**A Multiscale View of the Doping-Induced Tunable Wettability on Two-Dimensional Materials**

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**Abstract:**

The emergence of 2D-material-based liquid-phase devices calls for the need for understanding the wetting property at the 2D-material-liquid interface, and particularly the doping-induced tuning of wetting properties. In this letter, we propose a multiscale view of the doping-induced tunable wettability of 2D materials, by combining the reorientation effect of water molecules estimated by MD simulation, and the electrowetting effect calculated by continuum model. We reveal the electrostatic nature of the doping-induced wettability under both scale. We further evaluate the recent finding of doping-induced wettability tuning of graphene with the proposed model, by considering incomplete surface coverage of 2D materials. We find that minor surface incompleteness can cause great discrepancy in the measured value of interfacial wettability, requiring extreme care for interpreting the experimental results. In addition, we prove that a 2D material with higher density of states can essentially reduce the gating voltage in a 2D-material-based electrowetting device, and rank the tunability of the 2D materials as: MoTe$\_{2}$ > MoS$\_{2}$ > WTe$\_{2}$ > WS$\_{2}$ > germanene > silicene > graphene. Our multiscale analysis provides a comprehensive view of the wettability of 2D material interface, and we believe operational 2D-material-based liquid manipulating devices will be facilitate by the principles presented in this letter.

The emergence of two-dimensional (2D) materials has attracted broad interest in various research fields, inspired by their unique physical and chemical properties. Recent progress of scalable 2D material synthesis paves the way for their liquid phase 2D-material-based applications, for instance functional coating [@Prasai\_2012; @Rafiee\_2010; @Kim\_2014], nanotribology devices [@Yin\_2014; @Tang\_2016; @Feng\_2016], nanoporous desalination apparatus [@Surwade\_2015; @Rollings\_2016; @Jain\_2015], droplet manipulation [@Hern\_ndez\_2013; @Vijayarangamuthu\_2015], etc. To fully exploit the physics of the interface between 2D materials and liquid phase, a comprehensive understanding of the 2D-material-liquid interaction, and in particular, the wettability, is of great importance.

Wetting on atomically-thin 2D materials has long been a hot but highly disputed topic [@taherian2013what; @Kozbial\_2015; @Parobek\_2015; @Govind\_Rajan\_2016]. Accurate description of the intrinsic wettability of 2D materials is known to be challenging. Recent studies show that the wettability on graphene [@li\_effect\_2013; @Xu\_2013\_withwhat; @kozbial\_study\_2014] and MoS2 [@Kozbial\_2015; @Chow\_2015] is strongly affected by airborne contaminants. Meanwhile, the contact angle measurement technique which has been widely to determine the wettability on 2D materials, may also suffer inaccuracy from contact angle hysteresis caused by local defects [@raj\_wettability\_2013]. On the other hand, unlike bulk materials, the thickness of a 2D material falls within the effective range of dispersion interactions. As a result, the dispersion interaction between the substrate underneath the 2D material and liquid molecules is not fully screened by the 2D material, giving rise to the fascinating property known as the "wetting-translucency" [@rafiee\_wetting\_2012; @shih\_breakdown\_2012; @shih\_wetting\_2013]. Moreover, 2D semimetals (graphene, silecene, germanene, etc.) and 2D semiconductors (e.g, transition metal dichalcogenides (TMDCs)) possess significantly lower density of states (DOS) than bulk materials, making them easier to be doped by the underlying substrates [@Chen\_2013; @Varchon\_2007; @Giovannetti\_2008] or electrostatic gating [@Das\_2008; @Perera\_2013]. Due to the ubiquity of doping in 2D materials, it is worth investigating the relationship between the doping level and wettability. Several recent reports have addressed the issue of doping-induced tunability of graphene's wettability, from both atomistic simulations [@ostrowski\_tunable\_2014; @ren\_interfacial\_2015; @Taherian\_2015; @daub\_electrowetting\_2007] and experimental demonstrations [@hong\_mechanism\_2016; @goniszewski\_correlation\_2016; @ashraf\_doping-induced\_2016]. However, discrepancies exist between individual reports, concerning the origin and magnitude of the doping-induced wetting tunability. Moreover, to get a full perspective of such phenomenon, the gap between the nanoscale simulations and macroscopic experimental results needs to be filled, and the aforementioned issues of intrinsic wettability and wetting translucency should also be taken into account.

In this letter, we propose a multiscale approach to properly model the doping-induced tuning of 2D materials' wettability. We model the change of surface adhesion energy between water and 2D material as a combined effect of (i) reorientation of water molecules, characterized by molecular dynamic (MD) simulations and (ii) electrowetting due to formation of electric double layer, calculated by a continuum model based on modified Young-Lippman theory. By using graphene as an example, we demonstrate that, the electrostatic interaction plays a major role in both the reorientation and electrowetting effects. By further considering the surface coverage of 2D materials, we evaluate the previous reported result on the doping-induced wetting behavior of graphene using the proposed multiscale model. We find that the existence of minor defects can cause great discrepancy between the observed wetting property and theoretical values, requesting attentive interpretation of the experimental results. Moreover, we quantify the tunability of interfacial tension in a gate-controlled 2D-material-based electrowetting device as a function of the DOS of the 2D material, and rank several 2D materials according to their tunability. We show that 2D materials with higher DOS such as transition metal dichalcogenides (TMDCs), perform better than graphene by means of wettability regulation. Our findings provide a comprehensional view of the wettability of 2D materials, as well as guidance for operational liquid-phase 2D material-based devices.

Due to the complex dynamic nature of wetting [@Cassie\_1944; @Wenzel\_1936; @Gao\_2007; @Marmur\_2009], we only study the static wettability of 2D materials. We only consider water as the liquid phase, as most liquid-phase applications of 2D materials are also in aqueous environment. The macroscopic feature of wetting--contact angle , is connected to the interfacial adhesion energy by the Young's equation:

where is defined as:

where is the surface tension between the interface of the 2D material and the aqueous phase, and are the surface tensions of the 2D material and water in vacuum, respectively. is contributed by both the short-range dispersion interaction and long-range electrostatic interaction between the 2D material and water. The existence of additional charges in 2D materials gives rise to the reorientation of adjacent water molecules [@ostrowski\_tunable\_2014]. On the other hand, the formation of electric double layer (EDL) in an ionic solution near the interface also alters the interfacial adhesion properties, known as the electrowetting effect [@Lippmann\_1908], which has been widely used in microfluidic applications [@Mugele\_2005]. Owing to the additive nature of dispersion and electrostatic interactions, we propose that the change of interfacial adhesion energy is a combined effect of the reorientation effect and EDL formation :

A multiscale approach is needed to combine both effects as their effective length scales are different. We use molecular dynamics (MD) simulations for sampling the orientation effect adjacent to the 2D material; in addition a continuum model is implemented to describe the contribution of EDL formation, since state-of-art MD simulations fail to handle diluted ionic solution systems where the Debye length can be as long as 103 nm. Our multiscale modeling approach is schematically illustrated in Fig. <ref:fig:scheme-method>.

[file:../img/scheme-methods.pdf](../img/scheme-methods.pdf)

It is also noteworthy that our multiscale approach is compatible with the issues of the intrinsic wettability and wetting translucency of 2D materials. Since we are dealing with the change of interfacial adhesion energy as a function of surface charge, the absolute value of or (extracted from intrinsic wetting property and wetting translucency theory) can be treated as independent variables.

We model the charged 2D materials as rigid sheets with uniform surface charge density , either by substrate or electrostatic doping. We also assume that the 2D material has no dissociable groups which can change the aqueous pH value [@zuccaro\_tuning\_2015] and the 2D material is inert to electrochemical reaction at the interface [@bard\_electrochemical\_1980]. First we use graphene as a model system to show the effect of reorientation of water molecules on the interfacial adhesion energy. Different from previous approaches which used MD simulations to extract the contact angle of nanodroplets on graphene [@ostrowski\_tunable\_2014; @daub\_electrowetting\_2007; @ren\_interfacial\_2015; @Taherian\_2015], where the interfacial adhesion energy cannot be accurately measured due to changed contact area between water and graphene, here we propose to use a continuous water monolith in the MD simulation with periodic boundary conditions in the x and y directions to calculate the interfacial adhesion energy .

TODO Description for MD simulation

The adhesion energy in the MD simulation is defined as:

where is the area of the graphene sheet (same as the contact area between water and graphene), is the Avogadro's number, is the total internal potential of the 2D material-water system, and and are the potentials of the separated water phase and 2D materials, respectively. The adhesion energy can be further decomposed into the short-range Lenard-Jones potential term () and the long-range Coulombic interaction term (). Since and are unalterable in the MD simulation, the change of interfacial adhesion energy as a result of surface doping, is calculated as:

[file:../img/fig-pot-dens.pdf](../img/fig-pot-dens.pdf)

The changes of adhesion energy terms , and , as functions of , are shown in Fig. <ref:fig:pot-dens>(a). It can be seen that the contribution from dispersion interaction has a very small magnitude of negative change (less than 2.5 mJ) when ranges from -5 ~ 5 . On the other hand, we find that contributes majorly to , indicating the electrostatic nature of the doping-induced reorientation of water molecules.

TODO Validate the statement above

It is also interesting to find that, unlike its counterpart from dispersion interaction, has a asymmetric response to . We further plot the local density of water molecules , as a function of distance from the graphene plane, which can be seen in Fig. <ref:fig:pot-dens>(b). We consider 3 cases where the graphene layer is either charge-neutral, or , respectively. We find that the at the first water layer adjacent to graphene ($z \approx 3.2\ \mathrm{\AA}$) also responsed asymmetrically with . When , drops to ca. 80% of that in the electroneutral system, while at has a 8% increase in the density compared with the electroneutral system. The change of interfacial water density can be ascribed by the polarity of water molecules. When the graphene layer is positively charged, the O atom is more favorably facing the graphene surface, while H atom is more favorably facing the negatively-charged surface.

TODO Describe the density change

TODO More in-depth discussion?

It is noteworthy that although the process for investigating the magnitude of is similar for other 2D materials other than graphene, the result obtained here cannot be readily applied to other 2D materials, since the contribution of dispersion interaction and electrostatic interaction can be completely different [@Govind\_Rajan\_2016; @Chow\_2015]. Nevertheless, in real-world measurements, due to the existence of the contamination layer which has a typical thickness ca. 1~2 nm, the dispersion interactions contributed by surface charge can be nearly completely screened out; aqueous electrolytes can also greatly attenuate the electric displacement field, compared with the dipole water model used in the MD simulations. Therefore we propose that the effect of reorientation may not be easily observable in current experimental setups.

While the interfacial dispersion interaction vanishes several molecules away from the surface, the long range electrostatic interaction will cause the aqueous ions to rearrange at a much longer length scale, forming an EDL at the interface and decrease the interfacial surface tension by the phenomenon known as electrowetting. To model the effect of electrowetting, we first consider that a contamination layer with thickness covers the 2D material surface. Since the airborne contaminants are mostly hydrocarbon compounds, they can be treated as a dielectric layer with permittivity . We use the Gouy-Chapman-Stern model to describe the EDL in the aqueous phase, which consists a Helmholtz double layer with the same permittivity as water, and thickness , together with a diffuse layer where ionic distribution is described by the Gouy-Chapman equation. The potentials at the surface of the 2D material, the contamination layer surface and the outer Helmholtz plane (the interface between the Helmholtz double layer and the diffuse layer) are , and , respectively. An illustration of the model for the 2D-material-water interface is shown in Fig. <ref:fig:scheme-EDL>.

[file:../img/scheme-EDL.pdf](../img/scheme-EDL.pdf)

If we neglect specific adsorption of ions at the solid-liquid interface, electroneutrality ensures that the charge density of the 2D material balances the total charge density of the EDL [@bard\_electrochemical\_1980]:

From the Gouy-Chapman model of symmetric electrolytes we know:

where is the valency of the electrolyte, is the concentration of the electrolyte, is the Avogadro constant and is the Boltzmann constant. While the contamination layer is responsible for a potential drop across the solid phase, the solid-liquid interfacial potential which contributes to the , is only governed by . Therefore we conclude that the existence of a contamination layer does not affect the magnitude of $\Delta \Phi\_{\mathrm{2D-w}}}^{el}$.

The change of interfacial adhesion energy is calculated using the Gibbs adsorption isotherm equation: , where is the interfacial adsorption number at the solid-liquid interface. Since the Debye length is much smaller than the diameter of a macroscopic droplet, can be approximated by the total excessive charge density at the interface. Therefore can be derived from Eqs (<ref:eqn:psi-2D>) and (ref:eqn:psi-L):

where is the geometric capacitance of the Helmholtz double layer, is the capacitance of diffuse layer derived from the Gouy-Chapman equation, and is the Debye length of the electrolyte. The quantity is actually the Debye-Hückel-style capacitance of the EDL. Eq. (ref:eqn:Delta-Phi-exact) shows that consists of the contributions from the Helmholtz double layer and the diffuse layer, respectively. Note that at room temperature, when is large (e.g. ) and is small (e.g. mol),

*ψL*=347 mV

, which is much larger than , causing a significant discrepancy between the Gouy-Chapman capacitance and the Debye-Hückel capacitance . This effect is often ignored in previous studies concerning the electrowetting on graphene and other 2D materials [@ostrowski\_tunable\_2014; @daub\_electrowetting\_2007; @goniszewski\_correlation\_2016; @ashraf\_doping-induced\_2016], and the classical Young-Lippman equation (or ) is casually used instead, assuming the capacitance to be constant. Since most of the reported samples deals with pure water with extremely low , the Debye-Hückel capacitance is much smaller than the Gouy-Chapman capacitance, leading to an overestimation of . Therefore our derivation in Eq. <ref:eqn:Delta-Phi-exact> provides a more accurate approach to analyze $\Delta \Phi\_{\mathem{2D-w}}^{el}$ as a function of .

[file:../img/2d-ph-dependency.pdf](../img/2d-ph-dependency.pdf)

Consider that the aqueous phase contains a 1:1 electrolyte with concentration , the thickness of the Helmholtz plane $d\_{\mathrm{H}}=3\ \mathrm{\AA}$ [@mcclendon\_thickness\_1927], and the surface tension of water mJ at K, we calculate the magnitude of and as function of , as shown in Fig. <ref:fig:Delta-cos-dependency>(a). We discover that both the changes in the magnitude of interfacial adhesion energy and the contact angle become more pronounced when the concentration of electrolyte is lower. On the contrary, in conventional electrowetting model, is governed by the constant capacitance of the dielectric layer and is almost irrelevant to the . The results indicate that the variation of has a significant impact on and in the electrowetting on doped 2D materials. This is due to the fact that the interfacial potential is affected by both the surface charge and , as indicated by Eq. (ref:eqn:psi-L) and (ref:eqn:psi-2D). When is lower, a larger potential is required to be built upon the interface, giving rise to a larger change in the interfacial wetting property.

Although the "real" contact angle of a 2D material can be tedious to determine, it is still possible to estimate the magnitude of contact angle change due to the electrowetting effect, by assuming that the hypothetical contact angle on a charge-neutral 2D material layer. consists of the effect of intrinsic wettability, surface contamination as well the wetting translucency of the 2D material-liquid interface. Fig. <ref:fig:Delta-cos-dependency>(b) shows the magnitude of contact angle decrease as a function of both and , when mol (e.g. ideally pure water). Within the range of typical contact angles reported on graphene (ca. 40 ~ 100), and a doping level of ~ , we find that the maximum magnitude is only ca. 7 when doping level is as high as , essentially smaller than previously reported values which were measured both under smaller doping levels [@hong\_mechanism\_2016; @ashraf\_doping-induced\_2016]. Due to the saturation of CO2 in water and soluble contaminants, the effect of electrowetting may be even less prominent in real situations. Therefore we believe that the electrowetting effect theory on 2D materials alone, cannot explain the current findings of doping-induced wettability change on graphene.

Practically in a contact angle measurement, the amount of water varies from pL (using environmental scanning electron microscopy, ESEM) to (using goniometer). Unlike nanodroplet models used in MD contact angle simulations, the droplets used experimentally are large enough to be exposed to both pristine and defect 2D surface, and can therefore be trapped in the local minimal state caused by nanoscale defects [@raj\_wettability\_2013], giving rise to uncertainty of the measured contact angle. Meanwhile, it is widely observed that nanopores and macroscopic cracks exist in the transferred 2D material, increasing the adhesion interaction between the substrate and the water droplet.

[file:../img/scheme-crack.pdf](../img/scheme-crack.pdf)

We further consider the cases where the 2D material does not completely cover the substrate. In both the substrate-induced doping (see Fig. <ref:fig:scheme-crack>(a)) and the electrostatic doping (see Fig. <ref:fig:scheme-crack>(b)) systems, substrate surface charge still exists in non-covered regions: in surface doping the charged dopants (i.e. polyelectrolytes) will instantly build up a EDL near the substrate surface, while in electrostatic doping the electric displacement field still forms between the conducting 2D material and the gate electrode via the non-covered region, also causing the ions to accumulate at the substrate-water interface. The interfacial adsorption density of ions can essentially be larger than the surface charge density on 2D material, due to the partial screening of electric displacement field of the 2D material [@tian\_multiscale\_2016; @Shih2015PartiallyScreened; @Muruganathan\_2015; @Huttmann\_2015]. Since the electrowetting effect is amphipolar, the accumulation of cations and anions at the 2D material surface or the non-covered region both contribute to the decrease of the apparent surface tension . We assume that the electrowetting at the non-covered region is described by the classical Young-Lippman , where is the effective capacitance of the non-covered region (taken as the EDL capacitance in substrate doping, or the geometric capacitance of dielectric layer in electrostatic doping). We therefore describe as a combined effect of the electrowetting on both pristine 2D material surface and non-covered substrate surface, characterized by the surface coverage index :

It should also be noted that in electrowetting experiments where additional charge is doped to the 2D material via dielectric layer [@hong\_mechanism\_2016], the initial doping density should also be considered to explain the asymmetric electrowetting behavior. In an electrowetting system where a dielectric layer with geometric capacitance and external voltage is applied to the 2D material, the doping density in the 2D material is calculated as [@tian\_multiscale\_2016]:

where is the quantum capacitance of the 2D material, which is proportional to the density of states (DOS) at energy level : .

[file:../img/plot-fitting.pdf](../img/plot-fitting.pdf)

To examine the effect of incomplete 2D material coverage, we select two sets of reported experimental measurements of the wettability on doped graphene sheet, namely the contact angles of substrate-doped graphene measured by ESEM from Ref. [@ashraf\_doping-induced\_2016] and the contact angles of electostatically-doped graphene via goniometer from Ref. [@hong\_mechanism\_2016]. The contact angle at experimentally "charge-neutral" condition (graphene attached to SiO2 substrate for ESEM experiment or V in electrowetting experiment, however may not be 0 due to existence of ) is used as reference for calculating . We use Eq. <ref:eqn:apparent-gamma-combined> to extract and for both experiments, as seen in Fig. <ref:fig:f-nc-exp>. We observe that in both experimental data sets, the measured is essential larger than the theoretical value derived from the Gouy-Chapman-Stern model described here. Fitting results reveals both systems are lightly p-doped in the "charge-neutral" condition, which corresponds well with other experimental reports [@Shih2015PartiallyScreened; @goniszewski\_correlation\_2016]. The fitted values for both systems are as small as 3.7%-3.8%, indicating the graphene layers are mostly complete. It is very surprising to find out that due to large discrepancy of wetting behavior on the 2D material and the underlying substrate, the measured contact angle change can be greatly influenced by the existence of minor defects in the 2D material. Our calculations show that extreme care should be taken to interpret the true doping-tunable wetting behavior of 2D materials.

The doping-induced tuning of wetting on 2D materials opens a novel avenue for 2D-material-based liquid manipulating devices. Unlike conventional electrowetting on dielectric (EWOD) setup, no counter electrode is required in the liquid phase, ensuring simpler device design. Although Eq. <ref:eqn:Delta-Phi-exact> shows that the electrowetting effect of 2D material is only dependent on the surface charge , practically it is more favorable to achieve the desired electrowetting by applying a smaller . A usual setup for electrostatic doping of 2D material involves the use of high-k dielectric or ionic gating [@Das\_2008; @Radisavljevic\_2011; @Xu\_2011; @Newaz\_2012], where the is comparable with . Therefore the contribution of in Eq. <ref:eqn:doping-vm-2D> cannot be ignored. Combing Eqs. <ref:eqn:psi-L>, <ref:eqn:psi-2D> and <ref:eqn:doping-vm-2D>, we get:

and by substituting , we derive the ratio between and , named as :

at a certain , the larger is, the higher tunability in wettability of the 2D material will be. On the device side, it can be achieved if both and are larger. Increasing the value of can be implemented by replacing graphene--a 2D semimetal, with a 2D semiconductor, such as TMDC [@tian\_multiscale\_2016]. Here we evaluate a 2D-material-based electrowetting device consists of a 2 nm thick HfO2 dielectric layer with , and an 2D material sheet selected from graphene, silicene (2D allotrope of Si), germanene (2D allotrope of Ge), MoS2, MoTe2, WS2 and WTe2 (see Fig. <ref:fig:dcos-all-2D>(a)). The DOS and are calculated from first-principle simulations using HSE06 hydrid functional (see Ref. [@tian\_multiscale\_2016]). The magnitude of as a function of in devices based on different 2D materials is shown in Fig. <ref:fig:dcos-all-2D>(b).

[file:../img/dcos-all-2D.pdf](../img/dcos-all-2D.pdf)

As expected in Eq. <ref:eqn:beta>, at the same level, the 2D TMDC semiconductors (MoS2, MoTe2, WS2, WTe2) exhibit a much higher response than 2D semimetals (silicene, germanene and graphene). We can briefly rank the voltage tunability of the selected 2D materials by their DOS: MoTe2 > MoS2 > WTe2 > WS2 > germanene > silicene > graphene. Notably, TMDCs can achieve a as high as 0.15 when V is applied, corresponding a contact angle decrease at the magnitude of 10 when the intrinsic contact angle is ca. 90. A high-DOS 2D material further suppresses electrochemical reactions at the solid-liquid interface, as less electrochemical potential (i.e. the Fermi level ) is required. We conclude that a 2D material with higher DOS can essentially reduced the voltage needed for doping, pushing liquid-phase 2D-material-based devices to a more operational regime.

In conclusion, we propose a multiscale approach for modeling the doping-induced tunable wettability of 2D materials, by combining the reorientation effect of water molecules estimated by MD simulations, and the electrowetting effect calculated by a continuum model. Taking graphene as an example, we find that electrostatic interaction plays a major role at both scales for the graphene-water interface. We further show that, by considering the incomplete coverage of 2D material on the substrate, it is possible to evaluate the recent findings of doping-induced tuning of graphene's wettability with the proposed model. We find that minor surface incompleteness can cause great discrepancy in the measured value of interfacial wettability, and extreme care should be taken to interpret the observed electrowetting phenomena. In addition, we prove that a 2D material with higher density of states can essentially reduce the gating voltage in a 2D-material-based electrowetting device, and rank the tunability of the 2D materials as: MoTe2 > MoS2 > WTe2 > WS2 > germanene > silicene > graphene. Our multiscale analysis provides a comprehensive view of the wettability of 2D material interface, and we believe operational 2D-material-based liquid manipulating devices will be facilitated by the principles presented in this letter.