# Local Rearrangement in Adsorption Layers of Nanoconfined Ethane 

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#### Abstract

Fluids under nanoconfinement control many environmental and engineering processes. In particular, nanoconfined ethane commonly occurs in hydrocarbon production and gas separation applications. While previous research has measured the pore critical properties and self-diffusivity of nanoconfined ethane, the relationship between molecular organization and phase behavior in nanoporous media persists as a knowledge gap. Through experimental adsorption measurements and molecular dynamics simulations, we report the impact of pore wall proximity, pore size, and temperature on the structure of nanoconfined ethane. We offer evidence for an energetically favorable rearrangement of ethane molecules in the adsorption layer that may contribute to more accurate gas-in-place estimates and more efficient design of gas separation membranes.




## - INTRODUCTION

Numerous environmental and engineering applications depend on the phase behavior and dynamic response of nanoconfined fluids in both synthetic and natural nanoporous materials, such as catalysts, adsorbents, and membranes. ${ }^{1-6}$ Furthermore, fluids commonly occur in nanoporous media in nature, including in the subsurface,, ${ }^{4,7}$ in biological systems, ${ }^{8,9}$ and during cloud formation in the atmosphere. ${ }^{10}$ In particular, the focus of this work is on the physical properties of nanoconfined ethane, which are of great importance to many chemical, ${ }^{11-13}$ energy, ${ }^{4,14}$ and engineering processes. As the second most abundant component of natural gas, ethane is an economically valuable fuel. ${ }^{14}$ This fuel is increasingly produced from unconventional formations that are comprised of tight rocks with pore diameters on the order of 1 nm to $100 \mathrm{~nm} .{ }^{4}$ Moreover, the ethane-ethylene separation in porous membranes is a key step in the production of plastics and other polymers. ${ }^{13}$ Commonly, these membranes have pore size distributions that span the nanometer to micrometer range. Both of these applications require knowledge of how the structural response of ethane changes under confinement, especially near the pore walls. While the onset of capillary condensation and the pore critical temperature for various pore sizes have been measured, ${ }^{15,16}$ the fundamental mechanisms that lead to this phase transition remain active area of research. Moreover, because the molecular orientation affects gas transfer behavior in nanoporous membranes, ${ }^{17}$ differences in molecular orientation represent a critical consideration in designing selective molecular sieving membranes. ${ }^{18}$ Here, we investigate what the relationship is between phase behavior and molecular
organization, and how confinement affects such organization of ethane molecules.

Early studies of the phase behavior of small alkanes in model porous materials focused on understanding the shape of the hysteresis loop and quantifying the adsorption capacity for mesoporous silicas. ${ }^{19,20}$ Because the phase behavior of nanoconfined ethane impacts its local thermodiffusive properties, such characterization is of great importance to understanding the processes that control fluid transport under confinement. ${ }^{15,21}$ Previous studies have shown that pure ethane diffuses more slowly near the pore walls than near the pore center. ${ }^{21,22}$ Moreover, co-solvents such as carbon dioxide ${ }^{21}$ and ethylene ${ }^{13}$ have been shown to influence this diffusivity due to selective adsorption on the solid substrate. In this paper, we combine experimental measurements and numerical simulations to identify the fundamental interfacial phenomena that lead to changes in the local thermodiffusive properties. We demonstrate that, near the walls of quartz nanopores, ethane undergoes a quasi-2D rearrangement into an energetically favorable liquid phase with an enhanced structure.

## EXPERIMENTAL METHODS

For the experimental measurements, two porous silica samples were used: a homemade silica sample (see Supporting

[^0]

Information for the synthesis procedure) and a commercially procured AGC-40 silica sample (Advanced Glass \& Ceramics, $L L C$ ). Both samples were characterized following the same adsorption-desorption procedure with cryogenic $\mathrm{N}_{2}$ and via Brunauer-Emmett-Teller (BET) analysis, ${ }^{23}$ as shown in Figure 1a-d. Furthermore, Barrett-Joyner-Halenda (BJH)

transitions in samples created by mechanically mixing MCM-41 silicas with different pore sizes compared to the phase transitions measured in MCM-41 samples with a single pore size. Notably, in the current experiments, the adsorption isotherms are continuous and do not exhibit a discontinuous jump in adsorbed gas amount, which is characteristic of capillary condensation.

To analyze the phase behavior of ethane in these porous silica samples, we performed adsorption experiments with a magnetic suspension microbalance instrument (MSB, Rubotherm IsoSORP ${ }^{\circledR}$, Germany). This instrument (shown in Figure 1e) weighs the sample by measuring the force between the electromagnet and the permanent magnet, which maintains the sample in a freely suspended state. This contactless approach allows for measurements in a variety of gas atmospheres and for experimental conditions that span wide temperature and pressure ranges. In the current experimental study, we focused on conditions relevant to unconventional formations, i.e., we performed adsorption measurements between 293 K and 323 K along an isobar of 35 atm in the homemade sample and between 285 K and 323 K along an isobar of 31 atm in the AGC-40 sample.

## ■ MOLECULAR SIMULATIONS

To interpret the experimental data and to identify the fundamental interfacial phenomena that control any phase transitions in the porous samples, we also employed a combination of grand-canonical Monte Carlo (GCMC) and molecular dynamics (MD) simulations. GCMC simulations sample the grand-canonical $(\mu V T)$ ensemble, where the chemical potential, $\mu$, may be expressed as a function of the pressure, $P$, which was controlled in the experimental setup: ${ }^{27}$

$$
\begin{equation*}
\mu=k_{\mathrm{B}} T \ln \left(\frac{\phi P \Lambda^{3}}{k_{\mathrm{B}} T}\right) \tag{1}
\end{equation*}
$$

where $k_{\mathrm{B}}$ is the Boltzmann constant, $T$ is the temperature, $\phi(T$, $P)$ is the fugacity coefficient for ethane, and $\Lambda$ is the de Broglie thermal wavelength:

$$
\begin{equation*}
\Lambda=\sqrt{\frac{h^{2}}{2 \pi M k_{\mathrm{B}} T}} \tag{2}
\end{equation*}
$$

Here, $h$ is Planck's constant and $M$ is the molecular mass of ethane. Employing these relations, we calculated the chemical potential that was used as input for the GCMC simulations when investigating the phase behavior of ethane in cylindrical quartz pores along the isobar of 35 atm . We simulated systems at temperatures between 80 K and 400 K , running each simulation for at least $10^{7}$ Monte Carlo iterations or until density convergence was observed. The quartz pores had diameters between 1 nm and 20 nm , a range that spans the pore size distribution measured in the experimentally tested samples. The interactions between particles were represented using the TraPPE-UA force field for ethane ${ }^{28}$ and ClayFF for the $\mathrm{SiO}_{2}$ pores. ${ }^{29}$ These simulations were performed using the LargeScale Atomistic/Molecular Massively Parallel Simulator (LAMMPS) software package, ${ }^{30,31}$ and the setup details are presented in the Supporting Information.

## RESULTS AND DISCUSSION

The excess adsorption measurements for both the homemade silica and the AGC-40 samples are presented in Figure 2a, with the excess adsorbed amount increasing for smaller pore


Figure 2. Phase behavior of nanoconfined ethane. (a) Excess adsorption measured in adsorption experiments and computed from grand-canonical Monte Carlo (GCMC) simulations. (b) Average density of nanoconfined ethane in GCMC simulations (35 atm) as a function of temperature for a range of pore sizes. The vertical dashed lines represent the temperature conditions for the transverse density profiles in Figure 3 . Shaded regions in both panels corresponds to one standard deviation in simulation data. Experimental error bars represent the variation during the last hour of measurement.


Figure 3. Transverse density profiles of nanoconfined ethane at 35 atm in (a) 4-nm, (b) 8-nm, and (c) 20-nm pores. First adsorption layer (shaded in blue) persists to high temperatures. Second (shaded in orange) and further adsorption layers grow at lower temperatures. Profiles have been averaged axisymmetrically.
diameters. These results agree with observations from the literature that the excess adsorption is more substantial in smaller pores. ${ }^{32}$ Notably, Figure 2a shows no sign of capillary condensation. The excess adsorption of ethane decays continuously with increasing temperature in both samples beyond the point of first-order phase transition in bulk ethane: unconfined ethane boils at 290.4 K along the isobar of 35 atm and at 284.9 K at 31 atm . The interfacial processes behind this suppressed first-order phase transition in the porous samples were examined via GCMC and MD simulations.
The phase behavior of the GCMC simulations is also shown in Figure 2, where Figure 2a confirms that the simulated systems capture the phase behavior that was experimentally measured. The excess adsorption, $\Gamma_{\text {ex }}$, in the simulated systems was calculated as:

$$
\begin{equation*}
\Gamma_{\mathrm{ex}}(T)=\frac{\psi V}{A}\left[\rho(T)-\rho_{B}(T)\right] \tag{3}
\end{equation*}
$$

where $\rho(T)$ is the volume-averaged fluid density inside the pore from GCMC simulation, $\rho_{B}(T)$ is the bulk fluid density as given by NIST, $V$ is the pore volume, and $A$ is the pore surface area. In order to assess the porosity, $\psi$, of the simulated systems, we followed the approach of Yun et al. ${ }^{20}$ and determined the porosity value by fitting the simulation data to the experimental measurement at the lowest available temperature, where the adsorbate density represents the capacity of the adsorbent. The
agreement in the remainder of the excess adsorption curves suggests that the physical properties of nanoconfined ethane are only marginally impacted by the amorphous nature and by the connectivity of the pore network in the experimentally tested samples, two properties that were not modeled in the molecular simulations. The deviation between the experimental data point at 323 K and 35 atm likely stems from these two properties that differ between the homemade silica sample and the model system. Previous research ${ }^{33}$ has shown that pore connectivity may impact the excess adsorption in disordered materials. Similar reports ${ }^{26}$ were made on the impact of multimodal pore size distributions. Because the homemade silica sample was synthesized from spherical silica beads, the pores in this sample have a broader pore size distribution than in the AGC-40 sample (see Figure 1a-c) and they connect to each other in a complex topography. In contrast to this sample, the model used in the molecular simulations considers a single cylindrical pore with a prescribed diameter. Performing simulations on a realistic sample that could capture the impact of pore connectivity is prohibitively expensive with the current methods.

Furthermore, Figure 2b demonstrates the convergence toward bulk-like behavior. In the smallest pores $(d=1 \mathrm{~nm})$, inefficient molecular packing prevents the system to reach high liquid densities at low temperatures and this density slowly decreases at high temperatures. In contrast, in the largest pores ( $d=20 \mathrm{~nm}$ ), a relatively sharp gradient in average density is


Figure 4. Radial distribution functions of nanoconfined ethane. The impact of (a) pore wall proximity, (b) pore diameter, and (c) temperature is examined. (inset) Side-view snapshot of how molecules are delineated among the three regions for a 8 -nm pore at 275 K .
observed as the temperature increases. This observation agrees with the findings of Pitakbunkate et al., ${ }^{34}$ who reported that the critical temperature and pressure of confined ethane asymptotically approach the bulk values in pores with diameter of 15 nm or larger. However, these average densities obscure the fundamental changes that occur during the pore-filling process.
To quantify the structural behavior, we represent the density as a function of the wall-normal distance, $R$, i.e., in the form of transverse density profiles (TDPs). These profiles, whose representative examples are shown in Figure 3, indicate that high-density adsorption layers form near the pore walls for the whole range of examined temperatures in this study. The number of adsorption layers depends on both pore size and temperature. Because the examined pore sizes are on the order of several molecular diameters, the pore size imposes a physical upper bound on how many adsorption layers can form in this space. In contrast to this static upper bound imposed by pore size, temperature acts as a tuning knob for the number of adsorption layers. As temperature is lowered, additional layers form towards the pore centerline, eventually leading to a porefilling process. Because closely packed molecules may have electron cloud overlap that shields nuclear spins from applied magnetization, ${ }^{35}$ these high-density adsorption layers that persist to high temperatures may offer an explanation for the peak broadening that was reported in the literature for nuclear magnetic resonance spectroscopic measurements of nanoconfined ethane. ${ }^{36}$ Moreover, as expected based on the average density curves, in small pores (e.g., 4 nm in Figure 3a), the pore filling occurs gradually as temperature is lowered. In contrast to this gradual pore filling, the change in centerline density exhibits steeper gradient in large pores (e.g., 20 nm in Figure 3c). It is important to note that adsorption layers that are closer to the wall impose additional energy potential that may contribute to the formation of additional adsorption layers, ${ }^{37}$ if enough ethane molecules are present in the system. The density of each additional adsorption layer decreases due to the weaker interaction potential among ethane molecules than between ethane molecules and the quartz wall. This coupled relation between the presence of adsorption layers and the ethane density in the pores suggests that understanding the interfacial properties of adsorption layers is key to elucidating the mechanisms that lead to the pore-filling process that was experimentally observed.

To define an adsorption layer, we use the approach of Siderius et al. ${ }^{38}$, i.e., each adsorption layer is defined as the distance between two minima in the TDP at 180 K for a given pore diameter. The temperature of 180 K was chosen as a reference because at this temperature well-defined adsorption layers fill
the entirety of pores smaller than 4 nm in diameter. This definition yields adsorption layers with thickness of approximately one kinetic diameter of ethane ( 0.44 nm ). In the current study, we focus on examining the structural response of the first and second adsorption layer, as counted from the pore wall, and the fluid beyond the first two adsorption layers is treated as if it belongs to the core region of the pore. The first and the second adsorption layer are shown by blue and orange shading, respectively, in Figure 3. Notably, the thickness of the first adsorption layer is consistently greater by approximately $10 \%$ than that of the second adsorption layer. This difference originates from the surface roughness on the pore walls (Supporting Information, Figure S1) and, as such, may be influenced by the surface functionalization in various porous media. ${ }^{39}$

The structure of nanoconfined ethane in each of the three regions (i.e., first adsorption layer, second adsorption layer, and core) is characterized through the radial distribution functions (RDFs), $g(r)$. These correlation functions describe the local density variation of molecules in a fluid system around an average molecule in the system. A statistical description of the fluid structure is useful in calculating thermodynamic properties and understanding the local packing. To calculate the RDF from the intermolecular distances, $\mathbf{r}$, we performed an ensemble average over the count of molecules in spherical shells around each fluid molecule with OVITO: ${ }^{40}$

$$
\begin{equation*}
g(r)=\frac{1}{N^{2}} \sum_{i=1}^{N} \sum_{j \neq i}^{N}\left\langle\delta\left(\mathbf{r}-\left|\mathbf{r}_{j}-\mathbf{r}_{i}\right|\right)\right\rangle \tag{4}
\end{equation*}
$$

Here, $N$ is the total number of molecules in the system. In order to obtain a well-converged RDF, we replicated the final state of the GCMC simulations along the pore axis to obtain systems that contain at least 7,500 ethane molecules in the core region. This requirement resulted in systems with pore length between 32 nm and $1,845 \mathrm{~nm}$. Because periodic boundary conditions are used in the axial direction, no size effects are expected from this variation in pore length. By employing MD simulations, we equilibrated these new systems in the canonical ( $N V T$ ) ensemble. Statistics were collected during the last 60 ps of simulation time. Because we are investigating the structure of nanoconfined ethane, where fluid molecules are limited in their motion by the pore walls, we must account for excluded volume effects on the RDF. A correction for these effects was first proposed by Soper ${ }^{41}$ who found that the excluded volume effects on the RDF are especially important when the confining body and the fluid molecules are of similar dimensions. As outlined in the Supporting Information, we employed these


Figure 5. Average potential energy per molecule. (a) In core region, change in slope indicates phase transition at approximately 275 K. (b) In second adsorption layer, a phase transition is still noticeable. (c) In first adsorption layer, molecular potential energy increases linearly with temperature. Slope is same as for liquid-like regimes in core region and second adsorption layer.


Figure 6. Molecular orientation of nanoconfined ethane. (a) Schematic definition of orientation angle. Blue star is pore center; blue dashed line is the wall-normal vector, $\hat{u}$, and red dotted line is the molecular axis vector, $\hat{a}$. $(\mathrm{b}-\mathrm{f})$ Distributions of molecular orientation angles as function of proximity to wall, pore diameter, and temperature.
relations to correct the measured RDFs. ${ }^{41,42}$ Direct comparison of our results with an experimentally measured RDF of ethane at $181 \mathrm{~K}^{43}$ (Supporting Information, Figure S2) confirms the ability of the employed force field to accurately capture the local structure of ethane. By removing the impact due to excluded volume effects, any change in the RDF is due to physical processes that directly alter the local structure of nanoconfined ethane.

The impact of the pore wall proximity, pore diameter, and temperature are examined in Figure 4. Specifically, Figure 4a demonstrates the change of the RDF with pore wall proximity, indicating that the local structure is substantially enhanced in the first adsorption layer compared to the core region. This enhancement includes two aspects: (i) increasing number of ethane molecules in the first coordination shell between $4 \AA$ and $6 \AA$ from each fluid molecule compared to the far-field average density in this first layer; and (ii) formation of a second coordination shell evidenced by the appearance of a second peak in the RDF at approximately $9 \AA$ away from any molecule. We hypothesize that this enhancement of the local structure of nanoconfined ethane is due to fluid-wall interactions that control the organization of fluid molecules by altering the energy landscape. This hypothesis implies that the structural response of a fluid that is sufficiently far from the wall (i.e., in the core region) should not be impacted by the pore diameter, if the RDF
is appropriately corrected for excluded volume effects. Indeed, this behavior is observed when we compare the RDF of ethane molecules in the core region at a constant temperature for a variety of pore diameters in Figure 4b. The invariance in local structure of nanoconfined fluid with pore diameter persists for the examined range of temperatures. However, each temperature exhibits a unique RDF as shown in Figure 4c. In particular, as the temperature decreases the location of the first peak shifts to a smaller distance $r$, suggesting that at higher temperatures each molecule occupies a greater volume that prevents its nearest neighbors from approaching it. Moreover, we once again observe the same two trends as with the pore wall proximity: (i) the relative peak intensity grows and (ii) secondary and tertiary peaks appear as the temperature decreases. Based on these parallels between the variation of the local structure for nanoconfined fluid with increasing pore wall proximity and with decreasing temperature, we conclude that ethane in the adsorption layers undergoes a quasi-2D rearrangement to a liquid-like state alike the molecular rearrangement that accompanies phase transitions in bulk fluids. To examine the extent of this rearrangement, we analyze the molecular potential energy within the system.

To calculate the molecular potential energy, $E_{\text {pot,mol }}$ we consider all interactions among fluid molecules and between fluid molecules and the quartz substrate. These interactions are
defined based on the Lennard-Jones potential, ${ }^{28,29}$ in accordance with the simulation methodology (see Supporting Information). When the average molecular potential energy in the core region and in the second adsorption layer is plotted against temperature (Figure 5a,b), a transition, expressed as a slope change, is observed at approximately 275 K . This transition is especially pronounced in the core region. At temperatures beyond this transition, the average molecular potential energy in the core region remains invariant with change in temperature. This behavior implies that at 300 K and higher, ethane molecules that are sufficiently far away from the pore walls behave as dilute gas with minimal interactions with other fluid molecules. In contrast to this behavior, the average molecular potential energy in the first adsorption layer shows a linearly increasing trend with increasing temperature, as demonstrated in Figure 5c. The slope of this variation is found to be $10^{-2} \mathrm{kcal} /(\mathrm{mol} \mathrm{K})$, which is the same slope that defines how the average molecular potential energy increases with temperature in the core region at low temperatures, i.e., in the liquid-like regime. Based on the Lennard-Jones potential, an increase in the average distance between two neighboring molecules from $4.75 \AA$ to $5 \AA$ would lead to a slope of $10^{-2} \mathrm{kcal} /$ ( mol K ) in the average molecular potential energy. Indeed, Figure 4 c shows a shift of approximately $0.25 \AA$ in the first RDF peak location with temperature, indicating that this variation of $E_{\text {pot,mol }}$ is due to molecular rearrangement. Furthermore, the correspondence of the slopes of $E_{\text {pot,mol }}$ in the first adsorption layer and for the liquid-like regime in the core region supports our observation that the pore walls alter the energy landscape in their vicinity in a manner that encourages molecular organization alike the local structure of the fluid at low temperatures. This quasi-2D molecular rearrangement causes the enhanced local structure that is observed in the RDF of nanoconfined ethane in the first adsorption layer in comparison to the RDF of ethane in the core region.
In order to quantify the structural response that arises from this rearrangement in the adsorption layers, we measure the orientation of ethane molecules with respect to the pore walls. This orientation is examined in terms of the angle $\theta$, which, as shown schematically in Figure 6a, represents the angle between a unit vector along the major molecular axis, $\hat{a}$, and a wall-normal unit vector, $\hat{u}$. When $\theta_{i}=\pi / 2$, molecule $i$ is parallel to the pore wall, and when $\theta_{i}=0$, molecule $i$ is perpendicular to the wall. To remove any ambiguities due to varying system size, we analyze the distribution of molecular orientations, $n(\theta)$, that was normalized such that $\int n(\theta) \mathrm{d} \theta=1$. These distributions are shown in Figure 6b-f. While in the core region, as expected, there is no preferred orientation of ethane molecules, a broad distribution of molecular orientations exists in the adsorption layers. Notably, Figure 6 b shows that ethane molecules are more likely to adsorb parallel to the pore wall. As the distance from the pore wall increases, the population of parallelly oriented molecules decreases as the number of molecules with $\theta<\pi / 4$ gradually grows. While neither pore size, nor temperature have substantial impact on the distribution of molecular orientations in the core region (Figure $6 \mathrm{c}, \mathrm{d}$ ), the influence due to the pore walls varies with temperature (Figure 6f). Namely, the difference in molecular populations that are parallelly and perpendicularly oriented is more pronounced at high temperatures than at low temperatures. This notable delineation likely arises due to the decrease in residence time of ethane molecules in the adsorption layer. The molecules that have the longest residence time are those that are most strongly adsorbed to the pore walls, i.e.,
those molecules that have two methyl groups interacting with the pore wall due to their parallel orientation. Subsequently, these results confirm that the enhanced structure of nanoconfined ethane in the adsorption layers is due to close packing of fluid molecules near the pore wall. This close packing is attributed to the emergence of a preferred orientation among ethane molecules in the adsorption layers.

## ■ CONCLUSIONS

In summary, we performed adsorption measurements of highpressure ethane in porous silica samples and simulated equivalent systems with GCMC and MD simulations. The experiments indicated to a gradual pore filling process without a first-order phase transition between gas-like and liquid-like densities. These observations were interpreted via the simulated systems that provided evidence for a local rearrangement of ethane molecules in the adsorption layer.

Ethane molecules in the first adsorption layer rearrange in a structure like that of liquid ethane. This rearrangement was quantified via RDFs, which demonstrated that the observed nanoconfined ethane rearranges in a similar manner both by decreasing temperature in the core region (gas to liquid transition) and by pore wall proximity at constant temperature (core region to second adsorption layer to first adsorption layer). This rearrangement of the ethane molecules leads to locally enhanced structure and fluid density. The proximity of pore walls maintains minima in the energy landscape of the adsorption layer regions even at high temperatures, therefore enabling this locally enhanced structure to persist. These interactions suppress the phase transition that is reported in the core region, at a greater distance from the pore walls.

The energetically favorable rearrangement of nanoconfined ethane yields a closely packed organization of fluid molecules that are adsorbed parallel to the pore walls. Discovering this rearrangement and identifying its origins in the energetic interactions between ethane molecules and the pore walls is of great significance to the design of engineered gas separation membranes and to shale gas extraction technologies.

## - ASSOCIATED CONTENT

## (s) Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpcc.3c04869.

Porous silica sample synthesis procedure; experimental data analysis protocol; molecular simulations setup and force field parameters; and procedure to correct RDFs for excluded volume effects (PDF)

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## Notes

The authors declare no competing financial interest.

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