

Response to Editorial office

-Please remove "et al." from the References and add all author names

We have updated the references accordingly.

-Please embed all Tables/Figures in the text of the manuscript close to where they are first mentioned

We have moved all Figures/Tables accordingly.

-The text of Articles should be subdivided into the following sections: Introduction, Experimental Section, Results and Discussion, and Summary and Conclusions.

We have divided the text accordingly. Note that we do not have experimental section and the Results and Discussion section has been divided into subsections for better explanation.

-Please relabel all Figures in the Supporting Information for Publication file as Figures S1, S2, S3, etc...

-The pages in the Supporting Information should also be numbered consecutively (S1, S2, etc.)

The Figure labels and pages have been changed in the Supporting Information accordingly. Also the TOC is resized to fit the Langmuir definition (using the *langd5* option of *achemso* package in LaTeX).

Reviewer(s)' Comments to Author:

PLEASE NOTE: When reviewers point to specific line numbers in their comments, they are often referring to the line numbers inserted by ACS Paragon Plus in the PDF Proof of the manuscript. The PDF Proof is attached.

Response to Reviewer 1

Reviewer: 1

Recommendation: Major revisions needed as noted.

Comments:

The authors developed a multiscale theory to model the wettability at the interfaces of the doped 2D materials and discussed the effects of defects and airborne contaminations on wettability. They found that 2D materials with high quantum capacitances possess a wider range of tunability in the interfacial tension, the molecular reorientation of liquid molecules adjacent to the interface and the electrical double layer formed in the liquid phase dominate the contact angle change upon doping. However, the following questions should be reconsidered and discussed.

We thank the reviewer for his/her careful assessment of our theory. Please find our response as follows.

1. The presented work is more like static electrowetting on 2D materials supported by an insulator, because only the charge is considered and treated using an averaged density. Therefore, the title is not appropriate. Please refer to the paper about MD simulations of electrowetting: Phys. Rev. Lett., 104: 246101, 2010; Nanoscale, 7: 2561-2567, 2015.

We thank the reviewer for the comments about our present title. Nevertheless we think the current title is appropriate and fundamentally different from the two reports suggested by the reviewer. Our reasons are as follows:

- 1) As we discussed in the main text, the origin of the charges induced in 2D materials does not necessarily come from an electrostatic field, namely the electrowetting. The underlying substrate or the adsorbents on the substrate before deposition of 2D material can also dope 2D material and result in the same effect. Since we already specified the two different possibilities in the introduction, we believe that the current title can fully reflect the scope of this manuscript and is of broad interest.
- 2) Our multiscale model aims to understand the contact angle change on a sheet of doped 2D material observed experimentally. Therefore we included the effects of quantum capacitance and the effect of electrolytes, which cannot be revealed using classical MD simulations (the nanoscale wetting problem). On the other hand, we agree with the reviewer that the dynamic wetting behavior may be difficult to be resolved with our current model. We therefore added a short paragraph on Page 11 to reflect this fact. On Page 11: "Note that the current model can only reveal the static and macroscopic wetting behavior, while the effects of dynamic properties or surface roughness, as discussed by some recent MD-based nano-electrowetting studies, are not considered here."
- 3) Note that we understand in the case of substrate-induced doping of 2D materials, the charge distribution may not be spatially uniform and contains local potential fluctuation at the nanometer scale. Nevertheless, since we consider the macroscopic wetting behavior, we believe the local fluctuations are greatly smoothened, so the assumption of uniform charge distribution should remain valid here. Moreover, we already included the discussions about the effect of surface defects to address the discrepancy between theoretical and experimental results, complementary to the original model.

2. Please compare the order of magnitude of influence raised by the fermi energy, orientation and EDL from the aspects of both energy and geometry. In the case of high concentration of electrolyte, EDL should take priority to the other two. In the case of low concentration, the assumption of decoupling between the effects of dipole reorientation and EDL is doubtful.

We thank the reviewer for the suggestions. We did compare the magnitudes for different effects considered here. Specifically, we found that the reorientation effect (molecular scale) is slightly more predominant than the electrowetting effect (continuum scale) (Figs. 4b and 4c), and the change of Fermi energy level, or the quantum capacitance effect, has no net effect on the wetting behavior, as illustrated in eqs. (1), (3), and (7). In order to make it clearer, we have added more description in the abstract.

We agree with the reviewer that decoupling the reorientation and EDL effect may not fully describe the real liquid-solid interfacial behavior. We believe that at moderate electrolyte concentrations ($< 10^{-1}$ M), the two effects can be safely decoupled, since the screening length of Coulombic interaction is much larger than the effective distance of dispersion interactions. When $c_0 = 10^{-1}$ M, the Debye screening length is ~ 0.9 nm, which is slightly larger than the thickness of water boundary layer (~ 0.8 nm) in the MD simulations (see Figs. 3c and 3d), therefore the Coulombic contributions to the reorientation should be still valid. We do agree that such assumptions may break down for higher concentrations, since the screening length may be comparable or shorter than the effective distance of dispersion interactions. We also note that recent experimental and theoretical works (J. Phys. Chem. Lett. 2016, 7, 2157–2163, Phys. Rev. Lett. 2017, 119, 026002) reveal a more complex nature of highly concentrated electrolyte solution, that the screening length actually increases beyond the Debye-Hückel regime, instead of exponential decay from classical theories. The results indicate that our decoupled model may still be valid, provided an accurate description of the EDL at higher concentrations. Nevertheless, to keep the model simple and generally applicable, we have reduced the upper limit for the electrolyte we use for the EDL calculations to 0.1 mol/L, to be consistent with the decoupling assumption (see Figure 4). A brief discussion of our choice of concentration range is added on Page 19.

Note that as we indicated in the main text, for a diluted system (e.g., $c_0 \sim 10^{-7}$ M), the state-of-the-art MD framework does not allow us to consider the individual ions in the simulation box (in average 1 ion in 5×10^8 water molecules). Therefore, treating the EDL with a mean-field approach is practical.

3. From eqn. 3, materials with higher C_{2D} would have a smaller range of tunability in the interface tension, which is against the conclusion in the abstract.

We would like to stress that Eqn. 3 only deals with the surface tension change of a sheet of bare 2D material. After considering the water-2D material interface, the decrease of surface tension of 2D material (described by Eq. (3)) is cancelled out by the change of interfacial tension (see Eqs. (7) and (8)). Accordingly, Eq. (3) does not directly result in a contact angle change. We have added more description on Page 9 to clarify this point.

On the other hand, in Fig. 6, we actually compare the contact angle change as a function of the voltage applied. As described by Eq. (16), a high C_{2D} 2D material can store a higher σ_{2D} , thereby resulting in a higher contact angle change. To make it clear, we have added one sentence in the revised abstract, on page 25 as well as in the abstract.

4. When analyzing eqn. 5, why do the authors take surface energy of 2D material be invariant when charged? Please explain the reason. Surface tension of SPC/E water is 0.0636 N/m rather than 0.0728 N/m, please refer to the paper: J. Chem. Phys. 126, 154707, 2007.

We agree with the author that the surface tension value of SPC/E water is more appropriate here and therefore has used the new value in analysis of the MD results in the revised manuscript (page 12, 20 and Figure 4).

Nevertheless, as revealed in Eq. (5), the surface tension value only affects the calculated $\Delta\cos\theta$, while the MD-extracted $\Delta\Phi$ values remain unchanged. Accordingly, as shown in Figs. 4(b) and 4(c), the main conclusion that the reorientation effect is slightly more predominant than the EDL effect still holds.

Response to Reviewer 2

Recommendation: Publish as is.

Comments:

This is a very interesting theoretical paper on modeling the change of interfacial tension between a liquid and a sheet of 2D monolayer.

We thank the reviewer for his/her positive response about our work.

Response to Reviewer 3

Recommendation: Publish after minor revisions noted.

Comments:

This paper reports a multiscale theory study of the effect of doping on the wettability of 2D materials. This is a timely report as the wettability of 2D materials is sensitive to many factors. Previous theory work has not address many of the experimental factors, such as doping, contamination in a systematic way. Publication is recommended after the authors clarify the following minor issue.

Figure 5 and associated discussion treated the molecular doping and back gating in different ways. This is puzzling because electrostatically the two doping strategies produce the same effect: inject charge to graphene and leave a layer of counter charge at the surface next to graphene. The authors also assumed that σ_v is equivalent to σ_{2D} (above eq. 14), this is also puzzling because in the case of molecular doping, the absence of graphene would leave the substrate charge neutral (since there would be no charge transfer to graphene). Did I miss something here?

We appreciate the reviewer's positive response.

Indeed, modeling molecular and electrostatic doping effects are effectively the same since in both cases, charges are injected into the covered 2D material. Nevertheless, the physical pictures for the two cases are different when dealing with voids.

Specifically, in the case of molecular doping, the doping effect results from the surface charges on a substrate, which in turn transfer to the covered 2D material, as revealed by the charge transfer model (Yan et al. ACS Nano 2011, 5, 1535-1540). In the void region, the charges are directly in contact with the electrolyte solution, so we assume that the interfacial charges build up the EDL, similar to that on a 2D material surface. The effective capacitance (C_v in Eq. (14)) here is assumed to be $C_v \sim C_{DH}$, where C_{DH} is the EDL capacitance using Debye-Huckel approximation.

On the other hand, in the case of electrostatic doping, the charge density is controlled by the applied voltage, with no fixed charges on the substrate. The electric field builds up the EDL directly. In the void region, the charge density σ_{2D} is the same in both cases, while however, the effective capacitance is different since the gate voltage is applied through a gate dielectric layer, so that $C_v \sim C_d$, where C_d is the capacitance of the dielectric layer.

We understand the model may be oversimplified since σ_v can be influenced due to lateral diffusion, which is beyond the current scope of this report.

We have added further description on Page 21 to reflect our response here.