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


**Supplementary information:**

# Separation of Water–Alcohol Mixtures using Carbon Nanotubes under an Electric Field

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Figures S1 and S2 show pressures on the piston wall, left graphene wall, and right graphene wall under various external pressures at 0 and 2 V/nm, respectively. The pressures on piston wall and left graphene wall indicate pressure of molecules in the left reservoir. While the pressure on right graphene wall shows pressure by molecules in the right reservoir.

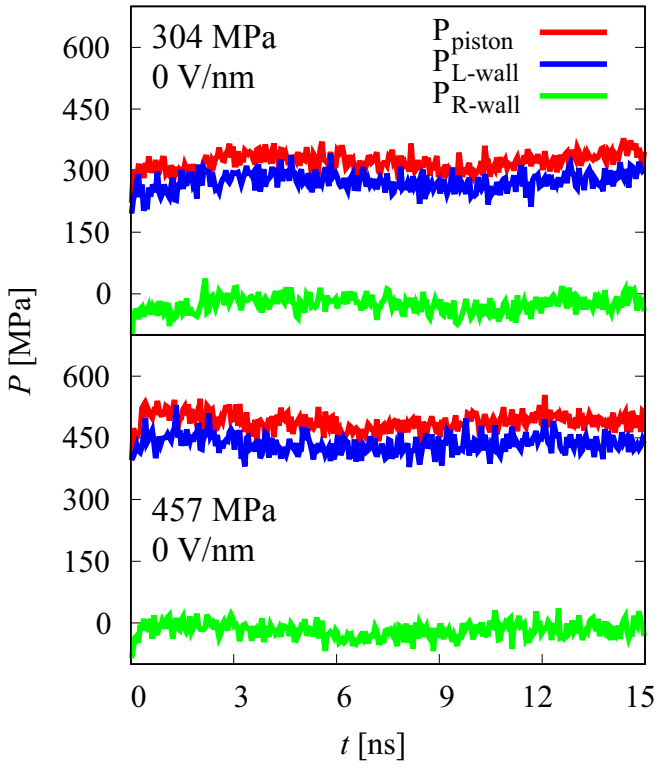


**Figure S1** Pressures on the piston wall, left graphene wall (L-wall), and right graphene wall (R-wall) at 0 V/nm with external pressures of 304 (top) and 457 MPa (bottom).

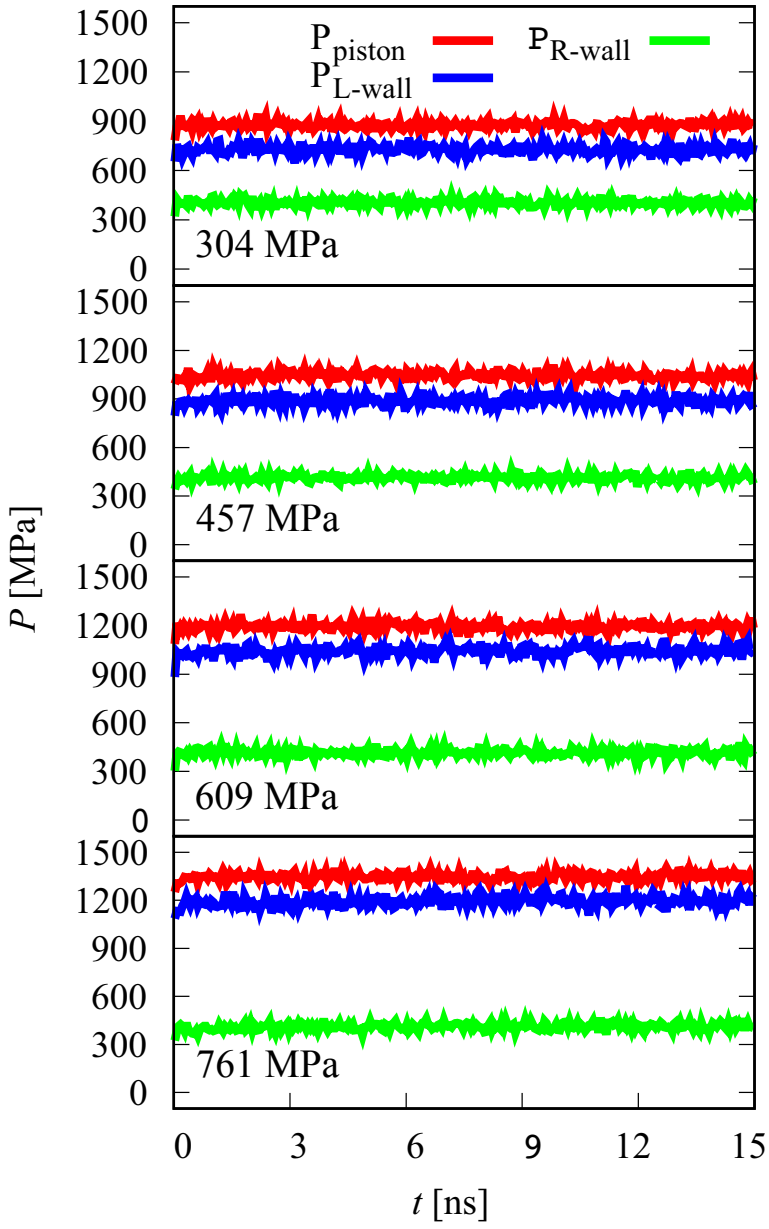


**Figure S2** Pressures on the piston wall, left graphene wall (L-wall), and right graphene wall (R-wall) at 2 V/nm with various external pressures of 304, 457, 609, and 761 MPa.

Density profile in the $z$ direction of the atoms of water and methanol molecules in the reservoirs at 2 V/nm is shown in Fig. S3. $\Delta z$ denotes the distance away from the graphene walls. The negative and positive values indicate the distance from the left and right graphene walls, respectively. The region around the CNT axis was excluded for the calculation, *i.e.*, from $r = 0$ (CNT axis) to $r = r_{CNT}$ (CNT radius) as shown by the white colored area in the inset of Fig. S3. We only considered the molecules in the orange colored region for the calculation of density distribution. Densities of the oxygen and methyl of methanol near the left graphene wall are higher than that of the oxygen of water. This implies that the Lennard-Jones interaction between the methanol molecule and the graphene wall is stronger than that between the water molecule and the graphene. With the higher piston pressure, the density of methanol near the left graphene wall increases.

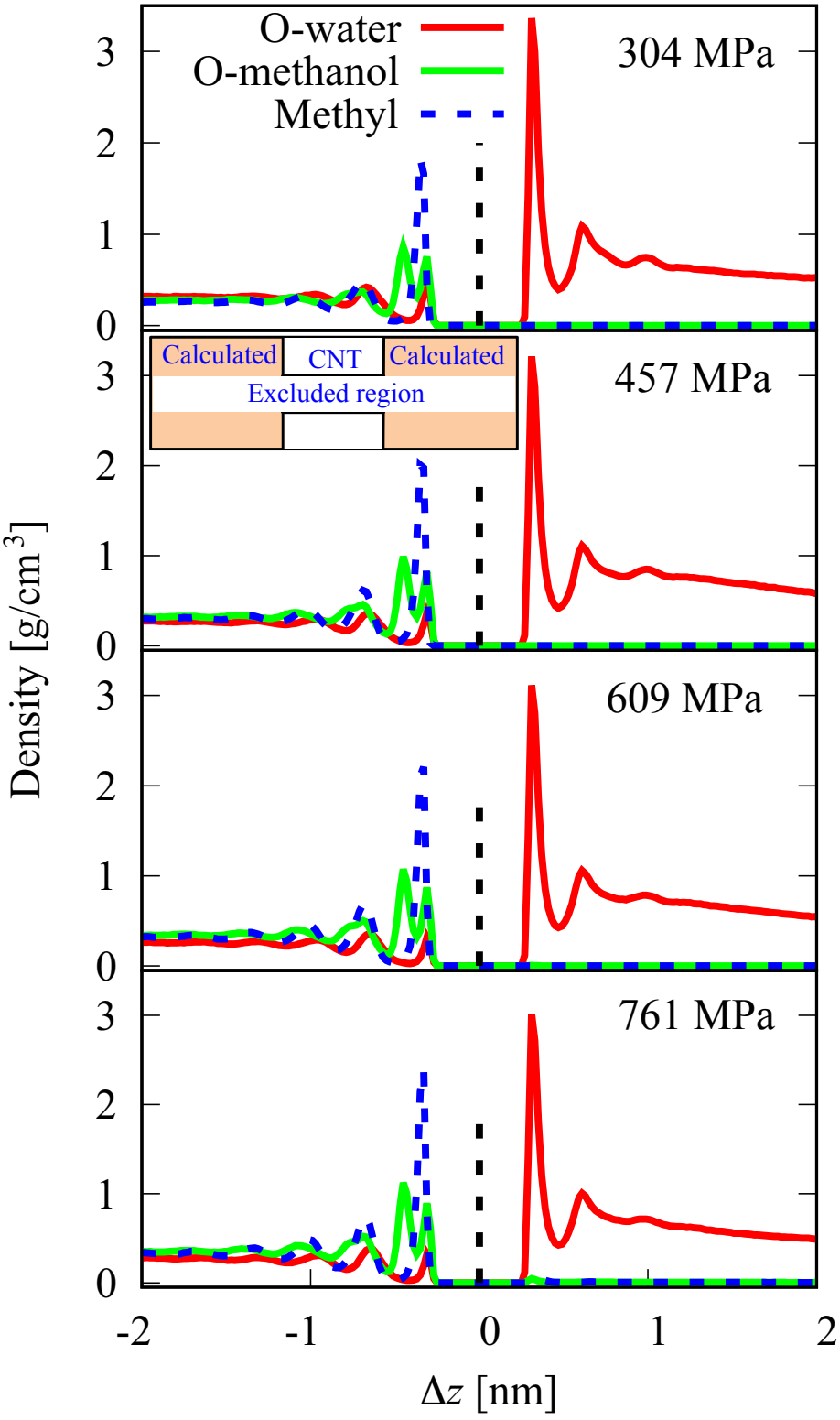


**Figure S3** Density distribution of the atoms of water and methanol molecules along the *z* axis at 2 V/nm and various pressures with (8,8) CNT system. Δ*z* indicates the distance from the graphene walls, where the negative and positive values are the distance from the left and right graphene walls, respectively. The region around the CNT axis (the white area in the inset) was excluded in the calculation. Only molecules in the orange region were considered in the calculation of density distribution.

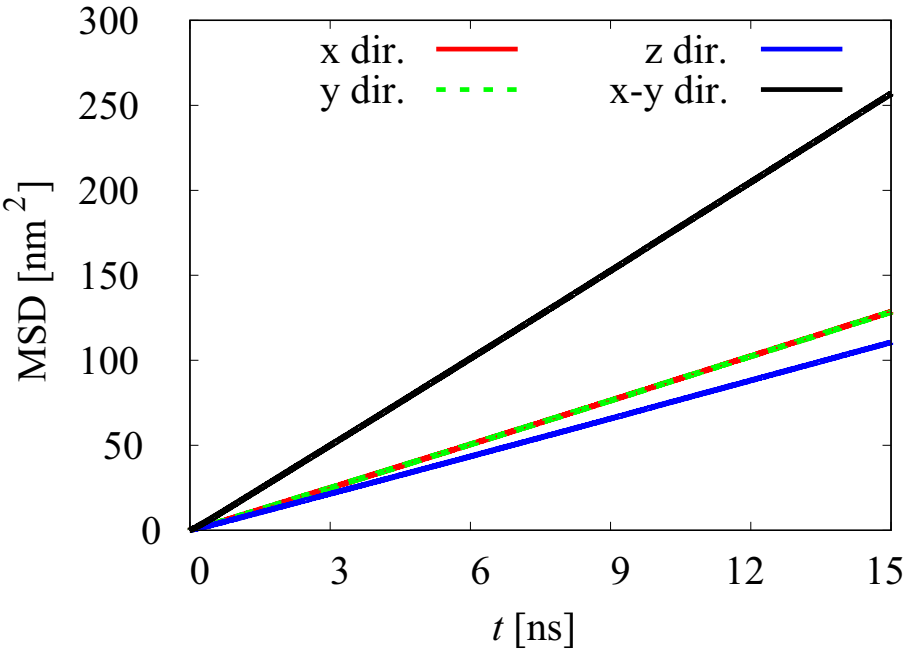


**Figure S4** Mean square displacement (MSD) in *x*, *y*, *z*, and *x* - *y* directions (dir.) of molecules in the left reservoir of (10,10) CNT system at 2 V/nm and external pressure of 304 MPa.

Figure S4 shows the mean square displacement (MSD) of molecules in the reservoir. The slope of the MSD in *z* direction (*z* dir.) is lower than that in *x* and *y* directions. This means that the diffusion constant in *z* direction ($D_z$) is lower than that in *x* and *y* directions ($D_x$ and $D_y$).

Table S1 is the diffusion constants in *x*-*y* and *z* directions of molecules in the left reservoir, *i.e.*, molecules in region between graphene piston and left graphene wall. The simulation system uses (10,10) CNT with 2 V/nm and various piston pressures from 304 to 761 MPa. The pressure affects dynamics of molecules in the reservoir. The diffusion constant decreases as the pressure increases. Diffusion in *z* direction is lower than that in *x*–*y*-direction due to the effect of walls (the piston and the left graphene wall).

**Tabel S1** Diffusion constants in *x*-*y* and *z* directions ($D_{xy}$ and $D_z$ ) of molecules in the left reservoir for (10,10) CNT system under 2 V/nm and various pressures.

| $P$ [MPa] | $D_{xy}$ [$10^{-5}$ cm$^2$/s] | $D_z$ [$10^{-5}$ cm$^2$/s] |
|---|---|---|
| 304 | 4.30 | 3.70 |
| 457 | 3.48 | 2.97 |
| 609 | 2.91 | 2.50 |
| 761 | 2.57 | 2.23 |

Figure S5 shows cumulative molecular pass (CMP) of a system with (8,8) CNT under piston pressure of 457 MPa. The left reservoir was filled with water–methanol mixture at very low water mole fraction, *i.e.*, 0.19. At 0 and 0.5 V/nm, both water and methanol molecules flow from the left to right reservoir through the CNT. Under 0 and 0.5 V/nm, water mole fraction of the CMP at 15 ns is 0.2, which is same as that in the left reservoir. This means no separation effect. In contrast, at higher electric fields of 1 and 2 V/nm only water molecules flow through the CNT while methanol molecules are rejected even through methanol mole fraction in the left reservoir is much higher than that of water. This indicates a high selectivity of CNT to permeate water.

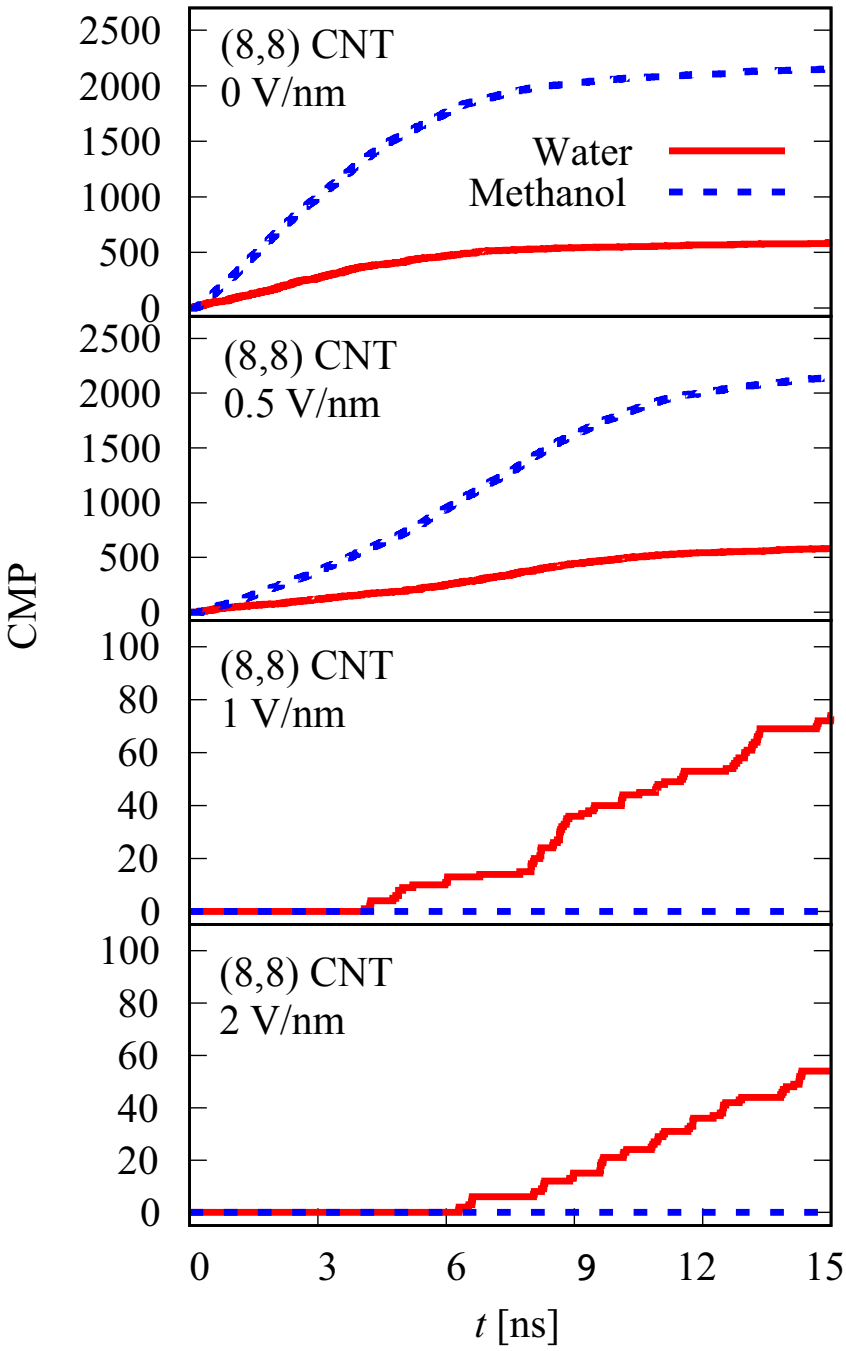


**Figure S5** Cumulative molecular pass (CMP) for (8,8) CNT system with various electric fields from 0 (top) to 2 V/nm (bottom) at piston pressure of 457 MPa. At $t = 0$ ns, water mole fraction in the left reservoir is 0.19.

Water molecules form double-wall structures in (10,10) CNT under 2 V/nm and piston pressure of 457 MPa (see Fig. S6). At higher pressure of 609 or 761 MPa, the structures are similar to those at 457 MPa. The structures are same as shown in previous studies. [1, 2]

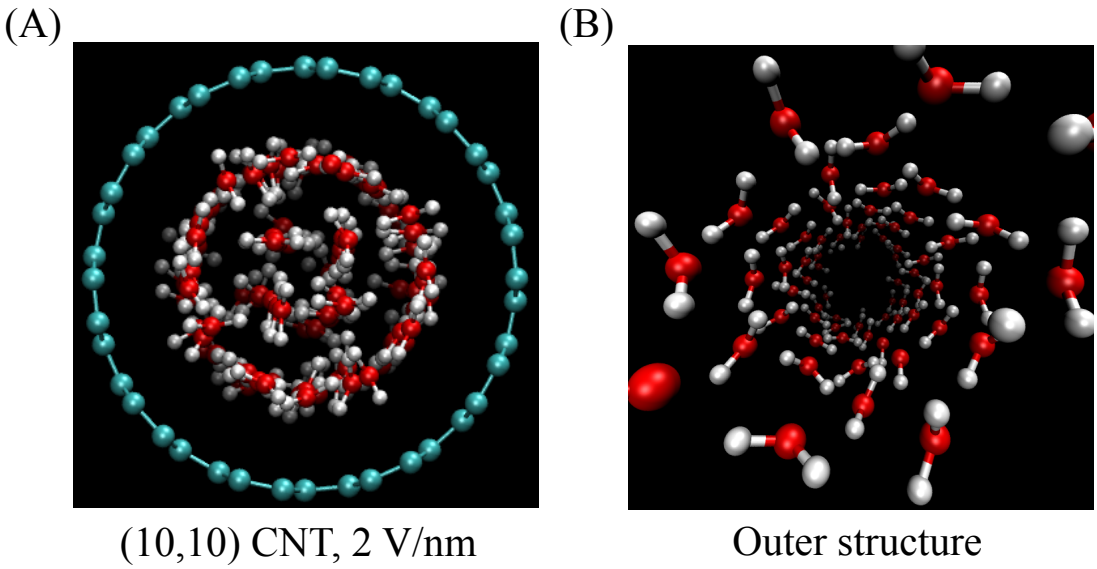


**Figure S6** (A) At 2 V/nm, water molecules in (10,10) CNT have double-wall structures, *i.e.*, inner and outer structures. (B) The outer structure of water molecules in (10,10) CNT with 2 V/nm.

Figure S7 shows structure of molecules in (25,25) CNT at various conditions. With 1 V/nm and 304 MPa, structure of water molecules in the CNT is not sufficiently strong and methanol molecules interrupt the structure (Fig. S7-A). Therefore, both water and methanol flow through the CNT. At higher electric field of 2 V/nm, water structure in the CNT becomes stronger and methanol molecules cannot interrupt the structure (Fig. S7-B). As a result, only water flow through the CNT. At higher pressure of 609 MPa, water structure cannot withstand disruption of methanol molecules and both water and methanol molecules permeate to the right reservoir (Fig. S7-C).

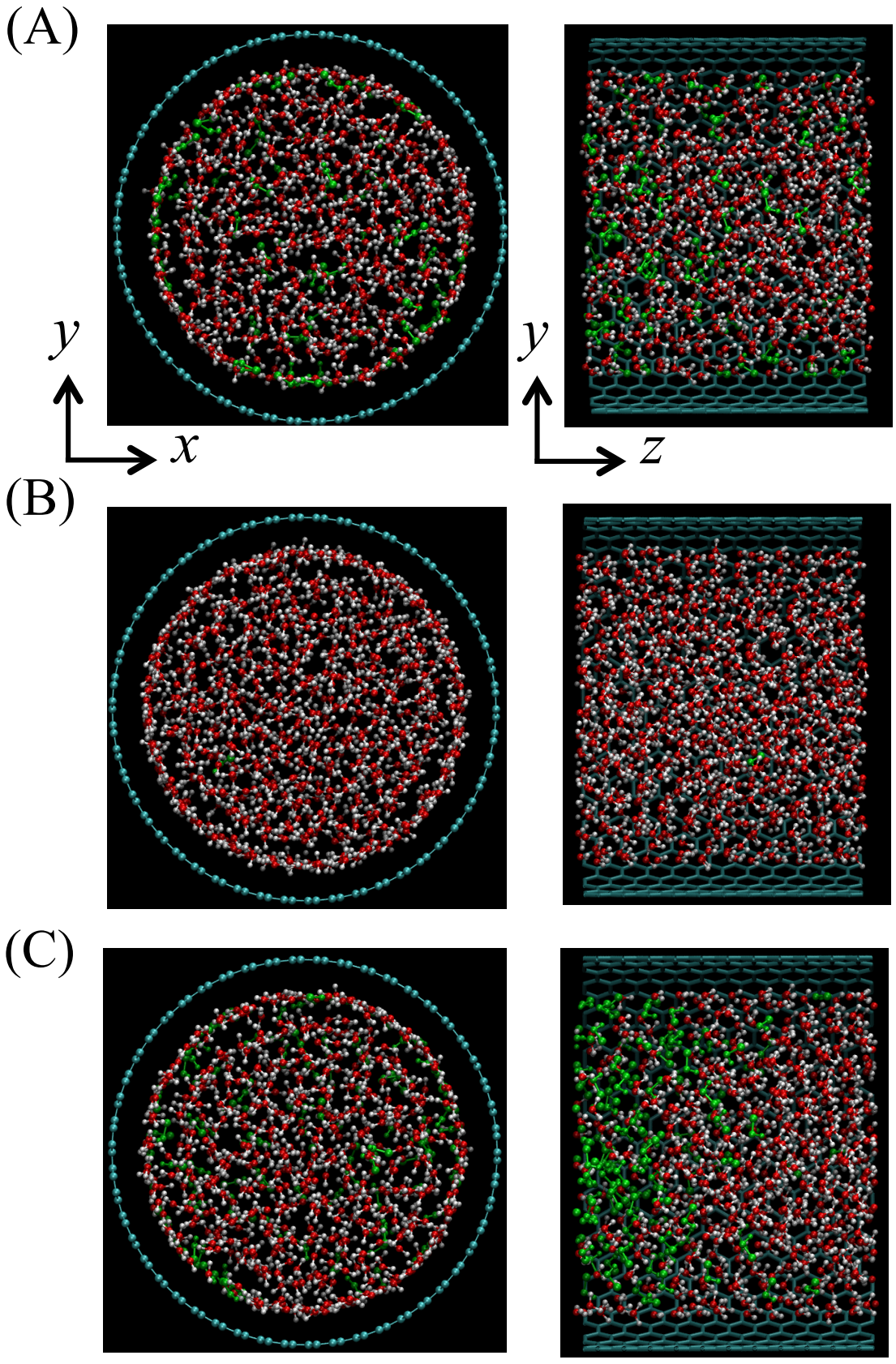


**Figure S7** Structures of water molecules (red and white) and methanol molecules (green) in (25,25) CNT with: (A) 1 V/nm and 304 MPa. (B) 2 V/nm and 304 MPa. (C) 2 V/nm and 609 MPa.

**References:**


1. Winarto, D. Takaiwa, E. Yamamoto, K. Yasuoka, *J. Chem. Phys.* 2015, **142**, 124701
2. Winarto, D. Takaiwa, E. Yamamoto, K. Yasuoka, *Nanoscale* 2015, **7**, 12659