

FOCUS REVIEW

Importance of water in the control of calcite crystal growth by organic molecules

Hiroki Nada

This review focuses on the effect of water on the binding conformation of an organic molecule at a hydrated calcite crystal surface. A recent molecular dynamics simulation suggested that water strongly affects the binding conformation of aspartic acid (Asp) at the crystal surface. The simulation also suggested that the binding conformation of the acid was different at various parts of the calcite surface, because of a difference in the structure of the water. This explains the change in the step morphology on [104] planes of calcite crystals caused by adding Asp in real systems. Similarly, recent simulations of other species of organic molecule have suggested that water affects the binding conformation of the molecule at the calcite surface. In this review, we discuss how water is crucial in the growth control of calcite crystals by organic molecules, which provides useful insights for the development of organic/inorganic hybrid materials.

Polymer Journal (2015) 47, 84–88; doi:10.1038/pj.2014.87; published online 22 October 2014

INTRODUCTION

The growth control of calcite crystals by organic molecules has attracted much attention in areas such as biomineralization,^{1,2} inhibition of scale formation in water³ and the development of new functional materials.^{4–6} The mechanism of calcite growth in the presence of organic molecules is therefore important in mineralogy, biology, environmental technology, crystal growth and materials chemistry. However, the mechanism is difficult to study experimentally and is still poorly understood.

Computer simulations, such as molecular dynamics (MD), are helpful tools for investigating the mechanism of calcite growth at the molecular level. Many simulations have been carried out to elucidate the binding conformations of various organic molecules at the surface of a calcite crystal,^{7–20} although most did not focus on the effect of water on the binding. Organic molecules strongly interact with both the calcite surface and the surrounding water, and, consequently, elucidating the effect of water on the binding conformation of molecules at various parts of the calcite surface is important to understand the mechanism of calcite growth in the presence of organic molecules.

Recently, an MD simulation was conducted to investigate the effect of water on the binding conformation of aspartic acid (Asp) at flat regions, step edges and kinks in the calcite surface.²¹ This simulation (hereafter, Asp-binding simulation) strongly suggested that water affects the binding conformation at each of these parts of the surface. MD simulations for other species of organic molecules by other research groups^{11,13,17–20} have also suggested such an effect. Thus, for many species of organic molecules, water may play an important role in the growth control of calcite crystals by organic molecules.

To highlight how water affects the growth control of calcite crystals by organic molecules, this review looks at the difference in the binding conformation of Asp for different parts of the hydrated calcite surface and its relationship to the growth control of calcite crystals in real systems.²¹ Studies of Asp interacting with the calcite surface contribute to clarifying the mechanism of calcite growth control during biomineralization.^{22,23} In real systems, Asp induces a step roughening at $[11\bar{4}]$ acute step edges on calcite {104} planes.²² It has been proposed that this effect originates from the selective binding of Asp to the acute step edges.²² The Asp-binding simulation supported this explanation and suggested that the selective binding arose from the structure of the surrounding water. We conclude by discussing the importance of water for the growth control of calcite crystals by organic molecules and the direction of future studies.

MD SIMULATION OF ASPARTIC ACID ON A HYDRATED CALCITE SURFACE

Simulation method

Calcite crystals have a rhombohedral morphology with six {104} planes. Thus, the simulation was performed for a system consisting of two flat {104} planes (the {104} system), a system consisting of two {104} planes with $[11\bar{4}]$ acute and obtuse steps, each of which had a molecularly smooth edge (the step system), and a system consisting of two {104} planes with $[11\bar{4}]$ acute and obtuse steps, each of which had two kinks at the edge (the kink system). The kink system contained two different types of kinks: one with a Ca^{2+} ion at the corner (Ca^{2+} kink) and the other with a CO_3^{2-} ion at the corner (CO_3^{2-} kink). For comparison, the simulation was also performed for a system consisting of two {110} planes (the {110} system).

Each system was a rectangular parallelepiped with a CaCO_3 calcite crystal sandwiched between two water phases (Figure 1). Each water phase contained an L-Asp monomer. Periodic boundary conditions were imposed in the x , y and z directions. To avoid the migration of Asp between two calcite surfaces via the periodic boundary, the system was elongated in the z direction by adding a vapor phase to each of the water phases. Illustrations of Asp, the Ca^{2+} and CO_3^{2-} ions, the {104} and {110} planes, the $[11\bar{4}]$ acute and obtuse steps, and the kinks at the step edges are shown in Figure 1.

The CaCO_3 potential model proposed by Raiteri *et al.*²⁴ was used to estimate the interactions within calcite. In this model, the interaction between a pair of ions is represented as the sum of the Coulomb potentials plus the sum of the Buckingham potentials. The CO_3^{2-} ion is treated as a rigid body and is thus a simplification of the actual CO_3^{2-} ion in this model. Nevertheless, the model adequately reproduces the structure and thermodynamic stability of real calcite crystals²⁴ and the structure of amorphous CaCO_3 .²⁵

The CHARMM22 force field was used to determine the potential parameters for Asp.²⁶ Asp was dissolved in liquid water and was assumed to be ionized with a charge of $-e$. The TIP3P model was used to estimate the interaction between pairs of H_2O molecules.²⁷ The H_2O – CaCO_3 interaction was estimated from the Coulomb potential between charged points: the Buckingham potential between an O atom of the CO_3^{2-} ion (O_c atom) and each of the O (O_w) and H atoms (H_w) in H_2O , and the Lennard-Jones (LJ) potential between the Ca^{2+} ion and O_w atom. The parameter values for the Buckingham and LJ potentials were the same as those calculated by Raiteri *et al.*²⁴ The Asp– CaCO_3 interaction was estimated with the Coulomb potential between charged points and the LJ potential between each Asp atom and each Ca^{2+} ion and O_c atom. The Buckingham and LJ potential parameter values for the Ca^{2+} ion, CO_3^{2-} ion, and H_2O molecule in this simulation are given in Nada.²¹

Calculations were carried out using a leapfrog algorithm with a time step of 1 fs. The total run was 6 ns for each simulation. The temperature was maintained at 298 K by a Berendsen thermostat with a coupling parameter of 0.1 ps.²⁸ During the simulation, the O–H and N–H distances in Asp were kept constant at their equilibrium values by means of the SHAKE algorithm.²⁹ The MD simulation was performed with the DL_POLY_2.2 MD simulation package.³⁰ The Ewald summation method was used to estimate the long-range

Coulomb potentials. Details of the simulation method are described in Nada.²¹

STRUCTURE OF WATER ON THE CALCITE SURFACE

The purpose of the Asp-binding simulation was the qualitative elucidation of the effect of water on the binding conformation of Asp at different parts of the calcite surface. Therefore, the structure of water on the calcite surface was investigated by means of an MD simulation for each of the systems without Asp.

As in earlier simulation studies,^{7,13,22,31} the Asp-binding simulation showed the formation of a layered water structure on the {104} plane (Figure 2a). As the structure of the {104} plane was energetically stable, all the Ca^{2+} and CO_3^{2-} ions at the outermost layer of the plane were stably arranged into the ideal lattice sites of calcite (Figure 2b). However, a layered water structure was not formed on the {110} plane (Figure 2a). This was because the structure of the {110} plane was not energetically stable and, therefore, the ideal crystal arrangement of Ca^{2+} and CO_3^{2-} ions was disrupted at the outermost layer of the plane (Figure 2b). The formation of a layered water structure on the {104} plane suggests that the water had a highly ordered structure compared with that of the bulk water.

Notably, a recent X-ray experimental study by Fenter and Sturchio³² suggested that the positions of Ca^{2+} and CO_3^{2-} at the outermost layer of a calcite {104} plane are slightly deviated from the ideal lattice sites. Nevertheless, the experimental study indicated a similar ordered water structure on the {104} plane as in MD simulations.^{31,32} Therefore, it is speculated that slight deviation of the positions of Ca^{2+} and CO_3^{2-} ions from the ideal lattice sites does not significantly influence the ordered water structure. More detailed experimental and simulation studies are needed to confirm this speculation.³¹

The Asp-binding simulation also showed a difference in the structure of water near the step edge between the acute and obtuse steps: the water near the obtuse step edge had an ordered structure, whereas that near the acute step edge did not (Figure 2c). The same differences were also detected in the kink system. Thus, the structure of water was different at different parts of the calcite surface.

BINDING CONFORMATION OF ASP ON THE CALCITE SURFACE

The Asp-binding simulation aimed to qualitatively elucidate the binding conformation adopted by Asp near the hydrated calcite surface, irrespective of the initial position of the molecule. Therefore, many trajectories were created for Asp, and each of the trajectories started with different initial positions and orientations. Recently, Raiteri *et al.*²⁰ also performed an MD simulation of Asp on a hydrated calcite {104} plane and analyzed the free energy of Asp binding near the plane. However, the present study is the first to elucidate the conformation of Asp at different parts of the hydrate calcite surface in detail.

Typical binding conformations that stably appeared during the simulation are summarized in Figure 3. For the {104} system, two types of binding conformation were observed: a direct binding conformation, in which the carboxyl O atoms of Asp were bound directly to the {104} plane, and an indirect binding conformation, in which Asp occupied positions separated from the plane by a layer of H_2O molecules. In the Asp-binding simulation, the occurrence ratio was much higher for the indirect binding conformation (0.875) than for the direct binding conformation (0.125).

For the {110} system, Asp preferentially adopted a direct binding conformation. For the step system, Asp preferentially adopted a direct binding conformation at the acute step edge but did not bind to the

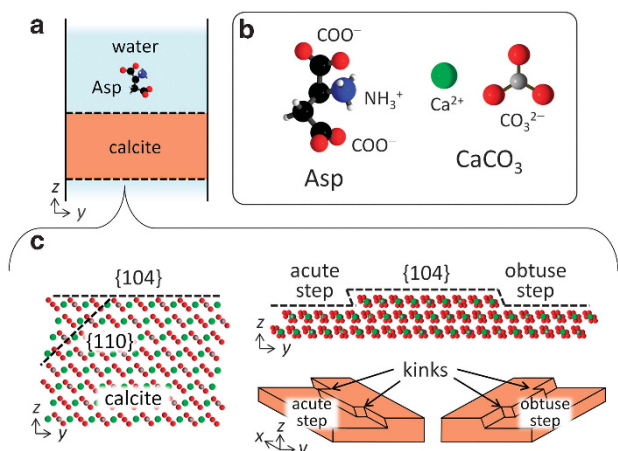


Figure 1 (a) Schematic of part of the simulation system, (b) structures of Asp and Ca^{2+} and CO_3^{2-} ions, and (c) schematic of a calcite crystal showing the positions of the {104} and {110} planes, the acute and obtuse steps, and the kinks.

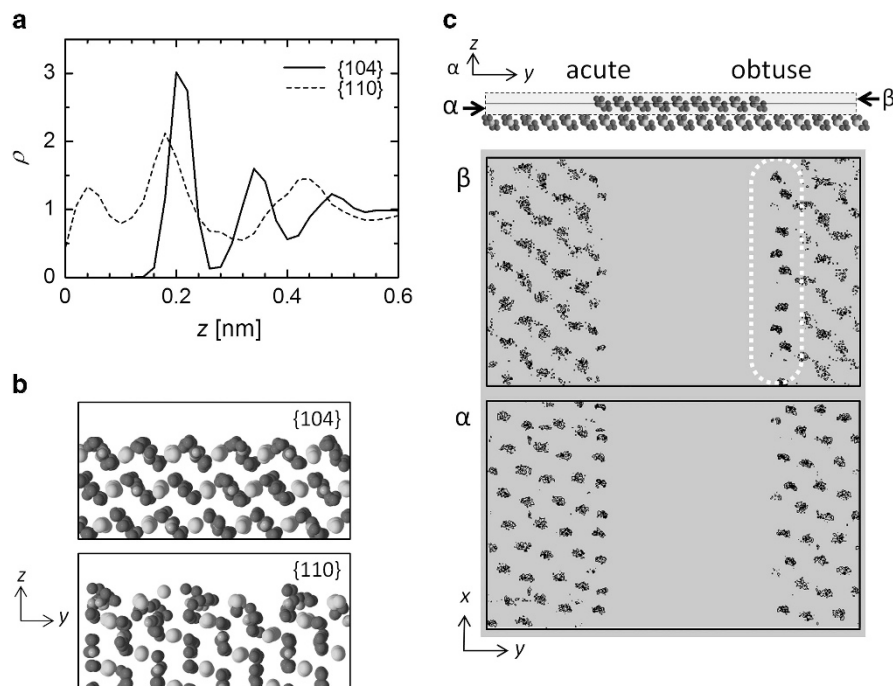


Figure 2 (a) Number density profiles of O_w atoms, ρ , along the z direction for the {104} and {110} systems without Asp. The origin of the z component was the outermost layer of Ca^{2+} ions in the calcite crystal. (b) The structures of the {104} and {110} planes obtained by MD simulation of the {104} and {110} systems without Asp. (c) Existence probabilities of H_2O molecules in two thin layers (α and β) on the {104} plane for the step system. The thickness of each layer in the z direction was ~ 0.13 nm. H_2O molecules in layer β were widely distributed near the acute step edge, whereas they were ordered near the obtuse step edge (region enclosed by the dashed oval). A full color version of this figure is available at *Polymer Journal* online.

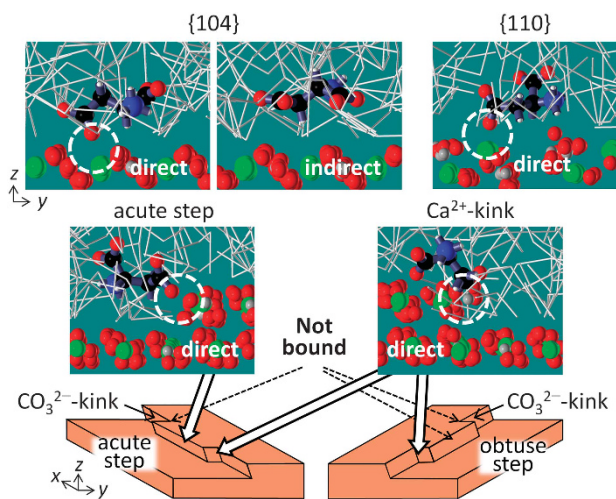


Figure 3 Snapshots of typical binding conformations of Asp at the calcite surface, which were obtained by the simulation. Direct and indirect binding conformations at the {104} plane, direct binding conformation at the {110} plane, direct binding conformation at the acute step edge, and direct binding conformation at the Ca^{2+} kink. Gray cylinders represent hydrogen bonds between the H_2O molecules.

obtuse step edge. For the kink system, Asp also adopted a direct binding conformation at the acute step edge as well as at the Ca^{2+} kink of both the acute and obtuse steps.

Whether Asp adopts a direct binding conformation at the calcite surface depends on the structure of water. Let us consider a change in the free energy of the system arising from the binding of Asp to the hydrated calcite surface (Figure 4). The direct binding of Asp to the calcite surface decreases the free energy of the system because it lowers

the Asp– $CaCO_3$ potential energy. However, for the {104} system, the direct binding to the {104} plane disrupted the ordered water structure, causing an increase in the free energy of the system. Actually, the free energy of the ordered water structure on the {104} plane was lower than that of the bulk water. Thus, for the {104} system, the indirect binding conformation was as stable as or more stable than the direct binding conformation. This explanation for the thermodynamic stability of the binding conformation is roughly consistent with the free energy calculation by Raiteri *et al.*²⁰ For the {110} system, the direct binding to the {110} plane did not increase the free energy of the system because an ordered water structure was not formed on the plane. Thus, the direct binding conformation was stable for the {110} system.

The difference in the binding conformation near the step edge between the acute and obtuse steps also arose from the difference in the structure of water near the step edge. The binding of Asp to the obtuse step edge was not favorable, because the disruption of an ordered water structure near the obtuse step edge due to the direct binding would increase the free energy of the system. However, the water near the acute step edge did not have an ordered structure, so the direct binding to the acute step edge did not increase the free energy of the system, which explains why Asp adopted a direct binding conformation at the acute step edge only. It is expected that water similarly affected the binding conformation near the kink.

Notably, the formation of an ordered water structure on the calcite surface gave rise to an activation energy for transitions between the Asp-binding conformations near the surface. Water was therefore crucial for both the thermodynamic stability of the binding conformation and the dynamics of Asp near the calcite surface. If the temperature was much higher than 298 K, different binding conformations might be stable due to the effect of entropy. An MD

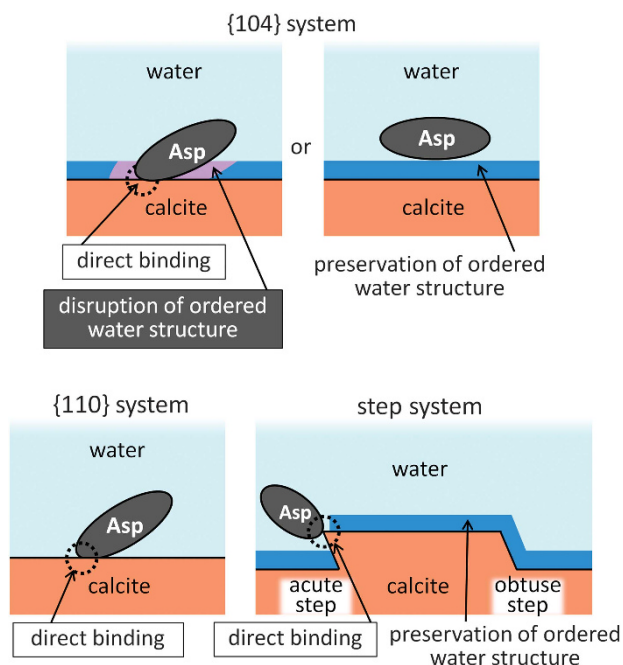


Figure 4 Schematic illustration of the relationship between the thermodynamic stability of the binding conformation and the structure of water at the calcite surface for each system. Blue regions represent an ordered water structure formed on the calcite surface. 'Direct binding' indicates a decrease in the free energy of the system; 'disruption of ordered water structure' indicates an increase in the free energy of the system.

simulation study for a wide range of temperature is needed to elucidate it.

DISCUSSION

It has been proposed that the step roughening at the acute step edge, which has been observed experimentally in the presence of Asp, originated from the selective binding of Asp to the acute step edge.²² The Asp-binding simulation result that the direct binding conformation occurred only at the acute step edge supports this speculation.²¹ Elhadj *et al.*²² attributed the selective binding of Asp to the acute step edge to a difference in the binding energy between the acute and obtuse steps. The Asp-binding simulation also detected a difference in the Asp–CaCO₃ potential energy between the acute and obtuse steps, but the difference was too small to explain this preferential binding. The simulation also suggested that the difference in the binding conformation of Asp near the step edge between the acute and obtuse steps, which is expected to cause a change in the step morphology in real systems,²² originated from the difference in the structure of water. Consequently, in the case of Asp at least, water has an important role in the growth control of calcite crystals.

In the Asp-binding simulation, an Asp monomer only was examined. However, Elhadj *et al.*²² investigated a change in the morphology of the step on {104} planes for Asp_n ($n = 1-6$). They found that for $n \leq 2$ the step roughening occurs at the acute step edge, whereas for $n > 2$ it occurs at the obtuse step edge. It would be particularly interesting then to perform an MD simulation study for the binding of Asp_n ($n > 1$) to the hydrated calcite surface in the future. The results would improve our understanding of the mechanism of change in step morphology caused by the addition of Asp.

Shen *et al.*¹⁷ reported that the binding of polystyrenesulfonate to the calcite {104} plane was much weaker than that to the calcite {100}

plane, and suggested that this was because the binding conformation at the {104} plane was strongly affected by water.¹⁷ Freeman *et al.*¹⁶ found that the binding conformation of ovocleidin-17 protein, a much larger organic molecule than Asp and polystyrenesulfonate, was affected by the structure of the surrounding water at the step edge of the calcite surface. Similar to Asp, water may play an important role in the growth of a calcite crystal in the presence of these organic molecules. Therefore, further extensive studies are required to determine the effect of water on binding conformation and its relationship with the growth of a calcite crystal for various species of organic molecules.

Aschauer *et al.*¹¹ performed an MD simulation of polyaspartic acid (p-Asp) and polyacrylic acid (PAA) on a hydrated calcite {104} plane. They also suggested that for both p-Asp and PAA the binding conformation was affected by water. Interestingly, the binding energy was negative for p-Asp but positive for PAA. They suggested that p-Asp bound to the surface because it produced an enthalpy gain, whereas PAA bound because it produced an entropy gain. As in the case of PAA, entropy may play an important role in stabilizing the binding conformation for other species of organic molecules. Precise calculations of the free energy of the binding conformation of an organic molecule at a hydrated calcite surface should also be performed. For the future studies suggested above, computer simulations such as MD simulations will be useful tools. It should be noted that choosing appropriate potential models is particularly important for simulating calcite, water and organic molecules together.³³

CONCLUSIONS

In this review, the effect of water on the growth control of a calcite crystal by organic molecules was discussed. The Asp-binding simulation suggested that water changes the step morphology on the (104) plane when Asp is present.²¹ Earlier simulations for polystyrenesulfonate,¹⁷ ovocleidin-17 protein,¹⁶ p-Asp¹¹ and PAA¹¹ also suggested that water affects the binding conformation for these molecules at the calcite surface. As in the case of Asp, water may affect the morphology of the calcite crystal in the presence of those molecules.

In conclusion, water may be an important factor in the growth control of calcite crystals by organic molecules. However, extensive studies of various organic molecules are needed to confirm this. It is interesting to note that the growth control of calcite crystals by organic molecules is analogous to the growth control of ice crystals by antifreeze proteins; the proteins control the growth of the crystal by binding to a specific plane and the surrounding water has an important role in stabilizing the binding conformation at the plane.³⁴⁻³⁷

The growth control of inorganic crystals by organic molecules is important for the development of hybrid materials.⁴⁻⁶ The simplest way to achieve effective growth control is through using suitable functional organic molecules. This paper suggests an alternative method: through improving the ability of organic molecules to affect the growth control by modifying the structural properties of solvent, which can be done with temperature, pressure and impurities. This may aid the design of an organic molecule for the development of hybrid materials.³⁸

ACKNOWLEDGEMENTS

This work was supported by a Grant-in-Aid for Scientific Research (no. 22107004) on Innovation Areas of 'Fusion Materials' (area no. 2206) from the Ministry of Education, Culture, Sports, Science and Technology (MEXT).

Some of the computations in this work were done using the facilities of the Supercomputer Center, Institute of Solid State Physics, The University of Tokyo.

- Mann, S. *Biom mineralization, Principles and Concepts in Biological Materials Chemistry*, Oxford University Press: Oxford (2000).
- Meldrum, F. C. & Colfen, H. Controlling mineral morphologies and structures in biological and synthetic systems. *Chem. Rev.* **108**, 4332–4432 (2008).
- Drela, I., Falewicz, P. & Kuczowska, S. New rapid test for evaluation of scale inhibitors. *Water Res.* **32**, 3188–3191 (1998).
- Sommerdijk, N. A. J. M. & de With, G. Biomimetic CaCO₃ mineralization using designer molecules and interfaces. *Chem. Rev.* **108**, 4499–4550 (2008).
- Kato, T., Sakamoto, T. & Nishimura, T. Macromolecular templating for the formation of inorganic-organic hybrid structures. *MRS Bulletin* **35**, 127–132 (2010).
- Zhu, F., Nishimura, T., Sakamoto, T., Tomono, H., Nada, H., Okumura, Y., Kikuchi, H. & Kato, T. Tuning the stability of CaCO₃ crystals with magnesium ions for formation of aragonite thin films on organic polymer templates. *Chem. Asian J.* **8**, 3002–3009 (2013).
- Cooke, D. J., Gray, R. J., Sand, K. K., Stipp, S. L. S. & Elliott, J. A. Interaction of ethanol and water with the {10 $\bar{1}$ 4} surface of calcite. *Langmuir* **26**, 14520–14529 (2010).
- Freeman, C. L., Asteriadis, I., Yang, M. & Harding, J. H. Interactions of organic molecules with calcite and magnesite surfaces. *J. Phys. Chem. C* **113**, 3666–3673 (2009).
- Freeman, C. L. & Harding, J. H. Entropy of molecular binding at solvated mineral surfaces. *J. Phys. Chem. C* **118**, 1506–1514 (2014).
- Yang, M., Stipp, S. L. S. & Harding, J. H. Molecular ordering of ethanol at the calcite surface. *Cryst. Growth Des.* **8**, 4066–4071 (2008).
- Aschauer, U., Spagnoli, D., Bowen, P. & Parker, S. C. Growth modification of seeded carboxylic acids: atomistic simulations. *J. Colloid Int. Sci.* **346**, 226–231 (2010).
- Duffy, D. M. & Harding, J. H. Simulation of organic monolayers as templates for the nucleation of calcite crystals. *Langmuir* **20**, 7630–7636 (2004).
- Zhu, B., Xu, X. & Tang, R. Hydration layer structure on calcite facets and their roles in selective adsorptions of biomolecules: a molecular dynamics study. *J. Chem. Phys.* **130**, 234705 (2013).
- Yang, M., Rodger, P. M., Harding, J. H. & Stipp, S. L. S. Molecular dynamics simulations of peptides on calcite surface. *Mol. Simul.* **35**, 547–553 (2009).
- Freeman, C. L., Harding, J. H., Quigley, D. & Rodger, P. M. Simulations of ovocleidin-17 binding to calcite surfaces and its implications for eggshell formation. *J. Phys. Chem. C* **115**, 8175–8183 (2011).
- Freeman, C. L., Harding, J. H., Quigley, D. & Rodger, P. M. Protein binding on stepped calcite surfaces: simulations of ovocleidin-17 on calcite {31.6} and {31.8}. *Phys. Chem. Chem. Phys.* **14**, 7287–7295 (2012).
- Shen, J.-W., Li, C., van der Velt, N. F. A. & Peter, C. Understanding the control of mineralization by polyelectrolyte additives: simulation of preferential binding to calcite surfaces. *J. Phys. Chem. C* **117**, 6904–6913 (2013).
- Freeman, C. L., Harding, J. H., Quigley, D. & Rodger, P. M. Structural control of crystal nuclei by an eggshell protein. *Angew. Chem. Int. Ed.* **49**, 5135–5137 (2010).
- de Leeuw, N. H. & Cooper, T. G. A Computer modeling study of the inhibiting effect of organic adsorbates on calcite crystal growth. *Cryst. Growth Des.* **4**, 123–133 (2004).
- Raiteri, P., Demichelis, R., Gale, J. D., Kellermeier, M., Gebauer, D., Quigley, D., Wright, L. B. & Walsh, T. R. Exploring the influence of organic species on pre- and post-nucleation calcium carbonate. *Faraday Discuss.* **159**, 61–85 (2012).
- Nada, H. Deference in the conformation and dynamics of aspartic acid on the flat regions, step edges, and kinks of a calcite surface: a molecular dynamics study. *J. Phys. Chem. C* **118**, 14335–14345 (2014).
- Elhadj, S., Salter, E. A., Wierzbicki, A., De Yoreo, J. J., Han, N. & Dove, P. M. Peptide controls on calcite mineralization: polyaspartate chain length affects growth kinetics and acts as a stereochemical switch on morphology. *Cryst. Growth Des.* **6**, 197–201 (2006).
- Gotliv, B. A., Kessler, N., Sumerel, J. L., Morse, D. E., Tuross, N., Addadi, L. & Weiner, S. Sprich: a novel aspartic acid-rich protein family from the prismatic shell matrix of the bivalve *Atrina rigida*. *ChembioChem* **6**, 304–314 (2005).
- Raiteri, P., Gale, J. D., Quigley, D. & Rodger, P. M. Deviation of an accurate force-field for simulating the growth of calcium carbonate from aqueous solution: A new model for the calcite-water interface. *J. Phys. Chem. C* **114**, 5997–6010 (2010).
- Tomono, H., Nada, H., Zhu, F., Sakamoto, T., Nishimura, T. & Kato, T. Effects of magnesium ions and water molecules on the structure of amorphous calcium carbonate: A molecular dynamics study. *J. Phys. Chem. B* **117**, 14849–14856 (2013).
- MacKerel, A. D. Jr, Bashford, D., Bellott, M., Dunbrack, R. L. Jr., Evanseck, J. D., Field, M. J., Fisher, S., Gao, J., Guo, H., Ha, S., Joseph-McCarthy, D., Kuchnir, L., Kuczera, K., Lau, F. T. K., Mattos, C., Michnick, S., Ngo, T., Nguyen, D. T., Prodhom, B., Reiger, W. E. III, Roux, B., Schlenkerich, M., Smith, J. C., Stote, R., Straub, J., Watanabe, M., Wiórkiewicz-Kuczera, J., Yin, D. & Karplus, M. All-atom empirical potential for molecular modeling and dynamics studies of proteins. *J. Phys. Chem. B* **102**, 3586–3616 (1998).
- Jorgensen, W. L., Chandrasekhar, J., Madura, J. D., Impey, R. W. & Klein, M. L. Comparison of simple potential functions for simulating liquid water. *J. Chem. Phys.* **79**, 926–935 (1983).
- Berendsen, H. J. C., Postma, J. P. M., van Gunsteren, W. F., DiNola, A. & Haak, J. R. Molecular dynamics with coupling to an external bath. *J. Chem. Phys.* **81**, 3684–3690 (1984).
- Ryckaert, J. P., Ciccotti, G. & Berendsen, H. J. C. Numerical integration of the Cartesian equations of motion of a system with constraints: Molecular dynamics of n-alkanes. *J. Comput. Chem.* **23**, 327–341 (1977).
- Smith, W. & Forester, T. R. DL_POLY 2.0: a general-purpose parallel molecular dynamics simulation package. *J. Mol. Graph.* **14**, 136–141 (1996).
- Fenter, P., Kerisit, S., Raiteri, P. & Gale, J. D. Is the calcite-water interface understood? Direct comparisons of molecular dynamics simulations with specular X-ray reflectivity data. *J. Phys. Chem. C* **117**, 5028–5042 (2013).
- Fenter, P. & Sturchio, N. C. Calcite (104)-water interface structure, revisited. *Geochim Cosmochim. Acta* **97**, 58–69 (2012).
- Raiteri, P., Demichelis, R. & Gale, J. D. Development of accurate force fields for the simulation of biomineralization. *Methods Enzymol.* **532**, 3–23 (2013).
- Jorov, A., Zhorov, B. S. & Yang, D. S. C. Theoretical study of interaction of winter flounder antifreeze protein with ice. *Protein Sci.* **13**, 1524–1537 (2004).
- Nada, H. & Furukawa, Y. Growth inhibition mechanism of an ice-water interface by a mutant of winter flounder antifreeze protein: a molecular dynamics study. *J. Phys. Chem. B* **112**, 7111–7119 (2008).
- Nada, H. & Furukawa, Y. Growth inhibition at the ice prismatic plane induced by a spruce budworm antifreeze protein: a molecular dynamics simulation study. *Phys. Chem. Chem. Phys.* **13**, 19936–19942 (2011).
- Nada, H. & Furukawa, Y. Antifreeze proteins: computer simulation studies on the mechanism of ice growth inhibition. *Polym. J.* **44**, 690–698 (2012).
- Sugawara-Narutaki, A. Bio-inspired synthesis of polymer-inorganic nanocomposite materials in mild aqueous systems. *Polym. J.* **45**, 269–276 (2013).