# Introduction

Two-dimensional (2D) materials, the crystalline films with a thickness of one atom or one molecule, combine optical transparency and the quantum-confined properties [@Novoselov\_2005; @Mas\_Ballest\_\_2011; @Novoselov\_2016] and have continuously influenced the development of nanotechnology since their emerging. Recent progress in the scalable production of large-area 2D materials [@Boott\_2015; @Li\_2016] has paved the way for the applications of functional surfaces and ultrathin membranes [@Prasai\_2012; @Feng\_2016; @Rafiee\_2010; @Yin\_2014; @Surwade\_2015; @Hern\_ndez\_2013]. The concept of van der Waals (vdW) epitaxy has been further extended to grow molecular heterostructures on 2D material-coated surfaces for a variety of applications [@Shi\_2012\_epitaxy\_graphene; @Kim\_2017\_remote\_epitaxy; @Novoselov\_2016]. The realization of these technologies essentially requires precise control over the molecular interactions at 2D material interfaces, which motivates fundamental research of their interfacial properties, in particular the wettability. An accurate determination of the interfacial tension, nevertheless, remains highly disputed [@taherian2013what; @Kozbial\_2015; @Parobek\_2015; @Govind\_Rajan\_2016]. Early literature on understanding the surface science of 2D materials has highlighted the effects of the airborne contaminants [@li\_effect\_2013; @Xu\_2013\_withwhat; @kozbial\_study\_2014; @Kozbial\_2015; @Chow\_2015] and the underlying substrate [@raj\_wettability\_2013; @rafiee\_wetting\_2012; @shih\_breakdown\_2012; @shih\_wetting\_2013], since the length scale for the van der Waals (vdW) interactions is comparable to the thickness of a monolayer. On the other hand, a subtle but important fact is that the 2D semimetals (e.g, graphene and silicene) and 2D semiconductors (e.g., transition metal dichalcogenides (TMDCs)) possess low density of states (DOSs) around the intrinsic Fermi level (), such that the effect of doping, either induced by the surroundings [@Chen\_2013; @Varchon\_2007; @Giovannetti\_2008], or by the electrostatic gating [@Das\_2008; @Perera\_2013], also comes into play. Recent advance in the *ab initio* calculations and scanning tunneling microscopy (STM) studies on the adsorbed molecules on graphene [@Muruganathan\_2015; @Huttmann\_2015] has provided some clues to the doping-dependent vdW interactions. Subsequently, the doping-induced change in the wettability of graphene has been observed in the contact-angle experiments [@hong\_mechanism\_2016; @goniszewski\_correlation\_2016; @ashraf\_doping-induced\_2016], and the molecular dynamics (MD) simulations [@ostrowski\_tunable\_2014; @ren\_interfacial\_2015; @Taherian\_2015; @daub\_electrowetting\_2007]. In this respect, however, most reports described the doping-dependent wettability with the basic Young-Lippmann equation (YLE) [@Lippmann\_1875], whereas the interplay between the orientation of liquid molecules at the interface [@Shen\_2006] and the electronic structure of the 2D materials is often ignored. In order to address the discrepancies among the literature, a general and complete theoretical picture that bridges the gap between different length scales, is clearly required.

In this letter, we propose the first theoretical framework to model the change of interfacial tension between liquid and a sheet of monolayer 2D material. Multiscale physical phenomena are considered. At the atomic scale, we formulate the dependence of surface energy of a 2D material on the doping density using the quantum capacitance (QC) calculated by the density functional theory (DFT). Next, the surface-charge-induced reorientation of liquid molecules adjacent to the interface is associated with an N-body system, which is resolved by molecular dynamics (MD) simulations, allowing quantification of the interfacial tension in the absence of electrolytes in liquid. The effect of the electrical double layer (EDL) induced by the electrostatic interactions between the 2D material surface charges and the ionic species in liquid, is then addressed at the continuum level. Practical considerations, such as the defect density and the surface contamination are also taken into account to provide a comprehensive understanding of the phenomena. Finally, we examine and validate our theory by comparing with the contact angle changes reported in the electrowetting and the substrate-induced doping experiments.

# Results and Discussions

## Surface Energy of Doped 2D Materials

Consider a liquid (*L*) droplet sitting on a flat, monolayer 2D material (*2D*) supported by a solid substrate, following the Young’s equation, the change of the equilibrium contact angle upon doping, is given by

where and are the surface tensions of the liquid phase and the 2D material considered, respectively, is the interfacial tension between the liquid and the contacting 2D material. We define for all the surface tensions considered and , where the subscript 0 corresponds to that in the case of intrinsic 2D material, with the doping density per unit area, . In the theoretical analysis presented here, we aim to model as a function of . Note that under the assumptions that (i) the change of in the doped 2D materials does not result in the interfacial electron transfer, namely, the electrochemical reactions, (ii) the doping effect does not change the surface energy of the underlying substrate, and (iii) the vdW and electrostatic interactions are perfectly additive and pairwise, one can decouple the effect of the underlying substrate. Therefore the debate of the “wetting transparency” [@rafiee\_wetting\_2012; @shih\_wetting\_2013], does not affect our analysis.

First, we model the dependence of on the doping level. Consider a closed system with constant pressure and volume containing a sheet of free-standing 2D material, following the Euler homogeneous function theorem of thermodynamics, the total internal energy of the system , is given by [@bard\_electrochemical\_1980], where is the temperature, is the entropy, is the chemical potential of the 2D material per unit lattice, is the number of unit lattices, is the area of the 2D material, and and are the electric potential and total charge in the 2D material, respectively. At constant , combining with the first law of thermodynamics and the differential form of , it follows:

relating the surface tension change of a free-standing 2D material as a function of its doping density . After bringing an amount of charge from infinity to a charge-neutral 2D material in the aforementioned system, the surface energy change is therefore given by:

where is the quantum capacitance of the 2D material [@davies\_two-dimensional\_1997; @Das\_Sarma\_2011], is the DOS as a function of , and corresponds to the Fermi level of the 2D material at the charge neutral point (CNP). Accordingly, eq <ref:eqn-delta-gamma-sigma-free-2D> provides a simple relation which depicts the surface tension change of a 2D material at the quantum-mechanical level. We have calculated the DOSs as a function of for a variety of 2D materials using the density functional theory [@tian\_multiscale\_2016]. Note that we take into account a fractional component of the exact exchange from the Hartree-Fock (HF) theory hybridized with the DFT exchange-correlation functional at the level of the HSE06 hybrid functional. Therefore, any limitation of the exchange and correlation functional utilized in the chemical description of the energy levels can be improved. The following 2D materials are considered: TMDC monolayers (MX2, M = Mo, W and X = S, Se, Te), silicene, germanene, phosphorene (monolayer black phosphorus), and graphene. The doping density in a 2D material is calculated by integrating the DOS from its intrinsic Fermi level, i.e., [@john\_quantum\_2004].

Figure <ref:fig:dgamma-sigma> presents the calculated as a function of for the 2D materials considered here. Clearly, the doping of 2D materials reduces their surface energy, or based on the classical definition, the work required to separate two stacked monolayers is lowered. Among the 2D materials, we find that graphene shows the highest degree of surface energy decrease, up to -16 mJ , or ca. 20% reduction of its intrinsic surface tension [@shih\_wetting\_2013], at = . However, as will be discussed later, it does not imply a reduced wettability because the quantum capacitance effect also reduces the interfacial tension, . A clear trend is that the surface energy decrease is more significant in the 2D semimetals (e.g. graphene, silicene, and germanene) than that in the 2D semiconductors (e.g. TMDCs). This reflects the fact that the effective mass of carriers in the 2D semiconductors is much higher than that in the 2D semimetals [@davies\_two-dimensional\_1997], therefore resulting in high DOS, as well as a high (see eq <ref:eqn-delta-gamma-sigma-free-2D>). This concept also explains why the surface energy decrease for silicene and germanene are lower than that for graphene [@Yan\_2013]. To our knowledge, the doping-induced surface energy change in 2D materials has never been investigated experimentally, which may be of interest for future study.

## Reorientation of Liquid Molecules

Next, we discuss the interactions between 2D materials and liquid. In a doped 2D material, the delocalized carriers are confined in the 2D plane. Therefore, following the spirit of the mean-field theory, we treat it as a continuously, uniformly charged surface. Since these charges are either generated by interacting with the underlying substrate, or electrostatically induced by gating, the electroneutrality still holds before in contact with liquid. The surface charges result in two consequences that may change , including (i) the reorientation of adjacent liquid molecules [@ostrowski\_tunable\_2014] and (ii) the formation of the electric double layer (EDL) at the liquid-solid interface, known as the electrowetting effect [@Lippmann\_1908; @mugele\_electrowetting:\_2005]. Under the assumption that the vdW and electrostatic (Coulombic) interactions are additive, which compose to the interfacial tension, we propose that the interfacial tension change is given by:

where and correspond to the contributions from the reorientation and the EDL effects, respectively, as schematically illustrated in Figure <ref:fig:scheme-method>. We also assume that is independent of the electrolyte concentration, since the concentration of liquid molecules is typically orders-of-magnitude higher.

First we discuss the orientation effect. Understanding the reorientation effect involves positioning and sampling the collective, time-averaged motion of liquid molecules near the interface, which is a standard molecular dynamics (MD) problem. Note that even with the state-of-the-art MD algorithms, it remains challenging to accommodate the calculations for the EDL, in which the length scale of electric field can be larger than one micrometer in diluted electrolyte solutions, e.g. pure water with self-ionized H3O+ and OH- ions. Here we consider the graphene-water interface as a model system. All MD simulations were carried out using the GROMACS 4.5 software package [@Hess\_2008]. Monolayer graphene was modeled as an infinite rigid sheet in the x-y plane. The carbon atoms of graphene were treated as uncharged Lennard-Jones (LJ) spheres with = 0.34 nm and = 0.223 kJ/mol [@Cheng\_1990], using the force-field parameters reported by Tummala and Striolo [@Tummala\_2008]. The doping effect is included by assigning an equal amount of charge , where is the surface density of carbon atoms, to each carbon atom. The range considered here approximately correspond to the partial atomic charge from −0.012 to 0.012 . Water molecules were modeled using the SPC/E model [@Berendsen\_1987] with bond lengths and angles of water molecules constrained using the SETTLE algorithm [@Miyamoto\_1992]. Lennard-Jones interactions were treated with a cutoff distance of 1 nm, with those between different atoms calculated using the standard geometric averaging rule. Long-range electrostatic interactions were treated using the particle mesh Ewald (PME) summation method [@Darden\_1993; @Essmann\_1995] with a short-range cutoff distance of 1 nm. The velocity-rescaled Berendsen thermostat was implemented to maintain a constant system temperature of 298.15 K [@Bussi\_2007]. All simulations were carried out under the NVT ensemble.

In order to precisely determine the interfacial interactions using MD simulations, instead of the commonly used model that compared the nanoscale contact angle by placing a nanodroplet onto a sheet of suspended 2D material [@ostrowski\_tunable\_2014; @daub\_electrowetting\_2007; @ren\_interfacial\_2015; @Taherian\_2015], we simulate the difference of the total potential energy, , between two separate systems that contain (i) only water molecules with two surfaces exposing to vacuum (L), and (ii) the same amount of water molecules with one surface in contact with graphene (placed at z = 0) and the other surface exposing to vacuum (GL) (see Figure <ref:fig:MD-res>(a) and <ref:fig:MD-res>(b)) . Periodic boundary conditions are used in all three directions of the simulation boxes in both systems. Additionally, a vacuum layer of 3 nm thick along the *z*-axis is placed to separate the periodic images of the graphene-water system. The total energy in both systems can be formulated as: and , respectively, where is the chemical potential per water molecule in the bulk phase, is the number of liquid molecules in the simulation box, and is the area of the *xy*-plane. A simulation box with large enough length of 21 nm in the *z*-direction is used, with a 18-nm thick block of water molecules, to minimize the effect of the long-range electrostatic interaction between the charged graphene and the water molecules at the water-vacuum interface, by ensuring that the time-averaged dipole moment for the water molecules at the water-vacuum interface is approaches zero (see Supporting Information Figure S1). One can show that , where is the interfacial energy, which is defined as , and combining with eq <ref:eqn-def-Young-Delta-theta>, the change of interfacial energy can be formulated as:

where corresponds to the contact angle change due to the reorientation effect. Note that in the current MD simulation setup, the surface tension of the 2D material remains unchanged (i.e. ), since the Fermi level of the 2D material remains unchanged with respect to (see eq <ref:eqn-delta-gamma-sigma-free-2D>). In all simulations we assume a constant surface tension of water . Accordingly, follows , where and correspond to the change for the vdW ad Coulombic interaction potentials, respectively.

Figure <ref:fig:MD-res>(c) shows the values of , and its contributions from the Lennard-Jones () and Coulombic interactions (), as functions of . We note that the change of adhesion energy in the doped graphene system is dominated by the Coulombic interaction. When the doping level of graphene is , the Coulombic interaction causes a decrease in the adhesion energy of -10~-15 mJ, while the vdW interaction, on the other hand, causes a slight increase in the adhesion energy by less than 5 mJ. In other words, concerning the reorientation of water molecules at large doping levels, the Coulombic interaction favors the decrease of , and thus the contact angle , while the vdW interaction slightly increases and . We shall note that due to the highly polar nature of water molecules, the average inter-molecular equilibrium distance in the absence of external electric field is shorter than the Lennard-Jones equilibrium distance. Increasing the doping density of the graphene sheet essentially enhances the electrostatic attractions between graphene and water molecules and further decreases the inter-molecular equilibrium distance, as reflected from the red shifts of the first peaks in Figure <ref:fig:MD-res>(d) for the two charged graphene cases compared to the charge-neutral case, which eventually leads to a slight increase in . The plot of as a function of in Figure <ref:fig:MD-res>(b) shows an apparent asymmetric shape. This is can be further revealed from the *z*-dependent local molecular density and charge density profiles of the water molecules, as shown in Figure <ref:fig:MD-res>(d) and <ref:fig:MD-res>(c), respectively. The molecular density of the first water layer adjacent to graphene increases when graphene is p-doped () and decreases when graphene is n-doped () compared with the case of charge-neutral graphene, indicating the polarity-dependent adsorption of water molecules on graphene. Similar trend can also be observed in the profiles. Interestingly, exhibits positive Coulombic contribution for slightly n-doped graphene, when , indicating that the reorientation of interfacial water molecules by small negative charges on graphene helps minimizing the Coulombic interactions.

TODO Explanation of the positive part of when ?

Although the MD simulation results show the Coulombic interaction between the doped graphene and water molecules dominate the reorientation effect, such conclusion may not be readily applied to other types of 2D materials. For 2D semimetal systems (silicene and germanene), the intensity of Coulombic interactions may vary due to the mismatch among the lattice constants. On the other hand, for the 2D semiconductors such as the TMDCs, in which their are already largely determined by the Coulombic interactions in the intrinsic case [@Govind\_Rajan\_2016; @Chow\_2015]. Therefore we anticipate that case-by-case studies and DFT calculations which deal with the post-doping charge redistribution, might be required.

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## Electrical Double Layer Effect

The EDL effect that decreases the interfacial tension has been extensively studied in the context of the electrowetting phenomena [@Mugele\_2005], in which the interfacial tension is reduced due to the adsorption of ionic species at the solid-liquid interface. Here we extend the concept to the 2D material-liquid systems. Consider a closed system containing an interface formed between liquid and a sheet of free-standing 2D material, by combining with the Gibbs adsorption theory [@bard\_electrochemical\_1980], following the procedure described to derive eq <ref:eqn-delta-gamma-sigma-free-2D>, one can obtain:

where and are the interfacial excess and the chemical potential of the ionic specie at the interface, respectively. Relative to that in the bulk phase (), the interfacial chemical potential of a charged solute , is given by , where is the valency of component , under the assumption that the interfacial electric potential equals . Similar to the approach of eq <ref:eqn-delta-gamma-sigma-free-2D>, the EDL-induced change of interfacial tension follows:

where is the interfacial charge density per unit area in the liquid phase, and is the EDL capacitance. Combining eq <ref:eqn-Delta-gamma-2DL-EDL-full> with eqs <ref:eqn-def-Young-Delta-theta> and <ref:eqn-delta-gamma-sigma-free-2D>, the contact angle change due to the EDL effect, is given by:

In other words, eqs <ref:eqn-delta-gamma-sigma-free-2D> and <ref:eqn-Delta-gamma-2DL-EDL-full> suggest that decreases both the and to the same extend, i.e. , such that the contribution of quantum capacitance cancels out in the YLE. As a result eq <ref:eqn-Delta-cos-EDL> shows that the contact angle change due to EDL effect , is only governed by the interfacial excess in the liquid phase.

For a electrolyte solution, with the molar concentration and the electrolyte valence , we describe the electric potential profile in liquid with the one-dimensional Gouy-Chapman-Stern model [@Stern\_1924\_theory], as schematically shown in Figure <ref:fig:res-EDL>(a). The EDL consists of a Helmholtz layer with the permittivity of liquid and thickness , next to the Gouy-Chapman (GC) diffuse layer where the electric potential profile follows the Poisson Boltzmann equation [@bard\_electrochemical\_1980]. The of the Gouy-Chapman-Stern model is equivalent to two capacitors in series, namely,

where is the capacitance of the Helmholtz double layer and is the differential capacitance of the GC layer, with corresponding to the electric potential at the GC interface. Consider a Gaussian enclosure including the 2D material layer and the EDL, due to a zero net electric field at the surface of the Gaussian enclosure, the electroneutrality of the system [@bard\_electrochemical\_1980] suggests:

And therefore, the electric potentials corresponding to the surface of the 2D material and the outer Helmholtz plane, and , are given by:

where is the Avogadro constant and is the Boltzmann constant, respectively. Accordingly, the final form of is given by:

where is the differential capacitance of the diffuse layer using the Debye-Hückel approximation [@bard\_electrochemical\_1980], and is the Debye screening length. Compared with the classical YLE, , where is the equivalent capacitance in YLE, one can show that is given by:

The above analysis leads to two important implications: (i) If a thin contamination layer (usually composed of charge-neutral hydrocarbon species [@li\_effect\_2013]) exists between the Helmholtz layer and the 2D material surface, the electroneutrality at the interface (eq <ref:eqn-neutrality>) still holds, such that remains the same (see eq <ref:eqn-Delta-cos-EDL-final>). In other words, despite the recent debate about the role of the airborne adsorbates in the contact angle measurement on 2D materials [@li\_effect\_2013; @Kozbial\_2015; @Xu\_2013\_withwhat; @Chow\_2015], we expect that the experimental characterization of the doping-induced contact angle change is more robust and reproducible. (ii) As shown in eqs <ref:eqn-GCS-capacitance-series> and <ref:eqn-Delta-gamma-2DL-EDL-full>, the equivalent capacitance in the YLE, , is not identical to the total capacitance in the EDL, . We notice that the literature in this field (e.g. Refs. [@ostrowski\_tunable\_2014; @daub\_electrowetting\_2007; @goniszewski\_correlation\_2016; @ashraf\_doping-induced\_2016]) often simply assumed that in the YLE, which significantly overestimates , when [@israelachvili03\_inter], as can be found in

Consider the interface formed between graphene and an (1:1) aqueous solution, using the parameters of Å [@mcclendon\_thickness\_1927], and at K, the calculated as a function of is shown in Figure <ref:fig:res-EDL>(b). Note that mol corresponds to the case of pure water system. We find that the contact angle change is stronger in a more diluted electrolyte solution, resulting from an increase in the Debye screening length , which in turn decreases both and . This is distinct from the that in the typical electrowetting experiment on a dielectric layer, in which is governed by the capacitance of the dielectric layer, so the contact angle change is almost independent of the of the electrolyte concentration [@Mugele\_2005]. Moreover, within the range of considered here ( ~ ), the calculated is always less than 0.06. In combination with the (equivalent to , see previous section) calculated by the MD simulations, the total change of contact angle due to the doping effect is shown in Figure <ref:fig:res-EDL>(c). The MD-calculated data of as a function of is fitted by a third order polynomial function (see Supporting Information Figure S3). We find that the reorientation effect is more predominant than the EDL effect, therefore the overall change of contact angle is less dependent on the solute concentration, compared with Figure <ref:fig:res-EDL>(b).

Together with the reorientation effect, the calculated change only reaches 0.06~0.08, corresponding to a maximum contact angle decrease of 3.5~4.5, for , if contact angle of graphene at CNP is 90. Such doping level is a typical range for both the electrostatic gating [@hong\_mechanism\_2016] and substrate doping [@ashraf\_doping-induced\_2016]. Clearly, the predicted contact angle change upon doping is still lower than those observed experimentally. In the next section, we discuss the practical considerations that may influence a 2D material-coated surface.

## Practical Considerations

To further adapt our analysis of the reorientation and the EDL phenomena to the experimental observations, some practical considerations need to be taken into account. In practice, in order to carry out the contact angle measurement, a large-area sheet of 2D material is required to cover the surface. Therefore, most of the experimental findings are based on the chemical-vapor-deposited (CVD) samples, which are inherently polycrystalline with grain boundaries and point defects [@Banhart\_2011\_defect]. In addition, the transfer of the ultrathin films onto a solid surface often results in nanometer- to micrometer- scale tears and wrinkles. Although our analysis has suggested that the charge-neutral polymer residues and airborne contaminations do not influence , here we show that the defect density plays an important role in determining the wettability of doped 2D materials.

Figure <ref:fig:f-nc-exp>(a) and <ref:fig:f-nc-exp>(b) illustrate how an electric field, either from the dopants on the substrate surface or from the electrostatic gating, penetrate through a void in a 2D material sheet and interact with the liquid phase directly. As a result, the EDL is built up adjacent to the substrate surface, with the surface excess and the effective capacitance . Since is equivalent to , together with the EDL and the reorientation effects discussed earlier, the modified YLE considering a 2D material with mixture of 2D-material-covered and void regions asvoids follows:

where is the void (defect) fraction in the 2D material. For the electrostatic gating involvesexperiments (see Figure <ref:fig:f-nc-exp>(a)), the 2D material quantum capacitor and the dielectric capacitor are connected in series, so that the voltage applied tobetween the gate electrode and 2D material, , is given by [@tian\_multiscale\_2016]:

where is the capacitance of the dielectric layer, and is the initial doping density of the 2D material, corresponding to .

Next, in order to examine the effect of incomplete 2D material coverage, two independent sets of experimental results, which measure the water contact angle on (i) substrate-doped graphene [@ashraf\_doping-induced\_2016] and (ii) electrostatically-gated graphene [@hong\_mechanism\_2016] are chosen to compare, with and in eq <ref:eqn-def-Delta-cos-mixture>, respectively. In each case the parameter and are determined by least-square fitting fitting of the experimental observation data with respect to , following eq <ref:eqn-def-Delta-cos-mixture>. Figure <ref:fig:f-nc-exp>(c) compares the calculated from the 2 sets of experimental data, as a function of . In both systems considered, we observe a slight degree of shift in the minima for the fitted curves, with respect to the CNP of graphene (). In other words, we observe in both cases, which is supported by most of various previous experimental observations [@Shih2015PartiallyScreened; @goniszewski\_correlation\_2016]. The fitted values of are reasonably small (3.6% for the electrostatically-gated graphene and 3.0% for substrate-doped graphene), clearly demonstrating that the contact angle change can be greatly influenced by the defect density. We believe this explains the discrepancy between the experimental observations and the multiscale theoretical framework proposed here.

Finally, we discuss the influence of 2D material choice under the electrostatic gating condition. The above analysis (eq <ref:eqn-Delta-cos-EDL-final>) has clearly suggested that the contact angle change effect only depends on , and therefore, except for the reorientation effect which might slightly changes on different 2D materials, our multiscale modeling framework is also applicable to quantify the wettability change of various doped 2D materials. In an electrowetting setup shown in Figure <ref:fig:dcos-all-2D>(a), where the 2D material is doped by electrostatic gating, the voltage applied to the gate electrode, , follows eq <ref:eqn-VG-gating>, so that the quantum capacitance comes into play. In other words, when a thick, low-dielectric-constant (low-) material is used, such that , one can infer that the contact angle change is clearly independent of 2D material used. On the other hand, when is comparable to , the choice of 2D material comes into play. Specifically, by combining eqs <ref:eqn-psi-GC> and <ref:eqn-VG-gating>, it follows:

And since , the first derivative of with respect to , namely , is given by:

The index here quantifies the tunability of the contact angle change by . Accordingly, a high degree of can be attained by increasing both and , thereby introducing the dependency on the choice of 2D material.

Here we demonstrate such phenomenon by considering an electrowetting setup composed of a thin, high- dielectric layer (2 nm HfO2 layer with the relative permittivity ) underlying a layer of monolayer 2D material (Figure <ref:fig:dcos-all-2D>(a)). As addressed earlier, due to the fact that of graphene-water system may not be readily applied to other 2D materials, we compare the $(\Delta
\cos \theta)^{\mathem{EDL}}$ as a function of , by using the DFT-calculated relations, as shown in <ref:fig:dcos-all-2D>(b).

Indeed, the gate-voltage-induced contact angle change on the 2D semiconductors is more pronounced compared to that on the 2D semimetals, as a result of their high quantum capacitance [@tian\_multiscale\_2016]. In particular, the for the TMDCs reaches up to 0.22~0.25, within the range of considered, suggesting the manipulation of a liquid droplet on a electrostatically-doped 2D material may be feasible [@Mugele\_2005; @Hayes\_2003\_nature\_EWOD]. In other words, a higher-quantum-capacitance 2D material reduces the voltage required to reach the same doping level, thereby inducing a wider tunability in their interaction with the adjacent liquid phase (e.g., Refs [@Yin\_2014; @hong\_mechanism\_2016]).

An interesting implication is that, together with the recent development in engineering 2D materials’ wetting translucency [@raj\_wettability\_2013; @rafiee\_wetting\_2012; @shih\_breakdown\_2012; @shih\_wetting\_2013], in principle, a 2D material less “transparent” (i.e. more screening) to both van der Waals and Coulombic interactions from the underlying substrate upon doping, since the interactions with 2D material itself become more predominant. More specifically, the doping level can be another control variable to modulate the molecular packing and epitaxial behavior on a 2D material-coated surface, which may bring new technology opportunity for a variety of applications.

# Conclusion

In conclusion, we present a multiscale theoretical framework concerning the wettability of doped 2D materials, by considering: (i) the change of 2D materials surface energy, (ii) the molecular reorientation of liquid molecules adjacent to the interface, and (iii) the electrical double layer formed in the liquid phase. Taking graphene as an example, we show that the Coulombic interaction dominates the change of liquid-2D material interfacial tension, at both atomistic and continuum length scales. We find that the latter two effects are the major mechanisms responsible for the wettability change at the 2D material interfaces upon doping.

The doping-induced reorientation of liquid molecules at the graphene-liquid interface is revealed by MD simulations, which also allow decoupling of vdW and Coulombic energy contributions to the interfacial tension in the absence of electrolytes in liquid. It is found that the interfacial energy change is dominated by the Coulombic interactions. Our results also reveal an asymmetric change of graphene-water interfacial energy upon doping, such that slightly n-doped graphene can reorient interfacial water molecules to minimize electrostatic attractions, and therefore, slightly increase the interfacial energy.

On the hand, the EDL effect is calculated by a continuum model. Our analysis suggests that the reorientation effect is more predominant than the EDL effect, On the graphene-water interface, we predict that the combined reorientation and EDL effects can induce a significant change of the interfacial surface tension , up to -15~-20 , at the doping level of . By adding the fitting parameter concerning the defect density, our theoretical framework can nicely describe the experimentally observed doping-induced contact angle change. Finally, based on the DFT-calculated quantum capacitances (QCs) for a variety of 2D materials, we predict that the wettability of 2D semiconductors (e.g. TMDCs) is more tunable under an electric displacement field, compared with 2D semimetals (e.g. graphene) due to their high quantum capacitances. Our findings reveals a complete picture for the modulation of the molecular interactions between liquid and a 2D monolayer upon doping. The multiscale theoretical framework proposed here is expected to shed light on the surface science of 2D materials, as well as to provide a quantitative estimation for the wettability of the doped 2D materials. We hope that the development for the 2D materials-based functional surfaces in liquid manipulation, energy harvesting, and molecular epitaxy will be facilitated by the fundamental principles and theoretical insights presented here.

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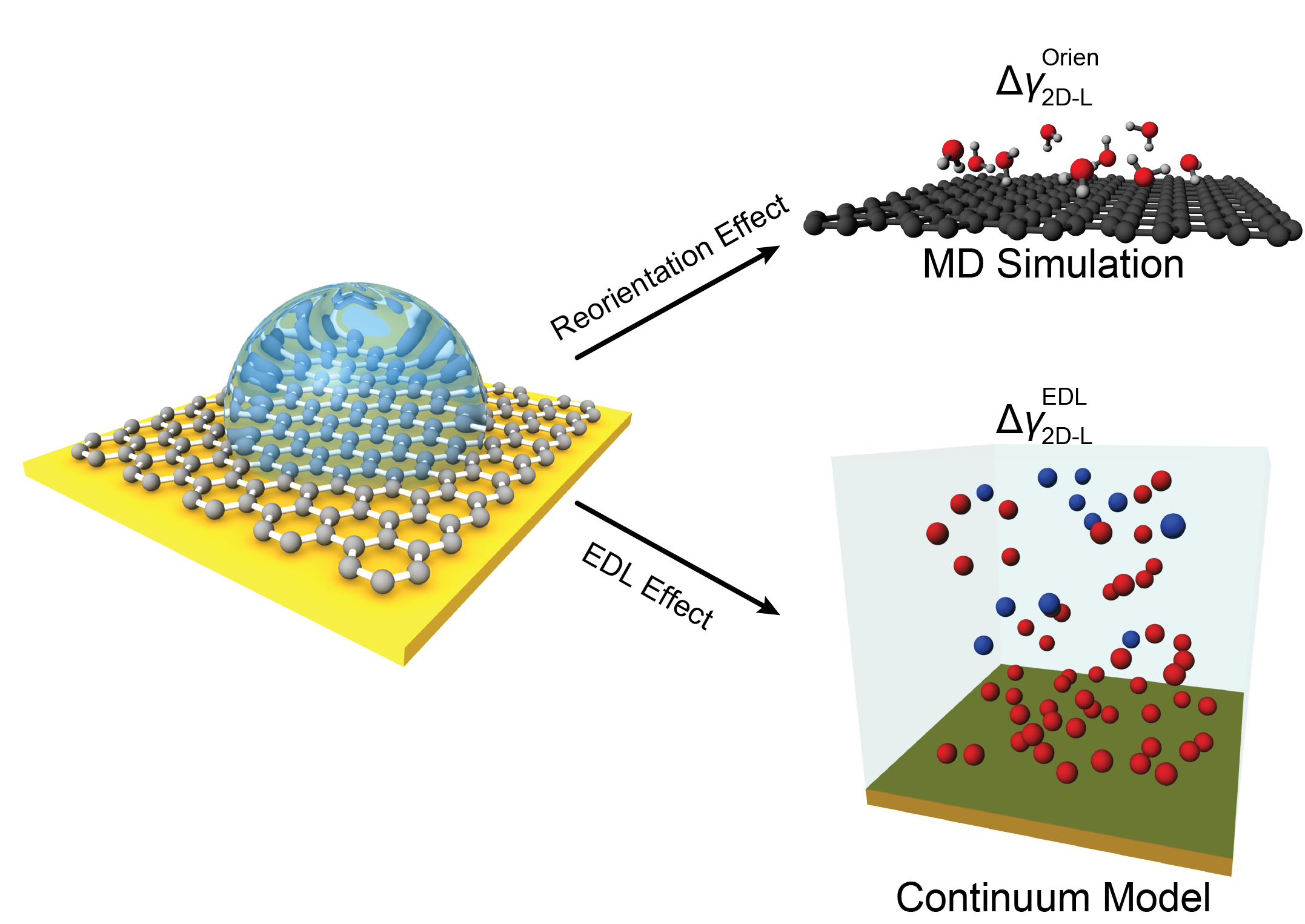
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# Figures

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