

# Water Self-Diffusivity Confined in Graphene Nanogap using Molecular Dynamics Simulations

M. Moulod and G. Hwang, <sup>a)</sup>

*Mechanical Engineering Department, Wichita State University, Wichita, Kansas, 67260, USA*

## I. WATER AND GRAPHENE STRUCTURES

Water and graphene models have been adopted from previous literatures <sup>1-11</sup> (Tables I and II). Water TIP3P and SPC/E models and rigid graphene are used.

Table I. Graphene Model Details

Graphene Model	
$m_C$ , AMU	12.0107
$C_{charge}$ , $e$	0.0000
$K_{C-C}$ , kcal/Å	350
$r_0$ , Å	1.53
$K_{C-C-C}$ , kcal/degree	50
$\theta_{C-C-C}$ , degree	120
$\epsilon_{C-O}$ , kcal/mol	Variable
$\sigma_{C-O}$ , Å	Variable

Table II. Water TIP3P Original and SPC extended (SPC/E) Models Details

Water Models	Water TIP3P model <sup>12-14</sup>	Water SPC/E model <sup>12-14</sup>
$m_O$ , AMU	15.9944	15.9944
$m_H$ , AMU	1.0084	1.0084
$O_{charge}$ , $e$	-0.834	-0.8476
$H_{charge}$ , $e$	0.417	0.4238
$K_{O-H}$ , kcal/Å	450	450
$r_{0,O-H}$ , Å	0.9572	1.00
$K_{H-O-H}$ , kcal/degree	55	55
$\theta_{H-O-H}$ , degree	104.52	109.47
$\epsilon_{O-O}$ , kcal/mol	0.1521	0.1553
$\sigma_{O-O}$ , Å	3.1507	3.166
$\epsilon_{H-H}$ , kcal/mol	0.0	0.0
$\sigma_{H-H}$ , Å	0.0	0.0
$\epsilon_{O-H}$ , kcal/mol	0.0	0.0
$\sigma_{O-H}$ , Å	0.0	0.0
$\epsilon_{O-O}$ , kcal/mol	0.1521	0.1553
$\sigma_{O-O}$ , Å	3.1507	3.166
$\epsilon_{H-H}$ , kcal/mol	0.0	0.0

## II. POTENTIALS

The following interatomic potentials for different interactions are used. The water structure is rigid for both models, thus the bond and angle coefficients are not important as they are fixed and their related potentials will be zero. For Graphene, the same structure is used and there is no interaction between carbon atoms<sup>13</sup>.

$$\varphi_{total} = \varphi_{bond} + \varphi_{angle} + \varphi_{van\ der\ walls} + \varphi_{coulombic} \quad (1)$$

$$\varphi_{bond} = \frac{1}{2}k_b(r-r_0)^2, \quad \varphi_{angle} = \frac{1}{2}k_\theta(\theta-\theta_0)^2 \quad (2)$$

$$\varphi_{van\ der\ walls} = 4\epsilon_{ij} \left\{ \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{ij}}{r_{ij}} \right)^6 \right\}, \quad \varphi_{coulombic} = \frac{q_i q_j}{e r_{ij}} \quad (3)$$

## III. PEAK WATER DENSITY VS NANOGAP SIZES

The peak local water density is related to the water-graphene interatomic potentials,  $\epsilon_{C-O} = 0.0478, 0.0937, \text{ and } 0.1646$  kcal/mol and nanogap sizes,  $L_z = 0.7$  to 4 nm. For the weak water-graphene interactions,  $\epsilon_{C-O} = 0.0478$  and 0.0937 kcal/mol, the local water densities monotonically increase as the nanogap size increases, and the increases are relatively moderate. However, for the strong water-graphene interaction,  $\epsilon_{C-O} = 0.1646$  kcal/mol, it increases until it reaches a peak at  $L_z = 3$  nm, and shows a small decrease as it further increases the nanogap size. It can be explained by the fact that after reaching the highest density, the repulsion forces between water molecules in the dense layer together with the attraction forces between water molecules inside and outside of dense layer overcome the surface attraction of graphene thus, adding more water molecules increases these forces and reduces the density. There is no significant difference between the two water models for the local density.

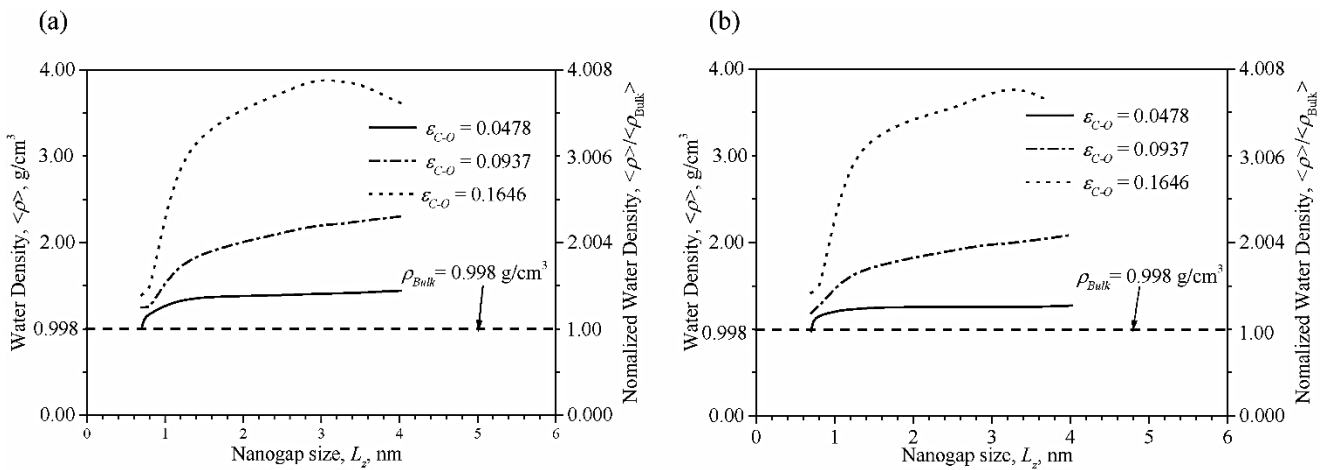
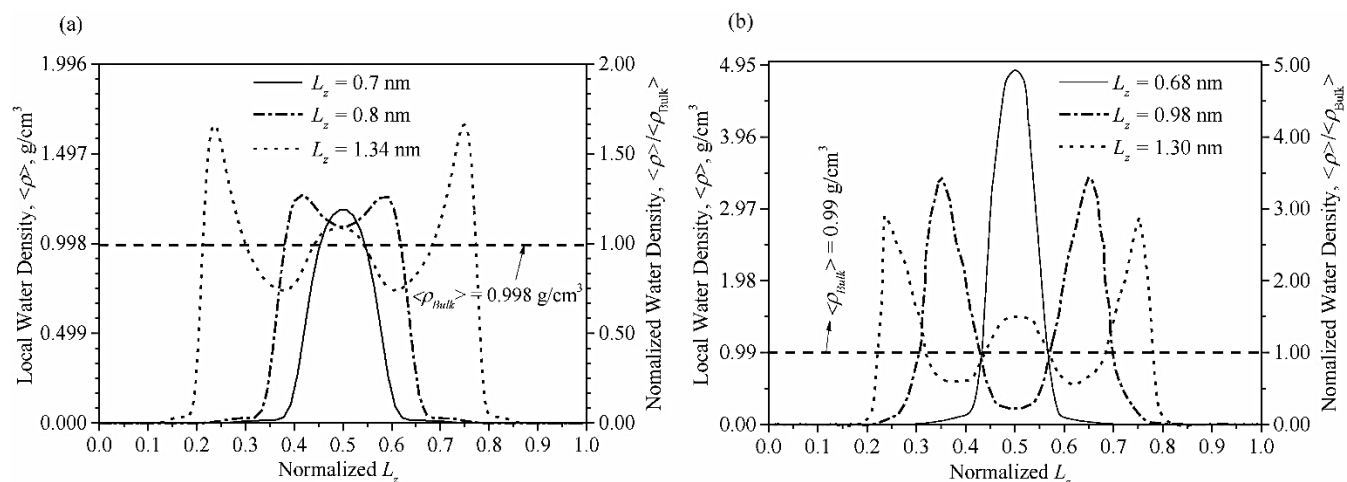


FIG S1. Variations of the peak water density as a function of the nanogap size,  $L_z$ , for three different water-graphene interatomic potentials,  $\epsilon_{C-O} = 0.0478, 0.0937, \text{ and } 0.1646$  kcal/mol, both for (a) TIP3P, and (b) SPC/E water models. The self-diffusivity of bulk water is also shown.

#### IV. LOCAL WATER DENSITY VS NANOGAP SIZES

**FIG S2 shows the local water density for different graphene nanogap sizes; (a) is the result of this study and (b) is the result given in the previous study<sup>15</sup>. Both results show the similar local density profiles for the similar size of graphene nanogap. However, the local density near the graphene surface in (b) is higher than that of this study due to higher water-carbon interaction ( $\sigma_{C-O} = 3.283 \text{ \AA}$  and  $\epsilon_{C-O} = 0.1156 \text{ kcal/mol}$ ) and use of an open nanogap system (water is freely accessible to the graphene nanogap).**



**FIG S2. Predicted local water density for different nanogap sizes for (a) present study,  $L_z = 0.7, 0.8,$  and  $1.34 \text{ nm}$ , using the SPC/E water model and  $\sigma_{C-O} = 3.19 \text{ \AA}$  and  $\epsilon_{C-O} = 0.0937 \text{ kcal/mol}$  (b) Choudhury & Pettitt, JACS, 2005 using Lorentz-Berthelot rules and  $\sigma_{C-O} = 3.283 \text{ \AA}$  and  $\epsilon_{C-O} = 0.1156 \text{ kcal/mol}$ . Right y-axis shows the normalized local and bulk water density.**

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