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ABSTRACT

Fundamental understanding of the subcritical/supercritical behavior of key hydrocarbon species inside nano-porous matrices at elevated pressure and temperature is less developed compared to bulk fluids, but this knowledge is of great importance for chemical and energy engineering industries. This study explores in detail the structure and dynamics of ethane (C₂H₆) fluid confined in silica nanopores, with a focus on the effects of pressure and different ratios of C₂H₆ and CO₂ at non-ambient temperature. Quasi-elastic neutron scattering (QENS) experiments were carried out for the pure C₂H₆, C₂H₆:CO₂ = 3:1, and 1:3 mixed fluids confined in 4-nm cylindrical silica pores at three different pressures (30 bars, 65 bars, and 100 bars) at 323 K. Two Lorentzian functions were required to fit the spectra, corresponding to fast and slow translational motions. No localized motions (rotations and vibrations) were detected. Higher pressures resulted in hindrances of the diffusivity of C₂H₆ molecules in all systems investigated. Pore size was found to be an important factor, i.e., the dynamics of confined C₂H₆ is more restricted in smaller pores compared to the larger pores used in previous studies. Molecular dynamics simulations were performed to complement the QENS experiment at 65 bars, providing supportive structure information and comparable dynamic information. The simulations indicate that CO₂ molecules are more strongly attracted to the pore surface compared to C₂H₆. The C₂H₆ molecules interacting with or near the pore surface form a dense first layer (L1) close to the pore surface and a second less dense layer (L2) extending into the pore center. Both the experiments and simulations revealed the role that CO₂ molecules play in enhancing C₂H₆ diffusion ("molecular lubrication") at high CO₂:C₂H₆ ratios. The energy scales of the two dynamic components, fast and slow, quantified by both techniques, are in very good agreement. Herein, the simulations identified the fast component as the main contributor to the dynamics. Molecule motions in the L2 region are mostly responsible for the dynamics (fast and slow) that can be detected by the instrument.

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I. INTRODUCTION

Nano-porous materials (i.e., solid materials having pore sizes <100 nm), such as zeolites, activated carbons, silicas, micas, etc., play a prominent role in chemical processing, particularly in separations,^{1–3} and as catalysts^{4,5} and catalytic supports.^{6–8} C–O–H-bearing fluids confined in such porous materials possess unique properties that enable future technologies in energy storage, novel

reactions and separations, fabrication of small devices of molecular dimensions, etc. In addition, fundamental nanoscale science, subsurface contaminant migration,^{9,10} geological sequestration of CO₂,^{11,12} development and extraction of energy resources particularly shale gas,^{13,14} and selectivity and reactivity in heterogeneous catalysts and composite materials^{15,16} all benefit from better understanding of the weak forces and subtle effects which determine nanoscale structures in confined fluid systems. Thus, how fluid

properties vary at the molecular level and how fluids interact with the solid host in confined geometries are important questions to the energy and chemical processing sectors.

Pore fluids have long been studied with regard to their different phase behaviors when compared to the bulk fluid properties. Pore confinement effects lead to shifts in phase transitions and related phenomena such as layering, wetting, freezing, boiling, capillary condensation, and immiscibility.^{17–19} Numerous adsorption experiments and molecular-level simulations^{20–25} targeting non-ambient conditions have been conducted to determine the thermodynamic behavior of C–O–H gases in a variety of representative solid nanoporous substrates. Porous systems that have been explored include coals,^{26–39} metal organic frameworks (MOFs),^{40–43} silica gels,^{44–49} zeolitic materials,^{50–57} activated carbon,^{26,58–62} clay minerals and organic matters,^{63–65} and shale matrices.^{29,66–69} The adsorption and structure of C–O–H gases in confined porous matrices under non-ambient conditions have also been investigated in previous studies using the neutron diffraction/scattering technique and molecular dynamics (MD) simulations.^{65,70–73}

However, the dynamic properties of fluids under confinement at non-ambient conditions are relatively less understood but provide important information complementary to the thermophysical properties. Common experimental tools for the dynamics of pore-confined hydrogen-bearing fluids include nuclear magnetic resonance (NMR) and quasi-elastic neutron scattering (QENS) experiments.⁷⁴ Pulsed field gradient (PFG) NMR has been a useful technique for the study of dynamics and transport of molecules in porous materials.^{75–87} In particular, PFG NMR provides information on diffusion in the intraparticle pores (within the particle) and interparticle space (between particles).^{77–87} This information is extremely useful for illustrating the differences between the pore-confined fluid behavior and the bulk fluid behavior.⁸⁴ The diffusion length scale detected by PFG NMR is in the range of 0.1 to hundreds of μm ,⁸⁰ that is, the approximate particle size of some porous materials (intraparticle)^{81,84} or their interparticle distances. Thus, PFG NMR is well suited to observe the long-range fluid dynamics in heterogeneous porous materials. For example, benzene exhibited different diffusivities (1–10 μm in the length scale) in different MCM-41 materials due to the varied transport resistances caused by the permeability of the outer surface of the silica particles. Furthermore, by measuring the anisotropic self-diffusion of *n*-hexadecane in MCM-41, the component perpendicular to the channels suggests the disorder in the parallel channels or defects of the pore walls.⁸¹ In contrast, the QENS experiment provides an effective length scale in nanometers.⁷⁴ Simulations can provide complementary information for experiments.

MD simulations alone have studied the structure and dynamics of C–O–H fluids in slit pores under geologically relevant conditions.^{88–94} Temperature and pressure effects, interfacial fluid structures, and diffusion behaviors were quantified for alkanes and their mixtures in these studies. In order to further understand the fluid dynamic properties in nano-confinement, the dynamic structure factor, a quantity which provides spatially resolved information on the dynamics, is investigated using quasi-elastic neutron scattering (QENS) in this study. Due to the large incoherent neutron cross section of hydrogen atoms, QENS is ideal for the study of hydrogen-containing fluids.⁹⁵ QENS has been used to examine confined ethane⁴⁹ and propane⁹⁶ in mesoporous silica materials at

elevated temperatures and pressures. Gautam *et al.*⁹⁶ found that fluid density and the presence of CO₂ strongly impact the mobility of propane, and the diffusion mechanism changes from continuous diffusion at lower pressure to jump diffusion at higher pressure. The confinement effect is more dominant at low pressures. Patankar *et al.*⁴⁹ reported that CO₂ enhances the mobility of ethane by displacing it from the pore surface through competitive adsorption. However, the C₂H₆–CO₂ mixture in that study was limited to just one composition. Additionally, measurements as a function of fluid density in the supercritical (SC) regime showed that diffusivity increases and residence times are reduced for interfacial pore ethane at supercritical densities.

A combination of QENS experiments and MD simulations has been used to document the structure and dynamics of interfacial fluids confined at planar surfaces^{97–100} or in varied geometries of pores.^{101–109} Normally, the self-diffusion coefficients can be directly compared between QENS experiments and those obtained from mean squared displacement (MSD) analysis in MD simulations. Another more direct comparison of time scales of motions can be made by calculating the intermediate scattering function [ISF, $I(\mathbf{Q}, t)$], which is the inverse Fourier transform of the dynamic structure factor $S(\mathbf{Q}, \omega)$ that can be obtained from the QENS experiment.^{100–102,104–109} The space resolution provided by the ISF, by virtue of its dependence on $\mathbf{Q}$ in addition to t , enables it to differentiate time scales involved in motion occurring at different length scales. MSD on the other hand integrates motion at all length scales. Due to this difference in the ability to resolve information on time scales of motion occurring at different length scales, the ISF can provide information directly comparable to the QENS experiments. This direct comparison between the simulated ISF and QENS experiments has helped resolve the contradictory information provided by simulated MSD¹⁰⁸ and experiments⁹⁶ on the dynamics of propane in nano-porous silica.¹⁰⁸ Both calculated functions, i.e., MSD and the ISF, are utilized in this study to obtain information on the dynamics of confined fluids.

Our previous study probed the behavior of ethane as a function of pressure up to 80 bars, in a pore diameter of ~ 11 nm, and in the presence of CO₂ at one C₂H₆–CO₂ mixture composition.⁴⁹ The results from that study indicated that further reductions in pore size and increases in pressure should have an even more profound effect on ethane dynamics, likely in the form of reduced mobility. The effect of varying the C₂H₆–CO₂ composition was left unexplored in the previous study. To test the hypothesis mentioned above and to explore the effect of varying the composition, we investigated the effects of (i) reduced pore size; (ii) increased pressure up to ~ 100 bars; and (iii) CO₂ addition using two different mole ratios of C₂H₆ and CO₂ on the dynamics of confined C₂H₆ in silica pores. Specifically, C₂H₆ adsorbed in 4-nm silica pores was measured at three pressures (30 bars, 65 bars, and 100 bars) at a fixed temperature of 323 K. Compositions of C₂H₆:CO₂ = 3:1 and 1:3 (mole ratios) were also measured at all these pressures. We used MD simulations to complement QENS experimental data for direct comparisons of diffusion coefficients and time/length scales of the dynamic motions. According to the phase diagrams of C₂H₆ and CO₂ (see Fig. S1 of the [supplementary material](#)), both bulk C₂H₆ and CO₂ are in their supercritical states under the above conditions. Thus, this study provides complementary and quantitative information on the structure and dynamics of confined C–O–H fluids in

temperature and pressure ranges relevant to engineered and natural energy systems.

II. EXPERIMENTS

A. Material characterization

Characterization included pore size, pore volume, specific surface area measurements (N_2 adsorption), and scanning and transmission electron microscopy (SEM and TEM) imaging. Detailed procedures are presented in Sec. II of the [supplementary material](#). The material purchased from Sigma-Aldrich is composed of spherical particles with a size of ~ 200 nm in diameter and 4-nm cylindrical channels regularly arranged in parallel in each particle, similar to the cylindrical pore structure of MCM-41 materials.

The obtained pore characteristics are listed in [Table I](#), with two of our previous studies^{49,96} mentioned above for comparison. The pore size in this study is smaller than the average pore sizes of our earlier work by factors of ~ 3 ⁴⁹ and ~ 4 .⁹⁶

B. QENS experiment

Quasi-elastic neutron scattering experiments were conducted at the disc chopper time-of-flight spectrometer (DCS)¹¹⁰ at the NIST Center for Neutron Research (NCNR), USA. The incident wavelength was set to 4.8 Å, and the instrument was used in low-resolution mode with a full width at half maximum (FWHM) of 118 μ eV at the elastic line. In this configuration, good quality spectra could be obtained in an energy transfer window of -3 meV to $+2$ meV. The silica sample (~ 5 g) was sealed in a cylindrical aluminum cell and centered in the path of the neutron beam. The dry sample measured at 323 K was used as the background. Three pressures with three different fluid compositions each were measured at 323 K, i.e., 30 bars, 65 bars, and 100 bars each for pure

C_2H_6 , $C_2H_6:CO_2 = 3:1$, and $1:3$ (mole ratios). C_2H_6 and CO_2 were supplied to two ISCO syringe pumps with maximum volumes of 500 ml. The pressure in the C_2H_6 cylinder was 38 bars, while that in the CO_2 cylinder was 59 bars. The measurement sequence for pure C_2H_6 started at 30 bars; then, the fluid in the pump was compressed to the subsequent 65 bars and 100 bars pressures and delivered to the sample cell for measurement. The protocol for the 3:1 mixture was to first measure the fluids at 65 bars since the initial total pressure of the two fluids after mixing is close to 65 bars, then compress it to 100 bars and measure, and then decompress the mixture to 30 bars and measure again. The 1:3 mixture was manipulated in the same way. A top-loading closed cycle refrigerator (CCR) was used to control sample temperature.¹¹¹

Compressed C_2H_6 and CO_2 were connected to the sample cell via a three-way valve. The composition of 3:1 was obtained by mixing 507.6 ml C_2H_6 with 109 ml CO_2 at room temperature; while the composition of 1:3 was obtained by mixing 270 ml C_2H_6 with 508 ml CO_2 at room temperature. These input amounts are equivalent to 1.322:0.454 (unit in mole) = $C_2H_6:CO_2 = 3:1$ and 0.703:2.115 (unit in mole) = $C_2H_6:CO_2 = 1:3$ at room temperature. Using the setup of two syringe pumps and a three-way valve, different defined fluid mixtures were produced as follows: (1) admit the required amount (in volume) of CO_2 into pump 1; (2) admit the required amount (in volume) of C_2H_6 into pump 2; (3) open the three-way valve to let CO_2 flow into the sample cell. Run pump 1 until syringe volume is 0 ml (i.e., all the CO_2 has been pumped into the sample cell); and (4) switch the three-way valve to C_2H_6 and control the pressure with the HL rated C_2H_6 pump (2). Run pump 2 until syringe volume is 0 ml. Let C_2H_6 and CO_2 mix in the sample cell for ~ 20 – 30 min. Use the C_2H_6 syringe pump (2) in constant pressure mode to control the pressure in the sample cell.

[Table II](#) provides the experimental conditions and the fluid bulk states at these conditions. Figure S1 of the [supplementary material](#) shows the associated phases of the bulk fluids in our experimental conditions on the phase diagrams of CO_2 and C_2H_6 .

TABLE I. Pore characteristics of the silica material compared to nano-porous materials in our previous studies as mentioned above.

Material	Pore size (nm)	BET surface area (m^2/g)	Pore volume (cm^3/g)
Mesoporous silica (this study, regular cylindrical)	3.7	570.5 ± 1.5	0.59
CPG-75 ⁴⁹ (heterogeneous pores)	11.1	148.5 ± 1.0	0.59
Silica aerogel ⁹⁶ (heterogeneous pores)	15.0	326.3 ± 3.4	2.50

TABLE II. QENS experimental conditions, compositions, and estimated bulk phases at 323 K.¹¹²

	Pure C_2H_6	$C_2H_6:CO_2 = 3:1$	$C_2H_6:CO_2 = 1:3$	MD simulations
30 bars	Gas	Gas, gas	Gas, gas	×
65 bars	SC fluid	Gas, gas	Gas, gas	✓
100 bars	SC fluid	SC fluid, gas	Gas, SC fluid	×

III. MD SIMULATIONS

Molecular dynamics (MD) simulations focused on the 65 bars pressure. The confined C_2H_6 fluid may undergo phase transitions when going from pure C_2H_6 to the 3:1 mixture at 65 bars indicated in Table II; thus, we can expect to observe larger changes in fluid dynamics caused by the phase transition and supercritical state of C_2H_6 . Fluids at 65 bars also avoid the potential complexity that supercritical CO_2 may bring at 100 bars. MD simulations were performed using the DL_POLY_4.06 package.¹¹³ To create the 4-nm cylindrical pore, a procedure similar to that used in earlier studies was followed.^{114,115} We started with the crystal structure of α -cristobalite¹¹⁶ in the space group of $P4_12_12$ ($a = 4.978 \text{ \AA}$ and $c = 6.948 \text{ \AA}$) and replicated a unit cell of $12 \times 12 \times 10$ times in three dimensions, resulting in a total number of 17 280 atoms. The crystalline sample was melted at 5000 K with an NPT simulation lasting for 100 ps with a time step of 1 fs. The molten simulation cell was then quenched to 300 K by sequentially running short NPT simulations lasting for 100 ps each at 4000 K, 3000 K, 2000 K, 1000 K, and 300 K. This approach was followed by a 100 ps NVT simulation at 300 K. The configuration output of all these simulations was used as the input of the next simulation. The simulation cell obtained is in the form of an amorphous silica material. Next, the 4-nm pore was carved out by removing certain Si and O atoms starting from the center of the simulation cell along the z-axis to the desired diameter. The number of removed Si and O atoms was kept at the ratio of 1:2. To mimic the silica material under ambient conditions, we decorated the unbonded Si and O atoms on the pore surface with OH and H groups. We carried out a short run of 50 ps to adsorb the OH and H groups to the surface. We observed that a fraction of the OH and H groups entered the interstitial space, which can be expected under ambient conditions for amorphous materials. Thus, the resulting total number of hydroxyl groups on the pore surfaces is 364, corresponding to a surface hydroxyl density of 4.1 OH/nm^2 , in good agreement with those determined by experiments ($2.6\text{--}4.6 \text{ OH/nm}^2$).¹¹⁷ The above simulation cell has a net charge of zero within the framework of CLAYFF force field.¹¹⁸

The force field for C_2H_6 and CO_2 used the TraPPE (transferable potentials for phase equilibria) parameters.¹¹⁹ Alkanes are modeled by the united atom (UA) formalism in TraPPE, wherein the C_2H_6 molecule is described by a dumbbell-type diatomic molecule composed of C–C. The C–C and C–O bond distances for C_2H_6 and CO_2 are fixed at 1.54 $\text{\AA}$ and 1.16 $\text{\AA}$, respectively. The Lennard–Jones potential is used to describe the bonded and nonbonded atom pairs. The charge of the solid substrate is derived from the CLAYFF model, where $\text{Si} = +2.1e$, $\text{O} = -1.05e$, $\text{O}_{\text{OH}} = -0.950e$, and $\text{H}_{\text{OH}} = +0.4250e$ for the O and H of the hydroxyl groups, respectively. The hydroxyl group is composed of OH groups and H groups that are bonded to the surface oxygen atoms. The oscillating modes for OH groups and H groups with surface oxygen atoms are treated as harmonic bonds, where the parameters follow the simple point charge (SPC) water model described by Berendsen *et al.*¹²⁰ The charge of the C pseudopotential of C_2H_6 is zero, whereas C and O atoms of the CO_2 molecule have charges of $+0.70e$ and $-0.35e$, respectively.

Simulations were conducted at 323 K with an NVT ensemble using the Nosé–Hoover thermostat: a setup that is consistent with our experiments. The simulations were carried out for 2 ns.

The Si and O atoms (including O in the hydroxyl group) were kept immobile, but the H atoms in the hydroxyl groups on the pore surface were free to move. The first 0.5 ns of the simulation was used for equilibrating the system. Attainment of equilibrium was ascertained by ensuring that the fluctuations in the total energy and temperature of the system are less than $\pm 7\%$ of their constant values and there is no systematic drift. The last 1.5 ns was taken as the production time to calculate average quantities of interest. The Velocity Verlet (VV) algorithm was used to advance the atom positions. Long-range Coulombic energy is estimated using Ewald summation with a precision of 10^{-6} . The Smoothed Particle Mesh Ewald (SPME) method developed by Essmann *et al.*¹²¹ is included in the DL_POLY_4.06 package. The time step was 1 fs for each step of movement, while the trajectories were recorded at an interval of 0.02 ps. Periodic boundary conditions were applied in all directions. A cutoff distance of 14 $\text{\AA}$ was used as recommended for the TraPPE force field.¹¹⁹ A pore wall thickness of more than 1 nm on each side in the simulation cell ensures that there is no interaction between the images of molecules in adjacent cells.

Three different fluid compositions were simulated at 65 bars to match the QENS experiments. For the pore fluid at a target pressure of 65 bars, the number of molecules was set to ($\text{C}_2\text{H}_6\text{:CO}_2$) 343:0, 270:90, and 90:270, respectively. These three compositions are referred to as “pure,” “3:1,” and “1:3.” Normalized to pore volume, 343 C_2H_6 molecules in the pore translate to a bulk pressure of ~ 65 bars. MD simulations match the compositional ratios, but the total pressures of the 1:3 mixed fluids were slightly lower than the target 65 bars. Dynamic properties of C_2H_6 will be primarily analyzed from the simulation results and compared with QENS experiments in which hydrogen-containing species dominate the spectra. In addition, MD simulations provide structure information of the confined fluids in the pores and the dynamic properties of CO_2 .

IV. RESULTS

A. QENS data

The QENS data were reduced and modeled using the data analysis package DAVE.¹²² Analysis of the spectra involved two approaches—one in which the spectrum of the empty nano-porous silica at 323 K was subtracted from the spectra of fluid filled samples and a second where no such subtraction was carried out. We observed that the first approach resulted in over-subtraction at some Q values. Therefore, the subtracted spectra were used only to estimate the relative contributions of elastic scattering. A more detailed analysis of all spectra was carried out without any background subtraction. This approach of not subtracting the matrix background was successfully used in previous studies.^{49,96,123,124} The over-subtraction caused by the decreasing intensity of the spectrum is likely due to the multiple scattering events contributed by C_2H_6 molecules. However, we used the dry background measured at 323 K as the resolution in the data analysis. This is justified because the dry silica sample measured at 323 K exhibited no quasi-elastic broadening and, therefore, represents the instrumental resolution.

Representative reduced spectra converted to the dynamical structure factor $S(\mathbf{Q}, \omega)$ are shown in Fig. 1. $S(\mathbf{Q}, \omega)$ is a property of the sample and is a function of momentum ($\hbar\mathbf{Q}$) and energy transfer ($\hbar\omega$) between the neutron and the sample in a scattering event. It provides information on the structure and dynamics of the sample. One should note that in our experiments the $S(\mathbf{Q}, \omega)$ always represents the incoherent dynamic structure factor of C_2H_6 because the incoherent neutron scattering cross section of hydrogen dominates the quasi-elastic scattering.

An attempt was made to separate the elastic and quasi-elastic components of the spectra by fitting the background subtracted data with a combination of a delta function representing the elastic component and a Lorentzian to represent the quasi-elastic component. This attempt resulted in reasonably good fits. The elastic incoherent structure factor (EISF), which is the fraction of the scattering signal that is elastic, obtained from these fits was found to be below ~ 0.1 for all $\mathbf{Q}$ values in all samples (Fig. S4 of the [supplementary material](#)). This indicates the absence of any localized motions, such as rotation.

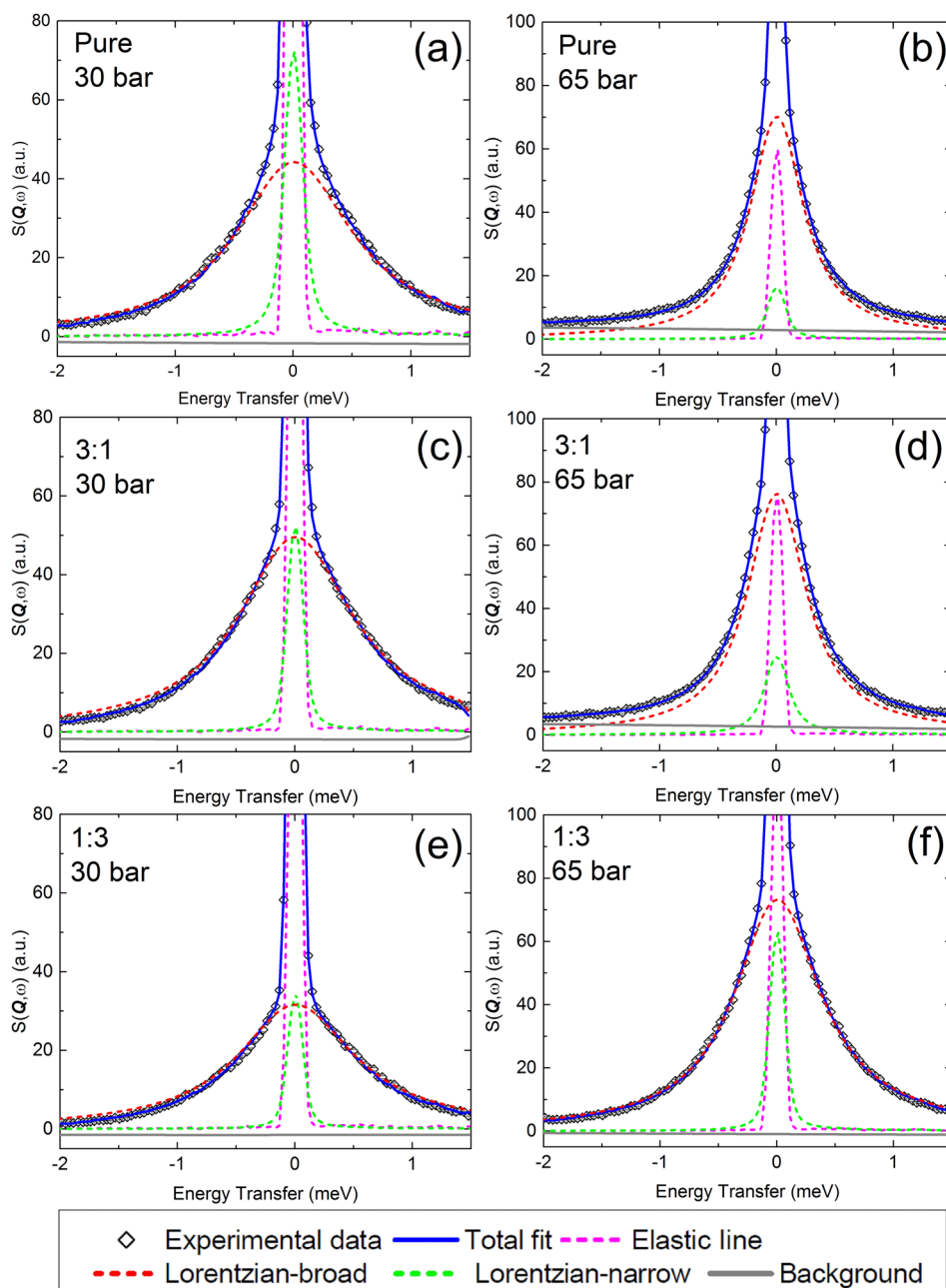


FIG. 1. Representative QENS spectra at 30 bars [(a), (c), and (e)] and 65 bars [(b), (d), and (f)] in three compositions. All spectra are at $\mathbf{Q} = 0.35 \text{ \AA}^{-1}$, without the matrix background being subtracted. Cap-tipped lines are the error bars of the experimental data.

Spectra that were not subtracted using the matrix background were also fit with this model of a delta function and a Lorentzian. The EISF resulting from these fits had values higher than 0.1 (up to 0.6) but also showed no significant Q dependence. These significantly higher EISF values are a result of no background subtraction and represent the elastic contribution from the matrix. The absence of contributions from rotational motions in the spectra allowed modification of the fitting function to further refine the quality. Thus, a combination of two Lorentzians was used to model the quasi-elastic broadening. The spectra without matrix background subtraction were fit using the following equation:

$$S(Q, \omega) = \{A(Q)\delta(\omega) + [1 - A(Q)][p_1 L_1(\Gamma_1, \omega) + p_2 L_2(\Gamma_2, \omega)] + [B_1 + B_2(Q, \omega)]\} \otimes R(Q, \omega), \quad (1)$$

where $A(Q)\delta(\omega)$ is the elastic component, $L_1(\Gamma_1, \omega)$ and $L_2(\Gamma_2, \omega)$ are the two Lorentzian components, p_1 and p_2 are the prefactors, and $[B_1 + B_2(Q, \omega)]$ is the linear background; these terms are convoluted by the resolution function $R(Q, \omega)$. The elastic component results from motions slower than the resolution of the instrument and static scattering from the silica and is modeled by a convoluted delta function $[\delta(\omega)]$ centered at zero energy transfer. The quasi-elastic components, modeled by the Lorentzian functions, represent the fast and slow components of translational motions. By fitting the spectra with Eq. (1), we determined the FWHM of the two Lorentzians (broad and narrow), $2\Gamma_i^e$ (where e denotes the experiment and $i = 1, 2$). Figure 1 shows the fits of the model function in Eq. (1) to the experimental spectra along with the individual components of the fitting function.

The Q dependence of the Γ_i^e obtained from the fits was investigated further to understand the mechanism of translational motions contributing to the QENS spectra. Confined fluids can exhibit diffusional motion that can be broadly classified into either Fickian diffusion or jump diffusion depending upon the strength of the intermolecular interactions. The Q dependence of Γ_i^e in the two diffusion models, i.e., Fickian and jump diffusions, can be expressed as

$$\Gamma_i^e = DQ^2 \quad (i = 1, 2) \quad (2)$$

and

$$\Gamma_i^e = \frac{DQ^2}{1 + DQ^2\tau} \quad (i = 1, 2), \quad (3)$$

respectively, where Γ_i^e is the half width at half maximum (HWHM), D is the self-diffusion coefficient, and τ is the residence time. The latter is a quantity that describes the time a molecule resides at a given position before jumping to another position. At lower Q values, Eq. (3) approximately equals DQ^2 , i.e., the form of Eq. (2), and then, it approaches $1/\tau$ at higher Q values. Thus, the slope of the initial stage determines the D , while the plateau at the later stage determines the τ . Figure 2 plots the relationship of Γ_i^e vs Q^2 for the 65 bars data for both the fast (main plot) and the slow (inset) components. For the fast component data, there is a tendency of the Γ_i^e values to plateau at higher Q values after increasing linearly at lower Q . This deviation from a linear behavior is a signature of jump

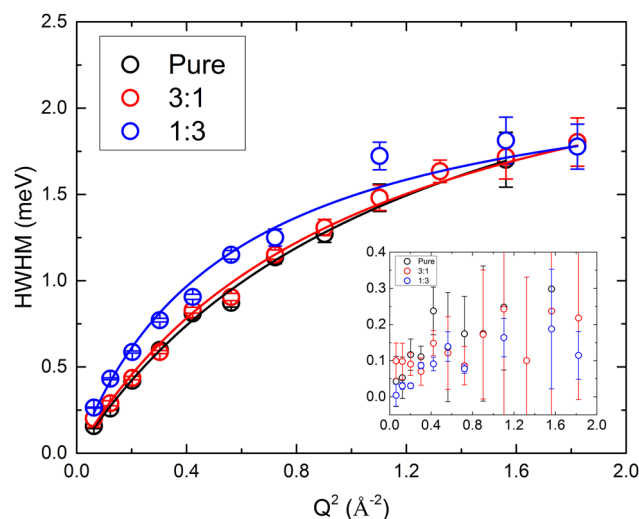


FIG. 2. Fast components in three compositions at 65 bars fit using the jump diffusion model. The inset shows the slow component in three compositions. No clear trend can be identified for the slow component.

diffusion represented by Eq. (3). The fast component in our three compositions was, therefore, fit using the jump diffusion model [Eq. (3)] in Fig. 2. However, the slow component shown in the inset of Fig. 2 does not show a clear trend and, therefore, was not fit with either model. The plots for 30 bars and 100 bars data are shown in Fig. S5 of the [supplementary material](#). The experimentally derived diffusion coefficients (D) are presented in Sec. V and compared with the D determined by MD simulations.

In addition to the slow and fast quasi-elastic components, represented by the two Lorentzian functions, a faster component from the solid background matrix is identified based on the fitted linear background variation with Q values. The offset of the linear background represented by B_1 in Eq. (1) is used to plot with Q values for every composition at each pressure, as shown in Fig. S6 of the [supplementary material](#). The general trend is that B_1 increases with increasing Q value, which can be a reflection of the “HWHM vs Q^2 ” relationship shown in Fig. 2. Therefore, the B_1 likely represents a much faster component that goes undetected in the energy window accessible by the QENS instrument used in this study.

B. Simulation results

1. Structure

Figure 3 shows the structures of C_2H_6 and CO_2 in the 4-nm cylindrical pore for the three compositions and their corresponding density profiles [center of mass (COM)] at 323 K and 65 bars from MD simulations. A quarter portion of the pore structure is displayed for clarity. The full range structures are shown in Fig. S7 of the [supplementary material](#). The simulation snapshots indicate that CO_2 molecules replace interfacial C_2H_6 molecules and adsorb on the pore surfaces, as shown in Figs. 3(b) and 3(c). The density profiles shown in Fig. 3(d) originate from the center of the pore. The boundary at the bottom between the gray shaded areas divides the bulk

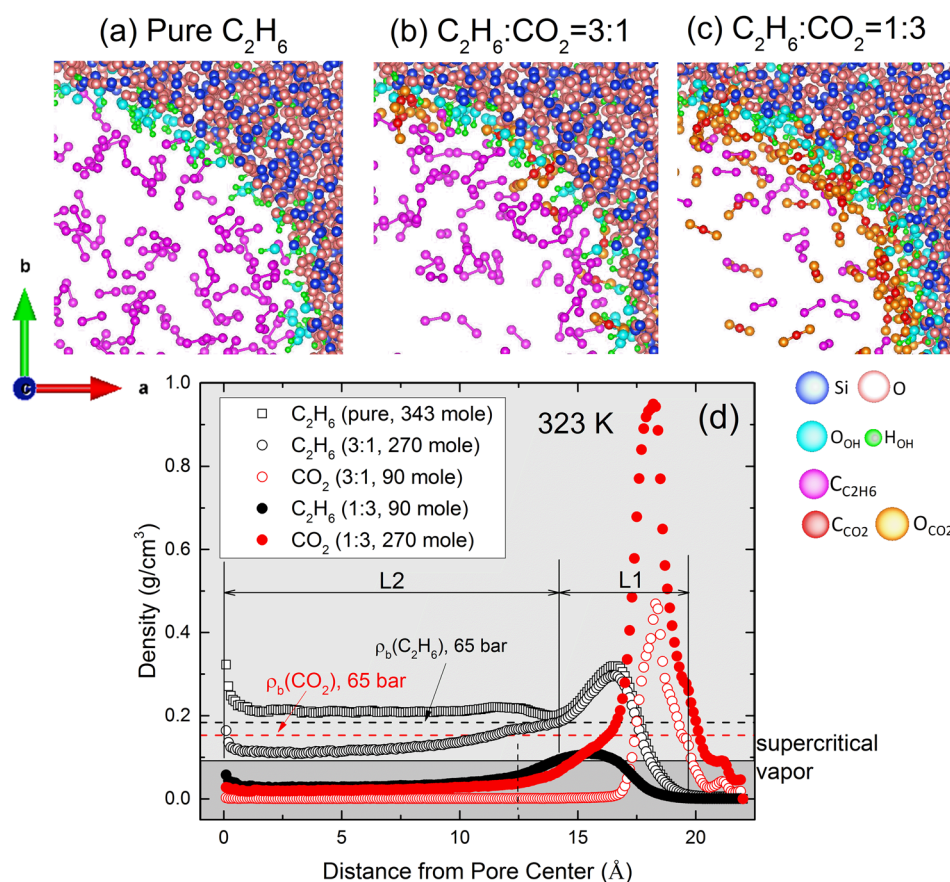


FIG. 3. Snapshots of C_2H_6 and CO_2 molecules in 4-nm hydroxylated cylindrical silica pores at 323 K in three compositions [(a)–(c)] and their corresponding density profiles (d). The two layer regions (interfacial L1 and bulk-like L2) of C_2H_6 are labeled in (d), where the black solid line is used for the pure and the 3:1 mixture and black dashed line for the 1:3 mixture to divide L1 and L2.

vapor from the supercritical phase according to the bulk density of C_2H_6 at 323 K.¹¹² The density profiles of CO_2 (in red) also reveal that CO_2 forms the dominant layer nearest to the pore surface. Due to the quadrupole moment of CO_2 and the corrugation of the pore surface, a minor peak of CO_2 forms in the proximity of the pore surface [beyond ~ 20 Å in Fig. 3(d)]. With increasing CO_2 amount in the 1:3 mixture, a weaker second peak of CO_2 is observed farther away from the pore wall [Fig. 3(d)]. For C_2H_6 , the first layer peaks for the loadings of 343 and 270 C_2H_6 molecules almost overlap, but the peak for the loading of 90 C_2H_6 molecules is displaced further from the surface due to the increased amount of CO_2 . We define the region of higher density for C_2H_6 close to the pore wall (~ 5 Å wide) as layer 1 (L1, interfacial) and the lower density region between the center of the pore and denser region as layer 2 (L2, bulk-like and unadsorbed). The two dashed lines in Fig. 3(d) identify the bulk densities of C_2H_6 (in black) and CO_2 (in red) at 65 bars, using the data from Ref. 112. Although the bulk density is a macroscopic property, different from the microscopic pore fluid density, we show these as reference points.

Due to the electrostatic interactions between the pore surface and the CO_2 layer adjacent to the pore surface, the latter can be expected to exhibit a preference in molecule orientation. A plot of the orientational distribution function is provided in Fig. S8 of the [supplementary material](#). These data indicate that the CO_2 molecules

are oriented at an angle of $\sim 45^\circ$ with the pore surface for the lower CO_2 loading. At higher CO_2 loading, this distribution is more isotropic.

2. Dynamics of the confined C_2H_6 and CO_2

Mean squared displacement (MSD) is used to describe the translational motion of molecules using their COM coordinates. The self-diffusion coefficient (D) determined from calculated MSD is based on the Einstein relation,

$$D = \frac{\text{MSD}}{2n_d t}, \quad (4)$$

where n_d is the number of dimensions in space, equal to three for overall MSD. The slope of the MSD vs t curve is taken at long times (after 100 ps), assuring the onset of diffusion. Figure 4 plots the MSD of C_2H_6 and CO_2 in their three compositions. The mixture of 1:3 leads to the fastest dynamics of C_2H_6 shown in Fig. 4, whereas the restricted CO_2 molecules that mostly reside on the pore wall show much slower dynamics. The D for C_2H_6 and CO_2 will be compared with the experimentally determined values and those of previous studies in Sec. V.

The Intermediate Scattering Function (ISF) is the spatial Fourier transform of the Van-Hove self-correlation function

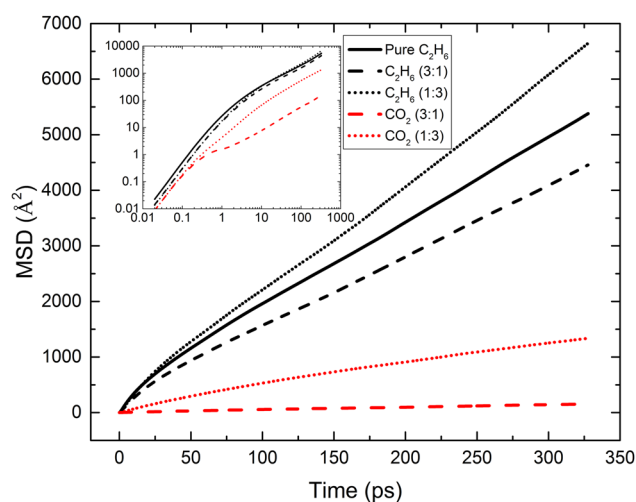


FIG. 4. Calculated MSD plots for pure confined C_2H_6 and CO_2 in three compositions. The inset is expressed in log-log scale.

$G(\mathbf{r}, t)$, which, in classical approximation, stands for the probability of finding a molecule at position “ $\mathbf{r}$ ” and time “ t ” given that it was at origin at $t = 0$. The temporal Fourier transform of the ISF is the dynamic structure factor $S(\mathbf{Q}, \omega)$, which is a quantity measured in neutron scattering experiments. In an MD simulation, the ISF can be calculated as

$$I(\mathbf{Q}, t) = \frac{1}{N} \sum_i \left\langle e^{i\mathbf{Q} \cdot (\mathbf{r}_i(t) - \mathbf{r}_i(0))} \right\rangle, \quad (5)$$

where $\hbar\mathbf{Q}$ is the momentum transfer, a quantity determined by the scattering angle in the experiment that has the dimension of inverse length, and $\mathbf{r}$ is the position vector of an interaction site in the simulation. The angular brackets denote an ensemble average and integrate the contribution from $\mathbf{Q}$'s for all directions with the same magnitude. Furthermore, the ISF corresponding to purely rotational and translational components of motion can be calculated from the simulated trajectories by decomposing the atomic coordinates in the lab frame into the center of mass coordinates in the lab frame and atomic coordinates in the center of mass frame. The translational ISF (TISF) can be calculated from the center of mass coordinates in the lab frame, whereas the rotational ISF (RISF) can be calculated from the atomic coordinates in the center of mass frame or a unit vector attached to them (see Fig. S9 of the [supplementary material](#)).^{100,125} If the atomic coordinates in the lab frame are used in Eq. (5), the corresponding ISF represents the sum of all motions exhibited by the molecule (translation, rotation, and vibration if it exists). The resulting ISF is called the overall ISF (OISF) in this study.

Taking the energy transfer window accessible by the instrument and the instrumental resolution we used in the experiment as energy boundaries, the measurable time scale for the motions of C_2H_6 molecules is 0.1–6 ps. Thus, to properly compare with the experiments, the MD-derived ISF needs to be modeled up to ~ 10 ps. In this range, the OISF exhibits two stages of decay, i.e.,

$$OISF = A_1 \cdot e^{-t/\tau_1^s} + A_2 \cdot e^{-t/\tau_2^s}, \quad (6)$$

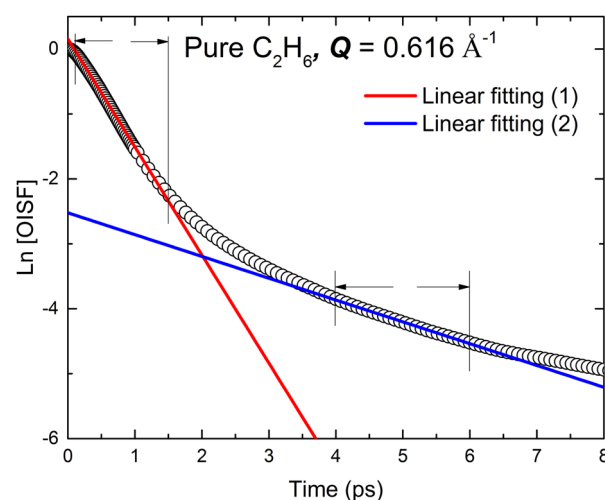


FIG. 5. $\ln[OISF]$ vs time using one Q value as a representative. Two separate linear functions are fitted in two representative linear regions as shown obtaining two different time decay constants τ corresponding to two Lorentzians in the experimental spectra. The two linear regions are marked by arrows, i.e., [0.1, 1.5] and [4, 6], on the time scale.

consistent with the experimental observation of two different populations of C_2H_6 molecules represented by two Lorentzian components in the QENS spectra. In fact, as shown in Fig. 5, the $\ln[OISF]$ vs time plot exhibits two different linear regimes in this time range. These two regimes are equivalent to the two Lorentzians in the $S(\mathbf{Q}, \omega)$ vs energy spectra, as an exponential decay function [Eq. (6), the straight line in logarithmic scale] forms a Fourier transform pair with a Lorentzian function. The slopes of the two linear regimes give the decay constants (τ_i^s) of the corresponding exponential decay functions. Figure 5 shows the plot of $\ln[OISF]$ vs time using a representative Q value, along with the two linear fits in their corresponding time ranges. The $\ln[OISF]$ plots and fits for the other two compositions are shown in Fig. S9 of the [supplementary material](#).

The results can be compared directly with the experimental HWHM values using the relation

$$\Gamma_i^s = \frac{\hbar}{\tau_i^s} \quad (i = 1, 2); \quad (7)$$

the comparison between Γ_i^e and Γ_i^s is presented in Sec. V.

V. DISCUSSION

A comparison between experimental and MD-derived diffusion coefficients is described first, followed by a discussion of the energy scales of the motions obtained from QENS and MD.

A. Diffusion coefficient (D) comparison

Table III lists the diffusion coefficients (D) of the fast component using the jump diffusion model (shown in Fig. 2) and the corresponding residence times τ . These data are compared to

TABLE III. Self-diffusion coefficient (D) comparison.

QENS experiment, 323 K, 4-nm silica						
	Pure C ₂ H ₆		C ₂ H ₆ :CO ₂ = 3:1		C ₂ H ₆ :CO ₂ = 1:3	
	D_b ($\times 10^{-9}$ m ² /s)	τ (ps)	D_b ($\times 10^{-9}$ m ² /s)	τ (ps)	D_b ($\times 10^{-9}$ m ² /s)	τ (ps)
30 bars	55.25 $\pm$ 3.90	0.45 $\pm$ 0.02	63.20 $\pm$ 4.90	0.44 $\pm$ 0.02	65.39 $\pm$ 1.17	0.46 $\pm$ 0.07
65 bars	24.46 $\pm$ 0.79	0.33 $\pm$ 0.02	27.19 $\pm$ 1.42	0.36 $\pm$ 0.03	41.32 $\pm$ 2.43	0.43 $\pm$ 0.03
100 bars	21.91 $\pm$ 0.82	0.30 $\pm$ 0.02	24.19 $\pm$ 2.46	0.38 $\pm$ 0.08	24.58 $\pm$ 2.76	0.34 $\pm$ 0.07
MD simulation, 323 K, D ($\times 10^{-9}$ m ² /s)						
65 bars	Pure C ₂ H ₆ 25.6		C ₂ H ₆ 21.4	CO ₂ 0.79	C ₂ H ₆ 33.6	CO ₂ 5.70
QENS experiment, Patankar <i>et al.</i> , ⁴⁹ 11-nm silica						
	Pure C ₂ H ₆ , 323 K		Pure C ₂ H ₆ , 38 bars (D_b , $\times 10^{-9}$ m ² /s)		Mixture, 27% CO ₂ in mole, 38 bars (D_b , $\times 10^{-9}$ m ² /s)	
	D_b ($\times 10^{-9}$ m ² /s)	τ (ps)				
38 bars	40.48 $\pm$ 1.70	1.56 $\pm$ 0.07	301 K	30.61 $\pm$ 1.33	33.35 $\pm$ 1.18	
50 bars	38.20 $\pm$ 1.73	1.76 $\pm$ 0.09	307 K	32.59 $\pm$ 1.60	36.75 $\pm$ 1.50	
60 bars	38.20 $\pm$ 0.88	1.45 $\pm$ 0.14	313 K	33.82 $\pm$ 1.12		
70 bars	36.65 $\pm$ 0.84	1.07 $\pm$ 0.16	318 K	36.31 $\pm$ 1.61	39.37 $\pm$ 2.31	
80 bars	32.78 $\pm$ 0.35	0.72 $\pm$ 0.11	323 K	40.48 $\pm$ 1.70	40.39 $\pm$ 0.89	

the D values determined from the MSD curves by MD simulations at 65 bars (Fig. 4). The notation of D_b is used here to represent the diffusion coefficient of the fast component determined by QENS experiments in the following discussion. The simulation-based D values for the confined CO₂ molecules at the pore walls are also listed in this table. The D_b values derived from QENS experiments are of the same order of magnitude as those in the work of Patankar *et al.*⁴⁹ for confined C₂H₆ (see Table III).

1. Pressure and pore size effects

Based on the QENS-derived data in Table III, increasing pressures reduce the mobility of the confined C₂H₆ molecules, leading to a decreasing trend in the overall D_b value for each composition with pressure. A similar pressure effect was observed in the work of Patankar *et al.*,⁴⁹ where the self-diffusivity of bulk-like C₂H₆ fluid (D_b) confined in the pores decreased with increasing fluid pressure from 38 bars to 80 bars in ~ 11.0 nm silica pores at 323 K, from 40.48 to 32.78 $\times 10^{-9}$ m²/s (Table III). The derived D_b values in this study are smaller than those in Ref. 49. However, the C₂H₆ fluids in these two studies are confined in different pore sizes, in addition to the fact that the dynamic behavior of the bulk-like fluids confined in either pores were fit using different models—the jump diffusion model in this study vs the continuous diffusion model in the work of Patankar *et al.*⁴⁹ This difference in the mechanisms of diffusion results from a stronger intermolecular interaction in the smaller pore that gives rise to a deviation from Fickian behavior. Ethane confined in even smaller pore size matrices, such as silica¹²⁶ and zeolitic materials,^{25,127–129} generally exhibits smaller D

values by one order of magnitude. However, these values are not directly comparable as they were measured at temperatures lower than 323 K used here. However, over greater length scales of up to micrometers, PFG NMR captures longer range diffusivities providing a window into molecular motion for time domains too slow for QENS. Long-range diffusion of C₂H₆ in the beds of NaX zeolite has been studied by Geier *et al.* (2002)⁷⁹ and Kärger *et al.* (2003),⁸² where the calculated mean free path is two orders of magnitude of the size of the single crystallite (20–30 μ m).⁷⁹ On their temperature dependent $D_{\text{long-range}}$ plot, the corresponding $D_{\text{long-range}}$ value for $P_{\text{C}_2\text{H}_6} = 50\text{--}80$ mbar at 323 K is $\sim 5 \times 10^{-7}$ m²/s. This value is one order of magnitude higher than pore-confined D_b values in Table III. However, the mean free path associated with this long-range diffusion also involves the factor of tortuosity that could enhance the diffusion path.⁸²

2. Composition effects

QENS experiments indicate that both the compositions of C₂H₆:CO₂ = 3:1 and 1:3 result in faster diffusivity of C₂H₆, validating the lubricating role of CO₂ for the transport of hydrocarbon species again (known as “molecular lubrication”) as in previous studies.^{49,89,90,96} The accelerating effect is stronger in the 1:3 mixture, especially for the pressure of 65 bars, consistent with the MD results at 65 bars. This indicates that the amount of CO₂ loading is a critical factor in enhancing C₂H₆ diffusion. In addition, the phase states of C₂H₆ and CO₂ fluids can be different at different fluid compositions and pressures (Table II), which can cause variable C₂H₆ diffusivities. For example, the enhancement is relatively strong at 30 bars

and 65 bars compared to 100 bars from 3:1 to 1:3. The insignificant increase at 100 bars going from 3:1 to 1:3 might be due to the possible bulk phase changes in both C_2H_6 and CO_2 between supercritical and gas from 3:1 to 1:3, as shown in Table II.

Between the experiment and MD simulation, the lack of good agreement with the trend in changing D between the pure phase and the 3:1 case at 65 bars might be because the MSD calculated from the simulation integrates all the motions, some of which might be beyond the energy window of the instrument. The QENS-derived residence times (τ) listed in Table III are reasonable estimates as its corresponding energy scale (~ 1 – 2 meV) is well within that of the fast component (Fig. 2). However, the orders of estimated τ values at each pressure do not follow the reverse order of estimated D values as expected, i.e., the greater the D , the shorter the τ . This might be due to the sparse data points and the larger error bars occurring in the higher Q region, which affects the accuracy of τ estimation. For each composition, the estimated τ values show a decreasing trend with the pressure increasing from 30 bars to 100 bars. This is consistent with the observation in Ref. 49 for pure C_2H_6 at 323 K from 38 bars to 80 bars listed in Table III. As they have pointed out, the decreasing trend might be due to the transition from fluid–pore interaction at lower pressures to fluid–fluid interaction at higher pressures.⁴⁹ In Sec. V B, energy scales of the two motions are directly compared between the two techniques.

3. The D values of confined CO_2

For the confined CO_2 , the overall D values in the 3:1 and 1:3 mixtures from MD are $0.79 \times 10^{-9} \text{ m}^2/\text{s}$ and $5.70 \times 10^{-9} \text{ m}^2/\text{s}$, respectively (Table III). In the work of Le *et al.*,^{89,90} the effects of CO_2 on the dynamics of alkanes in silica slit pores ($1.9 \text{ nm} \times 10.48 \text{ nm} \times 10.08 \text{ nm}$) were studied. As the unit pore volume is approximately twice the pore volume used in this work (89.43 nm^3), the corresponding CO_2 density in their work translates to twice the number of CO_2 molecules used in our work. They derived the in-plane D of CO_2 , which is comparable to the 1-dimension D along the pore channel direction (z -axis) in our study. Their in-plane D values for confined CO_2 in the presence of n -octane are $1.4 \times 10^{-9} \text{ m}^2/\text{s}$ (225 CO_2 :282 n -octane) and $2.7 \times 10^{-9} \text{ m}^2/\text{s}$ (448 CO_2 :282 n -octane) at 300 K⁹⁰ and $58 \times 10^{-9} \text{ m}^2/\text{s}$ (CO_2 : C_4H_{10} = 9:1, 300 molecules in total) and $50 \times 10^{-9} \text{ m}^2/\text{s}$ (CO_2 : C_4H_{10} = 9:1, 500 molecules in total) at 343 K.⁸⁹ The 1D values for the CO_2 in our study are determined to be $1.6 \times 10^{-9} \text{ m}^2/\text{s}$ (C_2H_6 : CO_2 = 3:1, 90 CO_2 molecules) and $13.6 \times 10^{-9} \text{ m}^2/\text{s}$ (C_2H_6 : CO_2 = 1:3, 270 CO_2 molecules). Our values are similar to the mixtures of CO_2 and n -octane at 300 K. This is most likely due to the similar CO_2 density (i.e., the number of CO_2 molecules in our cylindrical pores is half of that used in their slit pores). However, additional differences are caused by the different ratios of CO_2 and hydrocarbons, the in-plane and 1D definitions, and pore geometries.

B. Comparison of energy scales of motions

As discussed above, energy scales of motions derived from QENS experiment (Γ_i^e) only include translational motions, while MD simulation results (Γ_i^s) combine translation and rotation (OISF). Figure 6 compares the Γ_i values obtained from the experimental

QENS spectra using Eq. (1) and those obtained from Eq. (7) by converting the time parameters (τ_i^e) used to fit the $\ln[\text{OISF}]$ calculated from simulations. The two MD-derived components match reasonably well the two components derived from the QENS experiment, particularly the fast component. Only the fast motion of pure C_2H_6 shows a small discrepancy between simulation and experiment at higher Q . The two components (Γ_1 and Γ_2) vary by approximately one order of magnitude in terms of the energy scale. For the slow component, the error bars on the experimental data are large. This is because of the difficulties involved in obtaining a large and a small quantity simultaneously from fitting experimental data, making quantitative comparison between experiment and simulation for this component difficult. However, there is good qualitative agreement between the experiment and MD simulation for the slow component (see Fig. 6). The large error bars on the experimental data indicate that a combination of different instruments is required to better resolve this slow component. For example, Liu *et al.*¹⁰⁰ employed three QENS instruments with different energy windows and resolutions to probe the surface water dynamics on olivine surfaces and reached satisfactory agreement with the MD simulation which constrained three dynamic components. Such a practice can also benefit the understanding of the faster component in the system, as identified by the background variation mentioned above (Fig. S6 of the supplementary material).

The fitting of the calculated OISF was restricted to a time range that corresponds to the energy window of the DCS instrument used in the experiments. The derived energy scales are comparable with previous QENS studies that focused on the dynamics quantification of confined hydrocarbon fluids under non-ambient conditions.^{49,96} For example, Patankar *et al.* found that the dynamic energy range for confined C_2H_6 is also a few meV for the fast motion and a few hundreds of μeV for the slow motion, respectively, by the QENS experiment study using the Cold Neutron Chopper Spectrometer (CNCS) at Spallation Neutron Source (SNS), an instrument similar to the DCS.⁴⁹ For propane in mesoporous silica aerogel, a QENS instrument with better resolution had to be used to resolve the motion at smaller Q which had energies of $\sim$ tens of μeV , while the fast motion has an energy scale of $\sim 100 \mu\text{eV}$.

The layer specific ISF could provide insights on the motion distribution in the two distinct layers. In order to obtain the layer specific OISF, we selected ten representative molecules from L1 and L2 and used the trajectories at the longest duration in that specific layer to calculate the layer specific OISF (Fig. 7). The layer specific OISF for L1 and L2 for pure C_2H_6 were calculated using their trajectories with durations of 35 ps and 40 ps, respectively, confined to the specific layer regions (see trajectories in Fig. S11 of the supplementary material). In addition to the longest duration, the average residence time was also calculated (see Fig. S12 of the supplementary material), yielding a shorter average residence time than the longest duration we can identify in particular layers. In Fig. 7, the two linear fitted trends in red on the OISF are the same linear fits as in Fig. 5. As the L1 $\ln[\text{OISF}]$ has a linear section parallel to the slow component reflected in the total $\ln[\text{OISF}]$, a linear fit was performed on the section that covers the same time range as the total $\ln[\text{OISF}]$. The slope of the linear fit equals $-1/\tau$ and is labeled in this figure for comparison. The fit on the L2 $\ln[\text{OISF}]$ was performed in the time scale of the fast component shown in the total $\ln[\text{OISF}]$. The

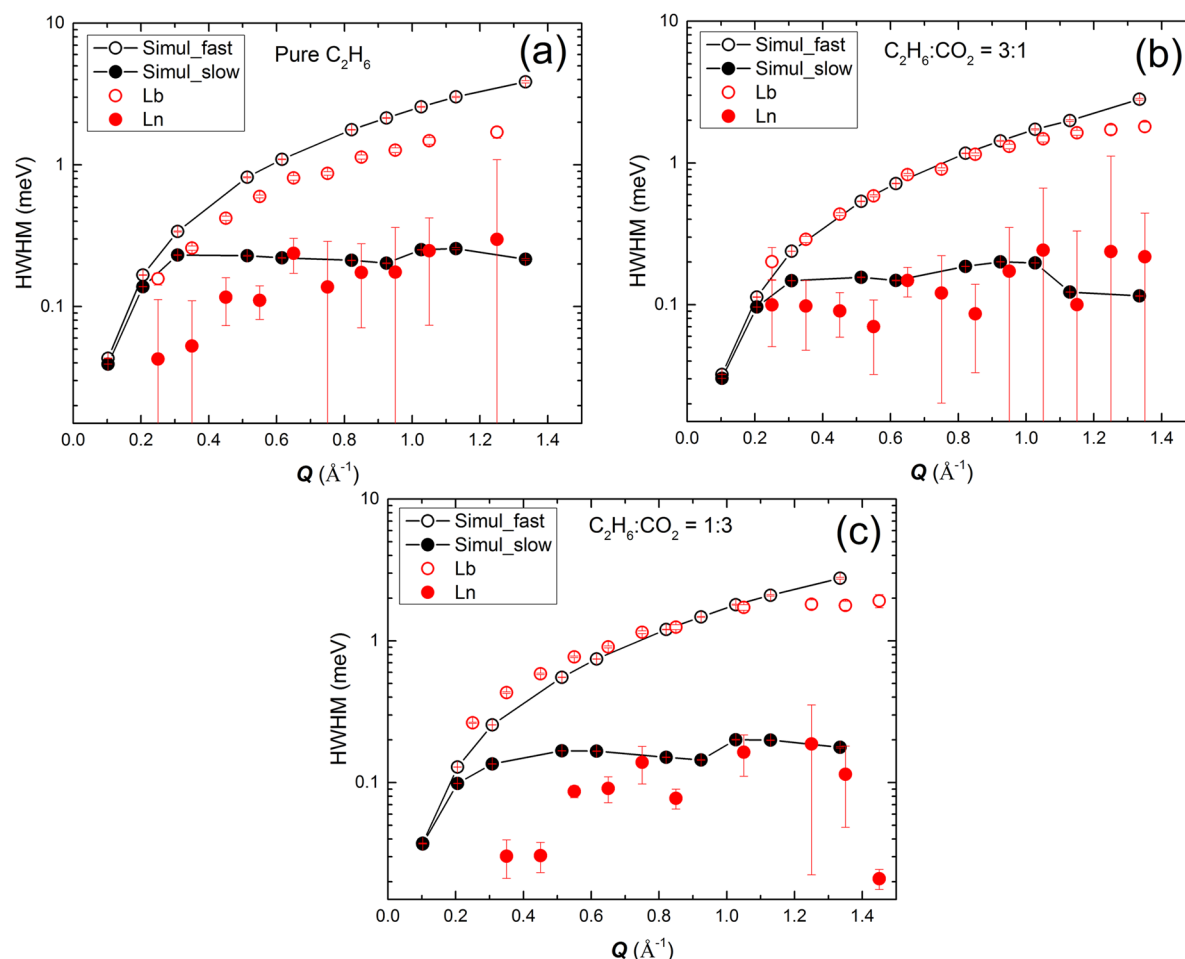


FIG. 6. Energy scale comparison of the QENS-derived data and MD simulation data at 65 bars for the compositions of pure (a), 3:1 (b), and 1:3 (c). All the error bars are shown in red. “Lb” and “Ln” denote the “Lorentzian-broad” and “Lorentzian-narrow” in Fig. 1, i.e., the fast and slow components, respectively.

slopes on the layer specific $\ln[\text{OISF}]$ are close to the fast and slow components determined from the total $\ln[\text{OISF}]$, i.e., -1.90 vs -1.66 and -0.30 vs -0.34 . This finding confirms that molecules in the L1 region mainly exhibit slow motions, while molecules in the L2 region mainly exhibit fast motions.

Figure S13 of the [supplementary material](#) shows the results for the mixtures of 3:1 and 1:3, which are similar to pure C_2H_6 . However, Fig. S13 also shows that L2 can be the primary contributor for both fast and slow motions, while L1 contributes more to slow motion than fast motion.

C. Relationship between the MD-derived TISF, RISF, and OISF

Our simulations suggest that the energy scales of the rotational motion of C_2H_6 are just barely covered by the energy window of the QENS instrument. This is illustrated by the RISF (Fig. S14 of the [supplementary material](#)) and the dipole autocorrelation

function (DACF, Fig. S15 of the [supplementary material](#)). This finding is in contrast to the experimental data, which suggest an absence of contribution from any localized motion (e.g., rotational motion) to the spectra. To probe this apparent contradiction between the experiments and the simulations, it is necessary to understand the relationship among the ISF corresponding to the translational (TISF), rotational (RISF), and overall (OISF) components of motion by MD simulations. Only the “pure” fluid data are considered here for consistency with Figs. 5 and 7. Figure 8 plots the three ISF curves using one representative Q value, as well as the product ($\text{PISF} = \text{TISF} \times \text{RISF}$) and the difference ($\text{DISF} = \text{OISF} - \text{PISF}$). Assuming the independence of the translational and rotational motions, the PISF and OISF should be identical.¹⁰⁶ The OISF and PISF overlap to a significant extent, exhibiting a negligible DISF supporting that the assumption of rotational and translational motion independence is valid. Additionally, in the time range accessible to the instrument, the OISF closely follows the TISF with only a slight perturbation by the RISF. Therefore, even though rotational motions fall within

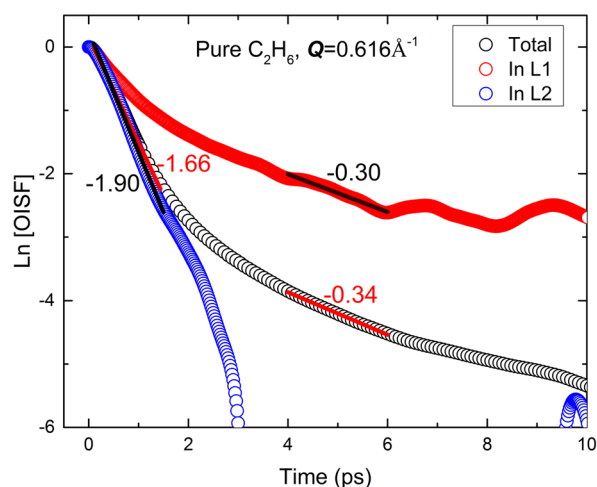


FIG. 7. Total OISF and the layer specific OISF for L1 and L2 at one particular Q value, expressed by $\ln[\text{OISF}]$. The red lines are the linear fitting results for the total OISF, while the black lines are the fitting results for the layer specific OISF.

the instrumental energy window, their contribution to the OISF is negligible and consideration of translational motions is sufficient. Hence, rotation is not expected to contribute much to the experimental spectra. Two other Q values are shown in Fig. S16 of the [supplementary material](#), suggesting similarly that rotation does not contribute significantly to the spectra. We also attempted to linearly fit the $\ln[\text{TISF}]$ and $\ln[\text{PISF}]$ curves, obtaining closer HWHM values to those from the OISF. This comparison is shown in Fig. S17 of the [supplementary material](#).

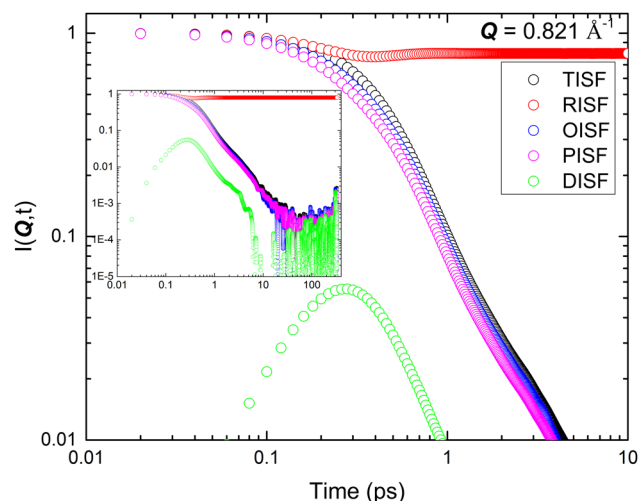


FIG. 8. A comparison between the TISF (black), RISF (red), OISF (blue), and PISF (magenta) for pure C_2H_6 . The light green is the difference of the OISF and PISF. The inset shows a wider range of plot.

VI. CONCLUSIONS

Complementary QENS experiments and MD simulations were carried out to study the structure and dynamics of C_2H_6 in nano-confined environments under non-ambient temperature and pressure conditions. QENS spectra were fit using two Lorentzian functions, yielding two dynamic components that closely match the MD simulation results with respect to the energy scales of the motions. The fast motion exhibits jump diffusion behavior, while the experimental data for the slow motion were difficult to model. Experimental results reflect the hindering effect of high pressure on diffusion dynamics, and both techniques show the enhancement effect of CO_2 (molecular lubrication) on the diffusivity of C_2H_6 . The strength of the lubrication effect of CO_2 depends on the composition of the mixture. A pore size confinement effect, where dynamics is slowed down in smaller pores, is also observed. On the other hand, MD simulations reveal the structure of the mixed fluids in the pores, i.e., CO_2 preferentially adsorbs on the pore wall, while C_2H_6 forms two distinct populations in the remaining space. Of these two populations of C_2H_6 , the molecular behavior in the layer which is more bulk-like and far away from pore wall (L2) dominates the observed dynamics. Molecules moving in the pore wall region (L1) mainly show slower dynamic motions, while molecules moving in the L2 region exhibit both fast and slow motions. Thus, two techniques together quantified the structure and dynamics of $\text{C}_2\text{H}_6/\text{CO}_2$ mixed fluids in different compositions under confinement. Our results can be used to fill the gap in our understanding of mixed fluids under non-ambient conditions and will be useful for chemical processing and subsurface energy exploration industries.

SUPPLEMENTARY MATERIAL

See the [supplementary material](#) for nano-porous silica material characterization, EISF results of the confined C_2H_6 fluid, HWHM results of confined fluids under 30 bars and 100 bars conditions, the discovery of a faster component in the system represented by the background variation with Q values, and additional structure and dynamic properties of the C_2H_6 and CO_2 fluids in nanopore confinement.

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Authors declare that there is no conflict of interest.

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