Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Molecular Dynamics Simulations of Propane in Nanoslit Silica Pore: Direct Comparison with Quasielastic Neutron Scattering Experiment

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Supplementary Material

Distribution in XY plane close to the pore surface

On an average, the distribution of center of mass (COM) of propane molecules in silica slit pore is homogenous with no visible structure. This is because the region in the pore away from the surface is geometrically very large as compared to the near surface surroundings and in this region, there is no preferred position that a typical molecule would like to occupy. This means that the inhomogeneity in the COM distribution close to the pore surface is suppressed by the homogenous distribution away from the surface making the overall distribution homogenous. However, if we limit the region of interest to a small layer close to the surface, a positional order can be seen. In Figure S1, we have plotted the center of mass position distribution of propane molecules in the XY plane between 2.0 and 2.3 nm. The contour colors represent the total number of molecules that occupy a given position in the XY plane at some time in the simulation. Thus regions colored red represent large instances of molecules occupying that region while blue colored regions had fewer instances of a molecule occupying it. Each pixel in the plots represents a square region with a side of 0.01 nm. At low pressure (left panel) although some structure can be seen, it is difficult to see a positional ordering. However, at higher pressure (right panel) a positional ordering can be seen very clearly. This ordering originates from the crystalline positional ordering of the SiO_2 matrix. At lower pressure, the number of adsorbed molecules is too small to make this ordering clearly visible. Similar to the positional ordering, we have also calculated the orientational ordering by calculating the cosine of the angle made by the CH_3-COM vector with the Z-direction. A value of 1 indicates this vector pointing parallel to the Z-direction, whereas a value of 0 indicates this vector being perpendicular to the Z-direction and hence parallel to the pore surface. These orientational distributions between 2.0 and 2.3 nm in the XY plane are shown in Figure S2. Here again, an ordering is relatively more clearly seen at higher pressure. The origin of this orientational ordering can also be found in the crystalline positional ordering of the pore surface. In a pore with an amorphous SiO_2, this positional and orientational ordering of propane molecules close to the pore might perhaps be absent.

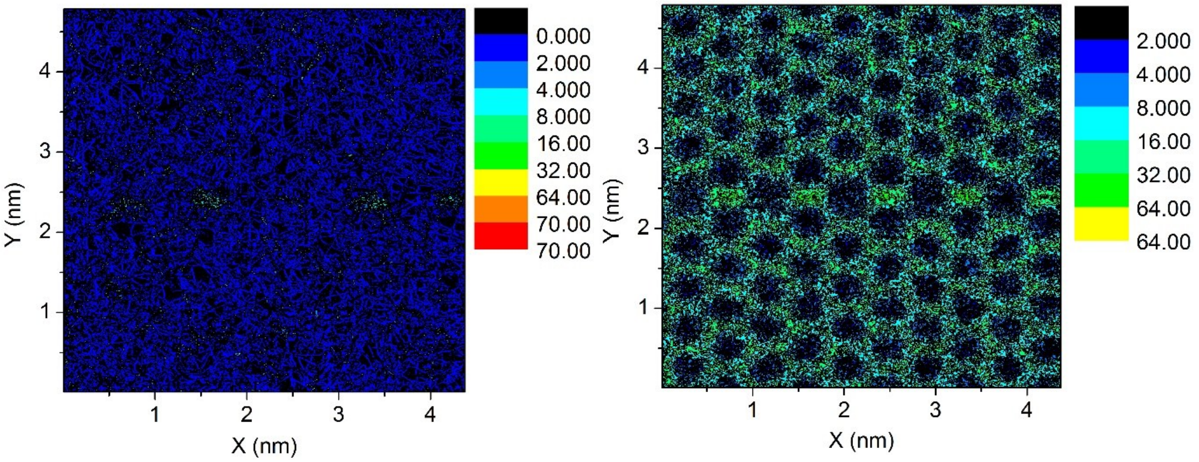

Figure S1. Density profiles of propane in the layer close to one of the pore walls (between 2.0 and 2.3 nm) at 8 bar (left panel) and 58 bar (right panel). A positional ordering can be seen more clearly at higher pressure.

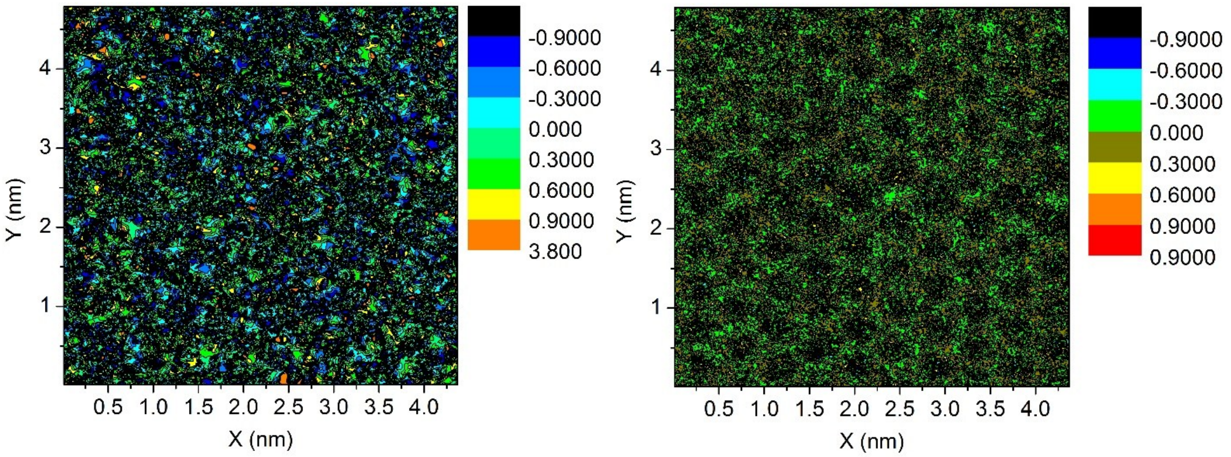

Figure S2. Variation of cosθ (θ is the angle made by CH3-COM unit vector with the Z-direction) close to one of the pore walls (between 2.0 and 2.3 nm) at 8 bar (left panel) and 58 bar (right panel). A slight tendency for orientational ordering can be seen at higher pressure.

Distribution along Z-direction – Distinguishing between two populations of molecules

Trajectories of the center of mass of 5 randomly chosen molecules are shown in Figure S3 for the two pressures at 337 K. It can be seen from these plots that a typical molecule is more likely to traverse the whole pore shuttling back and forth between the two opposite pore walls at low pressure. Compared to that, at higher pressure, a typical molecule remains confined in a narrow portion of the pore and seldom approaches both the opposite pore walls during the whole simulation time of 1 ns. This is because of crowding at higher pressure due to a larger number of molecules. We identified 10 molecules that remain within 0.3 nm (interface) from the pore wall continuously at a time at least for 50 ps. Similarly 10 molecules spending at least 50 ps continuously away from the interface were identified. The latter is easier because of the large geometric size of the pore relative to interface. This identification of 10 molecules each in interfacial and non-interfacial populations was done for both the simulations at 337 K. An example of a trajectory of 1 molecule chosen to represent interfacial population can be seen in Figure S3 for both the simulations, where the time interval when the molecule was present at the interface is highlighted with a green ellipse. Trajectories of the relevant time interval of these chosen molecules were combined to result in trajectories of 10 molecules for 50 ps. Quantities of interest were then calculated from these trajectories to represent the behavior in the two molecular populations.

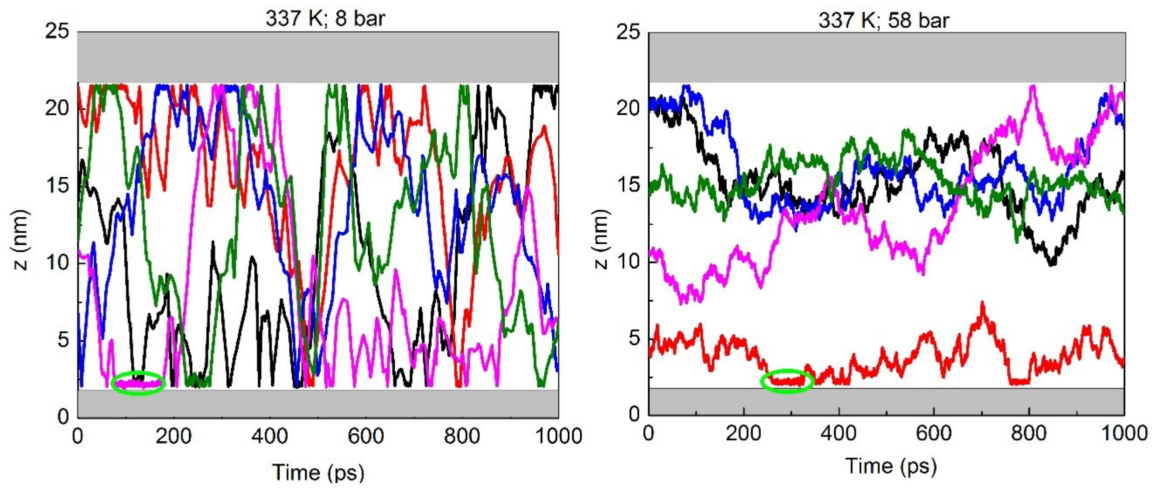

Figure S3 Trajectories in the Z-direction of the center of mass of 5 randomly chosen molecules. The SiO_2 slabs making the slit pore are represented by grey rectangles. Periods of continuous stay of a representative molecule close to the pore wall are highlighted by green ellipses (t ~ 100 - 150 ps for the low pressure and 270 – 320 ps for the high pressure).

Mean Squred Displacement of Interfacial and Non-interfacial molecules

The MSD of these interfacial and non-interfacial molecules is shown in Figure S4. It can be seen that even the molecules that are close to the pore wall have higher displacements at low pressure compared to that at high pressure. This is because of the crowding a typical molecule would encounter at higher pressure. Another interesting result is the duration of ballistic regime. For the higher pressure data, the ballistic regime extends to the same amount of time for molecules close to and away from the pore wall, suggesting that fluid-fluid collisions become equally likely as fluid-surface collisions. At lower pressure though, the ballistic regime persists longer for molecules away from the surface, as the fluid-fluid collisions are less likely to occur in the pore center than the fluid-surface collisions close to the surface. As the time range of these data is limited and the ballistic regime for the non-interfacial molecules at low pressures last up to a major part of this, extracting meaningful values of diffusion coefficients is not possible. An estimate of the effect of interface on the dynamics can be made however, by taking the ratio of MSD of the interfacial to non-interfacial molecules at a given time. At 25 ps, this ratio is found out to be 10.77 at low pressure and 1.55 at higher pressure. It needs to be mentioned here however that a contribution to this large ratio at low pressure comes from the long lasting of ballistic of non-interfacial molecules at low pressure. Another estimate of this effect can be made by comparing the prefactor (k) of t^2 in the relation between MSD and time (MSD = kt^2). The values of this prefactor for the interfacial and non-interfacial molecules is enlisted in Table S1. The value of k for the non-interfacial molecules do not vary with pressure. At higher pressure, the interfacial molecules have a slightly lower value of k whereas this values differs drastically at lower pressures. Thus the effects of interface are strongest at the lower pressure.

Table S1. Translational dynamics parameters for interfacial and non-interfacial molecules at 337 K.

Pressure	Molecule	k (m^2/s^2)	$MSD_{interfacial}/MSD_{non\text{-}interfacial}$ at 25 ps
8 bar	Interfacial	1410.3±10.3	10.77
	Non-interfacial	2245.9±28.2	

58 bar	Interfacial	2128.1±31.9	1.55
	Non-interfacial	2245.9±28.2	

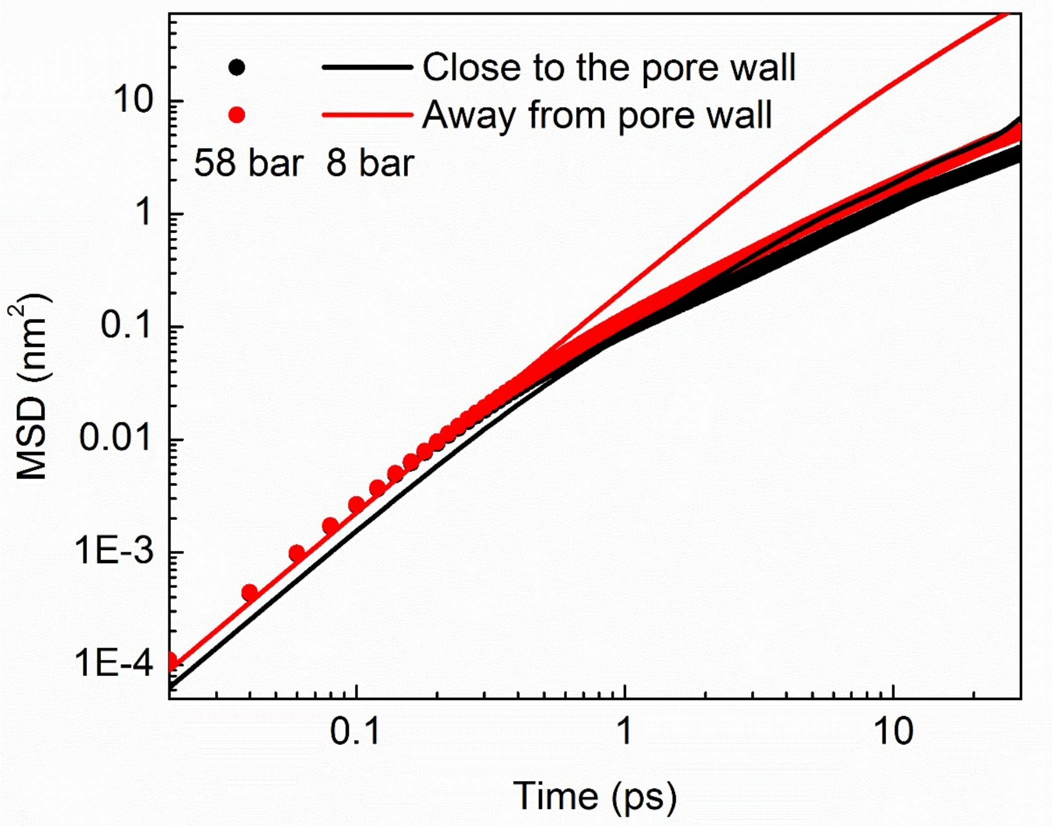

Figure S4. Mean Squared Displacements of the COM of 10 representative interfacial (black) and non-interfacial (red) propane molecules for the two pressures at 337 K. The higher pressure data are denoted by symbols whereas the lines denote the low pressure data.

Orientational Correlation Functions of Interfacial and Non-interfacial molecules

The orientational dynamics of interfacial and non-interfacial propane molecules was probed using the OCF corresponding to the 10 representative molecules from the two populations separately. Figure S5 shows the OCF of the order 1 and 2. At low pressure, a significantly larger change can be seen between the interfacial and non-interfacial molecules. This is evident in the first order OCF that show a conspicuous negative minima for the non-interfacial molecules. The first order OCF can be seen to represent the average value of the angular displacement and the first minimum in these functions can thus represent a measure of maximum angular displacement before a turnaround occurs. In particular, the cosine inverse of the value of the first order OCF at first minimum gives the maximum angle of displacement. This angle is calculated to be 101^0 for non-interfacial and 86^0 for interfacial molecules. The overall behavior of the OCF follow the OCF behavior for non-interfacial molecules. The rotational relaxation times of interfacial and non-interfacial molecules at the two pressures at 337 K are listed in Table S2. A slower decay of the OCF of interfacial molecules signifies a slower rotation as is expected due to the strong fluid-surface interactions. At higher pressure, neither of the two populations of molecules exhibit large angle jumps, however the rotation of interfacial molecules is slightly slower at high pressure similar to that at low pressure.

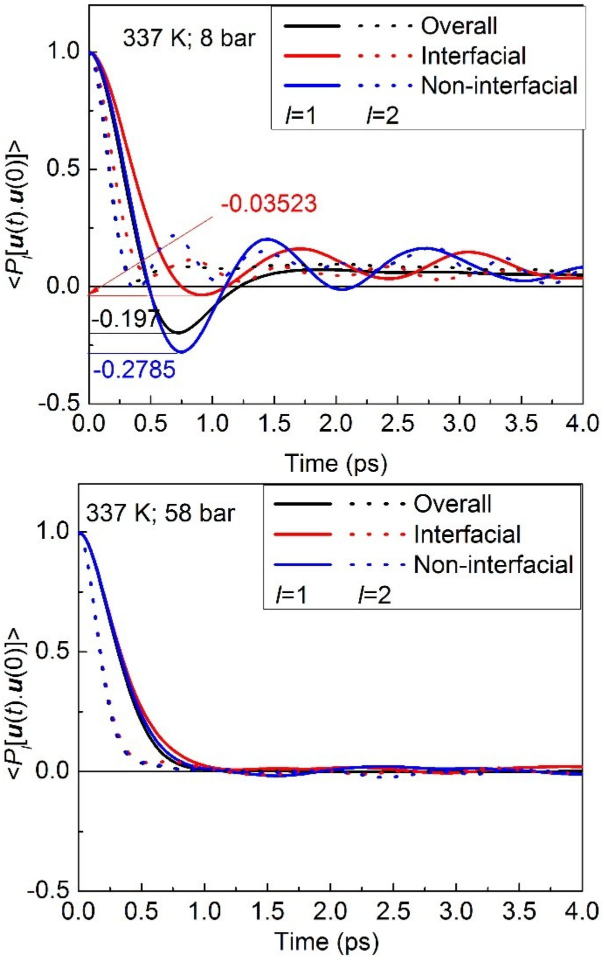

Figure S5. Orientational Correlation Functions in different regions at 337 K for two pressures. The first order functions are shown as solid lines whereas the dotted lines represent the second order OCFs.

Table S2. Time scales of rotational motion for the interfacial and non-interfacial molecules at 337 K.

T; P	τ_1(ps)	τ_2(ps)	τ_1/τ_2
8 bar Interfacial	1.906	1.139	1.673
8 bar Non-interfacial	0.514	1.041	0.494
58 bar Interfacial	0.470	0.151	3.112
58 bar Non-interfacial	0.472	0.146	3.233

RISF for the interfacial and non-interfacial molecules

The RISF calculated for the interfacial and non-interfacial molecules are shown in Figure S6. Although for lower pressure the RISFs for the two layers are not calculated for times long enough to have a stable value, it can be seen that beyond 10 ps, the RISFs for different regions become identical within the statistical uncertainties. This is true also for the RISFs at the two pressures. Thus, there is no change in the EISF values as the pressure or the location of propane molecules is changed. This means that the geometry of rotational motion remains unchanged for all the simulations in all regions of the pore.

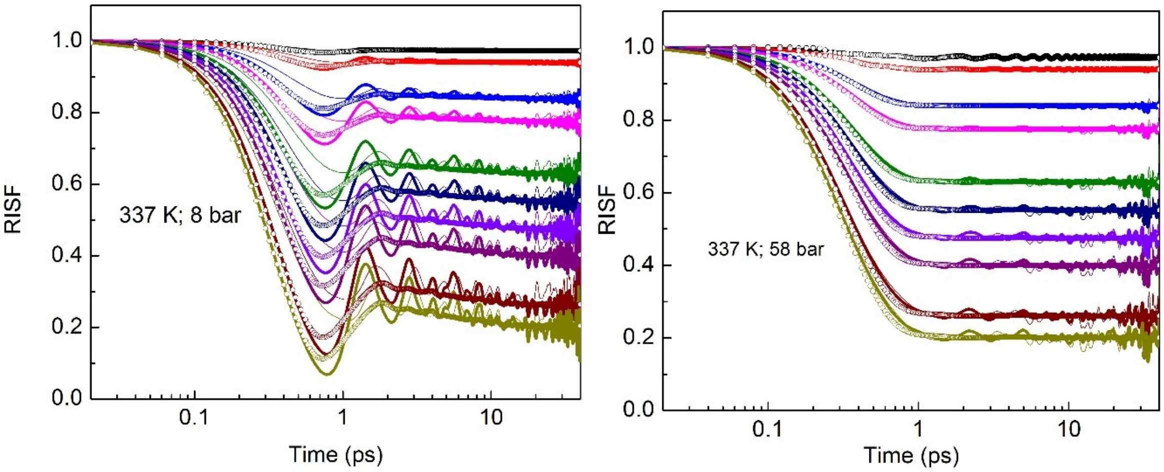

Figure S6. RISF corresponding to different Q values (different colors) between 0.29 and 2.01 Å^{-1} for interfacial molecules (thin lines), non-interfacial molecules (thick lines) and overall (symbols).