Supporting Information

Thermodynamics, Structure, and Dynamic Properties of Nanostructured Water Confined into B-, N-, and Si-Doped Graphene Surfaces and Carbon Nanotubes

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Table S1. The number of water molecules at different pore widths and densities in graphene systems

d (Å)	Density	Number of water molecules
6	0.2	46
	0.4	92
	0.6	138
	0.8	208
	1	230
8	0.6	184
10	0.6	230

Table S2. The number of water molecules at different CNT systems

CNT	Density	Number of water molecules
(14,0)	0.2	90
(15,0)	0.2	108

Table S3. The Lennard-Jones (LJ) parameters[58-60] used in this work

Interaction	ε (kJ/mol)	σ (Å)
C-C	0.2763	3.469
B-B	0.3971	3.453
N-N	0.6060	3.365
Si-Si	1.6789	4.295

S1. Effect of the doped atom distribution

To examine the effect of the doped atom distribution, we have distributed the doped atoms in the high (20%) doped systems with two states: periodically and randomly. The total energy, average number of the HBs, and self-diffusion coefficient of the confined water molecules between the graphene surfaces and into the doped CNTs with the two different doped atoms distributions have been presented at 300 K in Tables S4 and S5 in the supporting information. The O-H radial distribution functions of the confined molecules have been also presented in Fig. S8 in the supporting information.

According to Tables S4 and S5 and also Fig. S2, there are not much differences between the results in both states. However, it is shown that these differences are very small in the total energy, average number of HBs, and the RDFs whereas they become larger in the diffusion coefficient values. To more investigate this situation, we have presented the snapshots of the confined water molecules between the doped graphene (at different densities) and into the doped CNT in both states in Fig. S3 and S4, respectively. According to these figures, there is not much differences between the two states. However, according to Fig. S3, at low density (ρ=0.2 (g/cc)) for Si-doped system, we cannot observe the three discrete water chains in the random state (which was observed in the periodic state). The formation of the discrete water chains in the periodically doped graphene is due to the response of water molecules to the attraction of the periodic Si-doped atoms. By careful observation to Fig. S3 we can find that the confined water molecules create more ordered shapes in the randomly distributed doped atoms at higher density (ρ=1 (g/cc)) in both N- and Si-doped systems. This result is in agreement with the higher <HB> and smaller diffusion coefficient of confined water molecules in the randomly distributed doped atoms in the graphene system. However, according to Fig. S4, the confined water molecules into the periodically distributed doped atoms in the (14,0) CNT create more ordered pentagonal shape than the randomly distributed CNT. The <HB> of the confined water molecules is also greater for the random doped atoms distribution in (14,0) CNT.

Table S4. The total energy, average number of the HBs, and self-diffusion coefficient of the confined water molecules between the graphene surfaces with the two different doped atoms distributions.

Property	Periodic	Completely random
Total energy (kJ/mol)		
(20%) B-doped, ρ=0.2 (g/cc)	-34.5609	-34.8978
(20%) B-doped, ρ=0.6 (g/cc)	-42.1862	-42.3565
(20%) B-doped, ρ=1 (g/cc)	37.4004	40.3969
(20%) N-doped, ρ=0.2 (g/cc)	-36.4696	-34.6152
(20%) N-doped, ρ=0.6 (g/cc)	-43.2319	-42.4623
(20%) N-doped, ρ=1 (g/cc)	37.3900	39.4956
(20%) Si-doped, ρ=0.2 (g/cc)	-33.1217	-31.2261
(20%) Si-doped, ρ=0.6 (g/cc)	-36.4507	-33.9471
(20%) Si-doped, ρ=1 (g/cc)	78.9130	82.6609
Average number of HBs		
(20%) B-doped, ρ=0.2 (g/cc)	1.20	1.54
(20%) B-doped, ρ=0.6 (g/cc)	1.67	1.66
(20%) B-doped, ρ=1 (g/cc)	4.46	4.56
(20%) N-doped, ρ=0.2 (g/cc)	1.33	1.09
(20%) N-doped, ρ=0.6 (g/cc)	1.59	1.69
(20%) N-doped, ρ=1 (g/cc)	4.40	4.61
(20%) Si-doped, ρ=0.2 (g/cc)	0.63	0.74
(20%) Si-doped, ρ=0.6 (g/cc)	1.54	1.60
(20%) Si-doped, ρ=1 (g/cc)	4.90	5.09
Self-Diffusion (10^{-10} m^2/s)		
(20%) B-doped, ρ=0.2 (g/cc)	1.1173	1.5391
(20%) B-doped, ρ=0.6 (g/cc)	0.1177	0.0380
(20%) B-doped, ρ=1 (g/cc)	2.0367×10^{-3}	1.6642×10^{-3}
(20%) N-doped, ρ=0.2 (g/cc)	1.0878	1.494

(20%) N-doped, ρ=0.6 (g/cc)	0.1270	0.08969
(20%) N-doped, ρ=1 (g/cc)	3.1050×10^{-3}	1.2787×10^{-3}
(20%) Si-doped, ρ=0.2 (g/cc)	0.0868	0.04543
(20%) Si-doped, ρ=0.6 (g/cc)	5.8850×10^{-3}	4.5267×10^{-3}
(20%) Si-doped, ρ=1 (g/cc)	2.3683×10^{-3}	2.0700×10^{-3}

Table S5. The total energy and average number of the HBs of the confined water molecules into the (14,0) CNT with the two different doped atoms distributions.

Property	Periodic	Completely random
Total energy (kJ/mol)		
(20%) N-doped	-53.5644	-53.2744
Average number of HBs		
(20%) N-doped	1.92	1.82

Table S6. The total energy, average number of the HBs, and self-diffusion coefficient of the confined water molecules between the graphene surfaces with the random doped atoms distributions at the different pore widths.

Property	d= 6 Å	d= 8 Å	d= 10 Å
Total energy (kJ/mol)			
(20%) N-doped, ρ=0.6 (g/cc)	-42.4623	-44.1440	-41.3461
Average number of HBs			
(20%) N-doped, ρ=0.6 (g/cc)	1.69	1.78	1.6261
Self-Diffusion (10^{-10} m^2/s)			
(20%) N-doped, ρ=0.6 (g/cc)	0.08969	2.0388	18.3545

Table S7. The total energy and average number of the HBs of the confined water molecules into the different CNTs with the random doped atoms distributions.

Property	(14,0) CNT	(15,0) CNT
Total energy (kJ/mol)		
(20%) N-doped	-53.2744	-52.1898
Average number of HBs		
(20%) N-doped	1.82	1.88

Table S8. The total energy, average number of the HBs, and self-diffusion coefficient of the confined water molecules between the graphene surfaces with the random doped atoms distribution at the pore width of 6 (Å) at different temperatures.

Property	300 K	400 K	500 K	600 K
Total energy (kJ/mol)				
(20%) N-doped, ρ=0.6 (g/cc)	-42.4623	-34.2420	-27.4638	-21.9341
Average number of HBs				
(20%) N-doped, ρ=0.6 (g/cc)	1.69	1.65	1.68	1.72
Self-Diffusion (10^{-10} m^2/s)				
(20%) N-doped, ρ=0.6 (g/cc)	0.08969	2.6273	8.4892	12.5010

Table S9. The total energy and average number of the HBs of the confined water molecules into (14,0) CNT with the random doped atoms distribution at different temperatures.

Property	300 K	400 K	500 K	600 K
Total energy (kJ/mol)				
(20%) N-doped	-53.2744	-47.2033	-44.7744	-25.8500
Average number of HBs				
(20%) N-doped	1.82	1.90	1.88	1.80

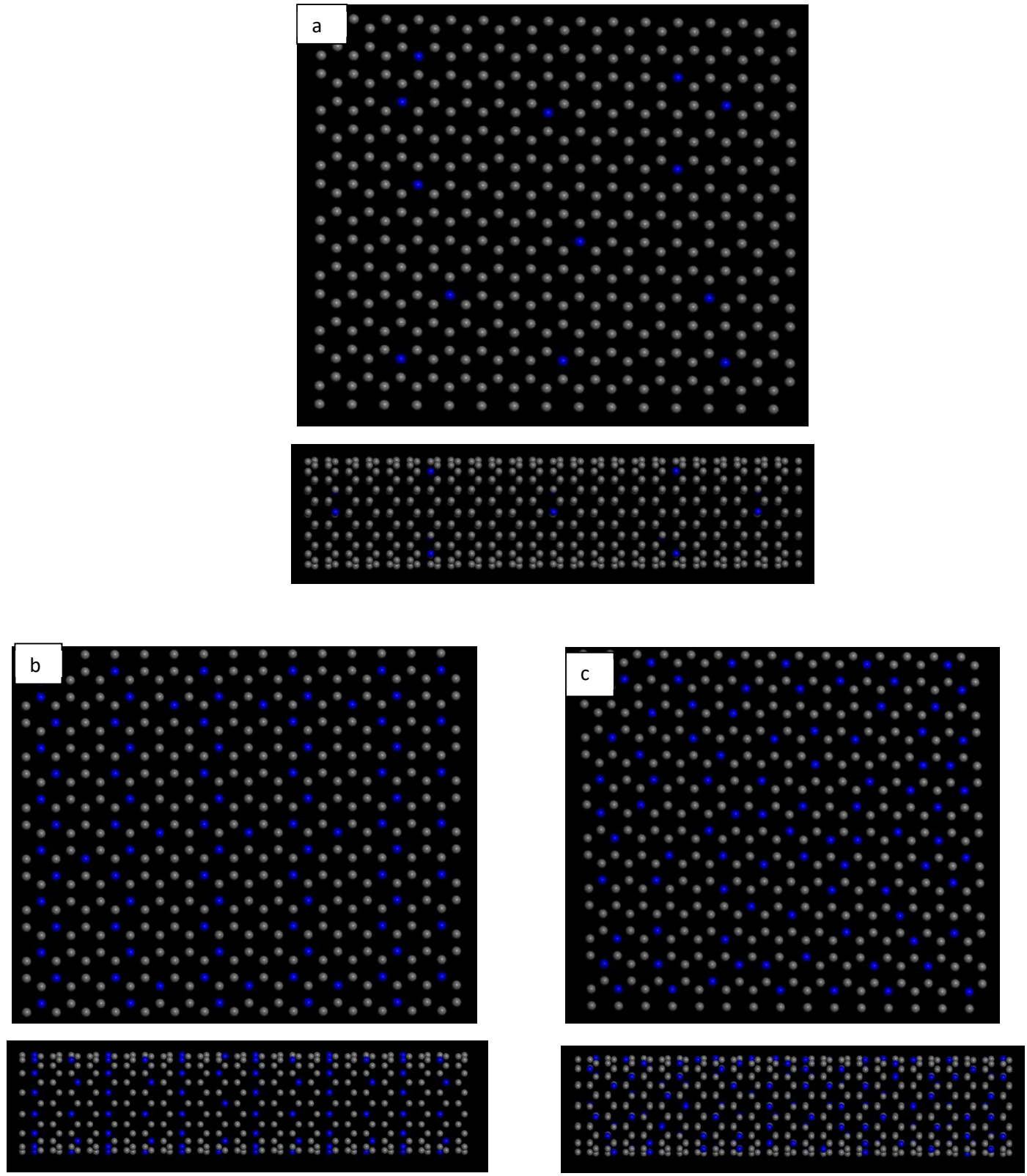


Fig. S1. The snapshots of the a) low (3%) doped graphene and CNT systems with random distribution and the b) high (20%) doped graphene and CNT systems with periodic and c) distributions. The carbon and doped atoms are in gray and blue, respectively.

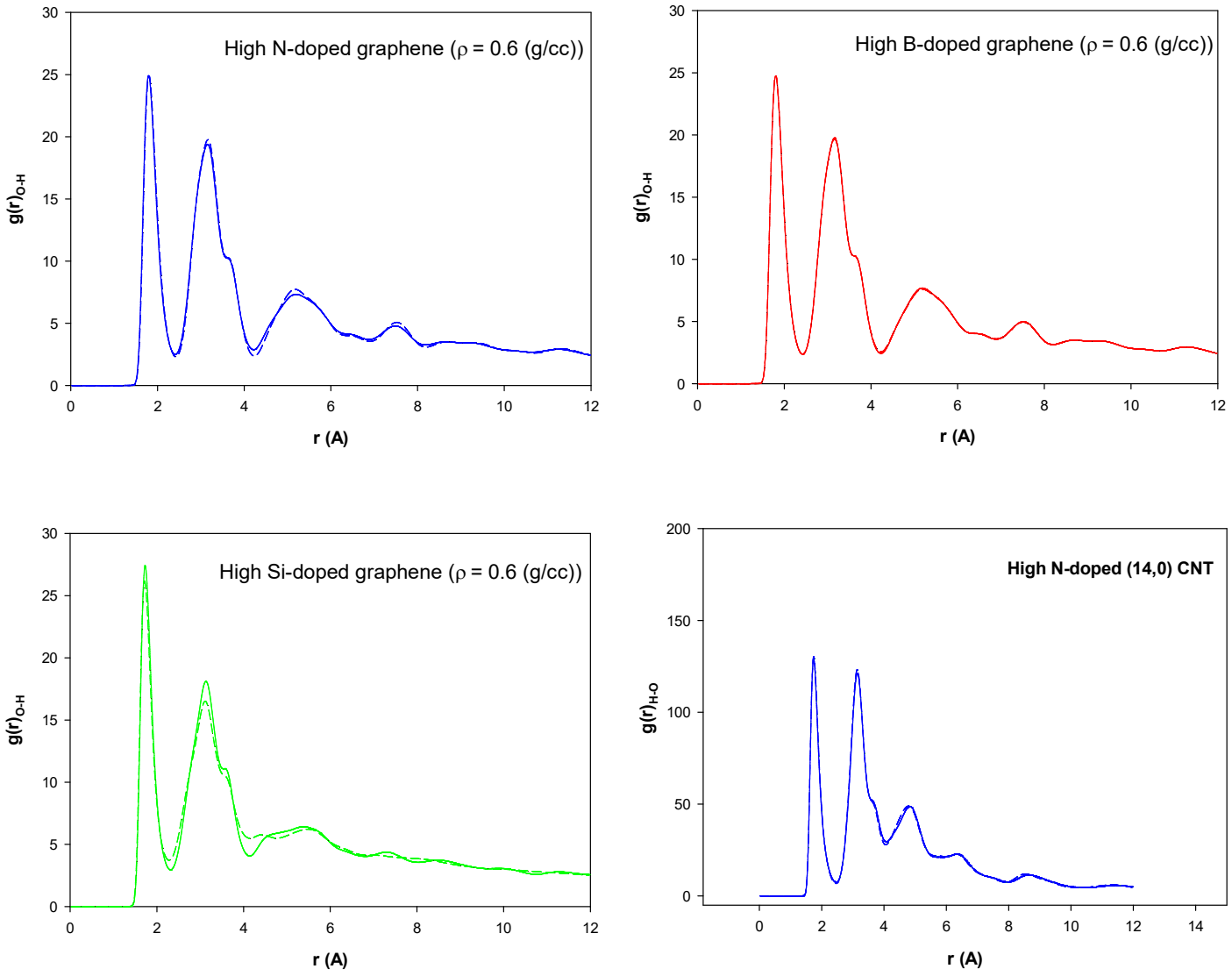


Fig. S2. The O-H RDFs of the confined molecules in the high doped systems with the two different doped atoms distributions: periodically (solid lines) and randomly (dashed lines).

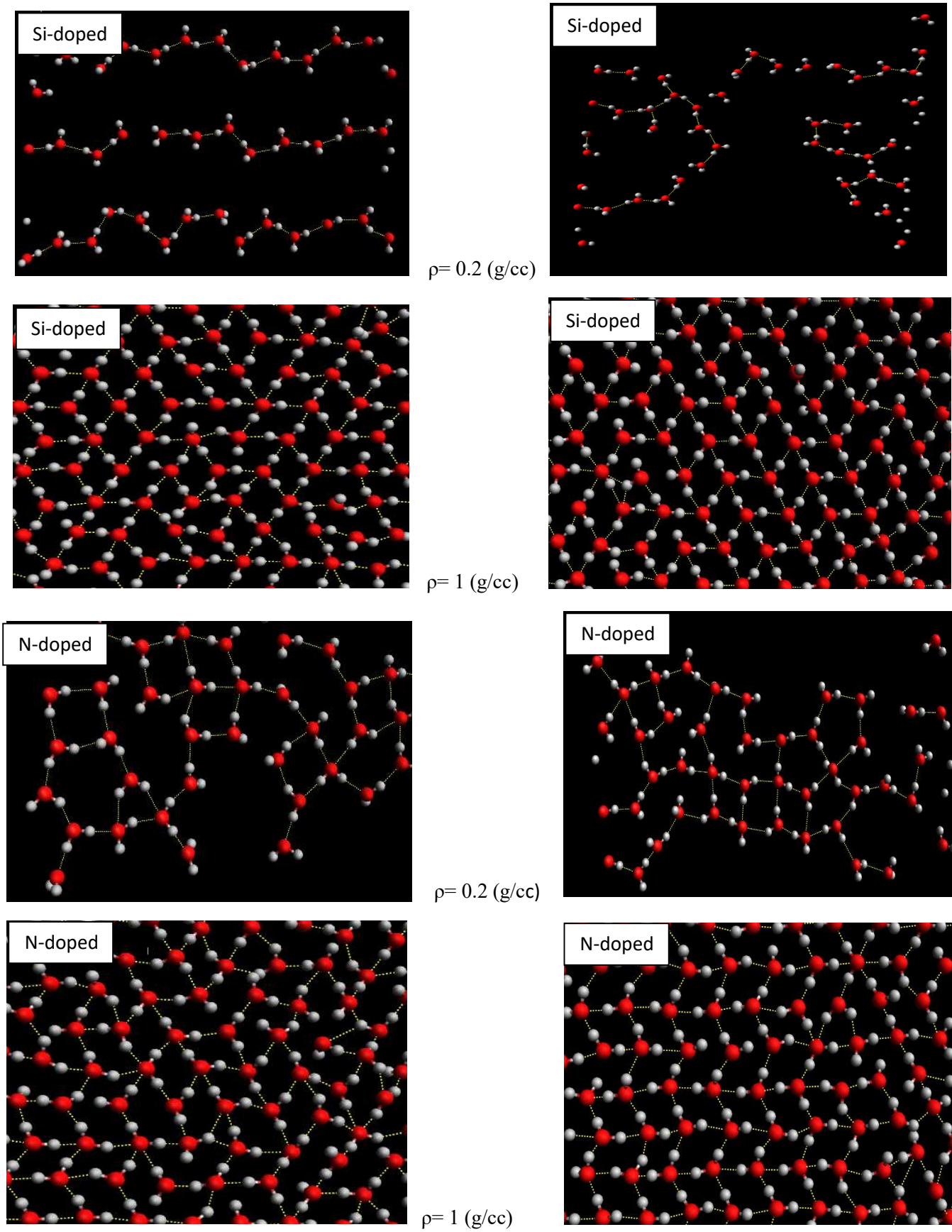


Fig. S3. The snapshots of the confined water molecules between in the high doped graphene at different densities with the two different doped atoms distributions: periodically (left side) and randomly (right side).

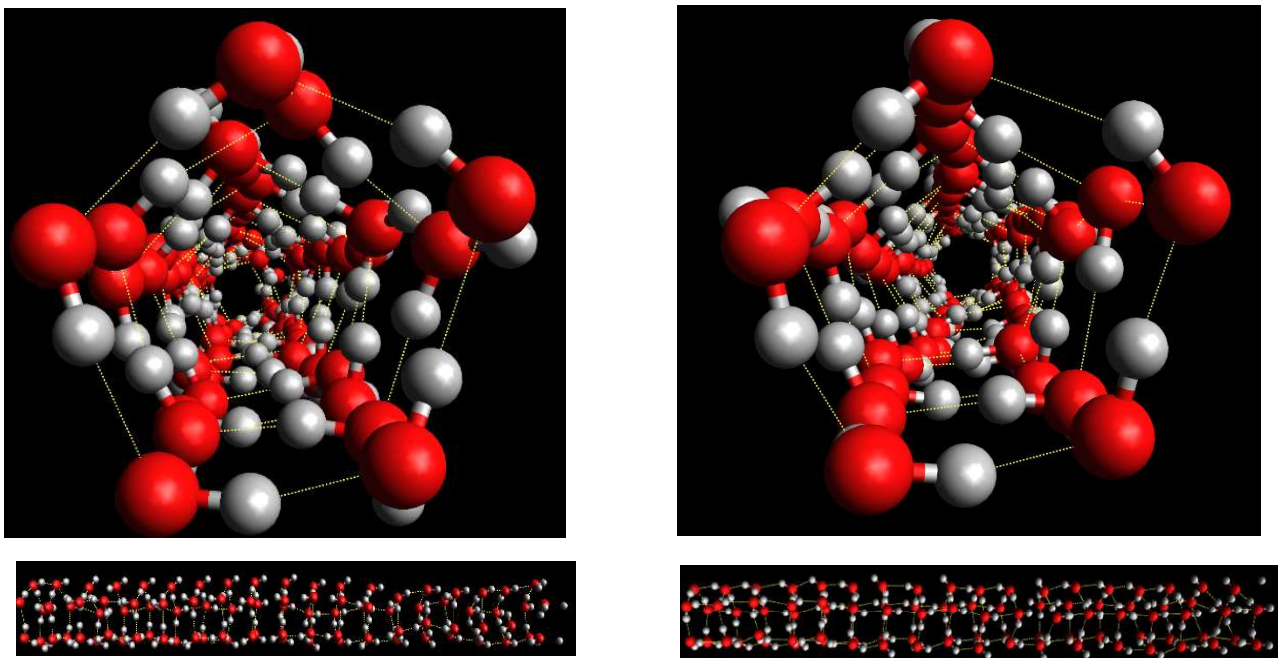


Fig. S4. The snapshots of the confined water molecules into the high N-doped (14,0) CNT with the two different doped atoms distributions: periodically (left side) and randomly (right side).

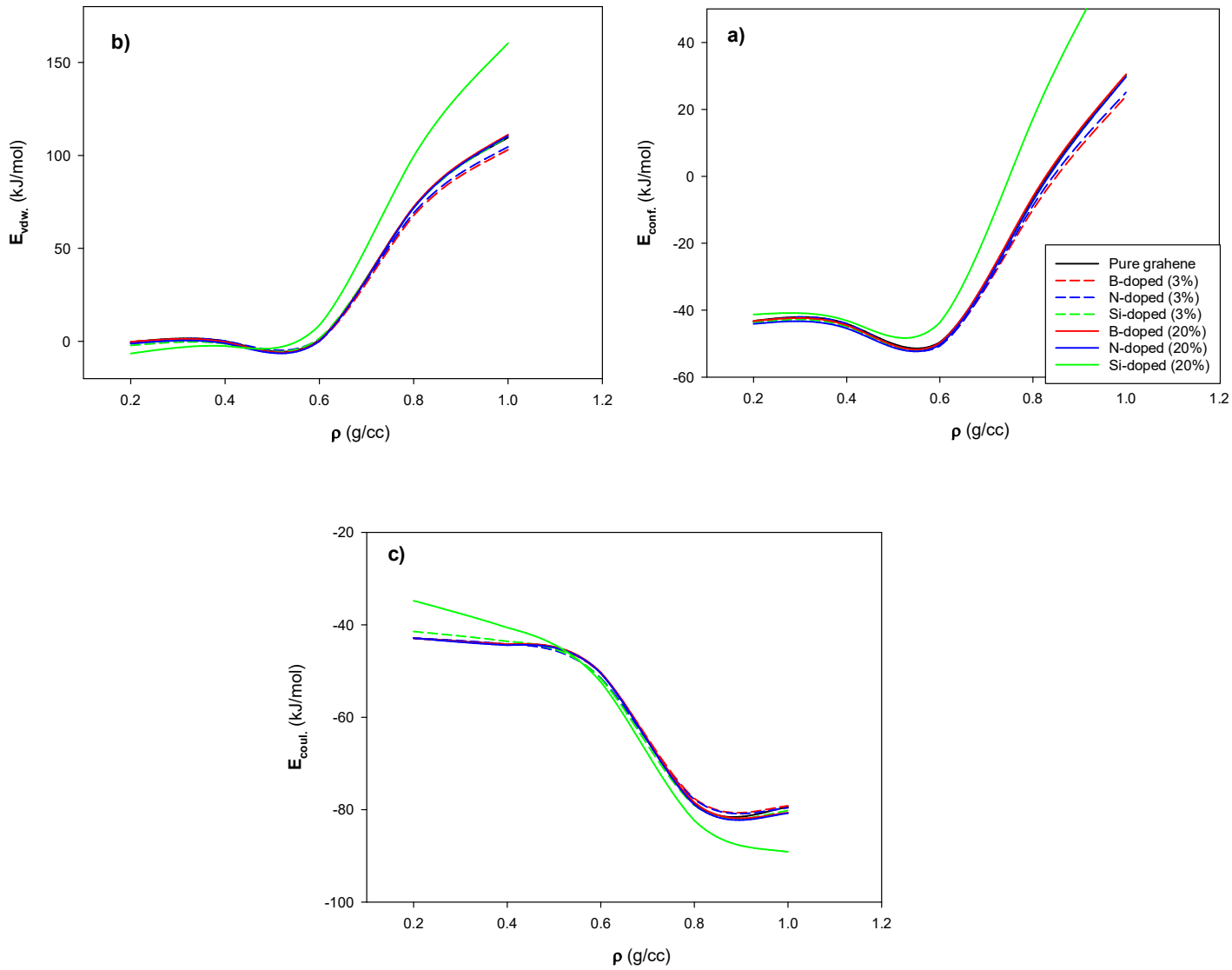
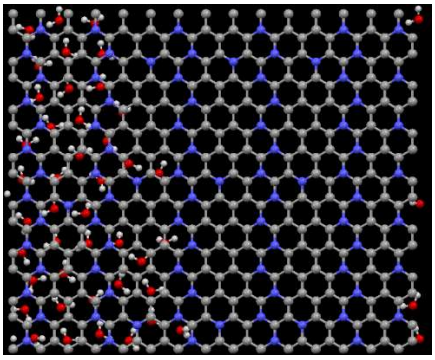
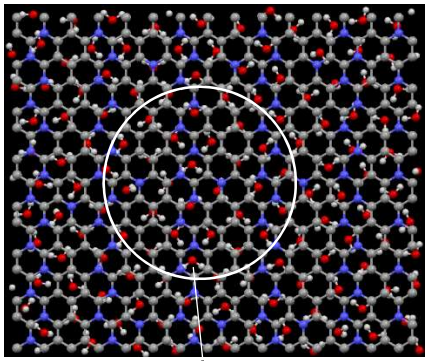


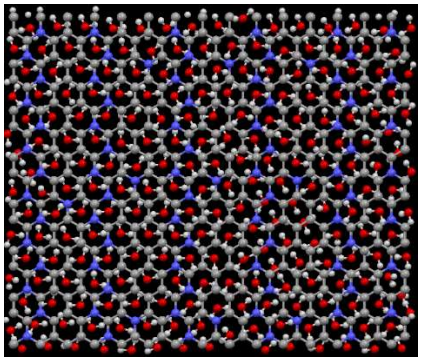
Fig. S5. The smoothed a) configurational, b) van der Waals, and c) columbic energy curves (per molecule) of confined water molecules with the different densities in the pure and the different doped systems.



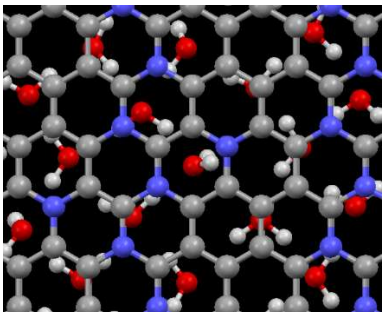
ρ= 0.2 (g/cc)

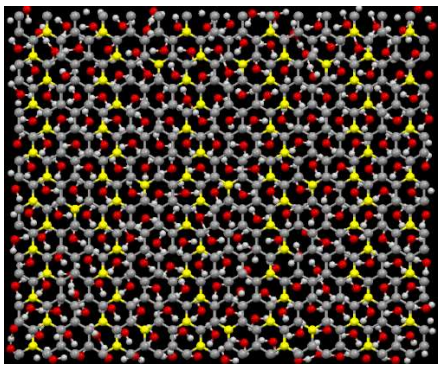


ρ= 0.6 (g/cc)

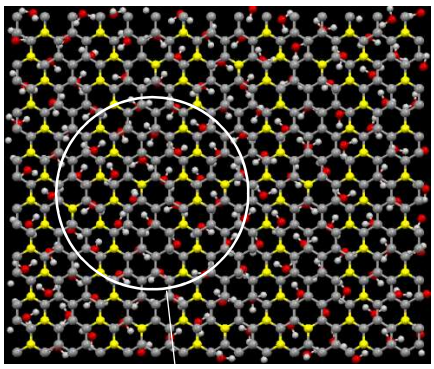


ρ= 1 (g/cc)

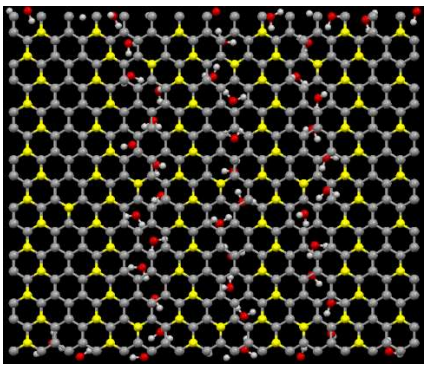




ρ= 0.2 (g/cc)



ρ= 0.6 (g/cc)



ρ= 1 (g/cc)

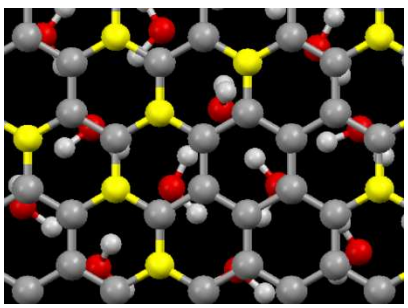


Fig. S6. The snapshots of the 20% N-doped (above) and 20% Si-doped (below) systems at the different densities. The carbon atoms are in gray, nitrogen atoms in blue, silicon atoms in yellow, oxygen atoms in red, and hydrogen atoms in silver.

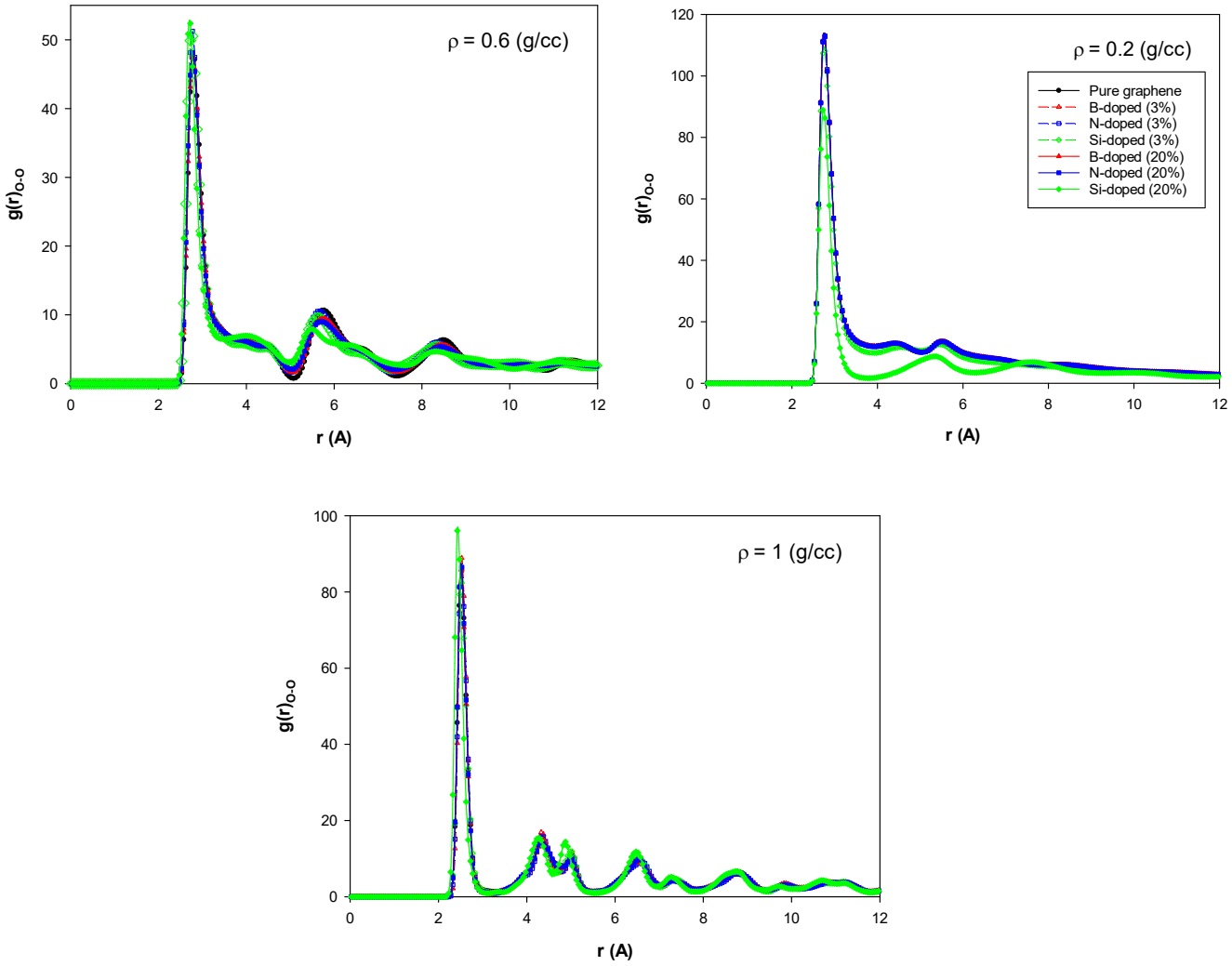


Fig. S7. The O-O RDF of the confined water molecules in the pure and the different doped systems at the different densities.

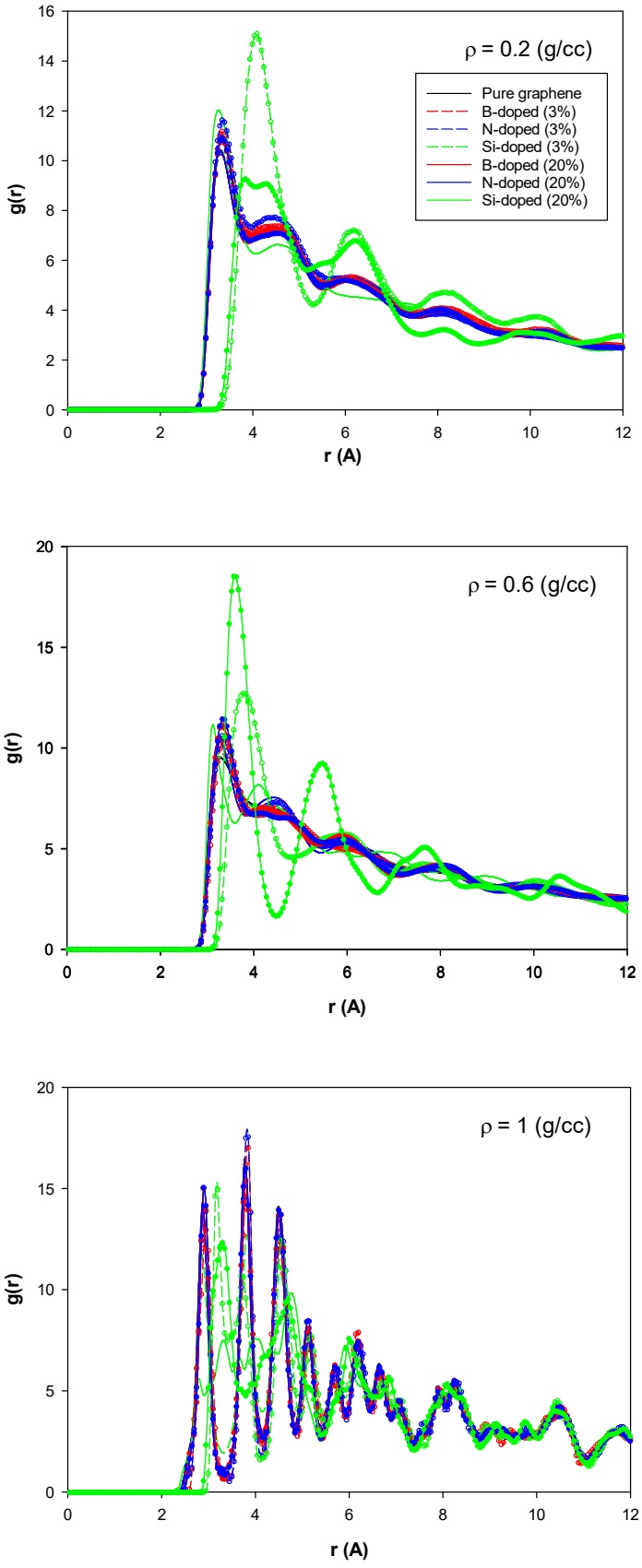


Fig. S8. The C-O RDFs (lines without symbols) and doped atom-O RDFs (lines with symbols) in the pure and the different doped systems at the different densities.

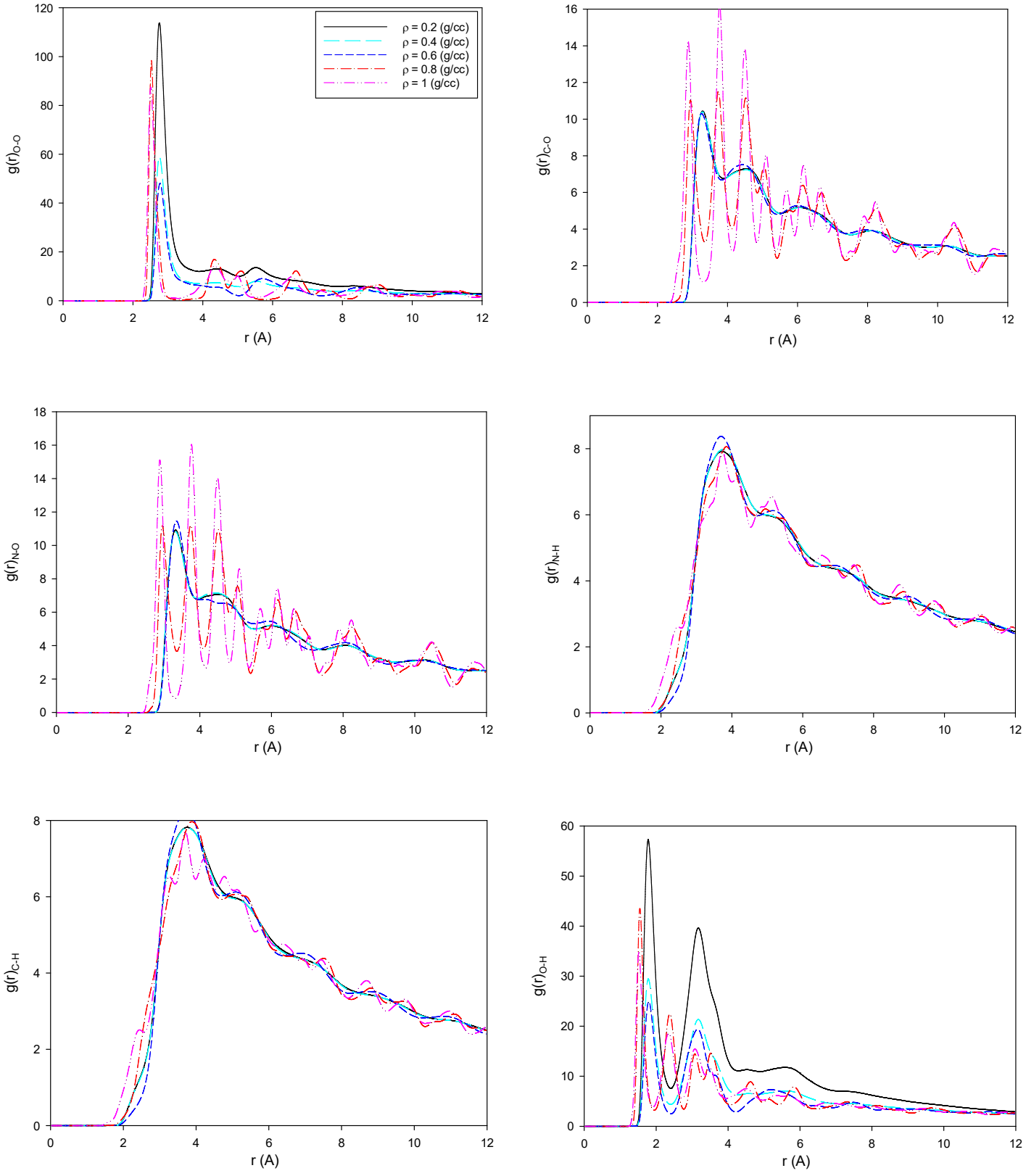
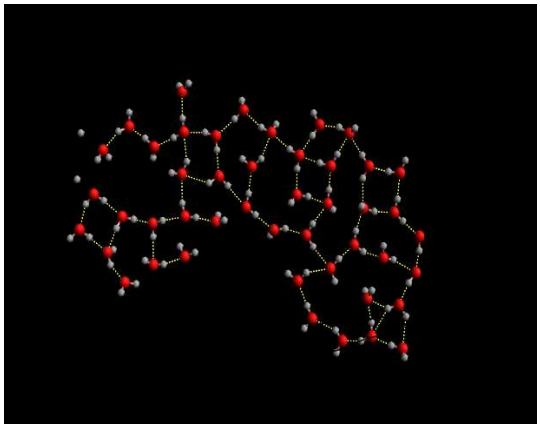
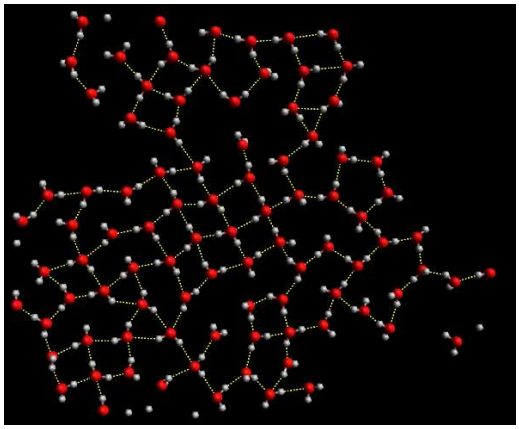


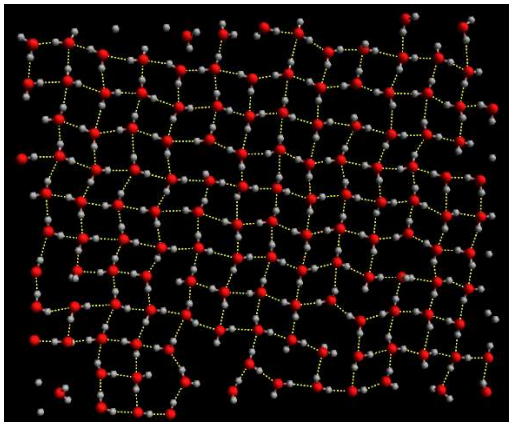
Fig. S9. The different RDFs of the confined water molecules in the high N-doped system at the different densities.



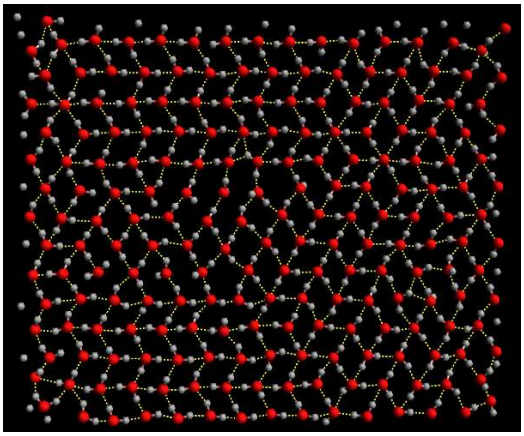
ρ= 0.2 (g/cc)



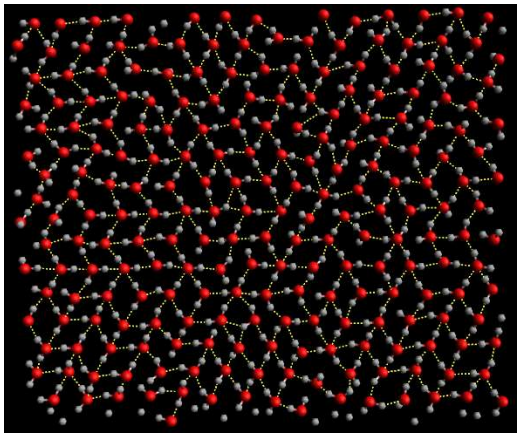
ρ= 0.4 (g/cc)



ρ= 0.6 (g/cc)



ρ= 0.8 (g/cc)



ρ= 1 (g/cc)

Fig. S10. The snapshots of the confined water molecules confined between the low N-doped graphene at the different densities. The oxygen atoms are in red and hydrogen atoms are in gray. The dashed lines shows the HBs (the bond length of 2.5 Å and the angle of 150º. Please note the void formation at lower densities.

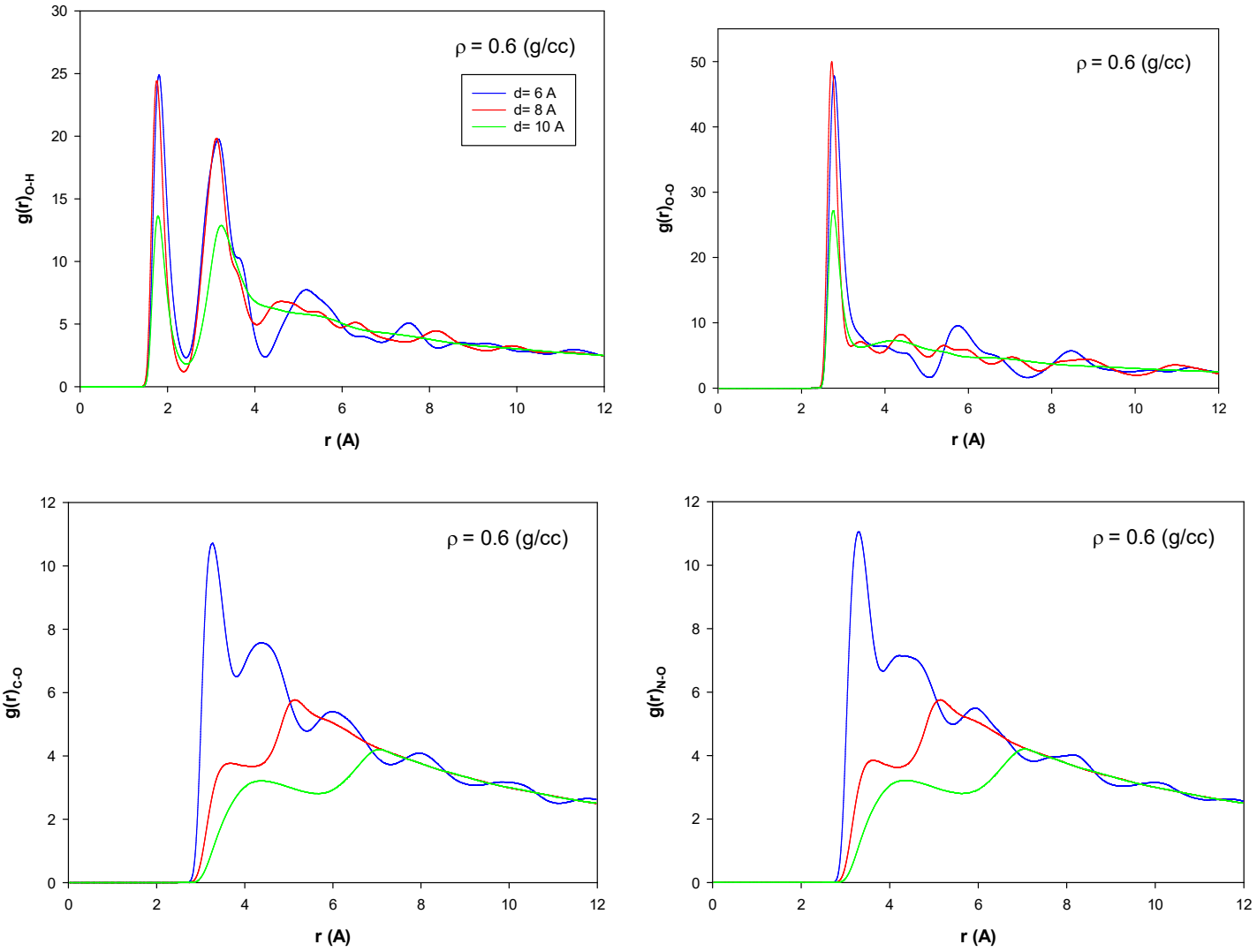


Fig. S11. The different RDFs of the confined molecules in the high N-doped graphene with the random doped atoms distribution at different slit pore sizes.

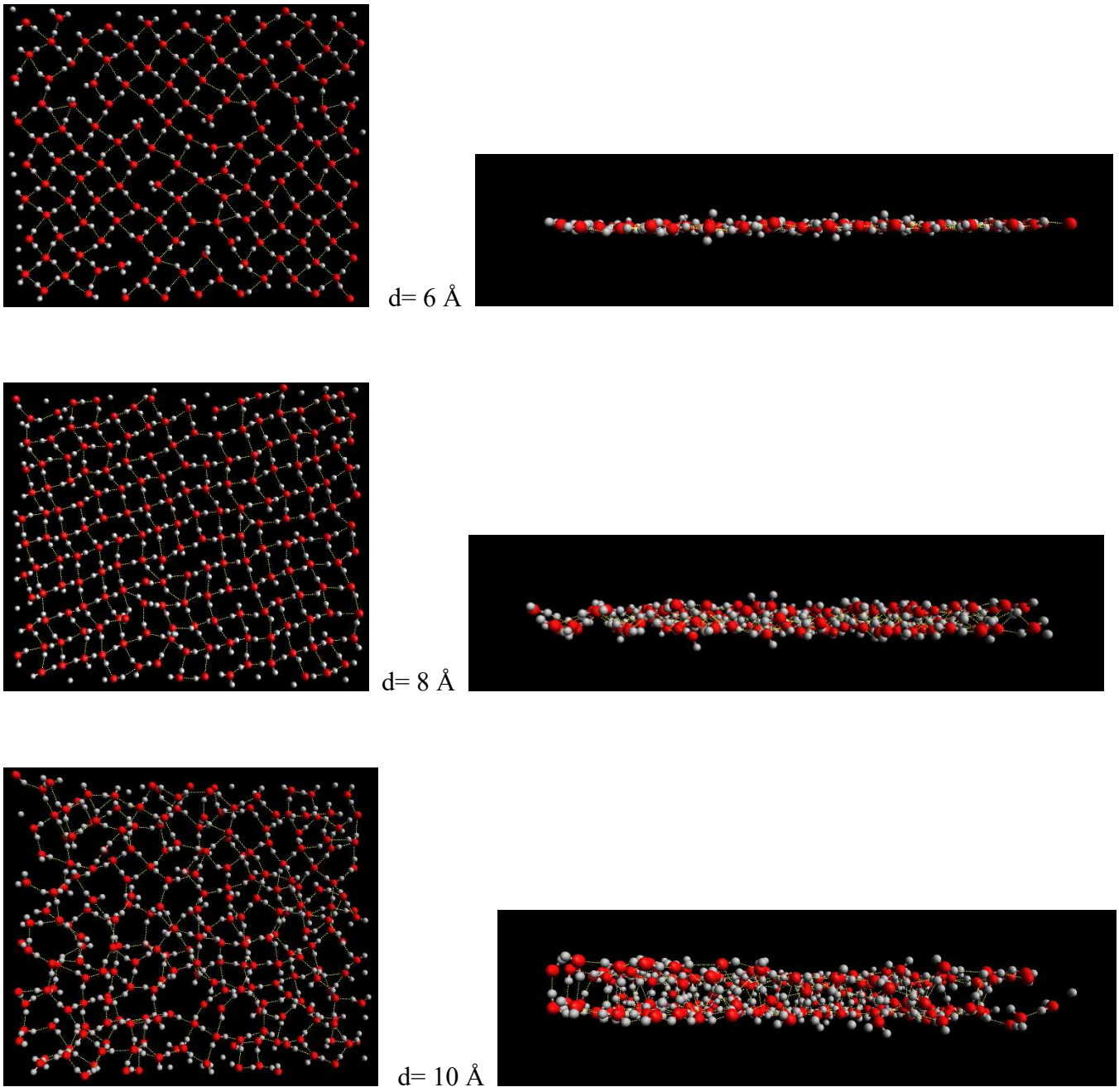


Fig. S12. The snapshots of the confined molecules in the high N-doped graphene with the random doped atoms distribution at different slit pore sizes.

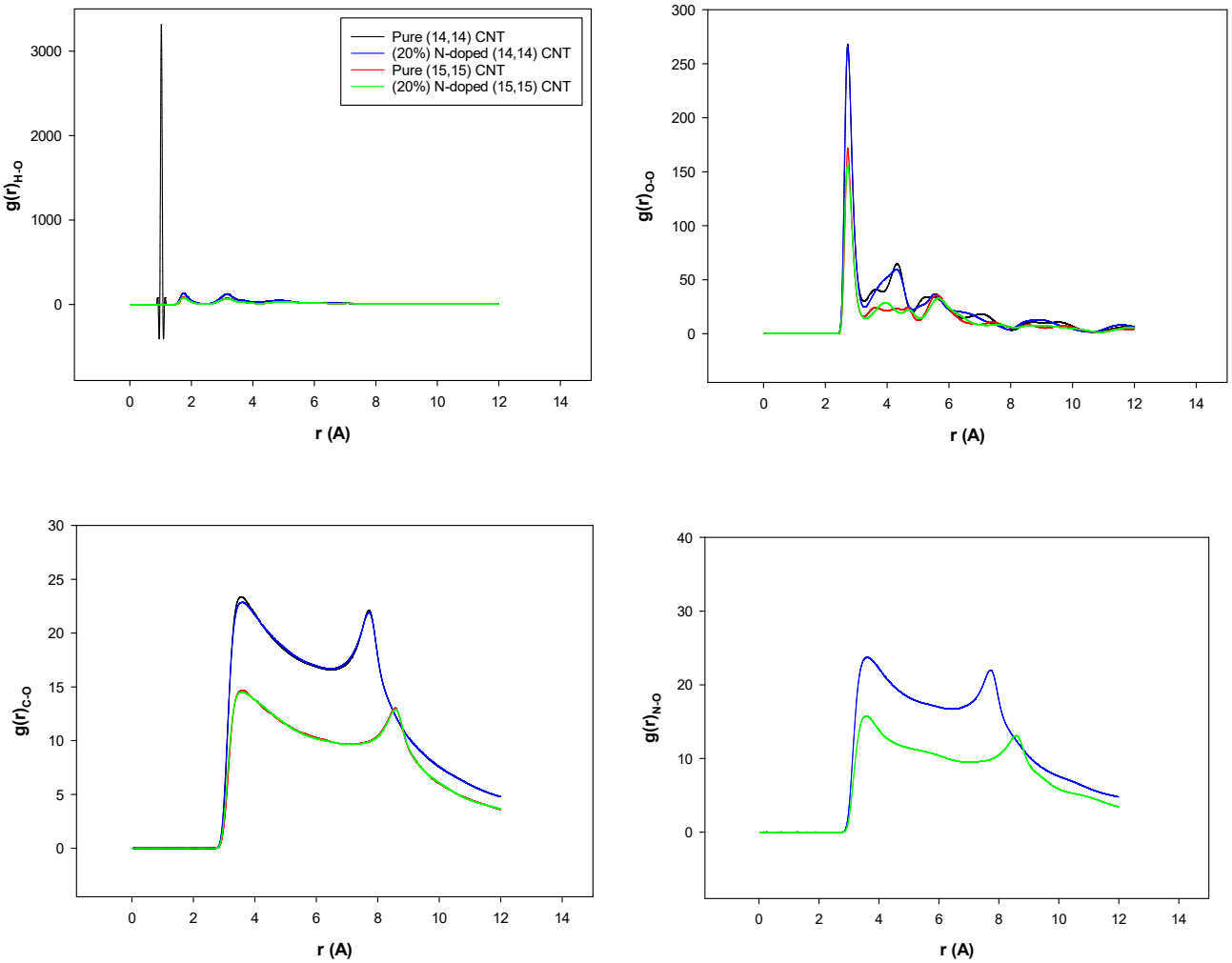


Fig. S13. The different RDFs of the confined molecules in the pure and high N-doped (14,0) and (15,0) CNTs with the random doped atoms distribution.

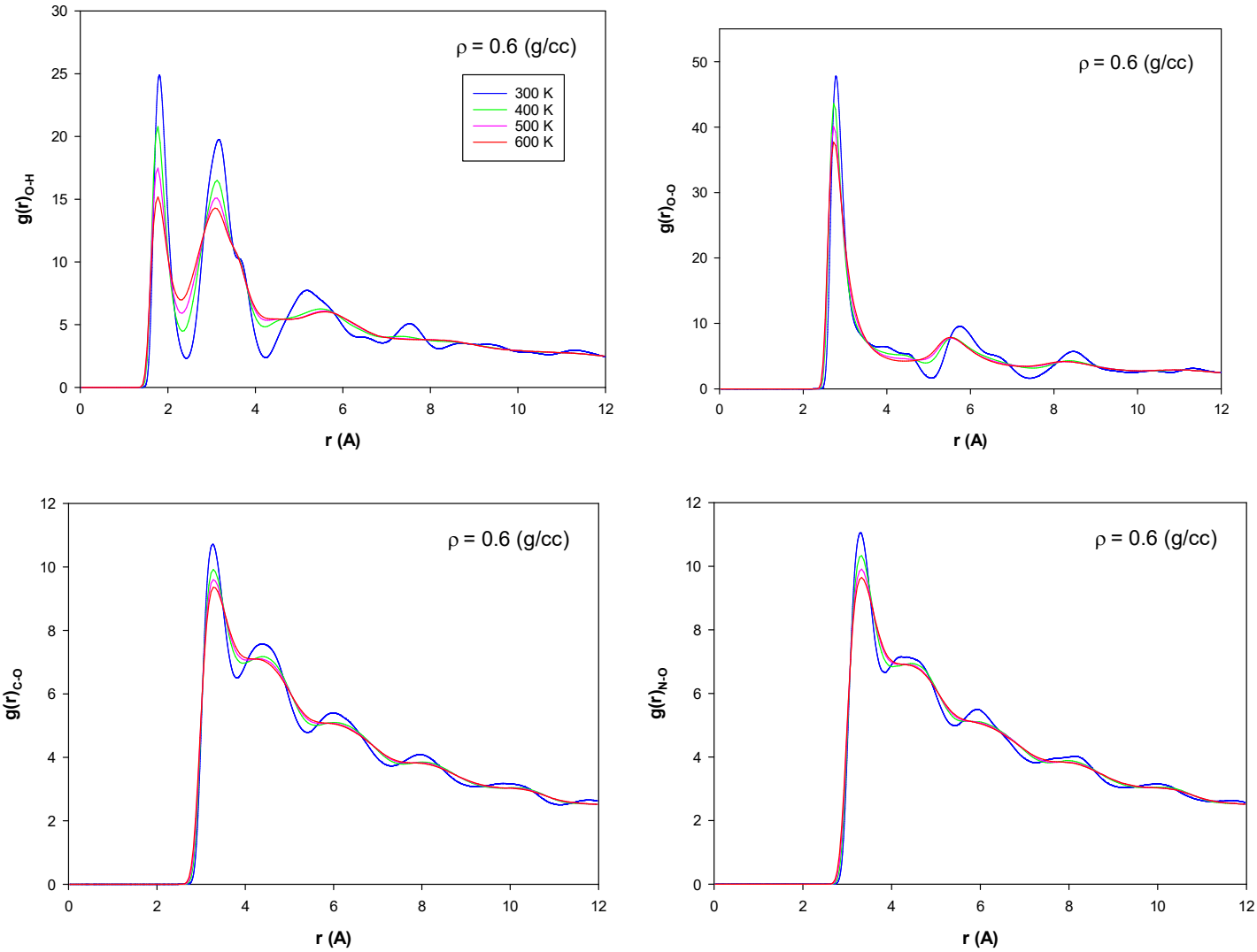


Fig. S14. The different RDFs of the confined molecules in the high N-doped graphene with the random doped atoms distribution with the slit pore of 6 (Å) at different temperatures.

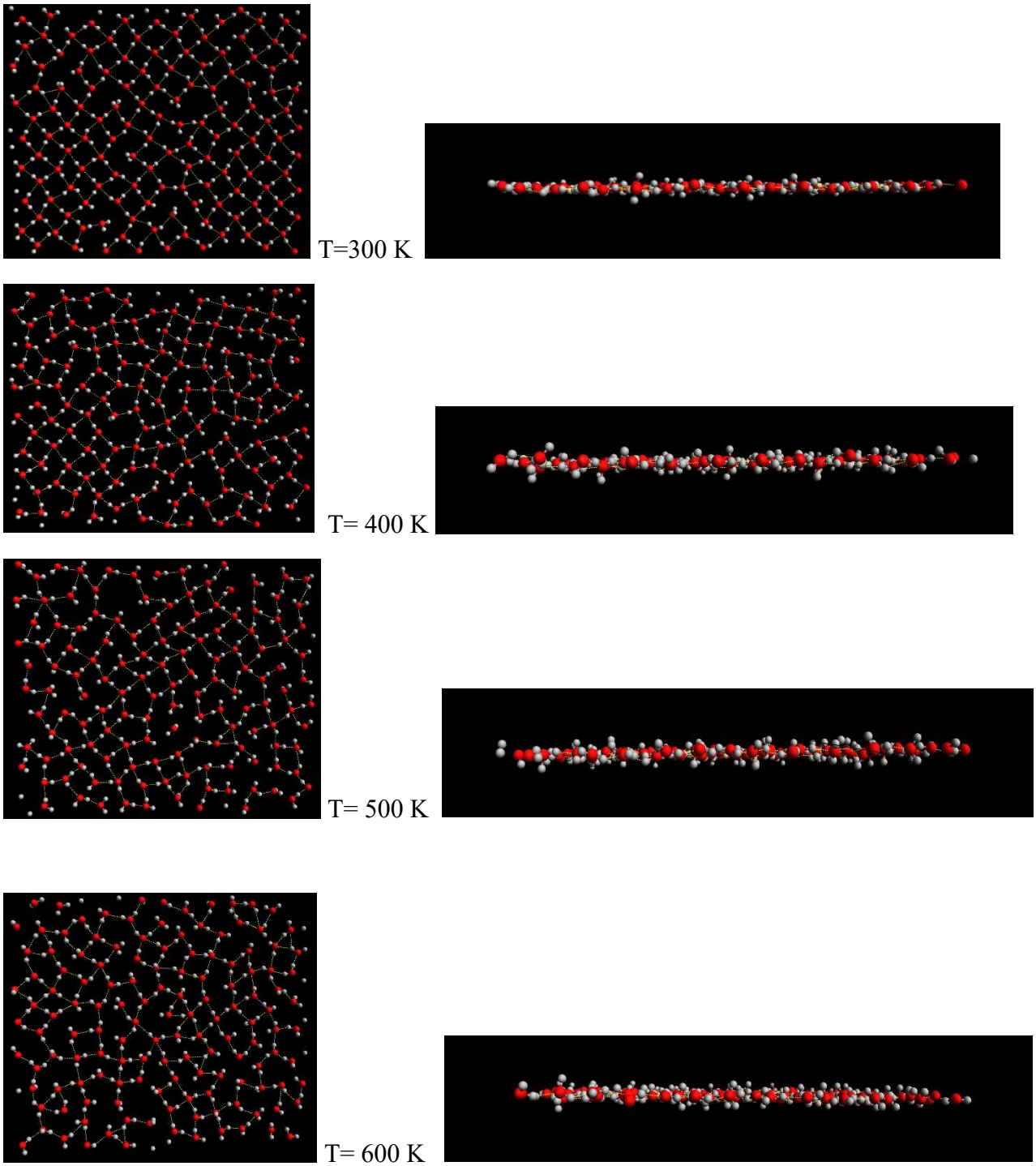


Fig. S15. The snapshots of the confined molecules in the high N-doped graphene with the random doped atoms distribution with the slit pore of 6 (Å) at different temperatures.

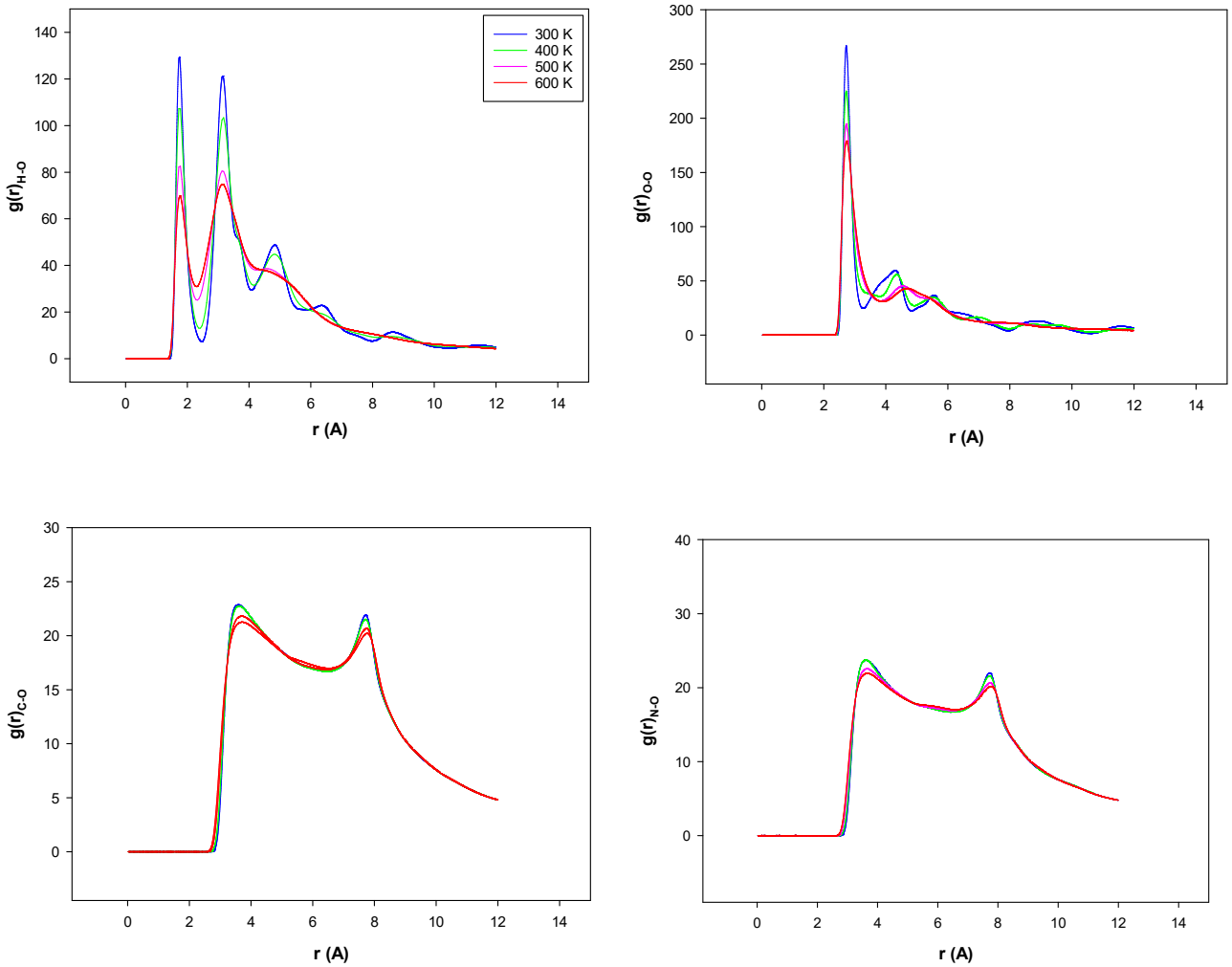


Fig. S16. The different RDFs of the confined molecules in the high N-doped (14,0) CNT with the random doped atoms distribution at different temperatures.