

## Wetting Transparency of Graphene

Javad Rafiee<sup>1</sup>, Xi Mi<sup>2</sup>, Hemtej Gullapalli<sup>3</sup>, Abhay V. Thomas<sup>1</sup>, Fazel Yavari<sup>1</sup>,  
Yunfeng Shi<sup>2</sup>, Pulickel M. Ajayan<sup>3\*</sup> and Nikhil A. Koratkar<sup>1,2\*</sup>

<sup>1</sup>*Department of Mechanical, Aerospace and Nuclear Engineering,*  
<sup>2</sup>*Department of Materials Science and Engineering,*  
*Rensselaer Polytechnic Institute, Troy, New York, USA*

<sup>3</sup>*Department of Mechanical and Materials Engineering,*  
*Rice University, Houston, Texas, USA*

**(1) Advancing and receding contact angles**

In addition to the sessile drop (as in Fig. 2a in manuscript), we also studied the wetting transparency with respect to the advancing and receding contact angles. Typical results are shown below for baseline silicon and silicon with monolayer graphene coating. The measured advancing contact angle for silicon (~36 deg: Fig. S1a) was very similar to monolayer graphene coated silicon (~35 deg: Fig. S1b). Similarly the receding water contact angle on silicon (~30 deg: Fig. S1c) was also similar to that of monolayer graphene coated silicon (~31 deg: Fig. S1d). The difference between the advancing and receding contact angles (i.e. the contact angle hysteresis) for the samples were in the range of 4 to 6 degrees.

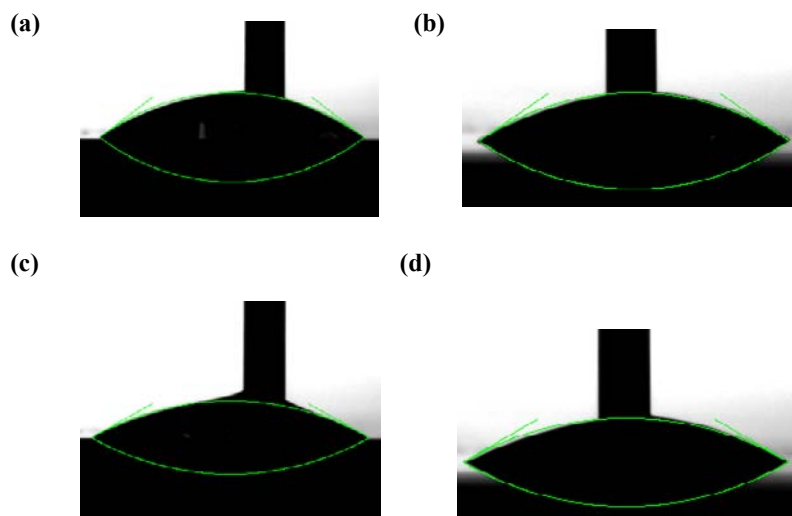


Figure S1: Advancing water front for baseline silicon (a) and the monolayer graphene coated silicon (b). Corresponding images for the receding water front for silicon (c) and monolayer graphene coated silicon (d).

**(2) Molecular Dynamics (MD) simulation approach:**

MD simulations are generally limited to nanometer-sized water droplets, which leads to non-negligible line tension force at the tri-phase junction. Therefore the apparent contact angle is usually system-size dependent. Werder et al<sup>1</sup> used MD simulations to calculate the contact angles of water on graphite with water droplets of different radii. Thus, by fitting the apparent contact angle as a function of droplet base radius to the modified Young's equation, they obtained the contact angle of a macroscopic water droplet through extrapolation to infinite droplet size. However multiple simulations with water droplet of different sizes are required and this is computationally inefficient. We utilize a new wetting system setup, which is free of system size effect on the contact angle. A slab-like simulation box is adopted which is thin in y-direction and long in x- and z-directions. Periodic boundary conditions are applied such that the water droplet is infinite in y-direction with a truncated cylindrical cross-section, as seen in Fig. S2. The advantage of this approach is that the contact line between water and substrate is straight, thus there is no contribution of line tension due to curvature. As a consequence, the macroscopic contact angle can be directly calculated through fitting the x-z projection of a nanometer-sized water droplet.

To test the system size dependency of our approach and to compare with Werder's classical approach<sup>1</sup>, we simulate a series of samples with 1000, 2000, 4000 and 8000 water molecules on top of graphite. The interaction parameters are identical to case 1 as in Werder's work<sup>1</sup>. For our approach, all of these simulation boxes are about 21.3 Å in y-dimension. The x- and z-dimensions are made large enough for each individual sample to prevent the interaction between the sample and its periodic images. The contact angles obtained using our method and those of Werder's (sample 1, 5, 6, 7 and 8 in Ref. 1) with similar system setup and force field

parameters have been organized in Table 1. The contact angles of our samples do not exhibit system-size dependency once the size of the droplet is larger than 2000 molecules. The contact angle is around  $109^\circ$ . This value is close to the macroscopic contact angle  $104^\circ$  by Werder *et al*<sup>1</sup>. Note that Werder's result might be biased by the smallest droplet, for which the contact angle has the largest uncertainty.

Reference:

1. Werder, T., Walther, J.H., Jaffe, R.L., Halicioglu, T. & Koumoutsakos, P. On the Water–Carbon Interaction for Use in Molecular Dynamics Simulations of Graphite and Carbon Nanotubes. *The Journal of Physical Chemistry B* **107**, 1345-1352 (2003).

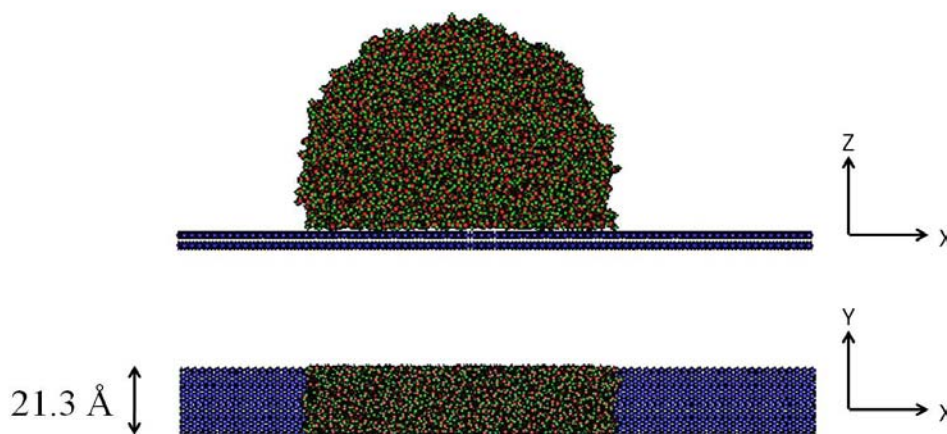


Figure S2: Side (top) and top view (bottom) of the snapshots for 4000 water molecules on double graphene layers. The dimensions are  $393.5 \text{ \AA} \times 21.3 \text{ \AA} \times 200 \text{ \AA}$ . Only part of the simulation system is shown. Blue, red and green dots are C, O and H atoms respectively.

Table. 1: Comparison of the contact angle predicted by Werder's approach and our approach. The system setup is water on double layer graphene. Same sets of force field parameters are used here for both approaches.

H <sub>2</sub> O molecules in the system	Contact angle (deg) by our new method	H <sub>2</sub> O molecules in the system	Contact angle (deg) by Werder's method
1000	121.1	1000	115.5
2000	109.8	2000	111.3
4000	109.2	4000	109.2
8000	110.9	8379	108.8
		17576	107.7
		$\infty$	103.9 <sup>a</sup>

<sup>a</sup> Obtained through linear fitting.

### (3) Effect of coating layer thickness on the wetting transparency effect

The continuum model (Eq. 3 in manuscript) was used to predict the effect of the coating layer thickness on the wetting transparency effect. Figure S3 shows the water contact angle transition from copper to graphite for carbon film coatings on copper with thicknesses of 0.34 nm, 0.7 nm and 1 nm. Even the ultrathin 0.7 nm or 1 nm coatings fail to provide wetting transparency. The wetting transparency effect becomes apparent only when one goes down to 0.34 nm (i.e. the thickness of graphene). This highlights the importance of graphene in its ability to provide ultra-thin conformal coatings on a variety of substrates.

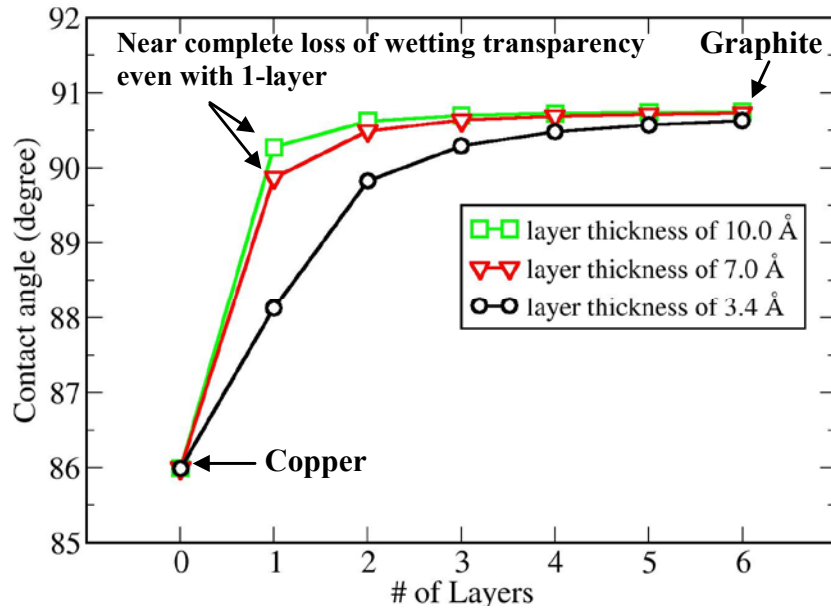


Figure S3: Effect of coating layer thickness on the water contact angle transition response.