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


**Supporting information for publications**

# Enhanced Fluidity of Water in Superhydrophobic Nanotubes: Estimating Viscosity using Jump-corrected Confined Stokes-Einstein Approach

*Golam Rosul Khan and Snehasis Daschakraborty**

Department of Chemistry, Indian Institute of Technology Patna, Bihar 801106, India

**Corresponding Author**

*Snehasis Daschakraborty*

Email: *snehasis@iitp.ac.in

**S1. Estimation of the Contact Angle:**

After the equilibration period, the center of mass of the droplet was calculated at 2ps intervals along the x-y plane. This information was used to establish the position of the z-axis following the method described by Ruijter et al. To analyze the droplet, two-dimensional (2D) binning was performed. Rectangular binning along the *z*-direction and cylindrical binning along the x-y plane, as previously described by Ruijter *et al.*[1], were used. The rectangular bins had a thickness of 0.2nm, and the radius of the cylindrical bins was determined based on equal volume for each bin. Interfacial points were estimated by fitting the radial density profile at each z-location. The interfacial points and interfacial thickness of the droplets were determined. Least squares fitting was applied to fit the interfacial points on the liquid-vapor interface into a circle, with certain criteria for discarding points close to the surface and with small radii due to density fluctuations. The contact angle of each droplet was then estimated by drawing a tangent line across the liquid-vapor interface from the droplet contact line. The center of the first layer of the graphite surface served as the reference point for contact angle calculations.

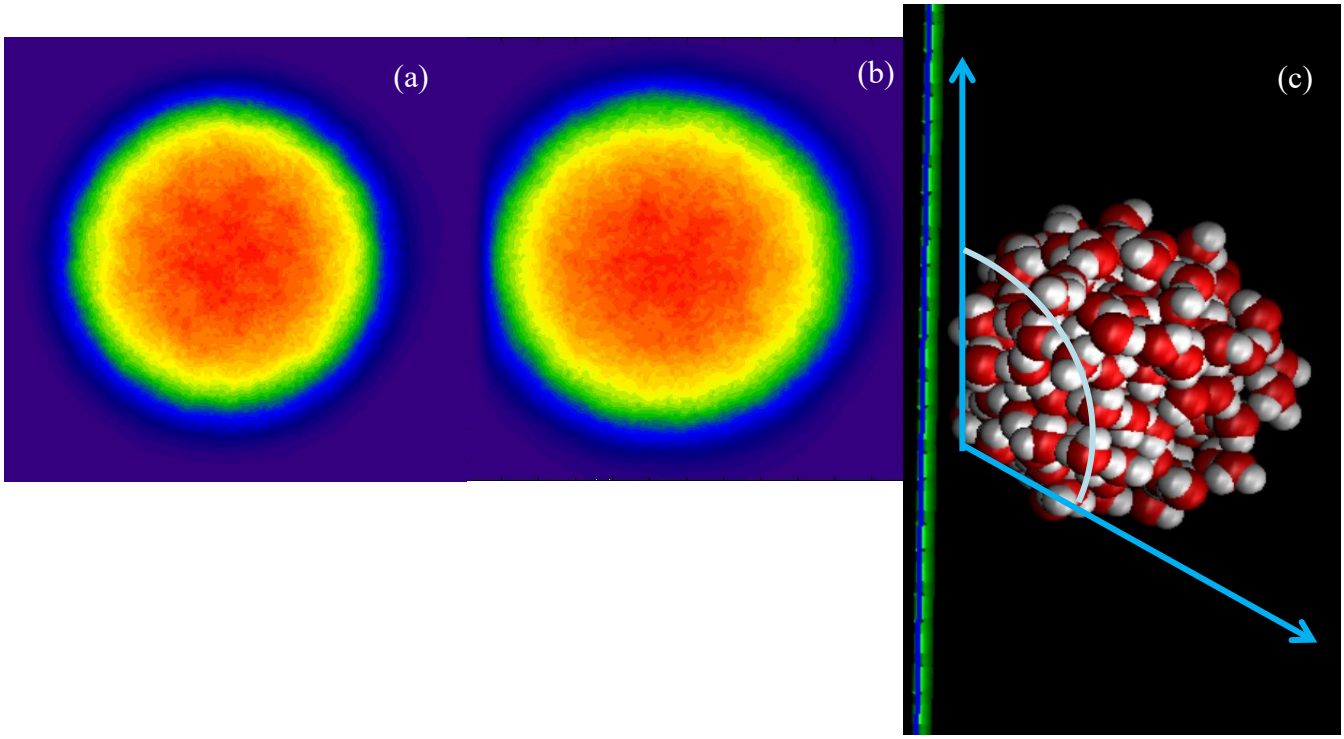


Figure S1. Density profiles of water in graphene sheet shown (a) top view,(b) side view and (c) contact angle of water droplet with graphene surface.

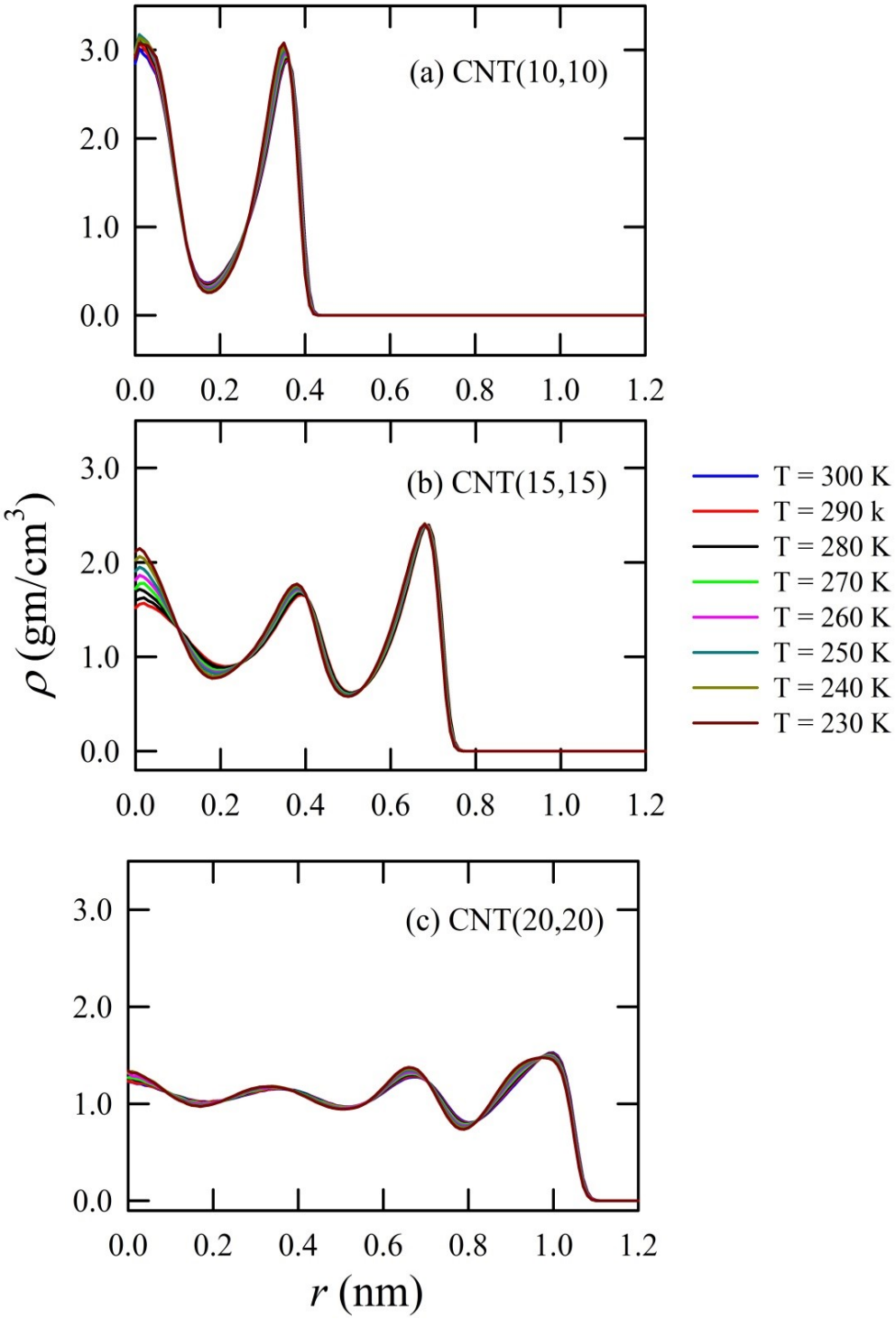



Figure S2. Radial density profiles of water inside the superhydrophobic CNTs.

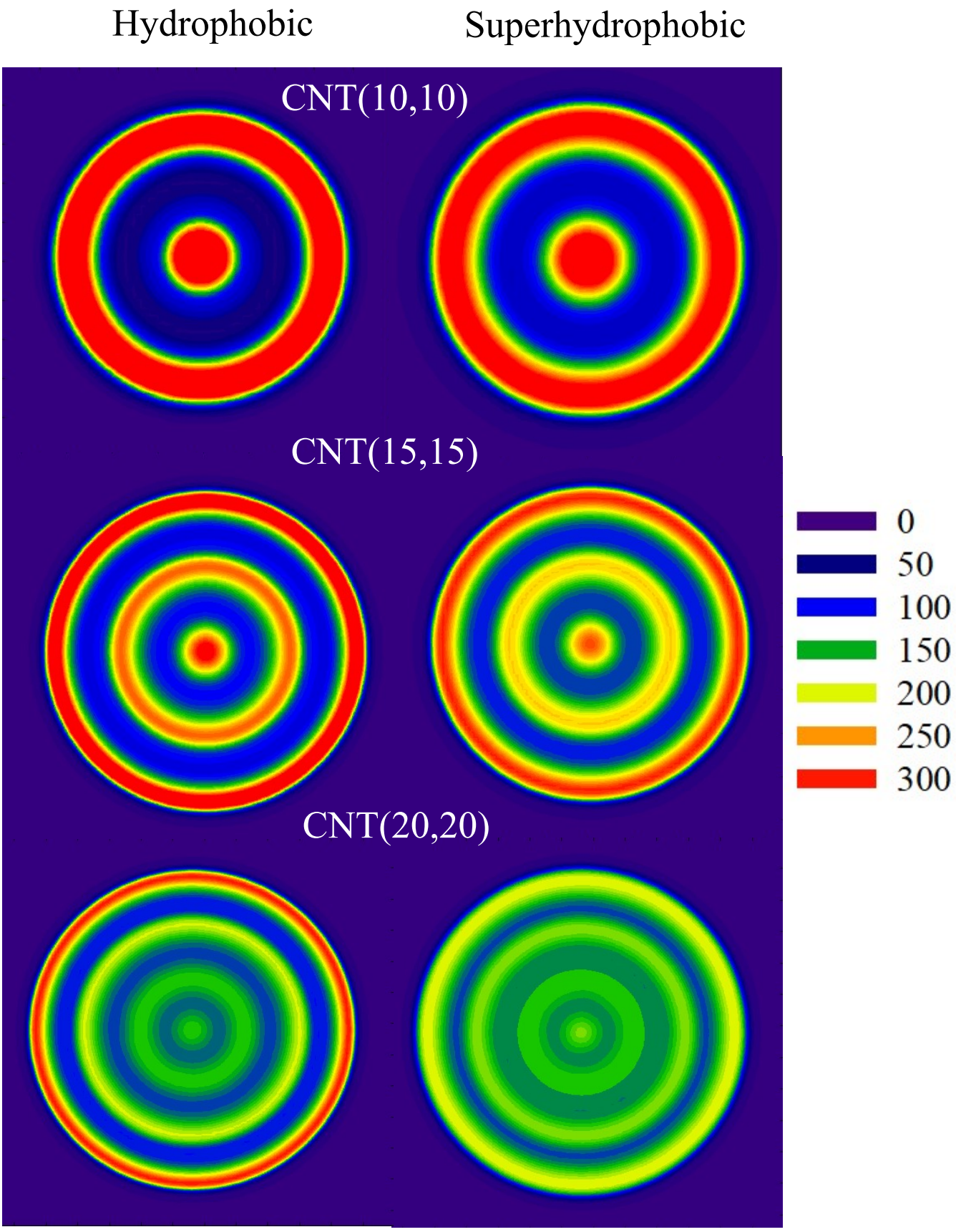



Figure S3. Two dimensional density maps of water inside water inside hydrophobic and superhydrophobic CNTs for 230 K.

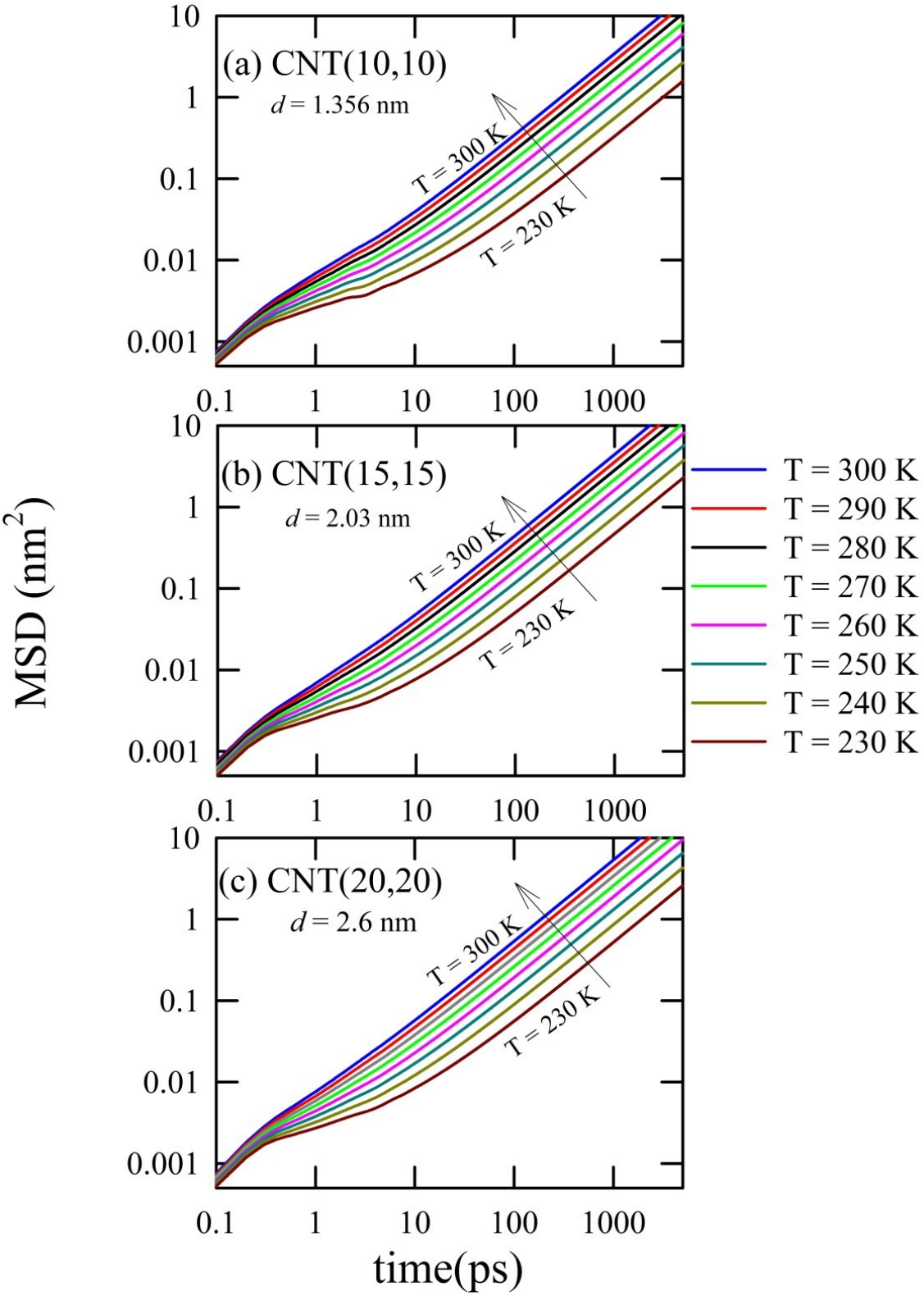



Figure S4. Mean square displacement (MSD) of water as functions of time at different temperatures for bulk water (a), and water inside the CNT (10, 10) (b), CNT (15, 15) (c) and CNT (20, 20) (d) superhydrophobic nanotube systems.

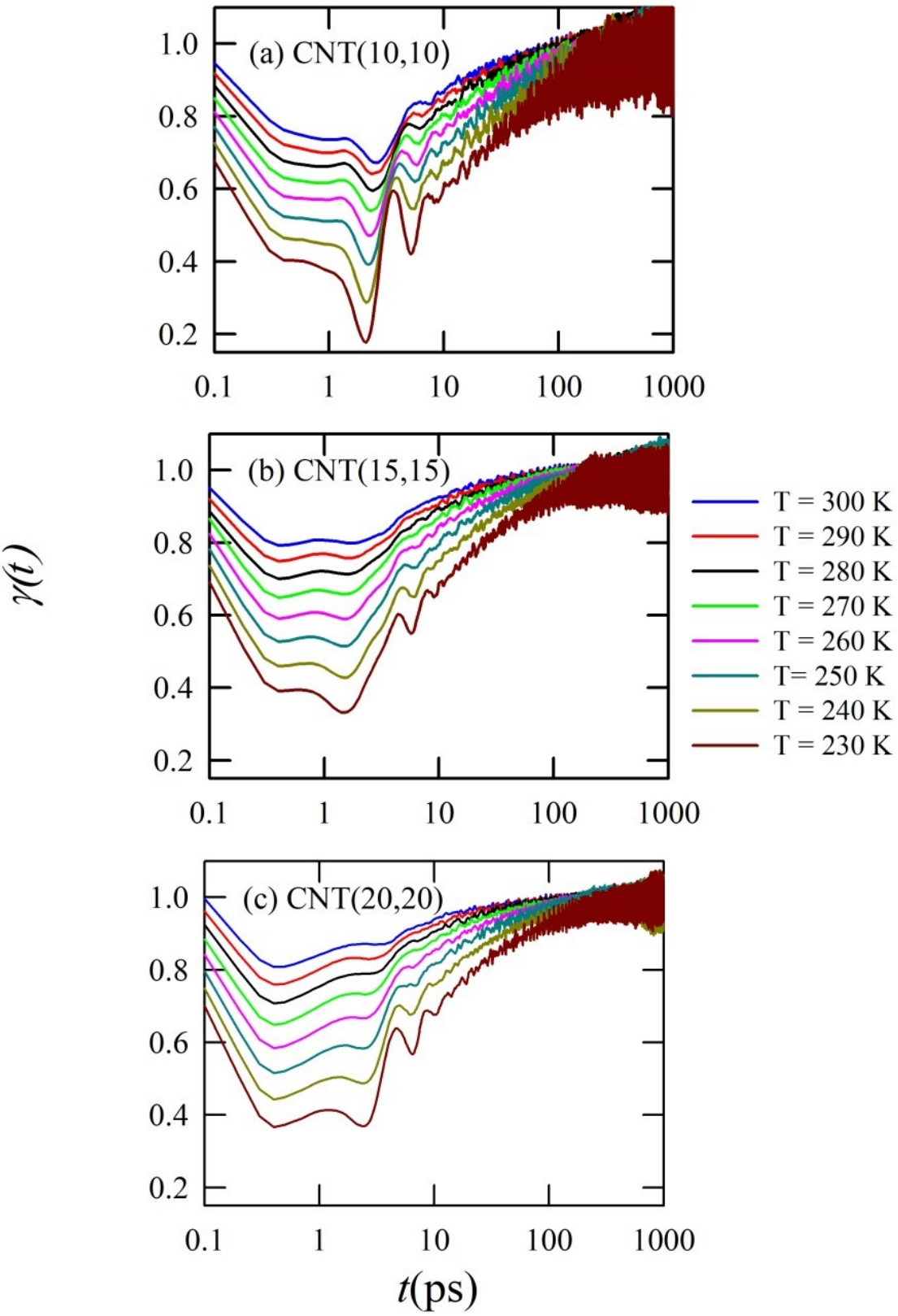
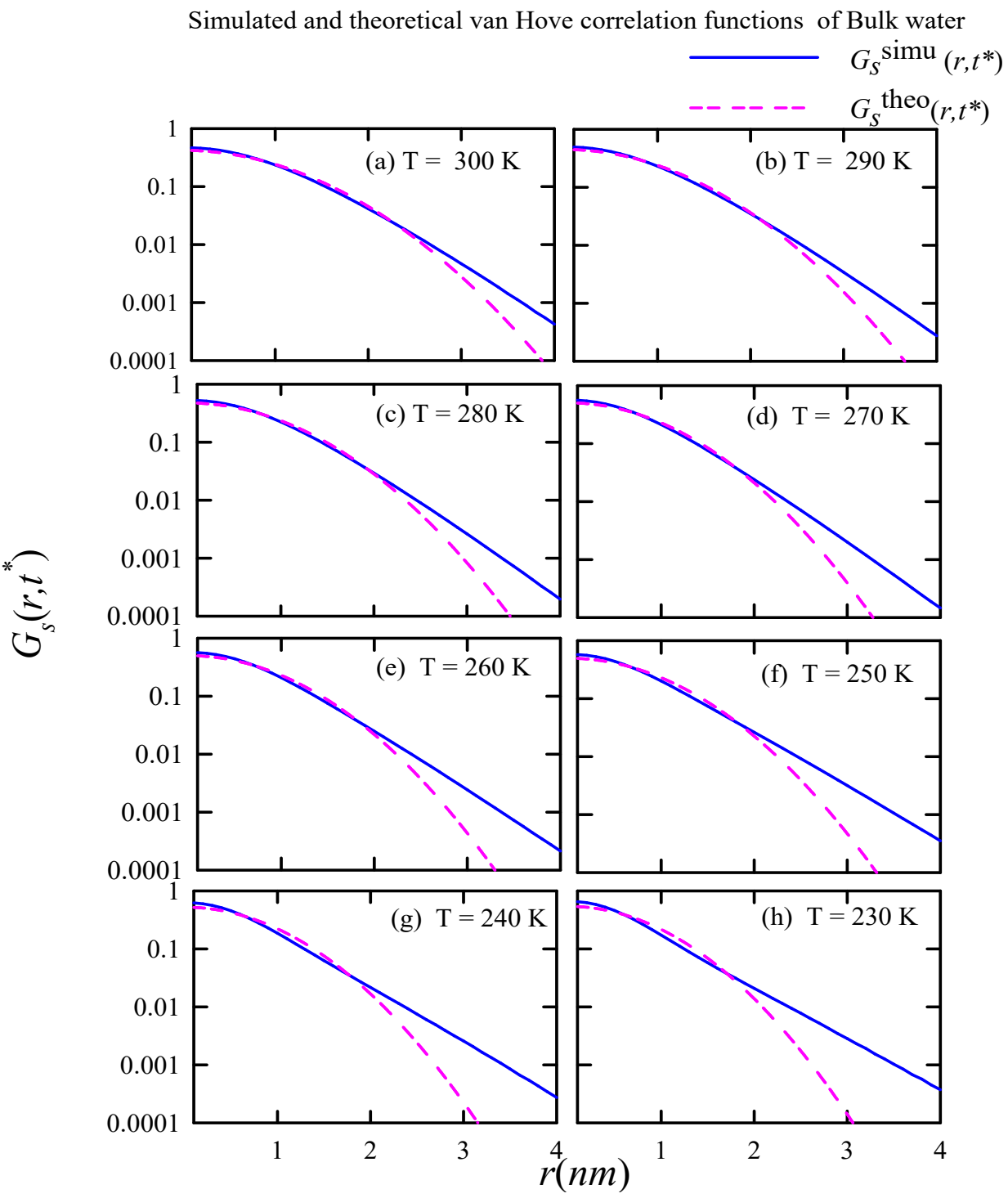
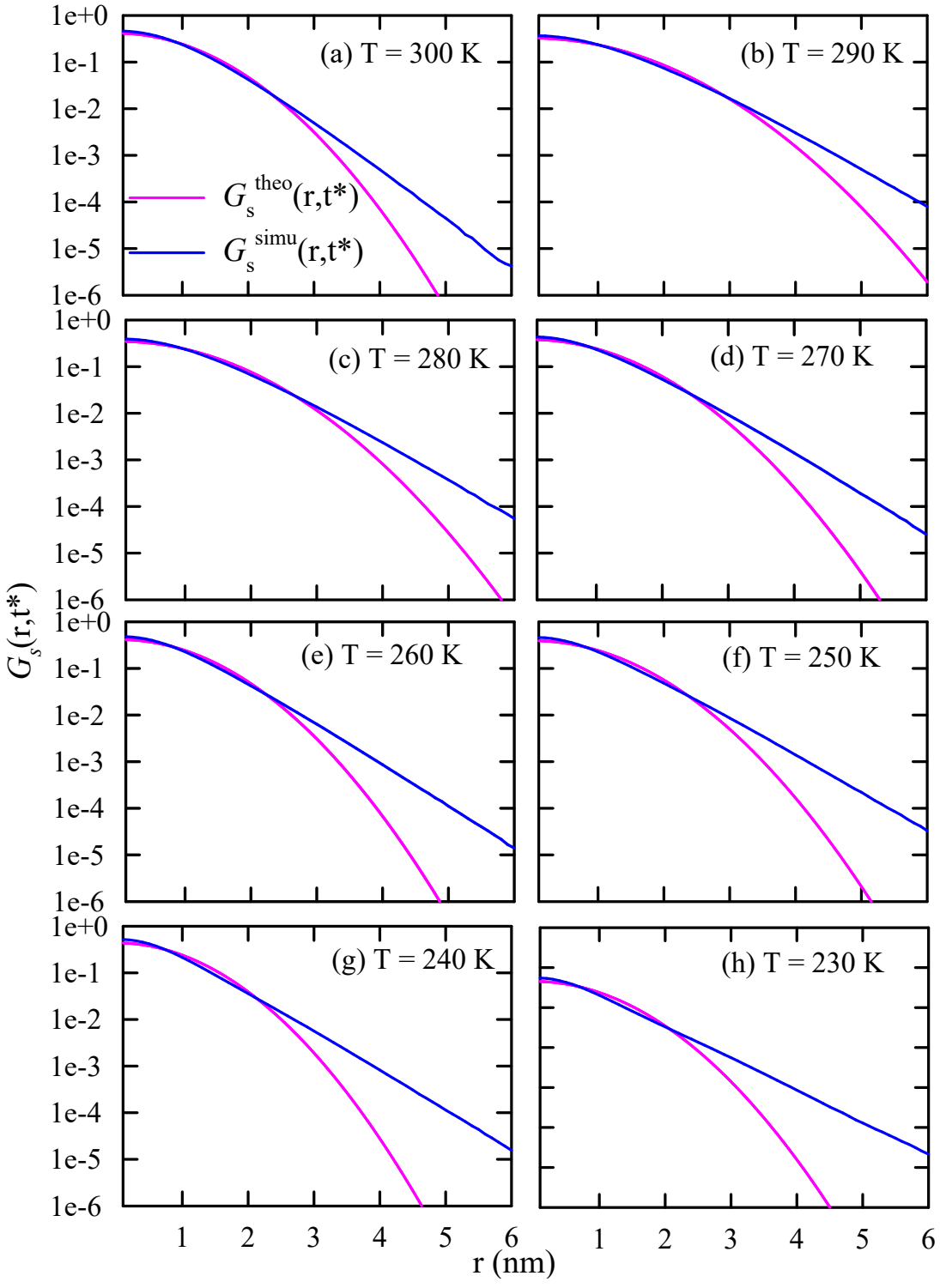


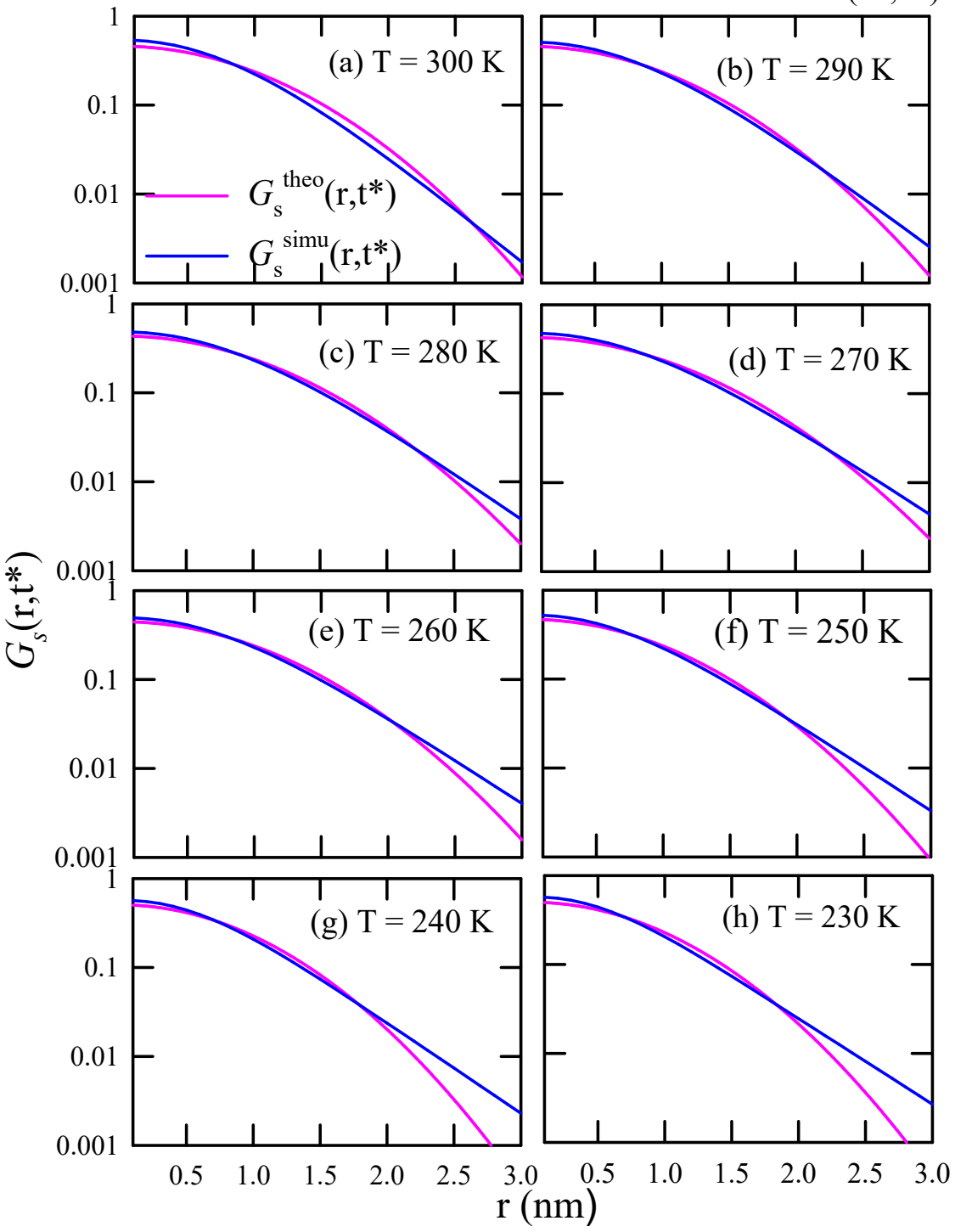

Figure S5. The exponent γ(t) calculated using the equation $\gamma(t) = d\ln(\mathrm{MSD}(t))/d\ln(t)$ for water at eight different temperatures ranging between 230and 300K for bulk water (a) and water in CNT(10,10) (b) , CNT(15,15) (c) and CNT(20,20) (d) superhydrophobic nanotube systems.


Simulated and theoretical van Hove correlation functions of Bulk water
$G_S^{simu}(r,t^*)$
$G_S^{theo}(r,t^*)$
(a) T = 300 K
(b) T = 290 K
(c) T = 280 K
(d) T = 270 K
(e) T = 260 K
(f) T = 250 K
(g) T = 240 K
(h) T = 230 K
$G_s(r,t^*)$
$r(nm)$
1
0.1
0.01
0.001
0.0001
1
2
3
4

Simulated and theoretical van Hove correlation functions of CNT(10,10)



Simulated and theoretical van Hove correlation functions of CNT(15,15) .



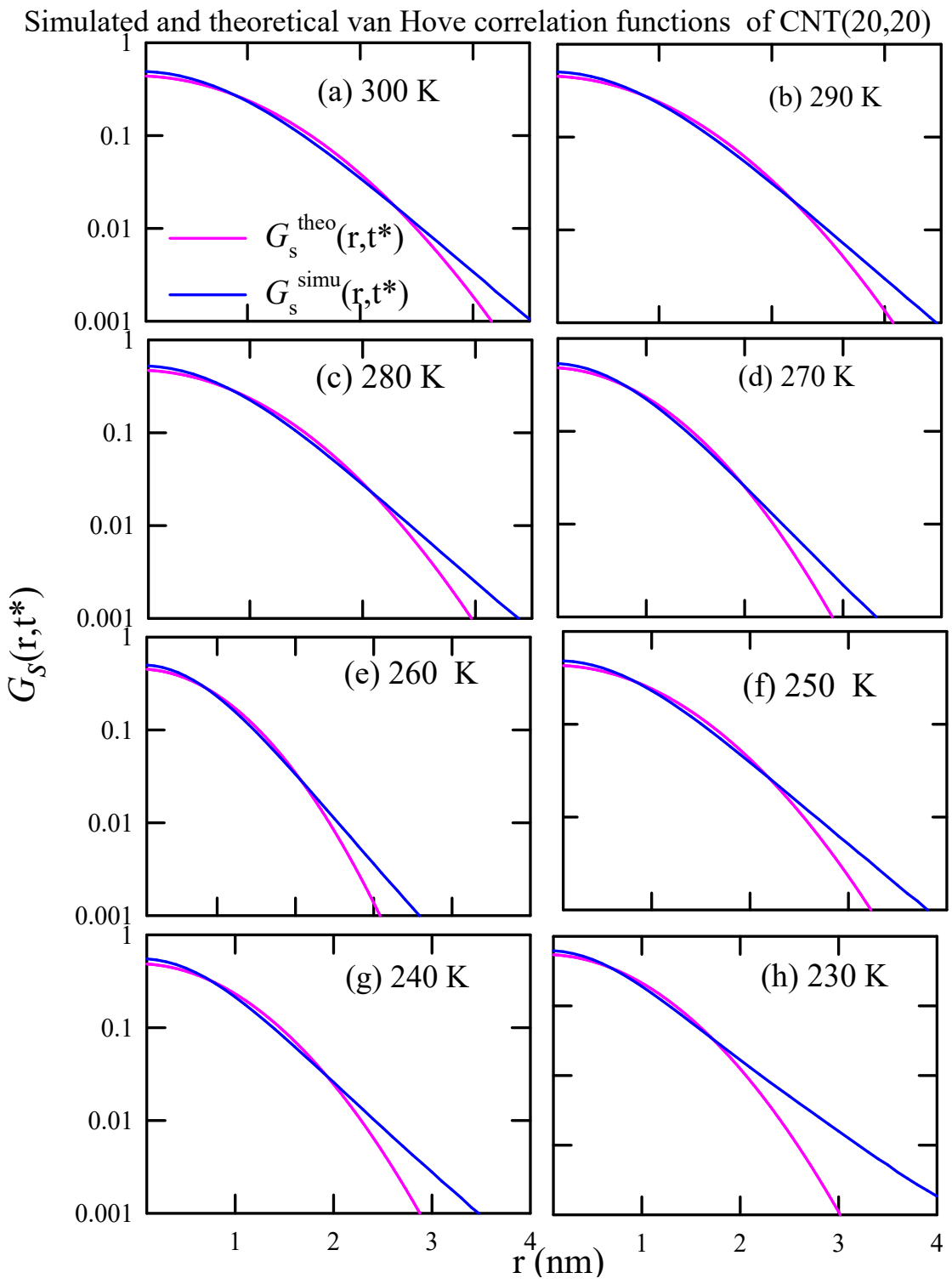



Figure S6. Comparison between simulated and theoretical van Hove correlation functions for all the temperatures studied water inside the CNT(10,10) , CNT(15,15) , and CNT(20,20) superhydrophobic nanotube systems.

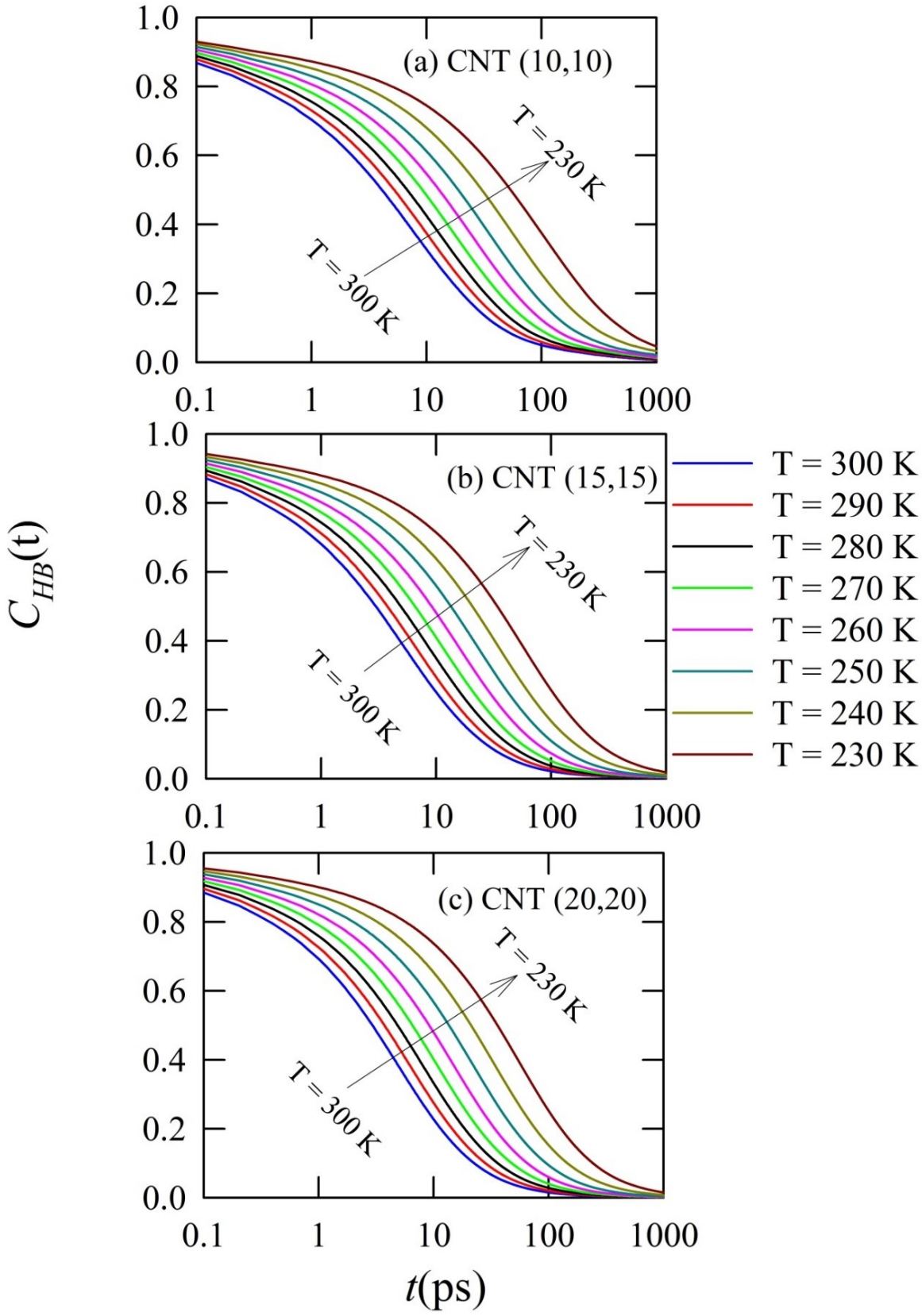



Figure S7**.**The water H-bond correlation function $C_{HB}(t)$ at different temperatures for water inside the CNT(10,10) , CNT(15,15) , and CNT(20,20) superhydrophobic nanotube systems.

**Table S1.** The temperature-dependent viscosity values $\eta$ for bulk water and water inside superhydrophobic CNTs using Green-kubo (GK) relation, Confined-Stokes-Einstein(CSE), and the Jump-corrected Confined-Stokes-Einstein(JCSE).

| Viscosity (cP) | 300 K | 290 K | 280 K | 270 K | 260 K | 250 K | 240 K | 230 K |
|---|---|---|---|---|---|---|---|---|
| Bulk Water | | | | | | | | |
| GK | 0.797 | 0.951 | 1.349 | 1.879 | 2.901 | 5.035 | 9.324 | 29.256 |
| CNT(10,10) | | | | | | | | |
| GK | 0.019 | 0.023 | 0.026 | 0.033 | 0.039 | 0.058 | 0.076 | 0.102 |
| CSE | 1.270 | 1.410 | 1.520 | 2.600 | 3.350 | 5.080 | 8.590 | 22.600 |
| JCSE | 1.260 | 1.420 | 1.520 | 2.400 | 3.040 | 4.420 | 8.110 | 18.400 |
| CNT(15,15) | | | | | | | | |
| GK | 0.054 | 0.062 | 0.078 | 0.099 | 0.129 | 0.173 | 0.234 | 0.335 |
| CSE | 1.080 | 1.180 | 1.290 | 2.010 | 2.440 | 3.610 | 6.340 | 14.100 |
| JCSE | 0.882 | 1.020 | 1.070 | 1.660 | 2.100 | 3.030 | 5.440 | 11.600 |
| CNT(20,20) | | | | | | | | |
| GK | 0.086 | 0.108 | 0.122 | 0.151 | 0.207 | 0.271 | 0.398 | 0.534 |
| CSE | 0.735 | 0.852 | 0.911 | 1.420 | 1.800 | 2.720 | 4.750 | 11.100 |
| JCSE | 0.727 | 0.840 | 0.890 | 1.400 | 1.760 | 2.580 | 4.640 | 10.500 |

**Table S2.** The ($C_{HB}(t)= a_1\exp(-t/\tau_1)+a_2\exp(-t/\tau_2)+a_3\exp(-t/\tau_3)$;$a_1+a_2+a_3=1$) fitting parameters of $C_{HB}(t)$ at different temperatures for four systems(bulk water and water inside superhydrophobic CNTs.

| | 300 K | 290 K | 280 K | 270 K | 260 K | 250 K | 240 K | 230 K |
|---|---|---|---|---|---|---|---|---|
| Bulk Water | | | | | | | | |
| $a_1$ | 0.22 | 0.22 | 0.21 | 0.20 | 0.19 | 0.17 | 0.18 | 0.16 |
| $\tau_1$(ps) | 0.47 | 0.59 | 0.78 | 1.14 | 1.96 | 3.66 | 7.84 | 14.56 |
| $a_2$ | 0.66 | 0.66 | 0.67 | 0.68 | 0.69 | 0.70 | 0.70 | 0.68 |
| $\tau_2$ (ps) | 6.40 | 7.90 | 10.47 | 15.22 | 25.51 | 49.26 | 90.09 | 188.68 |
| $a_3$ | 0.12 | 0.12 | 0.12 | 0.12 | 0.12 | 0.13 | 0.12 | 0.16 |
| $\tau_3$ (ps) | 36.23 | 44.44 | 58.48 | 85.47 | 138.89 | 250.00 | 454.55 | 769.23 |
| $\tau_{HB}$(ps) | 8.73 | 10.81 | 14.34 | 20.84 | 34.27 | 66.54 | 117.18 | 253.00 |
| $\Delta G^*$ | 9.98 | 10.08 | 10.31 | 10.70 | 11.29 | 12.16 | 12.72 | 13.58 |
| $\Delta G^*_{tot}$ | 36.48 | 37.28 | 38.54 | 40.43 | 43.17 | 46.98 | 49.54 | 53.28 |
| CNT(10,10) | | | | | | | | |
| $a_1$ | 0.47 | 0.46 | 0.45 | 0.43 | 0.40 | 0.38 | 0.39 | 0.35 |
| $\tau_1$(ps) | 1.53 | 1.88 | 2.38 | 3.03 | 3.60 | 4.74 | 8.61 | 11.92 |
| $a_2$ | 0.48 | 0.49 | 0.49 | 0.51 | 0.53 | 0.55 | 0.53 | 0.55 |
| $\tau_2$ (ps) | 18.80 | 22.83 | 28.49 | 36.23 | 45.05 | 60.61 | 103.09 | 161.29 |
| $a_3$ | 0.05 | 0.06 | 0.06 | 0.06 | 0.07 | 0.08 | 0.07 | 0.09 |
| $\tau_3$ (ps) | 400.00 | 476.19 | 555.56 | 666.67 | 666.67 | 769.23 | 1428.57 | 1666.67 |
| $\tau_{HB}$(ps) | 31.39 | 39.00 | 46.48 | 59.51 | 71.91 | 95.70 | 160.77 | 245.78 |
| $\Delta G^*$ | 13.08 | 13.14 | 13.05 | 13.05 | 12.90 | 12.91 | 13.35 | 13.52 |
| $\Delta G^*_{tot}$ | 42.33 | 42.99 | 43.12 | 43.61 | 43.53 | 44.05 | 46.02 | 47.12 |
| CNT(15,15) | | | | | | | | |
| $a_1$ | 0.45 | 0.45 | 0.44 | 0.43 | 0.40 | 0.36 | 0.39 | 0.30 |
| $\tau_1$(ps) | 1.17 | 1.47 | 1.88 | 2.50 | 3.03 | 3.76 | 7.09 | 7.46 |
| $a_2$ | 0.50 | 0.50 | 0.51 | 0.51 | 0.54 | 0.56 | 0.55 | 0.60 |
| $\tau_2$ (ps) | 12.08 | 14.84 | 18.69 | 24.10 | 30.03 | 39.06 | 64.94 | 83.33 |
| $a_3$ | 0.05 | 0.05 | 0.05 | 0.05 | 0.07 | 0.08 | 0.06 | 0.10 |
| $\tau_3$ (ps) | 138.89 | 172.41 | 208.33 | 263.16 | 285.71 | 333.33 | 625.00 | 625.00 |
| $\tau_{HB}$(ps) | 13.66 | 16.95 | 21.41 | 27.78 | 36.17 | 50.33 | 78.29 | 115.41 |
| $\Delta G^*$ | 11.09 | 11.51 | 11.24 | 11.34 | 11.41 | 11.58 | 11.91 | 12.08 |
| $\Delta G^*_{tot}$ | 37.93 | 39.77 | 39.23 | 39.98 | 40.61 | 41.59 | 43.18 | 44.15 |
| CNT(20,20) | | | | | | | | |
| $a_1$ | 0.33 | 0.32 | 0.32 | 0.32 | 0.30 | 0.29 | 0.29 | 0.26 |
| $\tau_1$(ps) | 0.74 | 0.94 | 1.26 | 1.70 | 2.18 | 3.18 | 5.33 | 8.00 |
| $a_2$ | 0.58 | 0.59 | 0.59 | 0.60 | 0.61 | 0.62 | 0.62 | 0.63 |
| $\tau_2$ (ps) | 7.67 | 9.57 | 12.36 | 16.31 | 21.55 | 30.96 | 48.54 | 76.34 |
| $a_3$ | 0.09 | 0.09 | 0.09 | 0.09 | 0.10 | 0.10 | 0.09 | 0.11 |
| $\tau_3$ (ps) | 60.98 | 76.34 | 99.01 | 129.87 | 163.93 | 227.27 | 370.37 | 526.32 |
| $\tau_{HB}$(ps) | 10.17 | 12.78 | 16.42 | 21.76 | 29.38 | 42.46 | 66.19 | 106.58 |
| $\Delta G^*$ | 10.36 | 10.48 | 10.62 | 10.79 | 10.96 | 11.22 | 11.58 | 11.93 |
| $\Delta G^*_{tot}$ | 35.86 | 36.69 | 37.59 | 38.59 | 39.59 | 40.93 | 42.61 | 44.26 |

**Table S3.** The table compares our simulated number of H-bond per water molecule and self-diffusion coefficient with some literature simulation studies, which considered TIP4P/2005 water model.

| Bulk water (TIP4P-2005) | Simulation | (Linse *et al.*)[2] | (Dubey *et al.*)[3] | (Hartkamp *et al.*)[4] | (Prasad *et al.*)[5] | (Belosludov ,*et al.*)[6] |
|---|---|---|---|---|---|---|
| $N_{Hb}$ | 3.655 | 3.662 | 3.645 | 3.65 | 3.85 | 3.55 |
| | | | | | | |
| Bulk water (TIP4P-2005) | Simulation | (Abascal *et al*)[7] | (Dubey *et al.*)[8] | (Hartkamp *et al.*)[4] | (V.Dubey *et al.*)[3] | (Hijes *et* al.)[9] |
| Diffusion Coefficient ($cm^2$/sec) | 2.10 | 2.08 | 2.217 | 2.35 | 2.384 | 2.450 |

**REFFERENCE**


1. M. J. De Ruijter, T. Blake and J. De Coninck, *Langmuir*, 1999, **15**, 7836-7847.
2. J.-B. Linse and J. S. Hub, *J. Chem. Phys.*, 2021, **154**.
3. V. Dubey, S. Erimban, S. Indra and S. Daschakraborty, *J. Phys. Chem. B*, 2019, **123**, 10089-10099.
4. R. Hartkamp and B. Coasne, *J. Chem. Phys.*, 2014, **141**.
5. M. Prasad and S. N. Chakraborty, *Comput .Theor. Chem.*, 2022, **1208**, 113527.
6. V. Belosludov, K. Gets, R. Zhdanov, V. Malinovsky, Y. Bozhko, R. Belosludov, N. Surovtsev, O. Subbotin and Y. Kawazoe, *Sci. Rep.*, 2020, **10**, 7323.
7. J. L. Abascal and C. Vega, *J. Chem. Phys.*, 2005, **123**.
8. S. Dueby, V. Dubey and S. Daschakraborty, *J. Phys. Chem. B*, 2019, **123**, 7178-7189.
9. P. Montero de Hijes, E. Sanz, L. Joly, C. Valeriani and F. Caupin, *J. Chem. Phys.*, 2018, **149**.