

Effect of Ion-Specific Hydration Forces on the Stability of Water Films on Calcite Surfaces

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ABSTRACT: The hydration force is indispensable for understanding short-range interfacial forces in aqueous systems. Perturbation of the hydration structure by ions generates an ion-specific hydration force. Surface-force measurements on calcite surfaces have suggested that Na^+ decreases the repulsive hydration force by directly adsorbing to the surface and disrupting the hydration layers. However, the influence of structural changes on the surface force remains unclear. We conducted molecular dynamics simulations for water films between calcite (104) surfaces and oil/water interfaces. Ion-specific hydration forces estimated by the simulations were consistent with the experimental results. Notably, the ion-specific hydration forces cannot be explained solely by the structure of water molecules because ions do not significantly change in the structure of the hydration layers such as density distributions and orientations. We propose a novel mechanism whereby ion-specific electrostatic potentials in the water films control the adhesive and repulsive nature between the interfaces. The directly adsorbed Na^+ on the calcite causes the monotonically decreasing electrostatic potential from the calcite surface, thereby enhancing adhesion. Ca^{2+} results in a convex shape of electrostatic potential curve, which enhances repulsion. Importantly, the shape of the electrostatic potential curve depends on the Stern layer structure and perturbation between the surface and interfaces. This study offers important insight for interpreting surface-force measurements in aqueous systems.

Introduction

Surface forces have crucial roles in aqueous biological and non-biological systems.¹⁻⁴ These forces impart stability of thin films on solid surfaces (i.e., the disjoining pressure). The formation of thin films is crucial in many applications, such as tribology,⁵ foam stability,⁴ and wettability.⁶ Balance between the disjoining pressure and other forces (e.g., capillary pressure) determines the thickness of thin films.^{4, 7-9} Thin films of wetting fluid on solid surfaces influence the dynamics of droplets near a contact line.^{9, 10} Water films on mineral surfaces play crucial roles in mineralization,¹¹ adsorption,¹² and phase behavior in confined spaces.¹³ Thin liquid films are stabilized by the disjoining pressure in foam systems. The shape of the disjoining pressure curves as a function of film thickness depends on the types of interfaces and media between them.^{4, 8} DLVO (Derjaguin–Landau–Verwey–Overbeek) theory can be used to predict the disjoining pressure.^{4, 14, 15} This theory takes into account the London van der Waals force and entropic repulsions under continuum assumption. This is a good approximation under conditions where the continuum assumption is valid: that is, under low salt concentration and for interaction ranges greater than a few nanometers.

Hydration forces, which are classified as non-DLVO forces, have gained considerable attention because of the significance of short-range forces in aqueous systems.¹⁶⁻²³ To understand the stability of thin films with thicknesses on the nano- or sub-nanometer scale, we must incorporate non-DLVO forces, such as hydration forces. Hydration forces are ion-specific²⁰⁻²² and are

influenced by a wide range of factors, such as the finite volumes of atoms (ions and water) and ionic dispersion forces.^{20, 21} Two regimes for hydration forces can be defined based on their exponential decay length: primary hydration forces (2–4 Å) and secondary hydration forces (10–30 Å).^{22, 23} Primary hydration forces can be linked to removal of bound water at interfaces,²³ whereas secondary hydration forces are caused by competition between water around solutes (ions) and water at interfaces.²³ Notably, the origins of hydration forces are still controversial, especially for secondary hydration forces.^{20, 22, 23} Understanding the influence of perturbations between interfaces under confinement is important for revealing the origin of ion-specific hydration forces.²²

Calcite is abundant in nature and crucial for processes such as oil production and geological CO_2 storage. Aging with oil transforms calcite surfaces from their originally water-wet state to an oil-wet state. The oil-wet state evolves by the adsorption of organic acids and the deposition of organic molecules.²⁴⁻²⁹ Ion-specific wettability alterations have gained considerable attention due to their implications for enhanced oil recovery from carbonate reservoirs.^{26, 27, 30, 31} The desorption of organic acids is facilitated by divalent cations in brine. Water films must be involved in the evolution of oil-wetness and the wettability alteration on calcite because of the initial water-wet state. Importantly, the influence of water films on the evolution of oil-wetness and the wettability alteration on calcite remains unknown.

The (104) plane is a representative surface of calcite. The Stern layer in the electric double layer on the calcite (104) surface has been investigated by X-ray,³²⁻³⁷ atomic force microscopy (AFM),^{35, 36, 38, 39} and theoretical simulations^{24, 36, 39-46} in aqueous systems. For example, Ricci et al. reported that Na⁺ can be directly adsorbed on the (104) surface of calcite (forming an inner-sphere surface complex), whereas Ca²⁺ cannot (forming an outer-sphere surface complex).³⁹ The combination of molecular simulations and microscopic experiments revealed the Stern layer structures at calcite surfaces.

Surface forces reflect the structure of cations at the (104) surface.^{30, 47-53} The adhesion force between a gold-coated AFM tip and the (104) surface was measured in different aqueous media (NaCl aq. and MgCl₂ aq.),³⁰ with Na⁺ and Mg²⁺ generating adhesive and repulsive forces, respectively. The authors suggested that Na⁺ disturbs the hydration layer on the (104) surface, with this disturbance weakening the repulsive primary hydration force and resulting in a shorter decay length. They suggested that Mg²⁺ beyond the diffuse layer generates secondary hydration forces at the (104) calcite surface and results in a longer decay length.³⁰ In addition, Mg²⁺ has been shown to enhance the hydrophilicity of the calcite surface by facilitating the desorption of carboxylate groups.²⁶ Dziadkowiec et al. also reported a similar enhancement in the repulsive force in the presence of Ca²⁺.⁴⁹ Stepwise force curves reflecting hydration layers were reported when AFM-tip approached the calcite surface.^{52, 53}

We point out that AFM and surface force apparatus (SFA) measure the interaction between hard surfaces.⁵⁴ Soft/hard or soft/soft interfaces are abundant in nature. Soft interfaces can change their shape under the influence of disjoining pressure. Changing the interfacial shape can also lead to rupture of confined spaces (e.g., thin films). Hydration forces have a key role in stabilizing thin films under these conditions. Notably, hydration forces may not be comparable among hard/hard, soft/hard, and soft/soft interfaces because of differences in perturbation. Types of disjoining pressure curves influence the stability of thin liquid film.⁹ The condition for the thermodynamic stability of the film can be expressed as follows;

$$\frac{d\Pi}{dh} < 0 \quad (1)$$

where Π and h represent the disjoining pressure and the water film thickness, respectively. The film ruptures when the system does not meet the condition. Importantly, certain ranges of film thickness are thermodynamically prohibited.

Although experiments have provided evidence of ion-specific hydration forces at the calcite surface, the relationship between the interfacial structure and hydration forces remains unclear. Simultaneous measurements of both interfacial structure and hydration forces are difficult. Molecular simulations are powerful tools for establishing a direct link between interfacial structures and hydration forces. For example, the surface force between interfaces was calculated using systems that control the thickness of confined spaces.⁵⁵⁻⁶⁰ In one study, the disjoining pressure for water films on a α -quartz surface was calculated and a highly repulsive force was observed between α -quartz/NaCl aq. and n -decane/NaCl aq. interfaces.⁶⁰ This study also demonstrated that water films were stable on the α -quartz surface under different NaCl concentrations and that repulsive force increased with decreasing NaCl concentration, following Poisson–Boltzmann theory.⁶⁰ However, the link between ion-specific interfacial structures and hydration forces remains unclear for classical electric-double-layer models. Importantly,

rupture of water films is important for understanding the evolution of oil-wetness on mineral surfaces.

This study focuses on the stability of ion-specific water films on calcite (104) surfaces. We provide direct evidence of ion-specific hydration forces under perturbation between oil/water and water/calcite interfaces through molecular dynamics simulations. The simulations provide insight into the electric-double-layer structure under confinement and the resulting hydration forces, and reveal a novel origin of ion-specific hydration forces.

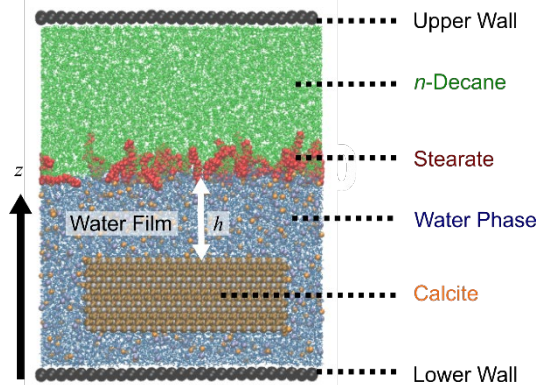


Figure 1. Systems used for molecular dynamics simulations. The oil phase consists of n -decane with or without stearate. The water phase is pure water, 1.0 mol/kg NaCl aq., or 1.0 mol/kg CaCl₂ aq. The calcite (104) surface faces the z -direction. The system has vacuum space above and below the upper and the lower walls, respectively.

Methodology

The simulation systems consisted of an upper and lower wall, oil phase, water phase, and calcite (Fig. 1). An external force was applied to the walls, which moved along the z -direction. The upper and the lower walls were used to control and calculate the pressure of the oil and water phases, respectively. Pressure was applied by adding a constant force on the center of mass of the walls. The pressure was calculated from the force on the walls by the oil and water phases. The oil phase was pure n -decane or n -decane + stearate (0.2 mol/kg). The stearate mimicked the polar components of crude oil and introduced a negative charge at the oil/water interface, where it remained at the interface at the concentration. The water phase was pure water, NaCl aq. (1.0 mol/kg), or CaCl₂ aq. (1.0 mol/kg). Counter cations (Na⁺ for NaCl aq. and Ca²⁺ for CaCl₂ aq.) were added to the water phase to attain charge neutrality in the system. The crystal structure of the calcite in the system was taken from Graf.⁶¹ We orientated the calcite (104) surface in the z -direction and set its area to be $9.98 \times 4.86 \text{ nm}^2$. The positions of carbon and calcium atoms in the calcite were fixed, whereas oxygen atoms were bound to the carbon atoms of the calcite and could move freely (i.e. free rotation of carboxylate in the calcite). The distance between the upper and lower walls was approximately 17 nm. The systems had vacuum spaces in the z -direction. The total size of each simulation systems was $14 \times 4.85756 \times 100 \text{ nm}^3$, including the vacuum space.

We used the force field for calcite reported by Xiao et al.⁶², which is widely used for interfacial molecular simulations.^{24, 43, 46} For water, we used the SPC/E model⁶³ and for Na⁺ and Cl⁻ we used an SPC/E-compatible model.⁶⁴ The parameters of aqueous Ca²⁺ were taken from Åqvist.⁶⁵ We used CGenFF⁶⁶⁻⁶⁸ to represent the oil molecules (n -decane and stearate). The ion

model is optimized to reproduce hydration free energy.^{64, 65, 69} CGenFF is selected because it well reproduces properties of organic molecules.⁷⁰ The Lennard–Jones interaction parameters (ϵ and σ) for the upper and the lower wall were set to 0.3 kJ/mol and 0.707 nm, respectively. Atoms did not pass through the walls with these parameters. The cutoff distance for the dispersion interaction was 1.4 nm with an analytical tail correction for long-range dispersion interaction. Electrostatic interactions were treated with particle-mesh Ewald summation with a slab correction.^{71–73} The temperature was controlled to 318 K by velocity rescaling with a stochastic term. We used GROMACS 2024^{74–76} for molecular dynamics calculations. Snapshots of the systems were obtained by visual molecular dynamics (VMD).⁷⁷

The systems were relaxed for 10 ns with the pressure on the upper and lower wall set to 1 MPa. The pressure on the upper wall was increased, such that the water film on the calcite (104) surface became thin. The differential pressure between the upper and the lower walls were set from 1 to 20 MPa while we monitored the film thickness. This calculation step took approximately 100 ns for each system. The atomic coordinates were recorded in this step. The atomic coordinates with a specific distance between the upper wall and the calcite surface were selected for the initial configuration in the disjoining-pressure calculations. These calculations were conducted by fixing the position of the upper wall and for a pressure of 1 MPa at the lower wall. The systems were relaxed to a certain water-film thicknesses in this step. The water-film thickness was defined as the distance between the z -coordinate of the calcite surface and the z -coordinate where the density of n -decane reaches half of its bulk density. The water-film thickness cannot be set explicitly. The disjoining pressure was defined as the pressure difference between the oil and water phases, and was obtained from the forces on the upper and lower walls. The time required to calculate the water-film thickness and the disjoining pressure was 200 ns in each system. The data from the last 100 ns was used for analysis. The standard deviation was calculated by dividing the last 100 ns into 10 blocks. Some of the CaCl_2 aq. systems showed longer relaxation times than the other systems. We extended the total calculation time up to 400 ns for monitoring pressure relaxation. The pressure relaxations of the different systems are shown in Figs S1–S5 in the Supporting Information. Structural analyses (e.g., density distributions) were conducted within the water film, excluding regions 1 nm from the calcite edges.

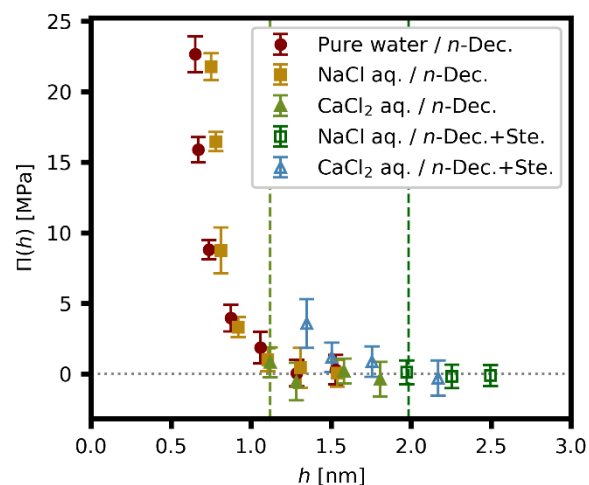


Figure 2. Disjoining-pressure curves between the calcite (104) surface and oil/water interfaces at 318 K. h represents the water-film thickness. The critical water film thicknesses are denoted by the dashed lines.

Results and Discussion

We observed the ion-specific behavior of the disjoining pressure in our simulations (Fig. 2). The pure water/ n -decane and the NaCl aq./ n -decane systems showed rapid increases in disjoining pressure with decreasing water-film thickness for thicknesses less than 1 nm (red circles and yellow squares). We interpret that the short-range, highly repulsive force is the primary hydration force based on the interaction range of 2–4 Å. The CaCl_2 aq./ n -decane + stearate system (blue open triangles) had a long-range repulsive force arising at a film thickness of 1.5 nm. This long-range force suggests the presence of secondary hydration forces in the system. The stearate remains at the oil-water interface at this separation (Fig. S6 in the Supporting Information). Consequently, no structural force arises due to the stearate. Notably, the water film ruptured in the other two systems (the NaCl aq./ n -decane + stearate and the CaCl_2 aq./ n -decane systems) below a critical thickness. We defined this critical thickness as the shortest thickness in the disjoining-pressure calculations where a flat oil/water interface was observed. The critical film thicknesses for the NaCl aq./ n -decane + stearate and the CaCl_2 aq./ n -decane systems were 2.0 and 1.1 nm, respectively. Snapshots of the systems are shown in Fig. 3. It was not possible to clearly define the critical film thickness (i.e., onset thickness of film rupture) in the CaCl_2 aq./ n -decane system because of the instability of the oil/water interface near the critical thickness. Film rupture is a phenomenon unique to systems containing soft interfaces. Stability of water films is achieved under the condition of Eq. (1). In systems with water-film rupture, the disjoining pressure did not meet this condition (i.e., $d\Pi/dh > 0$). Water-film thicknesses less than the critical thicknesses are thermodynamically unstable. Thus, adsorption of the oil molecules onto the calcite surface is facilitated in these systems (an oil-wet state). Disjoining pressures were found to be negative in the two systems with water films below the critical thickness. Values of the disjoining pressure in this region could not be obtained using the current simulation systems due to the instability of water film. Simulation systems that prohibit changes in the shape of interfaces can sample the disjoining pressure in this region. However, these systems cannot

reproduce the rupture of the water film allowing the reordering of interfacial components. We conducted independent simulations to validate the reproducibility of our observations (Fig. S7 in the Supporting Information). Reproducibility verifies that the simulation settings provide sufficient statistics in terms of system size and duration.

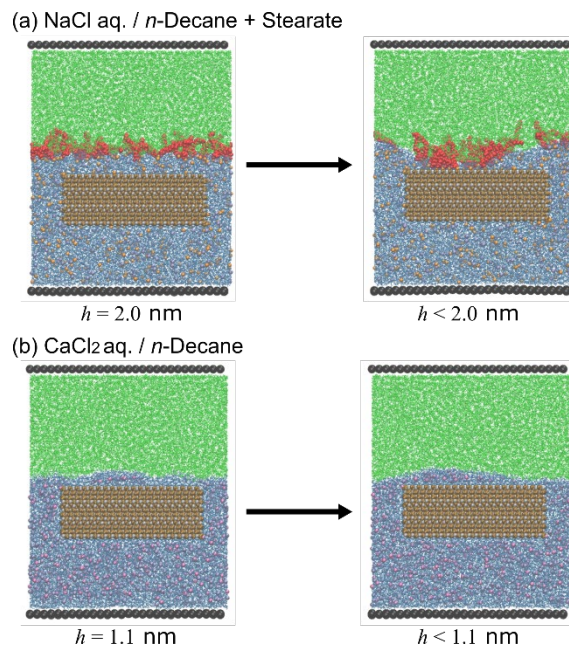


Figure 3. Snapshots of systems in which the water film ruptured (318 K). h represents the thickness of the water film and corresponds to the datapoints in the disjoining pressure curves (Fig. 2). The colors of the components corresponding to those in Fig. 1.

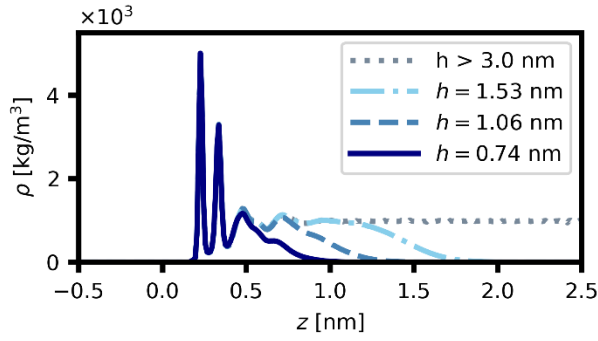
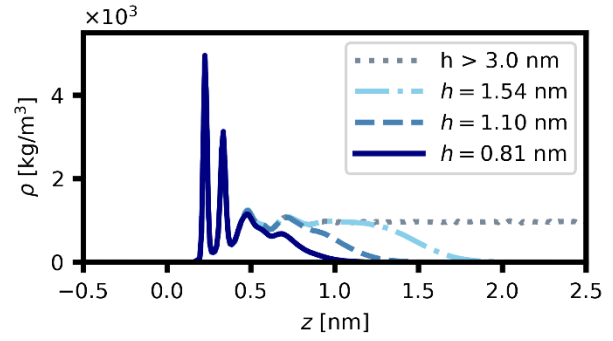
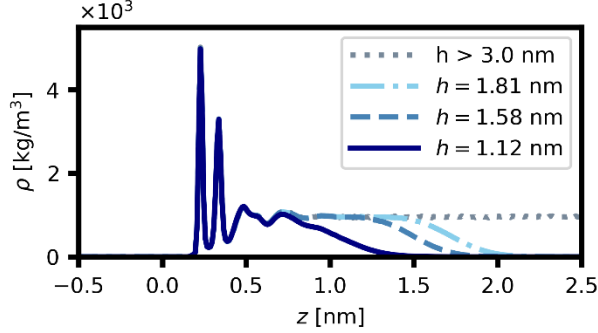
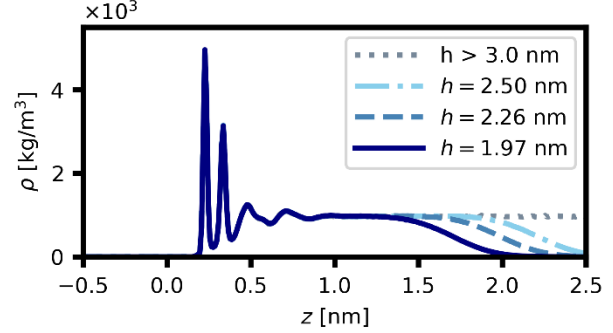
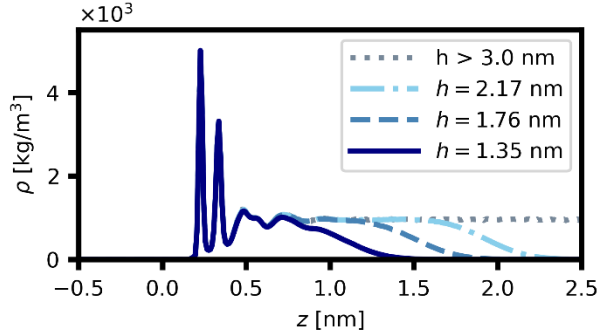
(a) Pure water / *n*-Decane(b) NaCl aq. / *n*-Decane(c) CaCl₂ aq. / *n*-Decane(d) NaCl aq. / *n*-Decane+Stearate(e) CaCl₂ aq. / *n*-Decane+Stearate

Figure 4. Density distribution of water molecules in water films (318 K). h represents the thickness of the water film and corresponds to the datapoints in the disjoining pressure curves (Fig. 2). $z = 0$ is the z -coordinate of the calcite surface.

The distributions of water molecules are consistent with those of previous studies,⁴¹⁻⁴³ and indicate the presence of highly ordered water layers at the calcite (104) surface (Fig. 4). Interference between the oil/water interface and the interfacial water structure took place for a water-film thickness of 1.0 nm (Fig. 4a and b). We conclude that the origin of the primary hydration force in the pure water/*n*-decane and the NaCl aq./*n*-decane systems is strongly bound water molecules at the calcite surface. The outer-most layer at 0.7 nm was excluded as the oil/water interface approaching the calcite surface (that is, the water films became thin, as shown by the dashed and solid lines in Fig. 4a and b). The other three layers near the calcite surface were not affected by the oil/water interface. The calcite (104) surface strongly binds water molecules. Energy associated with removing the water molecules causes the short-range repulsive force. This is consistent with the general idea of the primary hydration force. AFM measurements at the calcite surface have suggested that the decay length of hydration force is reduced by

the additions of Na⁺, which interferes with the hydration structure.^{30, 51} These measurements showed an adhesive force at high Na⁺ concentration (>150 mM) for gold tip-calcite. Notably, in the present study, similar decay lengths of the repulsive force were observed in the pure water/*n*-decane and the NaCl aq./*n*-decane systems (Fig. 2; red circles and yellow squares). The distributions of ions are shown in Fig. 5, with the direct adsorption of Na⁺ at the calcite (104) surface shown in Fig. 5a and Fig. S8a. These results agree with those of previous theoretical and experimental studies.^{24, 39, 43} Na⁺ may interfere with the hydration structure in the three layers near the calcite surface. However, our simulation indicated that the perturbations by directly adsorbed Na⁺ have only a minor influence on the primary hydration force even higher concentration (1.0 mol/kg) than the experiments,^{30, 51} in contrast with the mechanism suggested based on AFM measurements.³⁰

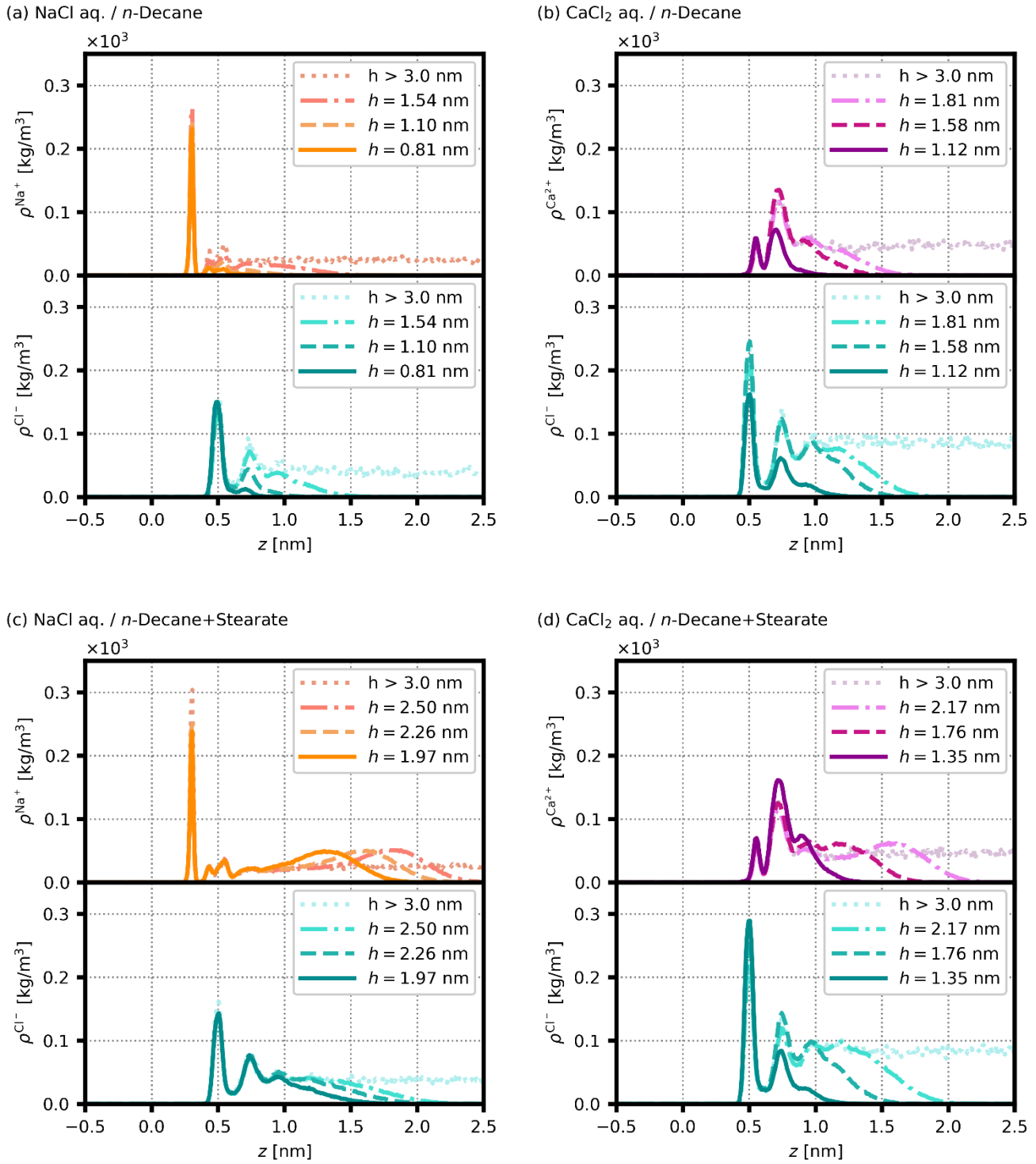


Figure 5. Density distribution of ions in water films (318 K). h represents the thickness of the water film and corresponds to the datapoints in the disjoining pressure curves (Fig. 2). $z = 0$ is the z -coordinate of the calcite surface.

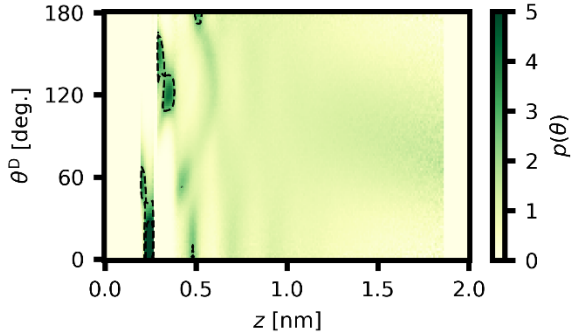
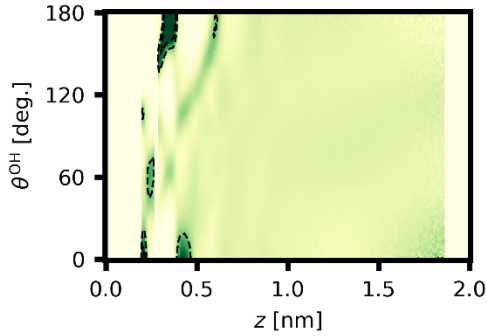
The long-range repulsive force is observed in the CaCl_2 aq./ n -decane + stearate system for a water-film thickness of 1.5 nm (open triangles in Fig. 2). Experiments indicate that divalent cations result in a longer decay length of hydration forces.^{30, 49} Our simulation shows a similar influence of divalent cations on hydration forces. The distribution of ions indicates interference

from the oil/water interface starts at $h \approx 1.4$ nm (Fig. 5d). Ca^{2+} adsorbs via water molecules at the calcite surface (i.e., outer-sphere surface complex) (Fig. S8b). Moreover, Ca^{2+} ions are farther from the calcite surface than Cl^- ions (Fig. 5b and d). Thus, these results indicate that the disturbance of hydration layer starts when the long-range repulsion is generated. Such

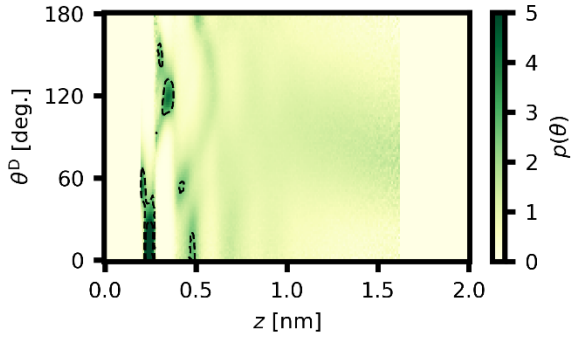
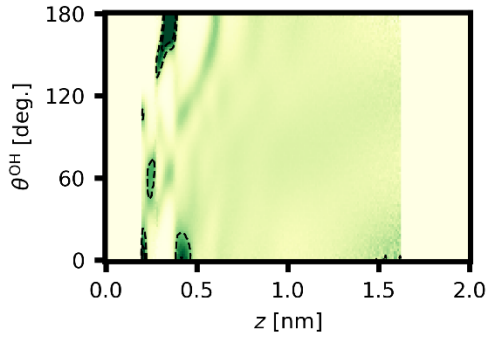
competition between water molecules around cations and water molecules at the calcite surface is an accepted mechanism of the secondary hydration force. However, the CaCl_2 aq./*n*-decane system does not exhibit a long-range repulsive force around $h = 1.5$ nm (Fig. 2), where the ionic distribution is disturbed by the oil-water interface (Fig. 5b). Therefore, we conclude that the

aforementioned competition alone cannot account for the long-range repulsion at the calcite surface, and another mechanism must be responsible for it.

(a) Pure water / *n*-Decane; $h = 1.53$ nm



(b) NaCl / *n*-Decane; $h = 1.31$ nm



(c) CaCl_2 / *n*-Decane; $h = 1.81$ nm

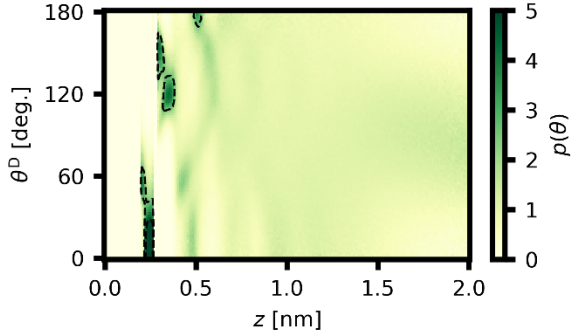
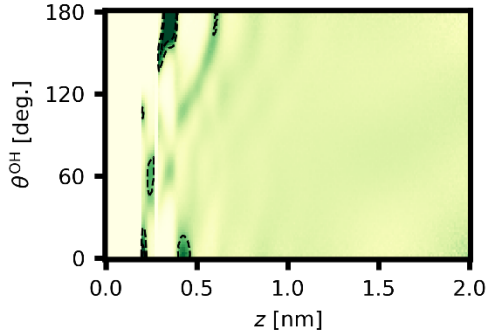


Figure 6. Probability distributions of the orientations of water molecules in water films (318 K). h represents the thickness of the water film and corresponds to the datapoints in the disjoining pressure curves (Fig. 2). $z = 0$ is the z -coordinate of the calcite surface. The superscripts “OH” and “D” represent OH and dipole intramolecular vectors, respectively. The dashed lines are contour lines at $p(\theta)$ of 2.5 and 5.0.

Our simulated density distributions of water and ions agree with previously published experimental results^{41–43, 45} that is, Na^+ is directly adsorbed and Ca^{2+} is located farther at the calcite surface. The density distributions of water were not influenced by presence of ions (Fig. 4). We now analyze the probability distributions of water orientations ($p(\theta)$) at the calcite surface, normalized as follows:

$$\int_0^\pi p(\theta) \sin \theta d\theta = 2 \quad (1)$$

The water orientations were defined by the angles between intramolecular vectors and a vector normal to the calcite surface.

OH vectors and dipole vectors were used as the intramolecular vectors. The probability distributions are shown in Fig. 6. The probability distributions are consistent with each other in the systems considered in this study (Fig. 6). The presence of ions and ion type did not influence the structures of water molecules at the calcite surface (Fig. 6). This is in line with recent surface X-ray diffraction measurements, where ions minimally change the interfacial structure at calcite (104) surfaces.³⁷ Thus, ion-specific hydration forces do not originate from changes in the hydration structures by ions.

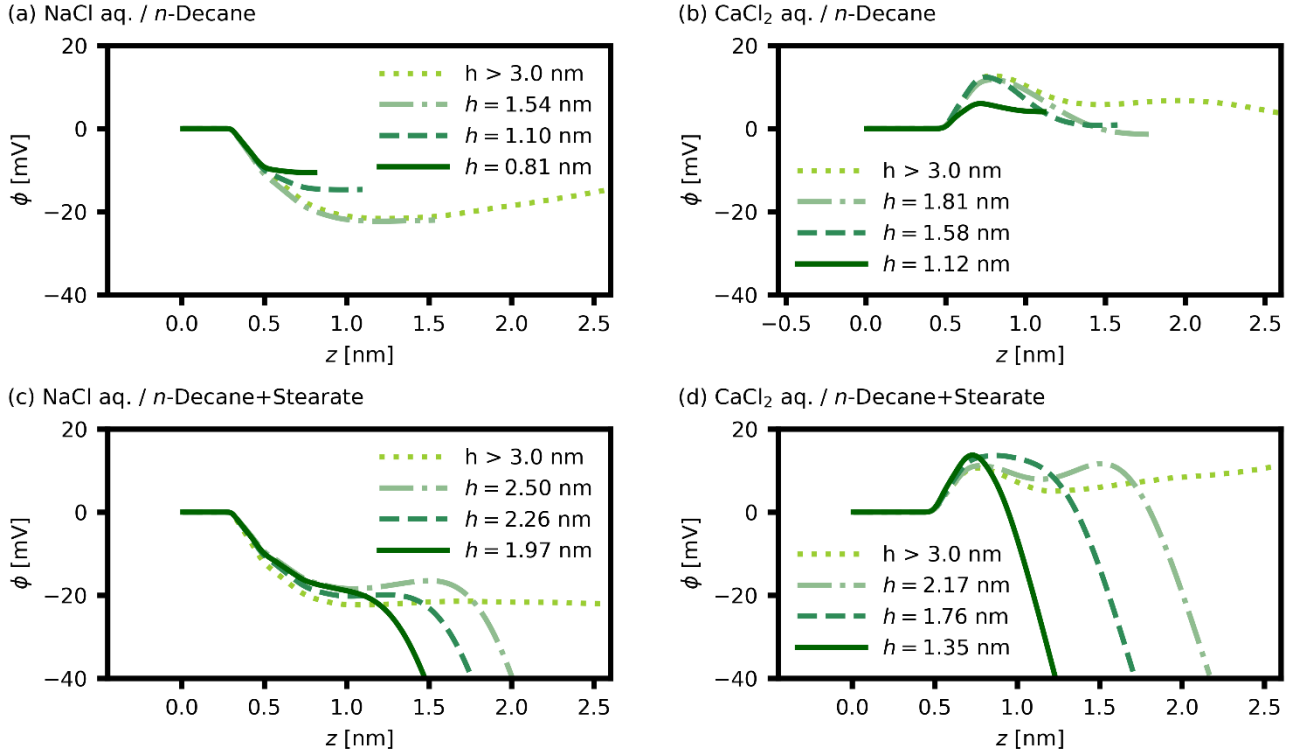


Figure 7. Electrostatic potentials calculated using Eq. (2) for different water-film thicknesses at 318 K. h represents the thickness of the water film and corresponds to the datapoints in the disjoining pressure curves (Fig. 2). $z = 0$ is the z -coordinate of the calcite surface.

We propose electrostatic interactions as a unrecognized mechanism interpreted previously as ion-specific hydration force. Figure 7 shows the electrostatic potentials ($\phi(z)$) calculated using the one-dimensional Poisson equation:

$$\frac{d^2}{dz^2} \phi(z) = -\frac{\rho_{\text{ions}}(z)}{\epsilon_0 \epsilon_r} \quad (2)$$

where ϵ_0 is the dielectric constant of vacuum and ϵ_r is the relative permittivity. We assumed $\epsilon_r = 71.5$ as the relative permittivity of water at 318 K.⁷⁸ ρ_{ions} is the charge density of ions. Only aqueous ions ($\text{Na}^+/\text{Ca}^{2+}$ and Cl^-) were considered in the term ρ_{ions} ; stearate, water, and atoms in calcite were excluded from ρ_{ions} . Considering the Debye length of less than 3 Å in our aqueous systems, the electrostatic potential calculated here differs from the electrostatic part of the DLVO force because it reflects the Stern layer structure, which represents atomic-scale characteristics. Importantly, the electrostatic potentials indicated ion-specific and oil-phase-specific behavior. The decrease in the electrostatic potential at the oil-water interface (Fig 7c, and d) indicates that the interface is negatively charged. The electrostatic potentials of the systems with NaCl aq. monotonically decreased from the calcite surface to the oil/water interface (Fig. 7a and c). The shape of the electrostatic potential curve for systems with CaCl_2 aq. was convex between the calcite surface and the oil/water interface (Fig. 7b and d). The disjoining pressures were determined from the shapes of the electrostatic potentials. A monotonically decreasing shape of electrostatic potential resulted in an adhesive force between the calcite surface and a negatively charged interface (i.e., interface between n -decane + stearate and water). The water film in the NaCl aq./ n -decane + stearate system became unstable owing to the adhesive force (due to the electrostatic potential) (Fig. 3a

and Fig. 7c). The oil/water interface that was negatively charged by stearates interacted with the calcite surface. In the previously mentioned AFM study with a gold-coated tip, the adhesion force increased upon addition of Na^+ .³⁰ The same mechanism may increase the adhesion force when considering that the gold-coated tip was negatively charged. The convex shape in the electrostatic potential curves indicated a repulsive force for both positively and negatively charged interfaces. The long-range repulsive force observed in the CaCl_2 aq./ n -decane + stearate originated from the repulsive nature of the electrostatic potential. The electrostatic potential curves for the calcite/water interface and the negatively charged oil/water interface originally had a convex shape. For a thick water films (Fig. 7d, $h = 2.19$ nm), the electrostatic potential showed two convex regions. The two convex-shaped potential curves influence each other to a greater extent as the water film thickness decreases (Fig. 7d, $h = 1.72$ nm). The repulsive force originated from the sharp convex feature at $h = 1.35$ nm. Perturbation is crucial for holding the convex shape of the electrostatic potential in CaCl_2 aq. systems. The convex shape was absent in the CaCl_2 aq./ n -decane system. As a result, no long-range force was observed. The perturbation of the electric double layer has a key role in maintaining the convex shape of the electrostatic potentials as the thickness of the water film decreases. The instability of the water film in the CaCl_2 aq./ n -decane system cannot be determined from the electrostatic potentials. Peng et al.⁴⁶ demonstrated that Ca in calcite provides attractive interactions with n -decane, which can yield the instability of the water film. However, further investigation is needed into the origins of the instability.

The shape of the electrostatic potential curve is determined by the Stern layer structure at the calcite surface. Adsorption of ions at the Stern layer is governed by dispersion forces between

ions and surfaces, ionic hydration, and ionic size and shape. The classical electric-double-layer model (e.g., Gouy–Chapman and Poisson–Boltzmann models) fails to predict electrostatic potentials because of ion-specific factors. Notably, only the valency of ions significantly influences the electrostatic potentials. Torrie and Valleau⁷⁹ demonstrated that divalent counterions result in non-monotonic shapes of the electrostatic potential curves in simply charged wall systems. Our results indicate that an ion-specific structure produces ion-specific electrostatic potentials. Na^+ can be directly adsorbed on the calcite surface. The direct adsorption results in the monotonically decreasing shape of electrostatic potential. The convex shape of the electrostatic potential curve originates from the non-direct adsorption of Ca^{2+} on the calcite surface (i.e., a Cl–first structure) (Fig. 5b and d). We predict that K^+ and Mg^{2+} would behave similarly to Na^+ and Ca^{2+} , respectively. Theoretical simulations demonstrated that K^+ can directly adsorb on calcite surfaces⁴³ and Mg^{2+} exhibits non-direct adsorption.⁴⁵ We expect similar electrostatic potentials and resulting surface forces for K^+ and Mg^{2+} as in our systems because of the similarity of the Stern layer structures. We conclude that the variation in electrostatic potentials and disjoining pressures are caused by the ion-specific Stern layer structure.

We introduce electrostatic potentials as a novel concept of attractive and repulsive forces. Our results are in line with the observation of adhesion force measurements on calcite surfaces. Na^+ increases the adhesion force while divalent cations decrease it.³⁰ Organic acids in crude oil are adsorbed on calcite surfaces altering wettability towards an oil-wet state. The disjoining pressure in the NaCl aq./n-decane + stearate system is nearly zero for water film thicknesses greater than its critical value (Fig. 2). This suggests that the rupture of the water film and stearate adsorption can occur without any driving force, such as capillary pressure. In other words, in this system, the calcite surface easily becomes oil-wet facilitating oil adhesion. Abdallah and Gmira³¹ demonstrated that the wettability of calcite surfaces aged with crude oil highly depends on the contacting brine composition. Wettability alteration to a water-wet state is facilitated by divalent cations, especially Mg^{2+} .^{26, 31} The concept of attractive and repulsive forces through electrostatic potential could serve as the hypothesis of ion-specific wettability on calcite surfaces.

We point out that electrostatic potential plays a role not limited to the oil-water-calcite system. The force curve measured by AFM for calcite system with CaCl_2 aq. (100 mM) indicates the onset of a repulsive background at separation distances from 1 nm to 2 nm.⁵² This agrees with the water film thickness of 1.5 nm, where repulsive force is observed between the negatively charged oil-water interface and the calcite surface. However, its significance varies from system to system, as disturbance of the interfacial structure highly depends on experimental setups. Javadi and Røyne⁵¹ reported adhesive forces between two freshly cleaved calcite surfaces at NaCl concentration of 100 mM. A different mechanism can be attributed to the adhesive nature because their experiments were conducted with symmetric systems, where adhesion arising from electrostatic potential cannot be expected. Notably, various ion-specific surface forces have a role on apparent total interfacial forces. AFM resolves ion-specific force curves that are stepwise, reflecting hydration characteristics.^{30, 49, 51–53} Diao et al.⁵² demonstrated that the water layer thickness excluded by the AFM tip varies with ion types ($\text{NaCl}/\text{CaCl}_2$) and concentrations. Our simulation showed that the structure of water is minimally influenced by presence of

ions, which agrees with surface X-ray diffraction.³⁷ Importantly, discrepancies can arise as signals from the AFM tip are influenced not only by the density distribution but also by the properties of hydration shell in addition to different experimental conditions. Molecular simulations of solid-water-solid systems in the future will be useful to decompose the ion-specific stepwise force and the electrostatic potential contribution and to link hydration characteristics with the force curve, as the softness of oil-water interface could hinder bumps in force from the hydration layer.

Conclusion

We investigated the stability of ion-specific water films on calcite (104) surfaces. The origin of ion-specific hydration forces at calcite surfaces cannot be explained solely by the energy required to remove water bound to solutes (i.e., ions) and the calcite surface. Ions do not significantly change the hydration structure near the surface. We propose an alternative mechanism based on electrostatic potential to explain long-range adhesive and repulsive forces (i.e., secondary hydration forces). This mechanism can explain experimental observations. The direct adsorption of Na^+ on calcite causes the shape of electrostatic potential to monotonically decrease. The Cl–first structure in the Stern layer in CaCl_2 systems results in a convex shape of the electrostatic potential curve. Importantly, the ion-specific Stern layer structure and interfacial perturbation affect the electrostatic potentials and resulting disjoining pressure. This study introduces the novel concept of attractive and repulsive force being generated by electrostatic potential related to ionic structuring, which is previously attributed to secondary hydration forces, in addition to the established mechanism involving water molecules.

ASSOCIATED CONTENT

Supporting Information. Pressure relaxations of the systems; snapshot of CaCl_2 aq. / n-decane + stearate system; disjoining pressure curves from two independent calculations; snapshots of an adsorbed cation at the calcite surface. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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ABBREVIATIONS

AFM, Atomic force microscopy; SFA, surface force apparatus; n-Dec, n-decane; Ste, stearate.

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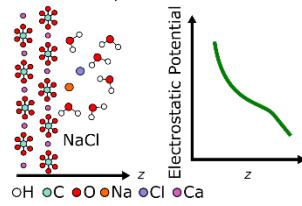
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