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Force Field for Water-Surface Interaction: Is Accurate Reproduction of Experimental Water Contact Angles Enough?

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**A new protocol based on quantum chemical calculations and molecular dynamics simulations was proposed to probe interaction between water and MoS2 surfaces. Zero-point energy was proven to significantly affect adsorption energy of water, and consequently parameters of the interaction force field. The water contact angle should not be considered as the sole criterion for evaluating the force field. Importantly, energetic ordering of different water-surface configurations should be considered as a clear manifestation of force-field accuracy.**

Measurement of water contact angles (WCAs) is a typical approach to investigate wettability of materials and surfaces. A droplet of water stably maintained on materials surfaces is the result of complex mechanical balancing among different interfacial interactions, in which water-surface interplay is intuitively typical. For a specific liquid-surface system, water contact angles are a unique and highly characteristic feature. Characterization of WCAs can help us understand physico-chemical properties and surface structures of materials.1

From the classical perspective, stabilization of a water droplet on surfaces can be attributed to equilibrium of classical atomic forces. Therefore, at molecular levels the formation and stabilization of water droplets on surfaces can be theoretically probed by making use of molecular dynamics (MD) simulations. Indeed, several MD works were conducted to study different aspects of nanodroplets on materials surfaces, for example advancing and receding, hysteresis, and evolution dynamics.2–4 In doing so, a force field (FF) with capability to describe correct interfacial interaction between water and surfaces is of paramount importance. Therefore, during the process of FF parameterization, reproduction of accurate WCAs is usually a key factor chosen for assessment of a newly developed parameters. Such assessments can be seen in development processes of various interfacial FFs for numerous materials such as graphene,5 boron nitride,6,7 molybdenum disulfide,8–10 and silica.11

With a wide range of potential applications in biological sensors12,13, water treatment,14–18 gas-sensing19,20 and electronic devices,21,22 single- and multi-layer nanosheets of MoS2 draw much attention from experimental and theoretical researchers. From the theoretical aspect, if one aims at high accuracy and small-size systems (up to few hundred atoms), density functional theory (DFT) might be the best choice. However, if nano-size systems and realistic models are considered, the MD method is always a feasible and obvious option. The point with MD methods is that a reliable and accurate FF to describe atomic interactions governing dynamic behaviours of materials is not always available and needs to be developed. Over the years, several sets of FF parameters were developed for simulating the MoS2 nanosheet23–25 and interfacial interactions between MoS2 layers with other molecules, particularly water8,9,26,27 and protein-related substances.10,28

As we can see, before any production MD simulation, reliability of the developed parameters used for interfacial simulations were eventually evaluated by considering their capability to reproduce the experimental WCA.8–10,26,27 The question arises here is that whether a FF which can accurately reproduce experimental WCAs can be safe enough for production MD simulations. In this work, we will show that several sets of FF parameters can produce the experimental WCA but not all of them can really describe energetic ordering of water configurations on the surface of MoS2 as the quantum chemical hypersurface does. Therefore, we propose energetic ordering as a new criterion to validate quality of parameters developed for water-surface simulations. This new criterion and WCAs are believed to be a synergistic pair of criteria which should be used to assess quality of FF parameters before any production MD run. We also prove that zero-point energy (ZPE) is believed to contribute to adsorption energy of water on the MoS2 surface. By using molecular dynamics simulations and quantum chemical calculations, the ZPE correction is estimated and ZPE-corrected adsorption energy of water on MoS2 is determined.

Fifteen geometrical configurations of water adsorbed on the MoS2 surface were optimized at the vdW-DF229 level of theory implemented in the Quantum Espresso 6.4.1 package.30,31 The optimized configurations were, subsequently, used in the MD calculations for evaluation of FF parameters developed in this work and in five other publications.8–10,26,27 All MD simulations were done with the Gromacs 2018.3 package. Full details of method selection, quantum chemical calculations, MD simulations, and nonbonded Lennard-Jones parameterization are provided in the electronic supplementary information (ESI).

Static adsorption energy of water on the basal plane of MoS2 was estimated to be 15 kJ/mol. Several configurations were found to have close interaction energies, ranging from 13.0 to 15.0 kJ/mol. These values are in good agreement with adsorption energy reported elsewhere.32,33 Geometrical structures of the strongest binding configuration and other close ones are given in Figure 1. Note that with a value of 15 kJ/mol, the static interaction between water and the basal plane of MoS2 can be considered as a weak interaction, and the insight into this interaction can be largely attributed to van der Waal forces.

Six sets (named as S1 to S6 in Table 1) of nonbonded FF parameters and water models extracted from literature were used to calculate interaction energies of fifteen water-surface configurations. The orderings of interaction are pictorially visualized in Figure 1. Obviously, two interaction orderings produced by two sets S1 and S2 are not in agreement with those produced by using the other four sets (S3 to S6), and not in agreement with the vdW-DF2 ordering (noted as DF2) as well. Remarkably, while two configurations C1 and C3 were identified to be among the strongest interactions at the vdW-DF2 level, they were completely identified as non-interaction, even repulsion at the S1 and S2 levels (see ESI for interaction energy). The S6 ordering behaves in a very similar way in comparison to the S1 and S2 ones. Among the six energetic orderings, S3 and S4 are in a good correlation with the vdW-DF2 ordering, except for the strongest binding configuration C1. Note that the S4 parameters were fitted from the random phase approximation (RDA) energy but with only 5 data points which may not enough for fitting parameters. This could be the reason why the S4 set cannot detect the strongest configuration C1. One, now, can see that even though different parameter sets can correctly describe specific properties of surface materials and reproduce accurate WCAs,8,10 they cannot consistently and correctly identify the most important geometrical configurations of water on the surface. Consequently, the dynamic behaviours of water on the surface cannot be simulated in such a way that would quantum mechanically happen. Note that with a similar procedure as done above, any set of interfacial FF parameters can be re-evaluated as long as contact angles of adsorbates on specific surfaces are experimentally available. Or in other words, here we propose a protocol based on quantum chemical energy and experimental contact angles to evaluate newly developed interfacial FFs.

Table 1 FF Well tested parameter sets with capability to accurately reproduce experimental WCAs reported in five different works

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| para. | para. set | | | | | |
| S110 | S210 | S39 | S426 | S527 | S68 |
| σMo | 0.480 | 0.480 | 0.443 | 0.393 | 0.420 | 0.255 |
| εMo | 0.293 | 0.293 | 0.485 | 0.192 | 0.254 | 0.544 |
| σS | 0.384 | 0.384 | 0.334 | 0.336 | 0.313 | 0.350 |
| εS | 1.255 | 1.255 | 2.085 | 1.121 | 1.184 | 1.046 |
| qMo | +0.50 | +0.50 | +0.50 | -0.60 | +0.00 | +0.76 |
| qS | -0.25 | -0.25 | -0.25 | -0.30 | -0.00 | -0.38 |
| water | TIP3P | SPC | SPCE | SPCE | SPCE | TIP3P |



Figure 1 Energetic ordering of several water configurations adsorbed on the basal plane of MoS2. S1 to S6 are orderings produced by FF parameter sets and water models listed in Table 1. DF2 and TW are energetic orderings determined at the vdW-DF2 level and by new FF parameters of this work, respectively. C1 to C15 are geometrical configurations of water on the basal plane of MoS2.

Our first attempt to fit the nonbonded parameters to static vdW-DF2 data points ended up with dynamically unpractical parameters because the obtained parameter set could not maintain droplets of water on the basal plane of MoS2. However just a mall change in interaction energy of the fitting data points can give rise to a stable droplet and change WCAs. This result reveals that contact angles are quite sensitive to energy of the fitting set. Weak static interaction ( ̴15 kJ/mol) between water and the MoS2 basal plane is believed to be the reason causing sensitive contact angles to energies of the fifing set. Therefore, any correction to interaction energy of the fitting data points can significantly contribute to the formation of water droplets. Note that the vdW-DF2 energies of the fitting points are bare static interaction energies without any further correction such as ZPE of water on MoS2 and marginal errors of the vdW-DF2 method.

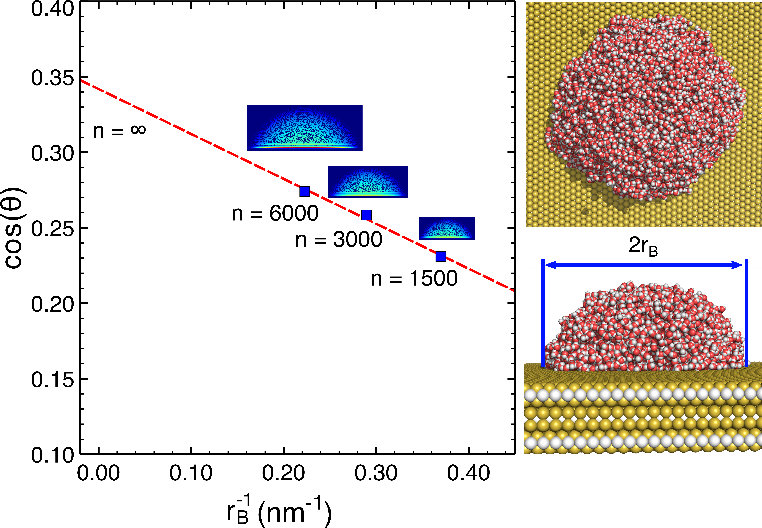


Figure 2 Three droplet sizes (1500, 3000, and 6000 molecules) of water on the three-layer MoS2 surface together with their representative top and side view. The water model TIPS3P was used for simulations of three sizes.

For weak facial water-MoS2 interaction in this work, ZPE correction should be taken into account. Indeed, by using three cluster models of water-MoS2 interaction (see ESI), we found that ZPE does affect the water-MoS­2 binding energy. In addition, we know that all interaction energies calculated using six sets of parameters above are clearly smaller than the static vdW-DF2 ones (refer to ESI). Therefore, we strongly believe that ZPE really plays important role in the formation of water droplets. Since ZPE correction to every water-MoS2 configuration and marginal errors of vdW-DF2 are hardly computed, we decided to fit nonbonded parameters of the CHARMM22\* force field34,35 to the experimental WCA. Importantly, the fifing process always ensures that the newly fitted parameters can relatively recover the vdW-DF2 energetic ordering of water-MoS2 interaction configurations.

Our newly fitted nonbonded parameters describing interaction between water and the basal plane of MoS2 ­can produce accurate the experimental WCA and energetic ordering of water-surface configurations. These parameters are given in Table 2. The macroscopic WCA was extrapolated from WCAs of three different sizes (see Figure 2) of nano droplets using Young’s equation given by

|  |  |
| --- | --- |
|  | (1) |

where is the water liquid-vapor surface tension, is the droplet base radius, and is the line tension. The macroscopic droplet contact angle was calculated to be 70o which is very close to the early WCA experimentally reported to be 69o.36 Energetic ordering of water-surface configurations obtained by using the newly fitted set of parameters was visually presented and marked as TW in Figure 1. Obviously, we can see that our new parameters can detect the strongest configuration and several other closer ones in good correlation with those determined at the vdW-DF2 level. Furthermore, quantum chemically unfavourable configurations are also correctly identified by this set. Briefly, our newly developed parameters can accurately reproduce the experimental WCA and well recover energetic ordering of all water-surface configurations. These two crucial features make our new interfacial FF parameters be quantitively capable of predicting the molecular dynamic interfacial behaviours of water on the MoS2.

A close look at our new parameters gives us more insights into the roles of MoS2 atomic layers in the interfacial interaction with water. Clearly, one can see that all epsilon values describing Mo-O and Mo-H interactions are quite small (0.04 kJ/mol), which means that the lower atomic layers of Mo in MoS2 layers play minor roles while the topper layer atoms of S contribute the most to the interfacial interaction with water molecules. An obvious difference between our new set of parameters and six sets above are that our new FF set treat surface-water interaction by considering two separated types: surface-oxygen and surface-hydrogen while the above sets use mixing rules. Such separation of treatment is believed to allow recovery of the strongest interaction configuration C1 (see Figure 1).

Table 2 Eight nonbonded FF parameters describing interaction between water and the basal surface of three MoS2 layers. Atomic charges of Mo and S are +0.50 and -0.25 e, respectively, taken from previously quantum chemical calculations.26,37

|  |  |  |
| --- | --- | --- |
| interaction | parameter | |
| σ (nm) | ε (kJ/mol) |
| Mo-O | 0.3000 | 0.0479 |
| Mo-H | 0.1500 | 0.0357 |
| S-O | 0.3020 | 1.4958 |
| S-H | 0.1870 | 0.0867 |

Predicted adsorption energy of water adsorbed on the pristine plane of MoS2 making use of our new FF is in the same range with the other two parameter sets S3 and S4 listed Table 1. While the S3 and S4 sets predict adsorption energies of 8.9 and 6.5 kJ/mol, respectively, our new parameters predict an amount of 7.8 kJ/mol. This value lies in between the two values of the sets S3 and S4, and more interestingly this value is excellent agreement with an estimation of 8.2 kJ/mol reported elsewhere.27 On the basis of adsorption energy predicted with the current parameter set, the ZPEs of all considered water-surface configurations are estimated to be 4.5 to 8.2 kJ/mol.

All in all, not all interfacial FFs are safe to be used in production MD simulations, even though they can well reflect structural behaviours of the surface materials and accurately produce the experimental contact angles. To ensure that newly developed FFs can be safely utilized in real interfacial simulations, we suggested a new criterion called “energetic ordering”, and proposed a protocol based on this new criterion and experimental contact angles to assess newly developed FF parameters. A new parameter set for molecular dynamical description of interfacial interaction between water and the MoS2 was developed and fully meet these two criteria.

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