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Enhanced Self-Diffusion of Adsorbed Methanol in Silica Aerogel

Jeongseop A. Lee¹, A. M. Mounce², Sangwon Oh³, A. M. Zimmerman¹, W. P. Halperin¹

¹*Department of Physics and Astronomy, Northwestern University, Evanston, Illinois 60208, USA*

²*Los Alamos National Laboratory, Los Alamos, New Mexico 87545, USA and*

³*Schlumberger-Doll Research Center, Massachusetts 02139 USA*

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Molecular transport of a two-component system of liquid and vapor in a porous medium can be anomalously increased owing to fast exchange between the two phases.¹ We have investigated this phenomenon measuring the self-diffusion coefficient of methanol adsorbed in a 98% porosity aerogel using nuclear magnetic resonance (NMR) field gradient techniques. We found enhancement of several orders of magnitude from which we determined the ballistic mean-free-path in the vapor phase. We have grown globally uniform anisotropic aerogels and applied the diffusion measurements to characterize the anisotropy. Our results are important for understanding the novel properties of superfluid ³He confined within an aerogel framework and for application to other physical systems.

PACS numbers:

I. INTRODUCTION

Molecular diffusion of fluids imbibed into porous materials has broad importance, for example in understanding the reaction rates in heterogeneous catalysis, the dynamics of water in geological structures, and the physical properties of quantum fluids at low temperatures. In some instances there can be significant consequences of enhanced mass transport when the fluid has simultaneously liquid and vapor components in sufficiently close proximity. One of the first observations of this phenomenon was reported by Karger *et al.*² for water in zeolites and investigated in some detail for water in sol-gel glasses by D'Orazio *et al.*¹ In the latter case the authors showed that enhanced diffusion results under conditions of, i) weak elastic scattering of the molecules in the vapor phase from the porous medium, and ii) fast exchange between the the vapor phase and the dense liquid or, as in our case, an adsorbed phase.¹ The latter condition ensures that all molecules are equivalent and that the effective diffusion of any molecule is given by the density weighted average of the diffusion coefficients of each separate phase. In our application we adsorb methanol in a high porosity silica aerogel which, for the adsorbed phase alone, would have a self-diffusion coefficient strongly suppressed compared with that of the pure liquid. But with the adsorbed phase in fast exchange with the vapor, the molecular transport can be greatly increased by many orders of magnitude.

We use fringe-field gradient NMR for self-diffusion measurements giving an absolute value of the diffusion coefficient in the direction of the magnetic field gradient, a method that is well-established. The time evolution of the NMR signal provides a clear signature of homogeneous dynamics, thereby confirming unambiguously that the condition of fast exchange is satisfied. The NMR signal is proportional to the number density of molecules which is completely dominated by the dense phase owing to the very dilute nature of the vapor. On the other hand the vapor phase has a very large diffusion coefficient in

contrast to the dense phase. Analysis of our diffusion measurements is greatly simplified by these two facts.

In the following sections we present our diffusion results and their analysis and discuss these in the context of novel behavior of superfluid ³He in the same porosity silica aerogel.³ The properties of the superfluid are strongly affected by elastic scattering of ³He atoms, a situation remarkably similar to the scattering of methanol vapor molecules in the aerogel framework. From our measurements of the diffusion coefficient we obtain the ballistic mean-free-path. Since the diffusion experiment is directionally specific we can determine the orientation dependence of the mean-free-path in a globally uniform but anisotropic porous medium. Our application of the methanol diffusion experiment has significance for recent discoveries in superfluid ³He in anisotropic aerogel where the anisotropy is responsible for stabilizing new quantum states.⁴

II. EXPERIMENTAL METHOD

A. NMR methods

Proton nuclear magnetic resonance (NMR) experiments were performed on methanol molecules adsorbed on the surface of silica aerogel with 98% porosity in a fringe-field of a 3 T superconducting magnet with gradient along the field direction of 0.60 T/m at room temperature. The diffusion coefficients and transverse relaxation times, T_2 , were measured using the Carr-Purcell-Meiboom-Gill (CPMG) sequence $(\pi_x/2 - \tau - \pi_y - \tau - \text{echo} - \tau - \pi_y - \text{echo} \dots)$.⁵⁻⁷

Methanol adsorption isotherms were obtained in a manner similar to gas adsorption experiments typically used for determination of the surface area of porous materials. However, the usual adsorption experiment is performed with the amount of adsorbate measured either volumetrically⁸⁻¹¹ or by weight.⁹ In the present work it is determined from the NMR proton signal calculated

from the area under the echo formed in a standard Hahn echo sequence¹², $(\pi/2 - \tau - \pi - \tau - \text{echo})$ with a pulse separation, $\tau = 175 \mu\text{s}$. For T_2 and diffusion measurements 10 CPMG pulse sequences were accumulated at each pressure, each having a train of 60 echoes with τ values ranging from $209 \mu\text{s}$ to $409 \mu\text{s}$. This series was repeated and the results averaged.

FIG. 1. Optical birefringence intensity distribution of the RSA aerogel through cross-polarizer, on-axis (left) and off-axis (right). The optical axes of the cross-polarizers are oriented $\pm 45^\circ$ from the vertical.

B. Aerogel samples

Two cylindrical aerogel samples with 98% porosity and ~ 6 mm in diameter were used, one homogenous and isotropic (HIA) and the other uniformly and globally anisotropic. The latter was achieved with larger catalyst concentrations that induce uniform radial shrinkage during sample growth, and is called RSA. They were grown with a one-step method and rapid supercritical extraction of the solvent.^{13,14} The surface area of the aerogel from nitrogen adsorption (BET)¹⁵ is $\sim 400 \text{ m}^2/\text{g}$ and the mean distance between silica strands, *i.e.* the aerogel correlation length, can be estimated from numerical calculations to be $\sim 50 \text{ nm}$.¹⁶

The homogeneity of the samples was characterized with optical birefringence technique and filtered white light.¹³ Inhomogeneity in the aerogel density, if present on length scales longer than the wavelength of light, will induce a preferred optic axis that would be apparent in an image of the sample placed between crossed polarizers. The resulting light intensity variation serves as a sensitive method of determining the aerogel uniformity and density anisotropy, Fig. 1. The HIA and RSA aerogels used in this study were found to have uniform intensity profiles with less than 10% variation from the average intensity. The radial shrinkage in the RSA aerogel was measured to be 15% and the optical axis orientation was found to be coincident with the cylinder axis, Fig. 1. The HIA aerogel had no measurable shrinkage consistent with the absence of optical birefringence.

Each sample was inserted into a home-made glass cylindrical NMR cell measuring 2.5 cm in length and 1.3

cm in diameter. The cell was sealed with a brass plug and O-rings and the sample was fixed in place by quartz wool with the end cap shielded from the NMR coil. Prior to methanol adsorption, the NMR cell and sample were pumped and flushed with helium gas in order to remove pre-existing surface molecules. Nonetheless, there was a weak proton background from the sample of $\sim 5\%$ of the proton signal at one monolayer coverage. It is likely that this corresponds to surface silanol groups in the aerogel and it was measured for all pulse conditions and subtracted from the data during analysis.

Methanol was loaded from a buffer volume of vapor in equilibrium with pure liquid in a reservoir. The adsorption process was monitored through simultaneous measurement of the sample pressure with a precision of 5% using a quartz pressure transducer from Paroscientific, Inc. taking into account temperature fluctuations in the sample. At the same time the NMR signal intensity was measured to obtain the methanol surface coverage, Fig. 1. The diffusion measurements were carried out at a constant temperature for various adsorption pressures ranging from near zero pressure to the vapor pressure of methanol at room temperature, $P_o = 13 \text{ kPa}$. The RSA was investigated for two orientations with the cylinder axis of the aerogel parallel and orthogonal to the direction of the field gradient. For the HIA sample diffusion measurements were carried out with the cylinder axis parallel to the field gradient.

FIG. 2. Isotherms for aerogels measured by NMR Hahn echo amplitudes. The solid lines are theoretical expectations from the BET analysis. Dashed lines trace experimental data and represent the actual isotherms used in fitting the measured diffusion coefficients.

III. THEORY

The integrated intensity from each echo in a CPMG pulse sequence, $M(t)$, can be used to determine both the transverse relaxation time, T_2 , and the diffusion coefficient, D . The overall decay of the echo intensity is given

by,¹⁷

$$M(t) = M_o \exp\left(-\frac{t}{T_2}\right) \exp\left(-\frac{\gamma^2 g^2 D \tau^2 t}{3}\right) \quad (1)$$

where $t = 2n\tau$ for the n th echo; the gyromagnetic ratio is γ ; and the field gradient is $g = \partial H / \partial z$. Each term in the exponent is linear in time. Therefore the magnetization decay, $M(t)$, is characterized by a single relaxation constant, T_{2cpmg} ,

$$M(t) = M_0 \exp\left(-\frac{t}{T_{2cpmg}}\right) \quad (2)$$

$$\frac{1}{T_{2cpmg}} = \frac{1}{T_2} + \frac{\gamma^2 g^2 D \tau^2}{3}. \quad (3)$$

The diffusion coefficient for the two-component system in fast exchange is given by,^{1,18}

$$D = \frac{\rho_{ads}}{\rho_{vap} + \rho_{ads}} D_{ads} + \frac{\rho_{vap}}{\rho_{vap} + \rho_{ads}} D_{vap}, \quad (4)$$

which is the density weighted average of the independent diffusion coefficients D_{ads} and D_{vap} of adsorbed and vapor molecules respectively, and ρ_{ads} and ρ_{vap} are correspondingly the number densities of each state. Both ρ_{vap} and D_{vap} can be calculated from the kinetic theory for an ideal gas and at the vapor pressure of methanol, D_{vap} is on the order of $10^{-3} m^2/s$ and increasing as pressure decreases, $\sim 1/P$ (Eq. 8). The density of the adsorbed species ρ_{ads} is much larger than ρ_{vap} and can be equated with the total density ρ proportional to the NMR intensity set equal to $\alpha\rho$, Fig. 2, where α is a proportionality constant. It has been reported that surface diffusion of most organic fluids in typical porous materials is reduced by roughly an order of magnitude from that of the pure liquid.^{19,20} Since the diffusion of pure methanol²¹ is $1.6 \times 10^{-9} m^2/s$, this is expected to be on the order of $10^{-10} m^2/s$. This reduction can be largely attributed to the geometrical form factor often represented by the phenomenological relation known as Archie's Law.²² Additionally, the interaction between adsorbate and adsorbent further reduces surface diffusion.²³ Accordingly, for a very high porosity aerogel, the surface diffusion coefficient can be expected to be reduced by more than two orders of magnitude as compared with the pure liquid. Consequently, the first term on the right side of Eq. 4 will be more than three orders of magnitude smaller than the second term and can be neglected.

In order to characterize the vapor state, we use the kinetic theory for an ideal gas. The velocity of the gas is

$$v_{gas} = \sqrt{\frac{8k_B T}{\pi m}} \quad (5)$$

where k_B is the Boltzmann constant and m is the molecular mass. The mean-free-path in the free gas phase is

$$\lambda_{gas} = \frac{1}{\sqrt{2}\pi d^2 \rho_{gas}} \quad (6)$$

FIG. 3. CPMG echo decays. This representative data is from the RSA sample with its cylinder axis oriented parallel to the external field at a relative pressure $P/P_o = 0.98$. Increases in pulse separation, τ , resulted in increased attenuation of subsequent echoes according to Eq. 1. The overall relaxation is a single exponential with relaxation constant, T_{2cpmg} consistent with the fast exchange limit.

where $d = 4\text{\AA}$ is the diameter of the methanol molecule²⁴ and the density of the gas ρ_{gas} is given by the ideal gas law,

$$\rho_{gas} = \frac{P}{k_B T} = \rho_{vap}. \quad (7)$$

FIG. 4. CPMG relaxation rate, $1/T_{2cpmg}$, versus τ^2 for the RSA aerogel in the parallel orientation. Each curve is for a different pressure ranging from $P/P_o = 0.11$ to 0.98 . The slope is proportional to the diffusion coefficient. For $P/P_o = 0.11$ diffusion is strongly suppressed.

The free gas diffusion constant from kinetic theory can be expressed in terms of the velocity and the mean free path.

$$D_{gas} = \frac{1}{3} v_{gas} \lambda_{gas} = \frac{2}{3\pi^{3/2} d^2 P} \sqrt{\frac{k_B^3 T^3}{m}} \quad (8)$$

However, in order to account for the additional restriction on diffusion owing to scattering from the porous structure, the free gas diffusion coefficient is modified by the Knudsen diffusion term, D_{Kn} .²⁵

$$\frac{1}{D_{vap}} = \left(\frac{1}{D_{gas}} + \frac{1}{D_{Kn}} \right) \quad (9)$$

where

$$D_{Kn} = \frac{1}{3} \lambda_a v_{gas} = \frac{1}{3} \lambda_a \sqrt{\frac{8k_B T}{\pi m}} \quad (10)$$

and λ_a is the ballistic mean-free-path within the sample, *i.e.* the angular average of all straight line paths beginning and ending at a surface.

With the above definitions and well-defined limits we can write a simple relation for the pressure dependent diffusion coefficient,

$$D(P) = \frac{\rho_{vap}(P)}{\rho(P)} \frac{1}{3} v_{gas} \left(\frac{1}{\lambda_{gas}(P)} + \frac{1}{\lambda_a} \right)^{-1}, \quad (11)$$

At most pressures, λ_{gas} is orders of magnitudes larger than λ_a , therefore the effect of λ_{gas} is negligible. Measurement of $D(P)$ and the NMR signal intensity can be fit with this equation for the entire pressure range with just two adjustable parameters, α and λ_a .

IV. RESULTS AND ANALYSIS

The isotherms for HIA and RSA aerogels follow the simple BET analysis at low pressures, $P/P_o < 0.5$ shown as solid curves in Fig. 2. At higher pressures multi-layer adsorption takes place not adequately represented by the BET theory. Two isotherms each with respect to two different orientations for the RSA aerogel identically match each other, as expected for the same sample rotated by 90° inside the NMR coil and with the same NMR conditions.

Decay of CPMG echoes at all τ values can be characterized by a single exponential, Fig. 3, indicating that the pore structure is uniform throughout,²⁶ and that diffusion is normal, *i.e.* not anomalous. The relaxation rates $1/T_{2cpmg}$ for the echo decay curves were found to be a linear function of τ^2 consistent with Eq. 3, as shown in Fig. 4, from which the diffusion coefficients and T_2 were calculated, Fig. 5 and 6.

The measured diffusion coefficients as a function of pressure in Fig. 5 are consistent with the theory, Eq. 11 adjusted to fit the data with the two unknown parameters, α and λ_a . Interestingly, we observe a maximum value in the diffusion coefficients near $0.5 P_o$. This results from a competition between changes in the gas density and the decrease in gas diffusivity with increasing pressure. The aerogel mean free path, λ_a for the RSA sample was found to be anisotropic, $\lambda_{a||} = 152.3 \pm 7.4$ nm and $\lambda_{a\perp} = 129.8 \pm 8.8$ nm both of which are significantly

FIG. 5. Experimental diffusion data and theoretical fit using Eq. 11. The fit is consistent with experimental diffusion data over the entire pressure region.

FIG. 6. Transverse relaxation times, T_2 obtained from the intercept of $1/T_{2cpmg}$ vs τ^2 plot in Fig. 4. We find that T_2 is linearly dependent on the amount of adsorbed methanol as expected for a surface relaxation process that is uniform throughout the sample. Dotted horizontal line marks T_2 of the background proton signal for the dry aerogels.

larger than for HIA, $\lambda_a = 85.9 \pm 9.3$ nm, a difference we attribute to the aerogel growth conditions for the separate samples. For the RSA at higher pressures the diffusion coefficient for the parallel orientation is larger than the perpendicular orientation as can be expected from the larger mean free path, $\lambda_{a||} > \lambda_{a\perp}$. The trend is reversed at lower pressures where we observe higher mass diffusivity for a smaller mean free path. The anisotropy ratio for the RSA, $\lambda_{a||}/\lambda_{a\perp} = 1.17$ is in excellent agreement with the radial shrinkage of 15%.

The diffusion coefficients we have measured are two orders of magnitude larger than that of pure liquid methanol and two orders of magnitude less than in the unrestricted vapor. The diffusion times ranged from 2 to 25 ms giving diffusion lengths varying from 30 to 150 μ m.

The intercept of $1/T_{2cpmg}$ vs τ^2 in Fig. 4 as function of pressure is an intrinsic transverse relaxation rate, $1/T_2$, which we find to be a linear function of methanol adsorption as shown in Fig. 6. This dependence is characteristic of fast exchange conditions giving a unique relaxation rate specific to the surface where the liquid relaxation rate measured for pure bulk methanol was 0.83 ± 0.01 s and is negligible in comparison. The slopes of the fits shown in this figure are equal to the surface T_{2s} divided by the number of relaxation sites. For each of the dry aerogel samples we measured $T_{2s} = 2.7$ ms, shown as a dashed line. Consequently the larger slope for HIA as compared to RSA samples indicates a smaller concentration of relaxation sites for HIA, presumably associated with different growth conditions. Similar behavior has been reported for other partially filled porous materials.²⁰

V. DISCUSSION

In our work we measure the methanol gas self-diffusion coefficient in silica aerogel with enhanced signal to noise associated with the fast exchange of the gas with adsorbed layers. The gas diffusion coefficient is thereby reduced by the ratio of the gas density to the local methanol density. A different approach was taken by Guillot *et al.*²⁷ who measured diffusion of ^3He gas with signal-to-noise enhanced by hyperpolarization. The aerogel had approximately the same porosity as in the present work and a similar NMR diffusion technique was used with very small magnetic field gradients in a standard MRI configuration. These authors reported an unexpected behavior of the echo decay rate deviating from a quadratic dependence on magnetic field gradient. This was interpreted as a distribution of diffusion coefficients attributable to non-uniformity in the aerogel that would necessarily be of mm scale, the approximate scale of the diffusion length in the experiment. In contrast, in our work classical diffusion behavior was observed in all aerogel samples and in bulk liquid. Owing to our stronger field gradients the diffusion length was an order of magnitude smaller than that of Guillot *et al.* It is possible that their aerogels samples had large scale inhomogeneity. However, this can be ruled out in the present work from our direct measurements using optical birefringence and measurements on similar samples with small angle x-ray scattering.^{3,13} Additionally, for ^3He imbibed into the aerogel structure, spatial inhomogeneity in the density of aerogels will produce a non-zero width in the transition temperature to the superfluid ^3He state, where the appropriate length scale to resolve such inhomogeneity is the superfluid coherence length $\lesssim 0.1 \mu\text{m}$. However, in similar aerogels we do not find any evidence for such inhomogeneity to high precision.²⁸

The ballistic mean-free-path is one of the key parameters in the Ginzburg-Landau theory for superfluid ^3He describing effects of the aerogel framework in suppressing

and altering the phases of the superfluid. At low temperatures the principal thermal excitations in liquid ^3He are Fermi-Dirac quasiparticles which scatter from boundaries and impurities just as does the gas of methanol in the present work. In the quantum fluid, isotropic scattering is argued to stabilize isotropic superfluid phases while anisotropic scattering will tip the balance toward anisotropic quantum states. One of our goals was to measure the mean-free-path and its anisotropy. Consistent with expectations based on other characterization methods¹³ the RSA appears to be anisotropic and recent reports indicate that this type of anisotropy stabilizes an anisotropic superfluid state.^{4,29} Additionally, a second anisotropic superfluid state emerges at even lower temperatures where the theory indicates that this is the manifestation of a biaxial state.³⁰ However, the requirements of this theory are for the elastic mean-free-path anisotropy for ^3He quasiparticle scattering in the aerogel to be $\lambda_{||} < \lambda_{\perp}$ in contrast to our findings for the elastic mean-free-path anisotropy for scattering of methanol molecules. Understanding this discrepancy will require further theoretical work. Nonetheless, we note that the absolute magnitude of the mean-free-path that we measure of ~ 150 nm is very similar to the measurements from ^3He spin diffusion³¹ and to the analysis of the phase diagram and heat capacity with similar aerogels.³ Furthermore, numerical simulations¹⁶ from a cluster aggregation model for the aerogel give estimates of the mean free path that are also consistent with our measurements.

VI. CONCLUSION

We have measured the self-diffusion coefficient for methanol gas molecules as a function of pressure and at room temperature in two 98% silica aerogel samples, one isotropic and the other uniformly anisotropic. The results are well described by a simple model taking the methanol gas to be ideal. Fitting the measurements with two adjustable parameters we determine the scattering ballistic mean-free-path and, for the anisotropic sample, the mean-free-path anisotropy. Physical characterization of the aerogel through a determination of the ballistic mean-free-path provides an important parameter in the theory for superfluid ^3He and for our understanding of the quantum states stabilized by anisotropy.

Secondly, we report the discovery of an enormous enhancement in diffusion coefficient for a dense adsorbed phase on a silica aerogel by as much as two orders of magnitude. Apart from the significance to understanding quantum fluids, this observation has practical applications for two component mixtures of fluids in porous media which might include, hydration of the calcium-silica-hydrate in cementitious materials, controlling chemical reactions and possibly those having directional sensitivity, filtration, and other engineering instances where gas diffusion plays an important role.

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