

NEUTRON SCATTERING STUDY OF DILUTE SUPERCRITICAL SOLUTIONS†

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**NEUTRON SCATTERING STUDY
OF DILUTE SUPERCRITICAL SOLUTIONS**

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ABSTRACT

Dilute solutions in supercritical solvents exhibit interesting microstructures that are related to their dramatic macroscopic behavior. In typical attractive solutions, solutes are believed to be surrounded by clusters of solvent molecules, and solute molecules are believed to congregate in the vicinity of one another. Repulsive solutions, on the other hand, exhibit a local region of reduced solvent density around the solute with solute-solute congregation. Such microstructures influence solubility, partial molar volume, reaction kinetics, and many other properties. We have undertaken to observe these interesting microstructures directly by neutron scattering experiments on dilute noble gas systems including Ar. The three partial structure factors for such systems and the corresponding pair correlation functions can be determined by using the isotope substitution technique. The systems studied are uniquely suited for our objectives because of the large coherent neutron scattering length of the isotope ^{36}Ar and because of the accurate potential energy functions that are available for use in molecular simulations and theoretical calculations to be compared with the scattering results. We will describe our experiment, the unique apparatus we have built for it, and the neutron scattering results from our initial allocations of beam time. We will also describe planned scattering experiments to follow those with noble gases, including study of long-chain molecules in supercritical solvents. Such studies will involve hydrocarbon mixtures with and without deuteration to provide contrast.

INTRODUCTION

Both theory and experiment have indicated that the important and interesting properties of dilute solutions in supercritical solvents are related to the molecular-level correlation of solvent molecules about solute molecules or solute molecules about solute molecules [*e.g.*, 1-8]. This work is an effort undertaken to measure directly some of these interesting microstructures by neutron scattering. Dilute binary solutions of noble gases with one of the components being argon have been chosen for study because of the ease of theoretical and computational study of these simple fluid systems and because the exceptionally large coherent neutron scattering length of ^{36}Ar facilitates sensitive isotope substitution experiments. The specific objectives of the work are to measure the three pair correlation functions— $g_{vv}(r)$,

$g_{uv}(r)$, and $g_{uu}(r)$ —for states close to the solvent critical point in dilute supercritical solutions using the neutron scattering techniques. (We will let the subscript v designate the solvent and the subscript u designate the solute. Then, the differential cross section from a wide-angle neutron scattering (WANS) experiment is given by

$$\frac{d\sigma}{d\Omega} = N \sum_i c_i (\overline{b_i^2} - \overline{b_i}^2) + \sum_{i,j} \overline{b_i} \overline{b_j} S_{ij}(k) \quad (1)$$

where N is the number of atoms in the beam, c_i is the concentration of atoms of type i , b_i is the coherent scattering length of atoms of type i , and $S_{ij}(k)$ is the partial structure factor. The latter is related to the corresponding pair correlation function by the Fourier transform

$$S_{ij}(k) = c_i \delta_{ij} + c_i c_j \rho \int d\mathbf{r} \exp(i\mathbf{k} \cdot \mathbf{r}) [g_{ij}(r) - 1]. \quad (2)$$

Then, the three individual pair correlation functions in a binary mixture of monoatomic fluids may be determined from a set of three experiments in which only the isotopic composition of one component is changed, thereby changing its coherent neutron scattering length, by solution of three independent linear equations (1). The bulk thermodynamic properties are directly related to spatial integrals of the pair correlation functions which are called Kirkwood fluctuation integrals, G_{ij}

$$G_{ij} = \int d\mathbf{r} [g_{ij}(r) - 1] = \lim_{k \rightarrow 0} S_{ij}(k). \quad (3)$$

Conveniently, the fluctuation integrals are obtainable as the $k \rightarrow 0$ limit of complementary small angle neutron scattering (SANS) experiments by the same isotope substitution technique.

APPARATUS

Figure 1a shows the cryostat for neutron scattering experiments on dilute binary supercritical solutions of noble gases. The cell (See Figure 1b for details) is cooled by a closed cycle He refrigerant unit. The cryostat is evacuated and the heat load on the cell is further reduced (to *ca.* 0.25 watt) by multiple layers of doubly-aluminized plastic film superinsulation. The cell temperature is monitored by a pair of Pt resistance thermometers to ± 0.010 K or better, and the temperature differential across the cell can be reduced to less than ± 0.010 K by applying a small electric current to one or the other of a pair of small resistors mounted in the top and bottom of the cell. The contents of the cell are mixed, through an internal draft tube, by a miniature turbine containing a small magnet and driven by an external magnet. Gas mixtures are prepared externally and introduced into the evacuated cell through a capillary tube. The pressure is monitored by an accurate ($\pm 0.025\%$ of full scale) bourdon-tube gauge and is adjusted with a piston-cylinder hand pump on the external supply.

For neutron scattering experiments, the cryostat, with ancillary equipment, is transported to the neutron source. The cryostat is positioned in the beam so that neutrons enter the cryostat through a window sealed into the wall, pass through the sample tube in the cell containing the sample, and out a second window. Experiments have been performed at the SANS instrument on the High Flux Isotope Reactor at Oak Ridge National Laboratory and at the Glass, Liquid, and Amorphous Materials Diffractometer (GLAD) WANS instrument at the Intense Pulsed Neutron Source at Argonne National Laboratory. Details of the apparatus and results of its early testing have been reported elsewhere [9].

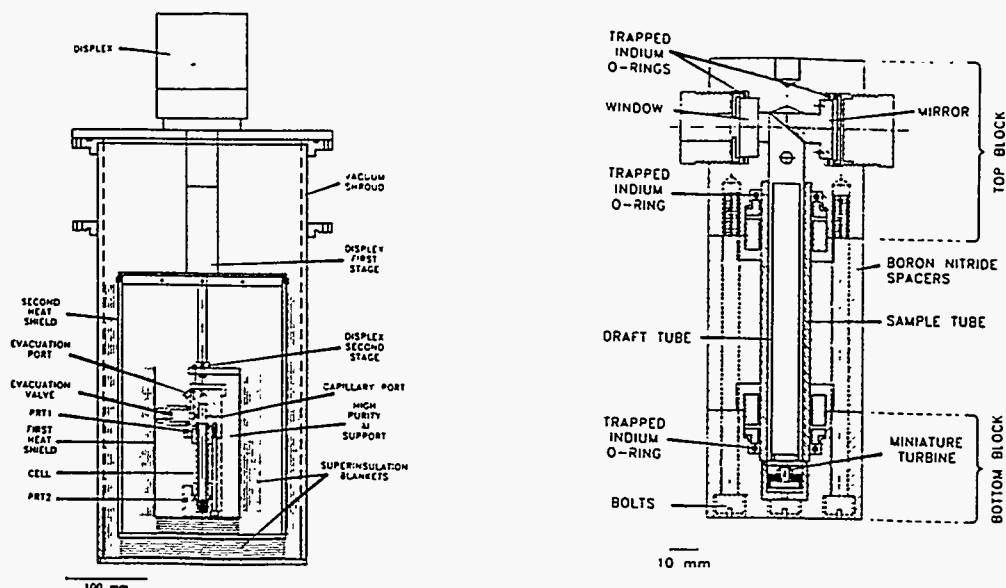


Figure 1. Apparatus. a) Schematic drawing of apparatus. b) Details of cell.

RESULTS

Figure 2a shows an Ornstein-Zernike plot of the SANS data for supercritical neon. Data for states near the critical point plotted in this fashion should be linear at small k and should extrapolate to give the isothermal compressibility, κ_T

$$S(0) = \rho k T \kappa_T \quad (4)$$

for a pure fluid. Figure 2b shows a plot of the intercepts from Figure 2a vs. temperature. Also shown for comparison are the results calculated from an accurate equation of state [10]. The satisfactory agreement indicates that the apparatus performs as required.

Figure 3a shows preliminary WANS results for pure neon at a near-critical state. Evident in the figure are Bragg peaks (from aluminum) and a relatively high noise level. Subsequent to these measurements the GLAD instrument has been modified to remove aluminum from the vicinity of the beam and to modify the beam stop which was the major contributor to the background noise in the signal. Figure 3b shows the much improved level of background noise of the GLAD instrument in later tests.

FUTURE WORK

Near-term plans call for SANS and WANS studies of isotopically enriched, dilute solutions of argon in supercritical krypton near the krypton critical point. This system is expected to be a weakly-attractive mixture [11]. In addition, SANS studies of additional pure noble gases (Ar, Kr, Xe) are planned to complete the studies begun previously [12].

When studies with the noble gas systems are completed, we plan to undertake a series of very similar studies in which both the solute and the supercritical solvent are hydrocarbons, taking advantage of the contrast in the coherent scattering between deuterium and hydrogen. We hope to report the results of these future studies in the 4th International Symposium on Supercritical Fluids.

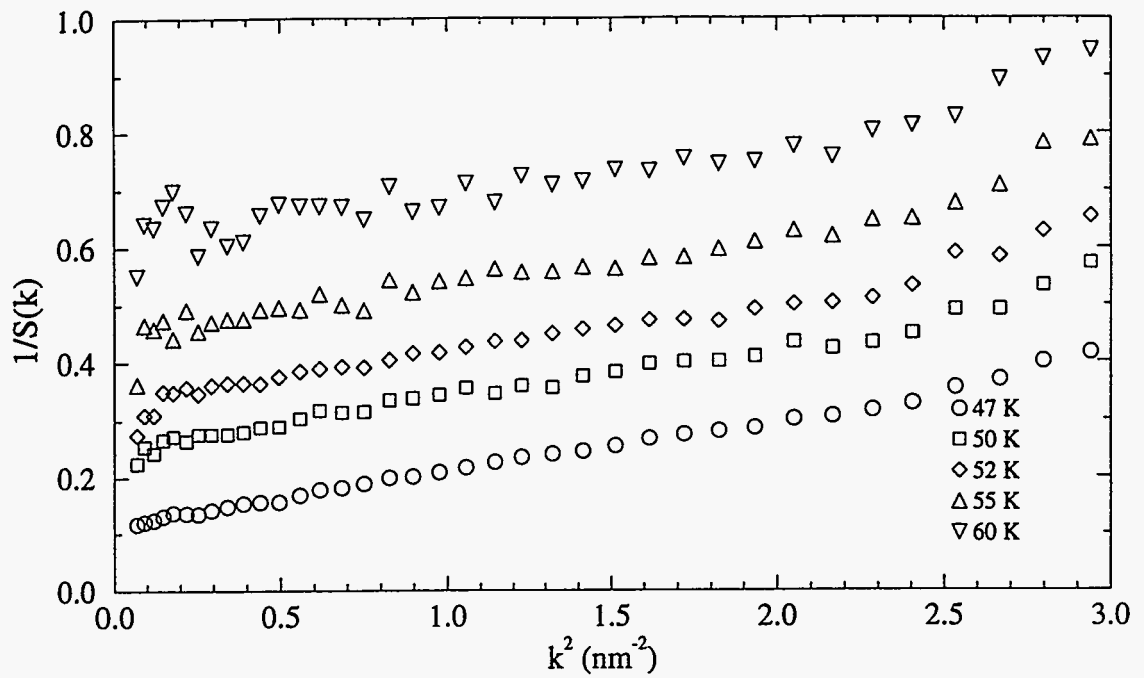


Figure 2a. Ornstein-Zernike plot of SANS data for pure Ne.

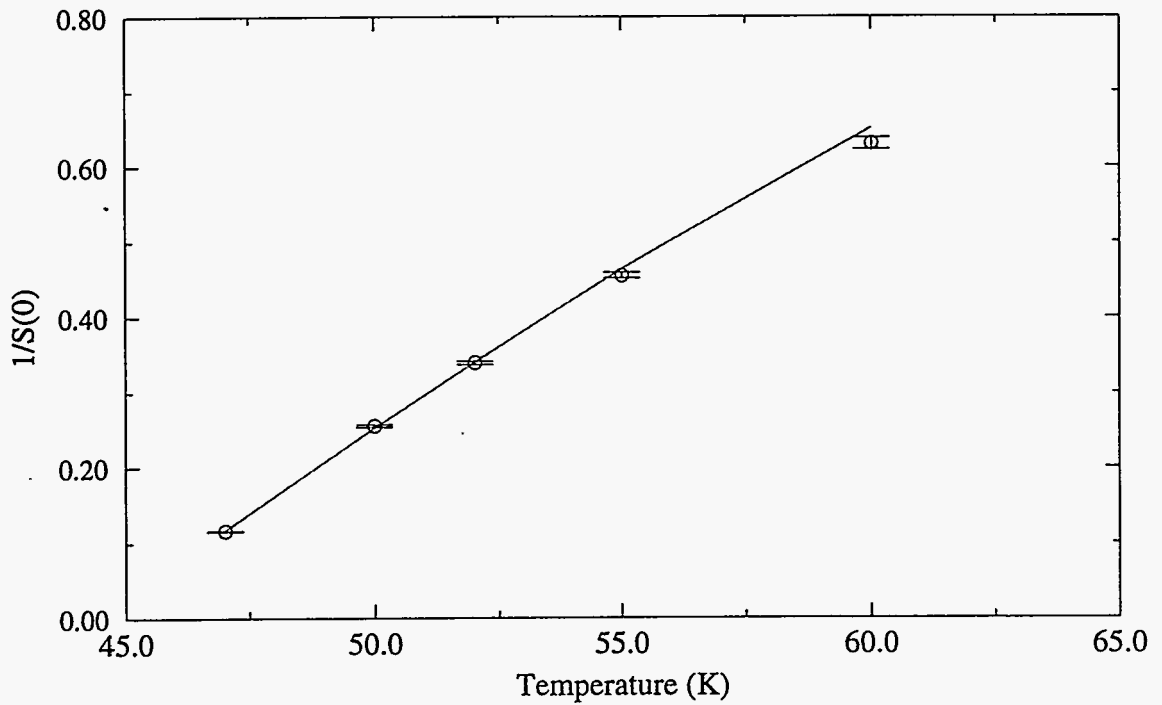


Figure 2b. Neon inverse isothermal compressibility from SANS data and from accurate equation of state [10].

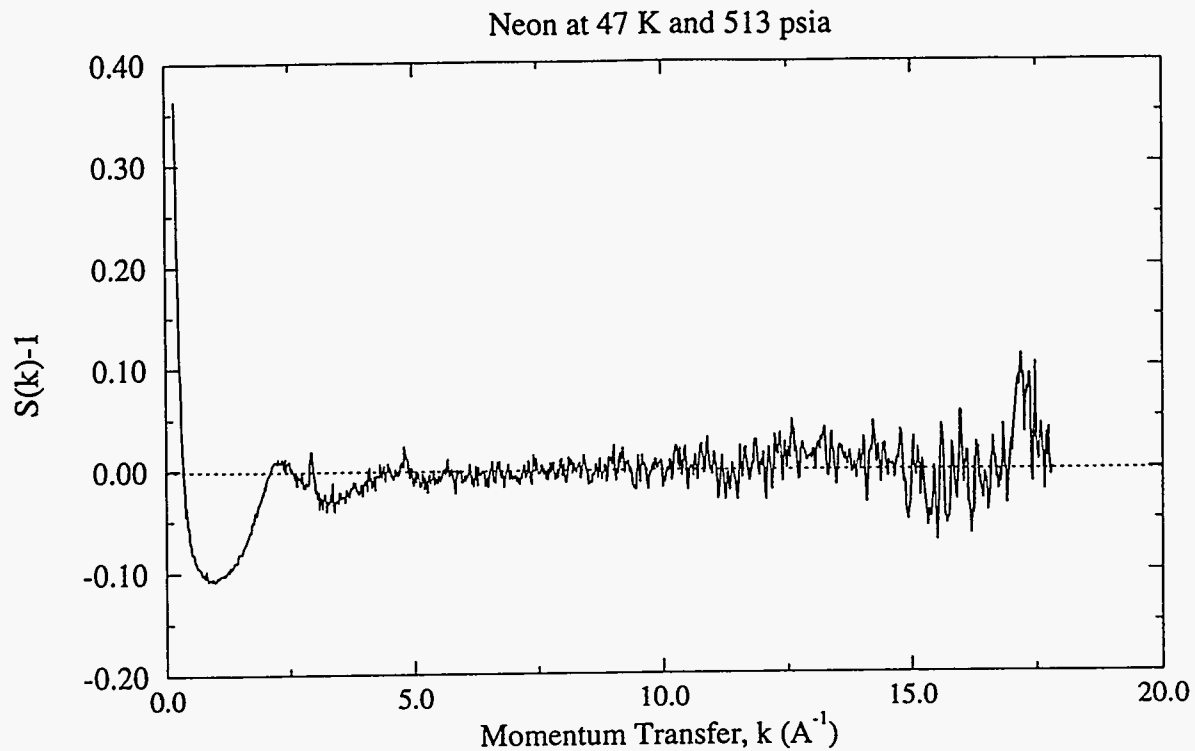


Figure 3a. WANS results from early experiment on GLAD, $S(k)$ for pure neon.

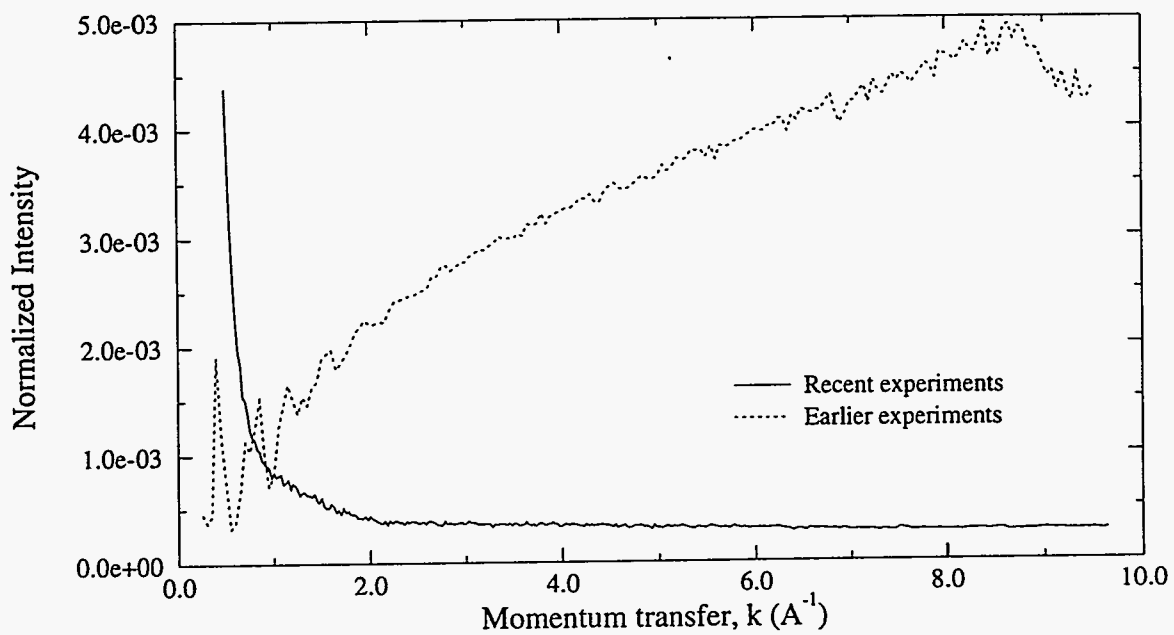


Figure 3b. Improved GLAD instrument background.

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