Does Expanding or Contracting MgO Lattice Really Help with Corrosion Resistance of Mg Surface: Insights from Molecular Dynamics Simulations

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ABSTRACT: In a humid environment, water droplets on the solid surface can act as a medium to accelerate corrosion. If the solid material has hydrophobic properties, the surface of the material will remain “clean” and corrosion may be retarded to a certain extent. In theory, MgO itself is a hydrophilic material, and we can apply additional stress or strain to change its lattice constant and adjust the wetting behavior of water on the MgO surface, resulting in changes of corrosion resistance. In order to study the effects of MgO lattice expansion or contraction on the wetting behavior of nano-water, molecular dynamics simulations have been performed in this work. It is found that the changes of the lattice constants on the MgO surface can significantly change the wetting tendency. It will alter the interaction forces between water molecules and MgO surfaces, which in turn changes the atomic density profiles, the orientation of OH bonds, and hydrogen bond networks. The contraction of MgO can actually result in the increase of wetting angles of nano-water droplets on the MgO surface and gradually exhibits hydrophobic properties.

1. INTRODUCTION

According to the Pilling−Bedworth (PB) theory,1 metallic materials which form bigger oxide crystal lattices than the substrate will lead to excellent corrosion protections, while those forming smaller oxidation volumes at the surface will result in poor protections. MgO/Mg has a PB ratio ($V_{MO}/V_M$) at 0.81 which is smaller than 1, and it is believed that the poor corrosion resistance of Mg alloys results from the incomplete coverage of MgO.2−8 Furthermore, MgO itself is a hydrophilic material, and water droplets on the MgO surface can act as a medium to accelerate corrosion in a humid environment. If the solid material has hydrophobic properties, the surface of the material will remain “clean” and corrosion may be retarded to a certain extent. In theory, MgO is a hydrophilic material, and additional stress or strain can change its lattice constant, affecting the wetting behavior of water on the MgO surface, resulting in changes of corrosion resistance. In order to study the effects of MgO lattice expansion or contraction on the wetting behavior of nano-water, molecular dynamics simulations have been performed in this work. It is found that the changes of the lattice constants on the MgO surface can significantly change the wetting tendency. It will alter the interaction forces between water molecules and MgO surfaces, which in turn changes the atomic density profiles, the orientation of OH bonds, and hydrogen bond networks. The contraction of MgO can actually result in the increase of wetting angles of nano-water droplets on the MgO surface and gradually exhibits hydrophobic properties.

Received: August 5, 2020
Accepted: December 4, 2020
Published: January 6, 2021

https://dx.doi.org/10.1021/acsomega.0c03755
ACS Omega 2021, 6, 1099−1107
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could strongly affect its wetting properties on a hydrophobic surface. However, on a hydrophobic surface, the interaction force is smaller than that for the hydrophilic surface. The water molecules in the first layer form a disordered structure and have a negligible influence on the wettability of the solid surface. On the ionic model, the surface with charges will alter the electrostatic interaction force between water molecules and the solid surface. Wang\(^{27}\) found that the wetting behavior on the polar hexagonal surface has a close correlation with the ordered water monolayer for the charge dipoles. He proposed that the solid surface has a critical length of the charge dipoles. When the dipole length is less than the critical value, the water molecules seem to have less electrostatic interaction force with the charge dipole on the solid surface, resulting in hydrophobic behavior.\(^{22}\)

However, there is still a lack of the microscopic structure details of water molecular arrangements on the charged solid surface with different lattice constants, such as OH bond orientations, hydrogen bond (HB) densities, atom density, and so forth. These features become extremely important in recent years.\(^{11,17,20,22}\) Qi\(^{17}\) suggested that temperature increases the number of HBs between the ordered water monolayer and the water droplet, which in turn enhances the hydrophilicity of the ordered water monolayer at the fcc model. Li\(^{20}\) also determined that ion hydration in the first layer can affect the wetting of the salt solution on the surface by transforming the orientation of water OH bonds and reconstructing an ordered water network. Therefore, we will pay more attention to the nanostructures in the first hydration layer, which is important to control the wetting behavior of water.

Now, a wide spectrum of analytical and imaging techniques could be used to observe the microscopic structure and dynamics of water molecules on the solid interface, such as synchrotron X-rays, IR, neutron scattering, diffuse X-rays, \(\text{nm}\) scattering, and so forth.\(^{11,20,28}\) However, the experiment needs to be in an ultrahigh vacuum condition and is very costly.\(^{27}\) On the other hand, scientists gradually pay more attention to the computer simulation methods, which can successfully predict the detailed information at the atomic level, that is, atom-molecules sites, OH orientation of water molecules, and distribution of HB structures. Molecular dynamics simulation, which is a powerful tool for studying the microscopic structure of molecules, has been widely used for studying the wetting behavior of water at various conditions.\(^{29–32}\)

In this paper, the effects of lattice constants on the wetting behavior of nano-water at the charged solid surface have been studied by molecular dynamics simulations. Magnesium oxide, as a natural oxide film preventing magnesium alloys from further corrosion,\(^{33}\) is chosen as the solid substrate. By analyzing the structure and dynamics of water molecules on the MgO surface, such as atomic density profiles, the orientation of OH bonds, HB network, and the interaction force between water molecules and the MgO surface, the effects of lattice constants and surface charges on the wettability of the MgO surfaces are explored at the atomic level. This provides theoretical guidance to improve the hydrophobicity and corrosion resistance of Mg alloys in the future.

2. SYSTEMS AND METHODS

2.1. Simulation Models and Parameters. In our previous work,\(^{16}\) the initial configuration of a water droplet on the top of the MgO substrate has been built, as shown in Figure 1. The lattice constant \(a_0\) is set to 4.212 Å, and a spherical water nanodroplet with a diameter of about 70 Å is placed on the MgO surface. Here, we use a factor \(L (a/a_0)\) to represent the change of lattice parameters that separate Mg and O atoms. There are six reduced lattice constants of MgO (\(a(a/a_0)\)) at 0.80, 0.85, 0.90, 0.95, 1.00, and 1.05, respectively. It should be stressed that the reduced lattice constants could resemble certain surfaces, suggesting both unrecognized possibilities associated with existing materials and potential for new materials that exhibit this property.\(^{23}\) The stable configuration is obtained within the simulation box of 210 Å \(\times\) 210 Å \(\times\) 147 Å. The effects of periodic images of the droplet can be effectively eliminated by this large simulation box. The thickness of the MgO substrate (lattice constant \(a_0\)) is set to 10.5 Å, according to theoretical studies.\(^{20,34}\) A software package, OVITO,\(^{35}\) is used to perform the visualization of simulation data, which has been widely used in previous molecular simulation studies.\(^{16,36}\)

In the simulations, the CLAYFF force field is chosen to describe the physical processes of MgO/water interfaces.\(^{37}\) It mainly contains Lennard–Jones (12–6) potential and Coulombic potential, which are chosen to describe van der Waals interactions and electrostatic forces, respectively. This force field has been proven to reproduce the substrate–water interface very well and is widely used.\(^{24,31}\) Similar to the previous studies,\(^{38}\) all atoms in the substrate are frozen.

\[
V = \sum_{i<j} \left\{ \frac{C_{ij}q_iq_j}{r_{ij}} + 4\epsilon_{ij} \left( \frac{\sigma_{ij}}{r_{ij}} \right)^6 - \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{12} \right\}
\]

(1)

The water is simulated using the extended simple point charge model\(^{32,35}\) in which many physical properties of water are agreed well with experimental data. The hydrogen atoms are located at 1 Å from the oxygen atom with an H–O–H angle of 109.47°. Bond distance and bond angle are fixed by employing the SHAKE algorithm.\(^{33}\) The cutoff distance for all interactions is set to 9 Å. In addition, the Lennard–Jones potential parameters for different atom interactions are determined by the Lorentz–Berthelot mixing rule.\(^{37}\) All force field parameters\(^{25,38}\) used in this work are summarized in Table 1.

The system is in a canonical ensemble \((NVT)\), where constant number of particles \(N\), volume \(V\), and specified temperature by a Nosé–Hoover thermostat are adopted.\(^{32}\) Periodic boundary conditions are applied in three dimensions in the simulation. The PPPM method\(^{43}\) is the Particle-Particle Particle-Mesh (PPPM) method for simulating many particle
systems interacting via long-range Coulombic potentials which has an accuracy up to 10−4 and has been used to calculate the long-range electrostatic interactions in this study. The Velocity–Verlet algorithm44 is used to solve the equation of motion. The length of each time step is 10−3 ps, and the total simulation time reaches 5 ns for equilibrium at 300 K. All simulations are performed using the large-scale atomic/molecular massively parallel simulator (LAMMPS) software.45

2.2. Calculation Method of PB Ratio. The volume ratio of metal oxide to metal, the PB ratio, is defined as3

\[
R_{PB} = \frac{V_{ox}}{V_{m}} = \frac{M_{ox}/\rho_{ox}}{n(M_{m}/\rho_{m})}
\]  

(2)

where \( M \) is the molar mass, \( \rho \) is the density, \( n \) is the number of metal atoms per molecule of oxide, and \( V \) is the molar volume. The PB ratio is the ratio of the volume occupied by a metal atom in the oxide to the volume occupied by the same metal atom in the substrate. As we knew, the crystal structure of Mg is hexachlorophene, and the units cell volume of Mg is \( a_{Mg} \times a_{Mg} \times a_{Mg} \) which has two Mg atoms per cell. However, the units cell volume of MgO is \( a_{MgO} \times a_{MgO} \times a_{MgO} \) and it has four Mg atoms per cell.

Thus, the PB ratios of MgO/Mg can be calculated as

\[
R_{PB} = \frac{V_{MgO}}{V_{Mg}} = \frac{a_{MgO}^3}{2\sqrt{2}a_{Mg}^3}
\]  

(3)

where the lattice constants of MgO (\( a_{MgO} \)) and Mg (\( a_{Mg} \)) are 4.212 and 3.192 Å in this paper, respectively. The change of MgO lattice parameters can be accompanied by the change of PB ratios. When the lattice parameter of MgO is \( L = 1.00 \), the PB ratio is \( \sim 0.81 \).

2.3. Calculation Method of Contact Angle. As shown in Figure 2, when a drop of water reached equilibrium on the

The density of each bin is calculated to obtain the density distribution of the droplets. The point of \( \rho(r,z) \) at 0.50 g·cm\(^{-3}\) is selected as the liquid–gas interface of the droplet.46 These interface points are adjusted by circular fit based on the least-squares method. The contact angle is obtained by tangential cutting at the intersection of the MgO surface.

2.4. Definition of HBs in Water Molecules. As shown in Figure 3, the geometric criteria are employed to determine the HB in this study. A HB is considered to form between two adjacent water molecules when it satisfies the following requirements:47,48 (1) the oxygen–oxygen distance is less than 3.5 Å. (2) The angle between the oxygen–oxygen axis and one of the oxygen–HBs is less than 30°. In addition, the position of one HB is defined as the midpoint between acceptor water oxygen and donor water hydrogen atoms.

3. RESULTS AND DISCUSSION

3.1. Contact Angle. Figure 4 shows the contact angle of the water droplet on the MgO when the system reaches equilibrium. The calculation method of the contact angle can be found in Section 2.3. As shown in Figure 4, it can be seen that the contact angle of water droplets on the MgO surface that we have calculated is 44.59° when \( L(a/a_0) \) is 1.00. It is similar to the contact angle at 47° obtained by Phan.38 Therefore, it is proven that our simulation model could accurately describe the wetting behaviors of the water droplets on the MgO surface.

When the ratio of lattice constants \( L \) increases from 0.80 to 1.05, The contact angle shows a gradual reduction tendency. The contact angle decreases from nonwetting when \( L = 0.80 \) at approximately 92.3° to complete wetting at 12.9° when \( L = 1.05 \). Specifically, the contact angle decreases slowly when \( L \) is from 0.80 to 0.90, and then it decreases quickly as \( L \) increases further. This phenomenon may be explained by the surface–water interactions, where they are more attractive as \( L \) increases, and changes the structural properties of water

| atom/ion | \( \varepsilon \) (kcal·mol\(^{-1}\)) | \( \sigma \) (Å) | charge (e) |
|----------|------------------|----------------|------------|
| O\(_{water}\) | 0.15542 | 3.16552 | −0.8476 |
| H\(_{water}\) | 0 | 0 | 0.4238 |
| Mg\(_{surf}\) | 9.03 × 10\(^{-7}\) | 5.26432 | 1.05 |
| O\(_{surf}\) | 0.15542 | 3.16552 | −1.05 |

Figure 2. Calculation method for the contact angle.

Figure 3. Geometrical criteria of HBs in water molecules.

Figure 4. Equilibrium contact angle as a function of different reduced lattice constants and different PB ratios, respectively.
molecules on the MgO surface. This leads to a monotonic decrease in contact angle and a relatively rapid decline at certain stages.

Therefore, it indicates that the changes of the lattice constant can adjust the wetting behavior of water on the MgO surface. MgO itself is a hydrophilic material. When additional stress or strain changes its lattice constant, the properties of MgO substrates can change from hydrophilic to hydrophobic. This feature could prevent the Mg alloys from water droplets and reduce the probability of corrosion.

On the other hand, when the MgO surface exhibits hydrophobic properties, its coverage on the surface of Mg and Mg alloys still needs to be considered. The PB ratio is often used to discuss the effectiveness of a protective layer.\(^1\),\(^5\),\(^8\)

It is the ratio of the volume occupied by a metal atom in the oxide to the volume occupied by the same metal atom in the substrate.\(^7\) When the MgO/Mg PB ratio is 0.81, the corresponding \(L (a/a_0) = 1.00\). The oxide layer is not compact and may not be able to protect the substrate from corrosion.\(^7\),\(^31\) If we reduce its PB ratio (<0.59) to decrease the wetting performance, as shown in Figure 4, the MgO surface will remain “clean” and corrosion may be retarded. However, the magnesium surface will not be fully protected, we still need to make further efforts to create new materials that are hydrophobic and completely cover the surface of magnesium.

### 3.2. Atomic Density Profiles

Because of the interaction force between the water molecules in the first hydration layer and the MgO surface, the water molecules next to the surface usually present an ordered structure different from the bulk. In the previous work,\(^20\),\(^21\) it is found that the ordered structure in the first hydration layer plays an important role in changing the contact angle. To quantify these effects, we report the density profiles for oxygen and hydrogen atoms of water molecules in the direction perpendicular to the MgO surface as \(L\) increases from 0.80 to 1.05, as shown in Figure 5. The reference \(z\) corresponds to the top plane of magnesium and oxygen atoms in the MgO surface.

When \(L = 1.00\), it could be seen that there is one peak in the oxygen atomic density profiles, which reveals the formation of a well-defined hydration layer at \(z = 2.45\) Å; and two adjacent hydrogen peaks are found at \(z = 1.65\) Å and \(z = 3.15\) Å. Those data agree well with the simulation results from Phan at 300 K.\(^38\) This first hydrogen peak is closer to the surface and below the first oxygen peak, suggesting that one of the OH bonds of water molecules belonging to the first hydration layer points downward to the surface.

Similar density distributions are found at \(L = 0.95\) and \(L = 1.05\), indicating that the orientation of water molecules is similar to the structure when \(L = 1.00\). However, the oxygen peak is found at 2.56 Å when \(L\) equals 0.95, farther away from the surface than the first oxygen peak at 2.30 Å when \(L\) equals 1.05 on the surface. The oxygen peak on the MgO \((L = 0.95)\) surface is also broader and less intense than that on the MgO \((L = 1.05)\) surface. In addition, the density of oxygen and hydrogen atoms in the first hydration layer is gradually increasing. These features show that interfacial water molecules are, to some extent, attracted strongly by the substrate surface when \(L\) increases from 0.95 to 1.05.

In Figure 5, it can be seen that the overall trend of the oxygen peak is gradually approaching the surface, indicating that the MgO surface is becoming more attractive to water molecules. However, when \(L\) changes from 0.80 to 0.90, the densities of H and O atoms do not change obviously. This indicates the interaction force between the substrate and water molecules does not increase significantly as \(L\) increases. Besides, the first peak for the hydrogen atoms of water becomes centered on the position of the first O peak. It shows that only a few OH bonds are pointing toward the surface, and more than one OH bond per water molecule is approximately parallel to the solid surface. However, the first hydrogen peak, which is below the first oxygen peak, is gradually observed as the \(L\) increases from 0.80 to 0.90. It suggests that the OH

![Figure 5](https://dx.doi.org/10.1021/acsomega.0c03755)
bonds of the water molecules have a tendency to transform from parallel to the surface to pointing toward the surface. Therefore, we found that the value of $L = 0.95$ is the critical point, where the density of water molecules in the first hydration layer increases, and the transformation of OH bonds begins. This implies that the interaction force between the water molecules in the first hydration layer and the substrate enhances greatly, resulting in the rapid decrease in contact angle.

3.3. Transformation of Water Orientation. To investigate the effects of lattice constants on the orientation of OH bonds in water molecules, the probability distribution of OH bond orientation in the first layer is reported. There are many approaches analyzing the OH bond orientation of water molecules. In this work, the angle $\theta_{\text{OH}}$ between the molecular OH vectors and the surface normal vector is considered to be OH bond orientation in water molecules. The detailed method can be found in the previous work.

Generally, the probability of OH parallel to the surface ($70^\circ < \theta < 120^\circ$) is the highest. Experimental and simulation results suggest that the water molecules in the first layer are almost parallel to the MgO(001) plane at low temperatures, which helps the water molecules to form HBs and increase the contact angle. As shown in Figure 5, when $L$ increases from 0.80 to 0.90, the probability of OH bonds parallel to the surface ($\theta = 0.95$) is the highest. Experimental and simulation results indicate that water molecules in the first hydration layer near the MgO(001) plane at low temperatures tend to form HBs, which increases the contact angle. In-plane radial distribution functions (RDFs) are also one of the best methods to quantify the structural characteristics of interfacial water. This 2D calculation method for RDFs is suitable for such a thin region ($\sim 1$ Å).

Figure 7. Density variations of HBs as a function of reduced lattice constants.

![Figure 7](https://dx.doi.org/10.1021/acsomega.0c03755)

![Figure 6](https://dx.doi.org/10.1021/acsomega.0c03755)

Figure 6. Probability distribution of OH bond orientation in the first hydration layer at different reduced lattice constants.

can be seen that the distribution of HB density exhibits a pronounced first peak, which corresponds to the first hydration layer. It suggests that water molecules in the first hydration layer have a strong tendency to form HBs. When $L$ increases from 0.80 to 0.90, the density of HBs in the first hydration layer is gradually reduced. This reduction in the density of HBs is affected by the transformation of OH bonds. As shown in Figures 5 and 6, the OH bonds of the water molecules have a tendency to transform from parallel to the surface to pointing toward the surface. The reason for the changes of water molecule structure is because of the increasing interaction force between the water molecules in the first hydration layer and the MgO surface. However, it can be found that the force increases slowly based on the insignificant change in the density of water molecules, as shown in Figure 5.

In addition, a new peak for interlayer HBs is gradually observed when $L$ is over 0.95. It shows that the interlayer HBs are formed between the upper hydrogen atom in the first hydration layer and the oxygen atom in the second layer. However, the distribution of HB density in the interlayer does not have this kind of peak when $L$ is changing from 0.80 to 0.90. It suggests that the interaction force between the water molecules in the interlayer is increased when the $L$ is over 0.95, which in turn decreases the contact angle.

Furthermore, this HB distribution in the interlayer is mainly caused by an increase in the force between the MgO surface and water molecules. The enhancement of the force can also be observed from the increase in the density of water molecules, as shown in Figure 5. It can result in the transformation of OH bonds, which results in the reduction of the HB density in the first hydration layer and the increase of the HB density in the interlayer. These features can be explained by analyzing the decrease in contact angle to some extent.

3.4. HB Network. HBs are correlated to the dynamical state of the water molecules, which has a strong impact on the wettability of the solid surface. The generation and destruction of HBs are the microscopic behavior of the basic dynamic process in the liquid. Zhu found that the ordering of the HB network within the first water layer can have a large influence on the wetting behaviors. Qiu found that the ordered water within the first hydration layer is broken as the temperature increases, leading to the formation of more HBs between the first and the second hydration layer (interlayer). This result demonstrates the enhancement of the interaction forces of water molecules in the interlayer and decreases the contact angle.

As shown in Figure 7, the distribution of HB density along the z-axis at different reduced lattice constants is reported.
previous studies, it is found that the RDFs for the second hydration layer are similar to the results of bulk water, indicating that the MgO surface perturbs the water structure at a short distance. Phan also suggested that only one water hydration layer is on the MgO surface. Therefore, we calculate the RDFs in the first hydration layer with different reduced lattice constants in this work.

As shown in Figure 8, when \( L \) changes from 0.80 to 0.90, it could be seen that the result for \( g_{\text{oo}}(r) \) and \( g_{\text{HH}}(r) \) obtained for different reduced lattice constants do not show significant differences, suggesting a slightly pronounced structuring of water in the first hydration layer. Interestingly, this RDF in the first hydration layer is similar to the results in bulk water. It means that the structural order of the surface water is not obvious at this time. When the \( L \) changes from 0.95 to 1.05, more pronounced structuring of water is observed, indicating significant water orientation ordering. This result implies that the interaction force between the water molecules and the substrate enhances greatly, resulting in the rapid decrease in contact angle.

4. DISCUSSION

In recent years, the influences of intrinsic properties on the wettability of the solid surfaces have attracted the attention of many scientists, such as lattice constants and surface charge. It is found that the interaction forces between the water molecules and the solid surfaces, changed with the lattice constants, could affect the structure of the water molecule in the first hydration layer, resulting in the changes of HB density. The wettability of solid surfaces, such as Pd, Pt, and Al surface, is mainly influenced by the HBs. Generally, the water molecules could form HBs in the first hydration layer, rather than in the first–second hydration layer. The number of HBs formed between the first hydration layer and the first–second hydration layer is a competitive relationship. The fewer number of the HBs in the first–second hydration layer will result in weaker interactions and the contact angle of the droplet increases. Xu investigated the effects of lattice constants on the wetting behavior of metal materials. They proposed that the fewer number of the first–second-layer H bonds results in weaker interactions between the first layer and the water molecules above the first layer. This will affect the wetting behavior of different solid surfaces. Zhu found that when the lattice constants are close to the length scale of projected oxygen–oxygen distance in bulk water, the HB network in the first hydration layer will be distorted because of the combined influence of potential of surface atoms and bulk water. It results in the reduction of the contact angle.

When the surface atoms are charged, the water molecules will be strongly attracted by the electrostatic interactions. Wang proposed that half of the water molecules in the first hydration layer will be attracted by the electrostatic interaction between the negatively charged O atoms in the water molecule and the positively charged atoms on the surface. For water molecules in the other half, the H atoms will point toward the surface because of the electrostatic interaction between the positively charged H atoms in the water molecule and the negatively charged atoms on the surface. This leads to the fact that the formation of HBs will be affected, thereby regulating the contact angle. At present, scientists find that the electrostatic interaction is mainly related to the dipole length and the amount of charge on the solid surface. In this work, we have studied the effect of lattice constants on the surface wettability of MgO. Therefore, we will mainly discuss the effect of lattice constants (dipole length) on electrostatic interactions.

There are currently two theories to explain electrostatic interactions with the changes of lattice constants. The first is the steric exclusion effect proposed by Wang. He postulated that when the size of water molecules is not commensurate with the crystal lattice of the solid surface, the positively charged H atoms and the negatively charged O atoms in the water molecules cannot match well with the atoms on the solid surface. The electrostatic interaction between neutral, albeit polar solids and water, can be ignored because of the steric exclusion effect.

As shown in Figure 9, it shows the surface structure of the MgO crystal. The red and yellow atoms are oxygen ion and magnesium ion, respectively. When dipole length (lc) is large enough, the Osurf and Mgsurf atoms on the surface could attract the HWater atoms and the OWater, so that some of the HWater and OWater atoms will be strongly attracted by the electrostatic interactions. When lc decreases to a smaller value, the steric exclusion effect prevents those atoms from staying very close to each other. The electrostatic interactions between water molecules and the charged surface atoms decrease quickly.
of water molecules cannot be arranged. Therefore, when the value of $l_c$ is smaller than the size of water, the electrostatic interaction could be ignored.

However, in addition to the steric exclusion effects, Govind Rajan$^{51}$ considered that the lattice constants could directly affect the electric potential and electric field above a surface. He calculated and found that electric potential over the MoS$_2$ basal plane is close to zero. It implies that electrostatic interaction energies between MoS$_2$ and water could be negligible. The interactions between MoS$_2$ surfaces and water are controlled by dispersion, rather than by electrostatic interactions, despite the existence of charges in the Mo and S atoms.$^{51}$ The theories proposed by Wang$^{24}$ and Govind Rajan$^{51}$ show that when the lattice constant reaches a critical value, the electrostatic interactions between surface atoms and water molecules can be ignored.

For the critical length of the MgO crystal, we find that when $L$ is equal to 0.95, the lattice constant is 1.996 Å. It is similar to the structure of NaCl(100), where critical length is 2.02 Å for $q = 1.0$ e, reported by Wang.$^{24}$ This indicates that the electrostatic forces on the MgO surface have less attraction to water molecules when the $L$ changes from 0.80 to 0.90. It is found that the interaction forces between the water molecules in the first hydration layer and the MgO substrates are mainly van der Waals forces. The van der Waals forces are less attractive to water molecules on the surface compared with the electrostatic forces. It leads to the fact that hydrophobic properties of the MgO surfaces and the contact angle do not change significantly. As Zhu reported previously,$^{22}$ lattice strains (2.72−2.90 Å) without charge dipoles have little effect on the wetting properties of the hydrophobic surfaces. In order to further prove that the electrostatic interactions can be ignored when $L$ is 0.80 to 0.90, we calculate the contact angle on the MgO surface without charges. It is found that the contact angle changes little compared with the MgO surface with charges. Furthermore, the structural order of the surface water in the first hydration layer is also not apparent when $L$ is from 0.80 to 0.90, as shown in Figure 8. It also implies that electrostatic interactions are small.

In the range of 0.95 $L$ 1.05, the dipole length of MgO exceeds the critical length. The water molecules in the first hydration layer are strongly attracted by the electrostatic interactions on the MgO surface. This strong force improves the structural order of the water molecules in the first hydration layer. It causes the transformation of water orientation, and the OH bonds trend to point toward the surface. These behaviors reduce the HB density in the first hydration layer and increase the HB density in the interlayer. The HB density in the interlayer could enhance the hydration layer and increase the HB density in the interlayer.

5. CONCLUSIONS

In this work, the effects of lattice constants on the wetting behavior of nano-water at the MgO surface have been investigated by molecular dynamics simulations. The atomic density profiles, OH bond orientations of water molecules, HBs, and RDFs are calculated to identify the microscopic mechanism of wetting behavior. The results can be concluded as follow:

1. When the ratio of the reduced lattice constants changes from 0.80 to 0.90, the interaction force between the water molecules in the first hydration layer and the MgO substrate is related to the van der Waals forces. While the charge dipole on the MgO surface has less attraction to water molecules, the electrostatic interactions could be ignored. This results in the weak interaction force by observing the density of water molecules in the first hydration layer. The structural order of the interfacial water is not clear, and the RDFs in the first hydration layer are similar to the results in bulk water. The OH bonds are mainly parallel to the surface, and the density of HBs is relatively high. These features cause the MgO surface to exhibit hydrophobic behavior, and the contact angle does not change significantly.

2. When the lattice constants increase from 0.95 to 1.05, the interaction force between the water molecules and the MgO substrate is mainly governed by the charge dipoles on the solid surface. The interaction forces are electrostatic interactions and van der Waals forces, respectively, which result in greater water molecule density and the transformation of OH bond orientation. This produces a reduction of HB density within the first hydration layer and the increase of HBs in the interlayer. Therefore, it leads to a rapid decrease in contact angle.

3. The water wettability of the MgO surface can switch from hydrophilic into hydrophobic when the lattice constant is contracting by 10%. This is surprisingly interesting for purposely engineering nanostructures where we can design hydrophobic properties of MgO or other new materials by contracting their lattice constants instead of expanding them, so as to achieve the objective of improving corrosion resistance in a completely new direction. In fact, many previous experiments have shown significant improvement in the corrosion resistance of magnesium alloys by anodizing their surface and it may well find its theoretical roots at the atomistic scale from our molecular dynamics studies.

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ACKNOWLEDGMENTS

The authors would like to thank the help from all members in the Integrated Computational Materials Engineering (ICME) laboratory at the Beijing Institute of Technology (BIT), and the financial support from the Key Laboratories at the Beijing Institute of Technology (funding #6142902180305 and #61409220124) are greatly acknowledged.

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**NOTE ADDED AFTER ASAP PUBLICATION**

This paper was published January 6, 2021, with an incorrect surname for author Shaokang Guan. The corrected version was posted January 19, 2021.