

Liquid-gas critical phenomena under confinement: small-angle neutron scattering studies of CO₂ in aerogel

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ABSTRACT. Small angle neutron scattering (SANS) is a well-established technique for investigating the behavior of confined binary liquid solutions, as it can probe the correlation length and susceptibility in pores on length scales $\sim 1 - 100$ nm. We applied SANS to explore the influence of confinement on critical behavior of an *individual fluid* carbon dioxide (CO₂) in a highly porous aerogel. The results demonstrate that quenched disorder induced by aerogel significantly depresses density fluctuations. Despite the negligible volume occupied by aerogel ($< 4\%$), the macroscopic phase separation of confined CO₂ into coexisting liquid and gaseous phases is suppressed and below the critical temperature of the bulk fluid frozen metastable microdomains are formed. Experimental data show that critical absorption is as important as the effect of confinement in defining the behavior of confined fluids.

1. INTRODUCTION

Phase transitions can be drastically modified by confinement and disorder. The liquid-vapor critical behavior in porous systems with quenched correlated disorder, such as aerogels, is of particular interest since it may provide an experimental realization of the Random Field Ising Model (RFIM) [1]. Theoretical considerations suggest that a new set of critical indices may appear in the fluid with quenched correlated impurities implying possible transition to a new universality class for confined systems. Experiments on the phase diagrams reported the bulk (Ising model) values of the critical index β of the coexistence curves of confined ⁴He and N₂ [2,3]. At the same time, studies of the superfluid transitions and heat capacity of ⁴He in aerogels demonstrated substantial difference between critical indices for bulk and confined fluid [4]. Evidently, much more experimental work is needed in order to elucidate the influence of quenched disorder on the phase behavior of confined fluids.

Small angle neutron scattering (SANS) is an ideal tool for investigating the correlation

length (ξ) and susceptibility (χ) of confined systems as it can probe the local structure and thermodynamic properties of fluids in small pores of the order on 1 – 100 nm. In this paper we report results of the first SANS investigations of the temperature variation of ξ and χ of carbon dioxide (CO₂) confined in porous matrix of an aerogel.

2. EXPERIMENTAL

A silica aerogel with ~ 96% porosity, a surface area of 400 m²/g, a density of 0.1 g/cm³, and pore size distribution peaked around the nominal pore diameters $2R_p \sim 60 \div 70 \text{ \AA}$ [5] was obtained from Oscellus Technologies, Livermore, CA. Aerogel was shaped into a cylinder (17 mm OD, 10 mm length) which fits tightly into a SANS high-pressure cell that has been used extensively for previous neutron scattering experiments with supercritical CO₂ - polymer mixtures [6]. Because the influence of the aerogel on the phase diagram of confined CO₂ is not known definitely, temperature scans in the range $80^\circ \geq T \geq 25^\circ \text{C}$ were performed at five different constant average densities of CO₂ (Matheson Gas Products, Inc, SFC purity 99.99%): $\rho_{\text{CO}_2} = 0.3, 0.4, 0.468, 0.55$ and 0.65 g/cm^3 , i.e. within $\pm 35\%$ deviation from the critical density of the bulk CO₂ $\rho_c = 0.468 \text{ g/cm}^3$ [7]. The pressure was measured using a precision digital pressure indicator (Sensotec, model AG-100) and the temperature of the cell was controlled to better than $\pm 0.2^\circ \text{C}$.

SANS experiments were performed on the KWS-2 SANS facility at the FRJ reactor in Julich, Germany. The neutron wavelength was $\lambda = 6.3 \text{ \AA}$ ($\Delta\lambda/\lambda = 10\%$). Three sample-detector distances of 14 m, 4 m, and 1.4 m were used for measuring scattering from empty aerogel to give an overall range of momentum transfer $0.003 < Q = 4\pi\lambda^{-1} \sin\theta < 0.2 \text{ \AA}^{-1}$, where 2θ is the scattering angle. Measurements of empty aerogel were repeated after each temperature scan and revealed no changes in the aerogel structure after exposure to CO₂. Scattering from bulk and confined CO₂ was measured in the appropriate Q-range ($0.007 < Q < 0.07 \text{ \AA}^{-1}$). The SANS data sets were corrected for instrumental backgrounds and normalized to an absolute ($\pm 5\%$) differential cross section per unit sample volume [$I(Q)$ in units of cm^{-1}] by means of pre-calibrated secondary standards [8].

3. RESULTS AND CONCLUSIONS

Several representative scattering curves from bulk and confined CO₂ as a function of temperature in the one phase region are shown in Fig.1. The values of ξ_{BULK} for bulk CO₂ as well as $I(0)$ proportional to the fluid compressibility χ were obtained by fitting $I(Q)$ to the Ornstein – Zernike formula

$$I(Q) = \frac{I(0)}{(1 + Q^2 \xi^2)} \quad (1)$$

The variation of ξ_{BULK} as a function of T is shown in Fig.2. As may be seen in Fig.2, ξ_{BULK} tends to diverge as $T \Rightarrow T_c$, and decreases rapidly below T_c at which point the formation of the meniscus is observed. On the log-log scale, the slope of $\xi_{\text{BULK}}(\tau)$ gives the critical index of the

bulk correlation length $\nu_{\text{BULK}}=0.61\pm 0.02$, which agrees within experimental error with the Ising model exponent $\nu=0.630\pm 0.001$ [9].

The scattering results for confined CO_2 can be interpreted quantitatively using an equation similar to that utilized previously to interpret SANS results on the influence of confinement on the liquid-liquid critical phenomena in partially miscible liquid solutions [10]:

$$I(Q) = \frac{I_{\text{LOR}}}{(1+Q^2\xi^2)} + \left[\frac{I_{\text{LSQ}}}{(1+Q^2\xi^2)} \right]^2 I_{\text{BGR}}(Q) + C \quad (2)$$

The angle-independent background ($C \sim 0.5 \text{ cm}^{-1}$) in Eq.2 arises mainly from H^1 atoms in the methoxy groups on the aerogel surface. The first (Lorentzian) term is identical to Eq.1 and describes the genuine scattering from critical fluctuations inside pores, whereas the second (Lorentzian-squared) term arises from the response of the order parameter (fluid density) to the “field” induced by aerogel and is related to the critical absorption [11]. The scattering from aerogel itself is taken into account in Eq.2 via the “background” term $I_{\text{BGR}}(Q)$, which represents scattering from CO_2 -saturated aerogel at $T=80 \text{ }^\circ\text{C} \gg T_c$, when contribution of the fluctuations of the order parameter is negligible.

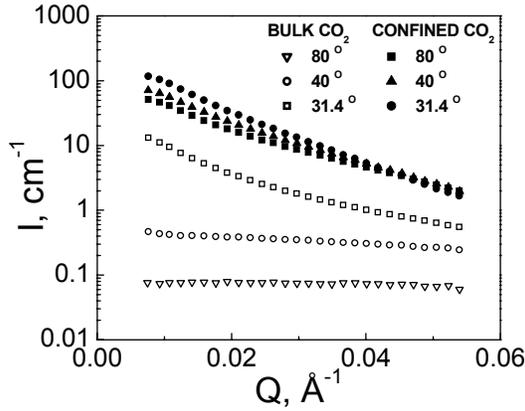


Fig.1. $I(Q)$ from bulk (open symbols) and confined CO_2 (solid symbols) at different temperatures. The average density of CO_2 is $\rho_c=0.468 \text{ g/cm}^3$.

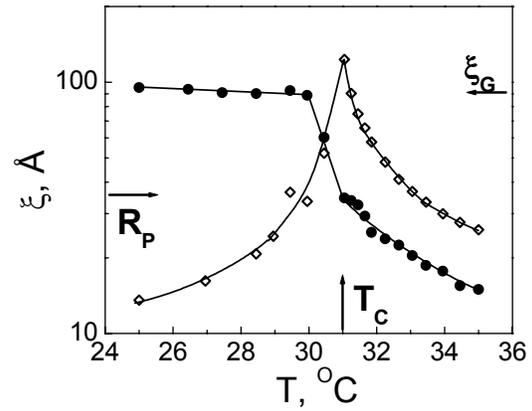


Fig.2. Correlation length of the density fluctuations of CO_2 in bulk (\diamond) and under confinement (\bullet). The average density of CO_2 is $\rho_c=0.468 \text{ g/cm}^3$.

We have found that in the one-phase region $T > 31 \text{ }^\circ\text{C}$ $I(Q)$ is best described (χ^2 below 2) by Eq.2 with the same value of ξ in both Lorentzian and Lorentzian squared terms, as theoretically predicted [12]. This is in agreement with results obtained for liquid solutions in rigid porous matrices of Vycor glass and silica gels. The temperature variation of the correlation length of confined CO_2 (ξ_{CONF}) at average density $\rho=\rho_{\text{C,BULK}}=0.468 \text{ g/cm}^3$ is

shown in Fig. 2. At $T > T_C=31$ °C, in the one-phase region, ξ_{CONF} is systematically smaller than ξ_{BULK} and the difference between the two parameters increases as $T \Rightarrow T_C$. These trends arise because ξ_{BULK} diverges and ξ_{CONF} saturates at the value corresponding to the pore radius $R_p \sim 30 \div 35$ Å. The log-log slope of $\xi_{\text{CONF}}(\tau)$ gives $\nu_{\text{CONF}}=0.5\pm 0.04$ in the range $\tau \geq 6 \times 10^{-3}$, which is close to the mean field value of $\nu=0.5$. At $\tau \Rightarrow 0$ ξ_{CONF} tends to round off at $\xi_{\text{CONF}} \sim R_p$. Below $T=31$ °C, ξ_{CONF} in Eq. 2 show a discontinuous change in the fit parameters and ξ_{CONF} tends to saturate at the value roughly corresponding the correlation length of aerogel $\xi_G \sim 90$ Å. At this point aerogel becomes strongly opaque, but exhibits no evidence of macroscopic phase separation (i.e. formation of meniscus). We speculate that this results from the formation of “frozen” metastable structural domains which mimic the correlated disorder introduced by the aerogel matrix. The intensity of scattering increases by two orders of magnitude and does not change with time at fixed temperature, which confirms the stability of the domains below T_C .

We interpret the lack of critical divergences of ξ and $I(0)$ as the result of the competition between the genuine critical fluctuations in the “core” of aerogel pores and critical absorption of CO₂ molecules on the silica strands of the aerogel, as both processes are characterized by a similar correlation length. We thus found no evidence of the RFIM behavior, which constitutes the major result of this study. The dilute quenched disorder induced by the host matrix works to suppress density fluctuations in the critical region due to a critical depletion mechanism and the correlation length of the order parameter does not exceed the characteristic pore size in the homogeneous region at all average densities of CO₂ studied [13]. Our results provide strong experimental evidence for individual fluids in aerogels to fall in the category of phase separation under confinement with critical absorption effects, in qualitative agreement with the single pore model [14].

4. ACKNOWLEDGMENTS

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