = 647.122 \pm 0.01$ K on IPTS 1968, a value which compares favorably with the value of 647.14 ± 0.1 K recommended by Levelt-Sengers et al. [1].

3.2. Comparison with Theory

In the treatment of dynamic critical phenomena, it is usual to separate the transport coefficients into background and singular contributions. This separation implies a similar separation of the overall decay rate Γ (or of D_T^*) written for pure fluids as

$$\Gamma = \Gamma_c \frac{C_p^c}{C_P} + \Gamma_B \quad \text{or} \quad D_T^* = D_c^* \frac{C_p^c}{C_p} + D_B^* \tag{3}$$

C_p^c is the critical part of the constant pressure-specific heat. It can be approximated in terms of the constant pressure-specific heat C_p and of the constant volume-specific heat C_V by

$$C_p^c = C_p - C_v \tag{4}$$

The background term is given by

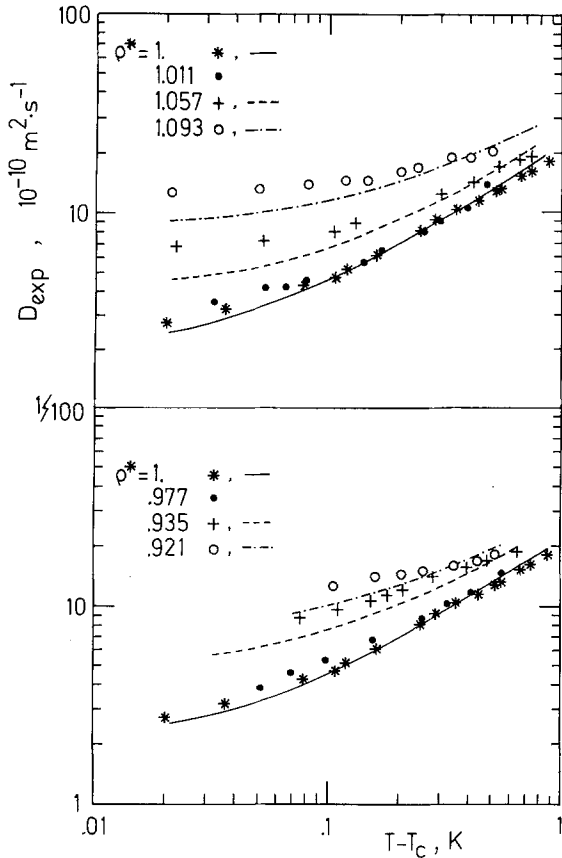$$D_B^* = \frac{\lambda_B}{\rho C_p} (1 + q^2 \xi^2) \tag{5}$$

Fig. 1. Thermal diffusivity of H_2O along $\rho \geqslant \rho_c$ and $\rho \leqslant \rho_c$ isochores. The lines are calculated values (see text).

where ξ is the correlation length, and λ_B the background thermal conductivity.

Mode-coupling theories and renormalization-group theories predict that D_c^* should asymptotically satisfy the following equation:

$$D_c^*(q\xi) = R \frac{k_B T}{6\pi\eta\xi} \Omega(q\xi) \qquad (6)$$

$\Omega(q\xi)$ is a universal dynamical scaling function and R is a universal constant. For the mode-coupling theory, the function $\Omega(q\xi)$ has been

estimated by Kawasaki and Lo [2] and by Burstyn and Sengers [3]. Burstyn and Sengers have derived a closed approximation of $\Omega(q\xi)$:

$$\Omega_{\rm B}(q\xi) = \Omega_{\rm B}(x) = \Omega_{\rm K}(x) \left(1 + \frac{x^2}{2}\right)^{x_\eta/2} \tag{7}$$

where

$$\Omega_{\rm K}(x) = \frac{3}{4x^2} \left[(1 + x^2 + (x^3 - x^{-1}) \operatorname{arctg} x)\right] \tag{8}$$

is the Kawasaki function.

In Eqs. (6) and (7), $x_\eta = 0.06$ and R takes the value $R = 1.03$.

From the renormalization-group theory, a slightly different approximation of $\Omega(x)$ has been proposed by Paladin and Peliti [4]:

$$\Omega_{\rm P}(x) = [\Omega_{\rm K}(x)]^{1-x_\eta} (1 + x^2)^{x_\eta} \tag{9}$$

where $x_\eta = 3/43$ and $R = 1.0375$. The maximum difference between $\Omega_{\rm B}(x)$ and $\Omega_{\rm P}(x)$ is only 1.2% in our experimental range $q\xi \leqslant 1.4$.

Other values of R have been obtained by Siggia et al. [5]. They vary from 0.79 to 1.2.

We have chosen to compare our experimental results with the expression of $D_{\rm c}^*$ proposed by Paladin and Peliti and R will be an adjustable parameter.

3.2.1. Critical Isochore

A discussion of the results has been presented in Ref. 6 and is briefly recalled here. For a comparison between experiment and theory, thermodynamic and transport properties of steam are needed. Moreover, the correlation length ξ must be estimated. Two sets of values are used. They differ by the expression of $\lambda_{\rm B}$, $K_{\rm T}$, and ξ. They are summarized in Table I.

Using the LIMHP set, the best fit of the critical isochore is obtained for $R = 1.075$, while a value of $R = 1.2$ is needed for an acceptable agreement between experiment and theory when the NBS set is used, a value which is actually considered too large. It can be shown that the difference between the two calculated curves is due mainly to the difference in the amplitude ξ_0 of the correlation length, the influence of the background term being small.

Considering the experimental errors on $(T - T_{\rm c})$ and $D_{\rm T}^*$, the agreement between experimental and calculated $D_{\rm T}^*$ values is satisfactory when choosing the LIMHP parameters.

Table I. Parameters Used for the Calculation of
Theoretical Values of D_T^*

	NBS	LIMHP
K_T	Scaled equation of state, Levelt-Sengers et al. [7]	Critical isochore [11] $K_T = K_T^\ominus \, \Delta T^{*-\gamma} [1 + a_x^+ \, \Delta T^{*\Delta}]$ $K_T^\ominus = 2.1375 \; 10^{-9} \; \mathrm{Pa}^{-1}$ $a_x^+ = 1.831$ $\gamma = 1.24; \Delta = 0.5$
C_v	Scaled equation of state [7]	
η	Improved representative equation, Watson et al. [8]	
λ_B	Thermal conductivity representative equation, Sengers et al. [9]	Tufeu et al. correlation [12]
ξ	$\xi = \xi_0^+ \left(\dfrac{\rho^2}{\rho_c^2} \dfrac{K_T}{K_T^0} \right)^{v/\gamma}$ (10) $\xi_0^+ = 1.31 \; 10^{-10} \; \mathrm{m}$ $v = 0.63; \gamma = 1.24$	Critical isochore [11] $\xi = \xi_0^+ \, \Delta T^{*-v} [1 + a_\xi^+ \, \Delta T^{*\Delta}]$ $\xi_0^+ = 1.212 \; 10^{-10} \; \mathrm{m}$ $a_\xi^+ = 1.177$ $v = 0.63; \Delta = 0.5$

Close to the critical point, when $(T - T_c) < 0.1$ K, the observed deviations can be explained partly by the vertical density gradient in the sample due to the divergence of the isothermal compressibility. It must be noted that the theoretical expression of D_T^* has been derived in the Ornstein–Zernike approximation and does not take into account so-called vertex corrections. Finally, due to the lack of experimental data very close to the critical point, the amplitude of the critical viscosity enhancement is not precisely known.

We must also note that, farther from the critical point, the experiments are performed in a range where the asymptotic conditions are not fullfilled, i.e., where crossover contributions should be taken into account. The theoretical approach of the problem is only beginning. Based on the mode coupling theory, an expression of the transport coefficients in the crossover region has been proposed by Olchowy and Sengers [13]. This modified mode coupling expression leads to a D_T value which does not differ significantly from the one calculated with the original mode coupling expression.

3.2.2. Noncritical Isochores

In the temperature and density range of the present study, the minimum value of the correlation length ξ estimated using Eq. (10) [10] given

in Table I and the scaled equation of state [7] is of the order of 80 Å, i.e., only slightly lower than the minimum value of ξ estimated along the critical isochore. Consequently, the experimental results obtained for the noncritical isochores can be compared to the theory by following the same procedure as above.

Along the critical isochore, the best agreement between theory and experiment has been obtained with the LIMHP set of thermodynamic and transport properties. Unfortunately, the method used by Garrabos [11] to predict the isothermal compressibility K_T and the correlation length ξ has not been extended outside the critical isochore. We have already noted that the difference between the values of D_T^* calculated with the two data sets is due mainly to the difference between the correlation length amplitude ξ_0. So we propose to estimate the correlation length outside the critical isochore using Eq. (10) given in Table I, with $\xi_0 = 1.212$ Å, while K_T, C_p, and C_v will be calculated from the scaled equation of state proposed by Levelt-Sengers et al. [7]. The background thermal conductivity λ_B has been evaluated by Tufeu et al. [12].

We again take the scaling function $\Omega_P(q\xi)$ proposed by Paladin and Peliti [4] and keep the value $R = 1.075$.

The calculated values D_T^* as a function of $(T - T_c)$ are reported in Figs. 1a and b for $\rho \geqslant \rho_c$ and $\rho \leqslant \rho_c$. T_c is related to T_t by [14]

$$\frac{(T_c - T_t)}{T_c} = \left(\frac{|\rho - \rho_c|}{B\rho_c}\right)^{1/\beta} \tag{11}$$

with $B = 1.993$ and $\beta = 0.324$

The agreement between calculated and experimental values can be considered as acceptable for $(T - T_c) > 0.2$ K. When approaching the transition temperature the deviations become important and increase with $\Delta\rho$. At $(T - T_c) = 0.55$ K, the deviation between experimental and calculated D_T^* is smaller than 5% for all densities, but for $(T - T_c) = 0.1$ K the deviation reaches 20% for $|\rho - \rho_c|/\rho_c = \pm 0.09$. Normalizing at $\rho = \rho_c$ the experimental and calculated curves $D_T^*(\rho)$ at $(T - T_c) = $ const., we note that the experimental variations of D_T^* in term of $|\rho - \rho_c|$ are larger than the calculated variations. It seems that a similar observation can be made from the comparison carried on by Olchowy and Sengers [13] between experimental and calculated values of D_T^* for CO_2 at $(T - T_c) \simeq 0.26$ K.

Systematic experimental errors can explain the observed deviations. Impurity effects must be considered. The duration of the measurement was the same for all isochores (~ 36 h), so the amount of impurities due to the corrosion of the cell must be the same for all the samples and certainly very small considering the facts that no shift of the transition temperature was

observed and that the measured critical temperature was close to the estimated value. Temperature gradients in the cell must also be considered, even if they have been controlled by acting on the compensation furnaces at the ends of the main part of the thermostat. Due to the divergence of the thermal expansion coefficient, the temperature gradients would induce density gradients which would increase when approaching the transition. However, it is our opinion that the gradients must be very small because

  (i) their effect would be larger for the critical isochore; and

  (ii) one would observe antisymetrical effects when $\rho > \rho_c$ and $\rho < \rho_c$, antisymetrical effects which cannot be experimentally reproduced with a shift of the critical density.

We have now to examine the validity of the values of the parameters used for the calculation of D_T^*.

For the theoretical calculation of D_T^*, the isothermal compressibility K_T is implicitily taken into account in the calculation of the background term (C_p and ξ) and in the critical part (ξ). A change in K_T behavior, which implies a modification of the equation of state in this range, would modify the calculated behavior of D_T^*. Moreover, the evaluation of ξ using Eq. (10) is an approximation outside the critical isochore.

At this point, it is evident that confirmation of our experimental results is needed before any definitive statement can be made concerning the observed differences between experimental and theoretical values of D_T^*.

4. CRITICAL FLUCTUATIONS IN H$_2$O–NaCl SYSTEMS

Recently some studies have been performed on the critical behavior of dilute NaCl in H$_2$O. Pitzer et al. [15, 16] measured the densities and the compositions of the coexisting liquid and gas phases as a function of pressure at constant temperature. From their experimental results, they concluded that the data cannot be represented by nonclassical exponents as in pure fluids and that the addition of small amount of salts suppresses large-scale fluctuations which are dominating near the critical point of pure fluids. Turner [17] studied the influence of gravity on these systems near the transition in the one-phase region. He estimated that electrostriction phenomena play an important role when the compressibility of the system diverges, i.e., near the critical transition. He concluded that it is impossible to approach the true critical transition under normal gravity and that a pseudo transition is observed which occurs well before the true critical transition. Therefore, it appears quite interesting to study the behavior of critical fluctuations of H$_2$O–NaCl systems in the one-phase region when approaching the transition.

The critical density of H_2O–NaCl systems as a function of composition is not precisely known. So we measured the decay time of the critical fluctuations as a function of temperature for different densities close to the critical density of pure steam at a fixed composition ($x = 0.1\%$, mol/mol) and we assumed that the critical density was obtained when we measured the highest decay time for a fixed distance from the transition. The transition yemperature measured for $x = 0.1\%$ was $381.3°C$, in good agreement with the results of Pitzer et al. [15, 16] and Olander and Liander [18]. The density of the system was $329\ \text{kg} \cdot \text{m}^{-3}$. The decay time τ of the system is shown in Fig. 2 as a function of the temperature distance to the observed transition, together with the decay time of steam along the critical isochore. The behavior observed in the two systems is quite different. For the H_2O–NaCl system and for pure steam, the same values of τ are obtained up to $(T - T_t) \sim 0.3$ K within experimental errors. Then for H_2O–NaCl, τ increases much less rapidly to a limiting value $\tau = 6.3\ \mu s$ at the transition.

The analysis of the behavior of τ is not simple for the H_2O–NaCl system since the path $x = \text{const.}$, $\rho = \text{const.}$ is not a thermodynamically relevant path to define theoretical critical exponents. However, following Griffith's arguments [19], along this path, "weak" and "strong" divergences of thermodynamic properties can be predicted. For example, the isothermal compressibility K_{Tx} at constant composition x should be asymptotically "weakly" divergent, but this weak divergence can be observed only very close to the critical point; for dilute solutions, the
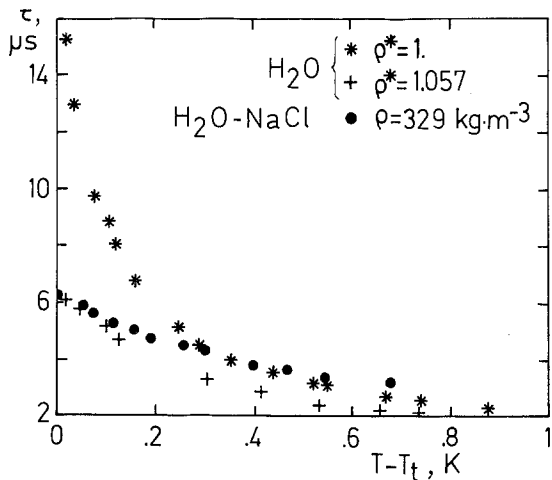

Fig. 2. Decay time of critical fluctuations in H_2O and in the
H_2O–NaCl system.

behavior of K_{Tx} is in practice comparable to that predicted for K_T of pure fluids (γ divergence). For our H_2O–NaCl system, in the temperature range $0.05 < (T - T_t) < 0.15$ K, τ varies as $(T - T_c) \sim 0.1$, which is a weak divergence compared to the pure fluid behavior. If we assume the same behavior for τ and K_{Tx}, the weak divergence of τ could not be experimentally seen at the temperature where it has been observed, and consequently, the variation of τ as a function of $(T - T_c)$ cannot be explained by the followed path.

The limiting value of τ obtained at the transition for the H_2O–NaCl system is close to the limit of τ measured for pure steam at $(\rho/\rho_c) = 1 \pm 0.06$; therefore the measurement of τ could be made in a zone where the density departs from the critical density by an amount of the order of 6%, if we assume that all thermodynamics and transport properties are the same for H_2O–NaCl and pure steam (amplitude of the correlation length, thermal conductivity, etc.). These density gradients can be explained by electrostriction phenomena. However, this effect cannot be as large as predicted by Turner, who suggests a 2.5 to 3 K shift of the critical transition for the 0.1% considered composition. If Turner is right, our measurements taken at 0.5 K from the transition would be, in fact, located at 3 to 3.5 K from the true critical temperature; this is incompatible with the measured value of the decay time (3.5 μs).

Our conclusion is that the electrostriction phenomena and induced stratification in the sample probably pertube the measurement of τ, but these effects are certainly less considerable than stated by Turner.

5. CONCLUSION

Our attempt to study critical fluctuation dynamics in steam and in a H_2O–NaCl system, performed under difficult conditions, shows some features which justify additional experiments. It clearly appears that measurements of the correlation length are needed. Moreover, the behavior of the decay time τ outside the critical isochore must be confirmed (eventually in a system easier to study); it is amazing to note here that almost all the comparable experiments have been made along the critical isochore alone. For the H_2O–NaCl system, the possible stratification problem must be cleared up in order to perform measurements in homogeneous samples. Then many experiments must be made at different densities and compositions in order to derive the behavior of the critical decay rate along relevant paths.

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