

Effect of Bicarbonate Ions on the Crystallization of Calcite on Self-Assembled Monolayers

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We use molecular dynamics simulations to investigate the nucleation of calcite crystals on self-assembled monolayers. We show how the presence of bicarbonate ions adsorbed on the monolayer surface can both aid nucleation and control the orientation of the growth of the crystal. Using a simple model of the nucleation process and calculated interfacial energies, we calculate the enhancement (with respect to the homogeneous nucleation rate) of the nucleation of calcite on the (01 $\bar{1}2$) and (0001) faces. The calculations show clearly that the (01 $\bar{1}2$) face is favored over the (0001) face and that the nucleation rate is enhanced for self-assembled monolayers made from molecules containing an even number of carbon atoms in the alkyl chain over those containing an odd number.

Introduction

Self-assembled monolayers (SAMs) of alkanethiols, with functionalized headgroups, have been widely used as substrates for the crystallization of minerals. Such experiments attempt to reproduce the remarkable control over crystal orientation exhibited by organisms in biomineralization. While complete control of crystal orientation has not been achieved in the laboratory, limited control is feasible. One notable result is the behavior of calcium carbonate growing on self-assembled monolayers (SAMs) of alkanethiols terminated by carboxylic acid groups, themselves on a gold substrate. Here, calcium carbonate exhibits a strong tendency to nucleate as calcite, growing on the (01 $\bar{1}2$) plane. Moreover, this effect depends on the length of the alkyl chain. Chains with an even number of carbon atoms produce (01 $\bar{1}2$)-oriented growth; chains with an odd number of carbon atoms produce either no oriented growth or growth on a different crystal face.¹

The prevalence of the (01 $\bar{1}2$) calcite orientation on SAMs has been attributed to templating and matching of the headgroup orientation with the carbonate angle orientation. This explanation is not without problems. The (01 $\bar{1}2$) surface of calcite is commensurate with the SAM in one direction only, and there is a significant lattice mismatch in the perpendicular direction. The (0001) orientation, however, is completely commensurate with the SAM, and thus we might expect the SAM to nucleate calcite with this orientation. Although both (0001) and (01 $\bar{1}2$) are polar surfaces in calcite (and therefore can only be present if the interfacial structure can cancel the macroscopic bulk dipole²), the (01 $\bar{1}2$) interface with the SAM must also accommodate the lattice mismatch. We have previously shown² that both conditions can be satisfied by the introduction of line defects at the calcite/SAM interface. These defects can accommodate the lattice mismatch, but their formation energy is rather high, such that the energy of the (01 $\bar{1}2$) calcite/SAM interface is higher than that of the (0001) calcite/SAM interface. We would, therefore,

expect nucleation in the (0001) orientation. In this paper, we present an alternative model for the (01 $\bar{1}2$) calcite/SAM interface in which the mismatch is accommodated using bicarbonate ions. Since the experimental solutions are supersaturated with these ions, it is reasonable to expect them to play a role in the nucleation and growth of a carbonate mineral. In the model we shall discuss, the bicarbonate ions are incorporated into the plane of the SAM along lines parallel to the commensurate direction. The ions compress the monolayer molecules, resulting in both a good lattice match and zero net dipole moment.

In this paper, we investigate both the odd–even effect and the preferential nucleation of the (01 $\bar{1}2$) orientation over the (0001) orientation. We model thin films of calcite in the (01 $\bar{1}2$) and (0001) orientations on both 16-mercaptohexadecanoic acid (MHA) and 15-mercaptopentadecanoic (MPA) monolayers, with both carbonate and bicarbonate terminations. We calculate angular order parameters for the thin film for the four interfaces considered. With the help of a simple model of heterogeneous nucleation theory and calculations of the relevant interfacial energies, we show the influence of interfacial energy on the nucleation barrier. The results demonstrate that bicarbonate ions play a very significant role in determining the orientation of calcite growth on SAMs.

Methods and Procedures

We model interfaces between the flat polar calcite surfaces, (0001) and (01 $\bar{1}2$), and the $\sqrt{3} \times \sqrt{3}$ R30° configuration of MHA and MPA on gold, to study both the odd–even effect and the prevalence of (01 $\bar{1}2$) calcite growth on SAMs. The (0001)/SAM interface is coherent because the calcite surface structure closely matches the hexagonal SAM structure, but the (01 $\bar{1}2$)/SAM interface is coherent in one direction only. The surface unit cell of the (01 $\bar{1}2$) face of calcite is 4.97 Å \times 6.63 Å, and that of the monolayer is 4.97 Å \times 8.61 Å.

In order for crystal growth to occur in a polar crystal direction, it is necessary to cancel the macroscopic dipole moment induced by crystal planes of alternating charge. This is normally achieved in simulations by terminating the crystal with a layer with a charge density half that of the crystal planes. In the case of the (0001) surface, the dipole is canceled by the fully ionized mono-

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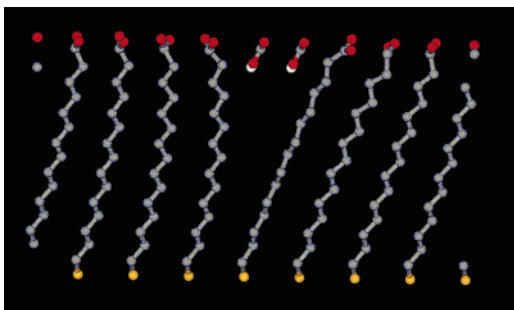


Figure 1. MHA SAM with bicarbonate ions. The resulting charge density is half that of the (01 $\bar{1}2$) calcite crystal planes. The C atoms are colored gray, O atoms red, H atoms white, and S atoms yellow.

layer because each headgroup has a charge of $-1e$ and each Ca ion of the surface has a charge of $+2e$, where e is the electronic charge. The upper face of the crystal is terminated by a half-layer of CO_3^{2-} ions or a full layer of HCO_3^- ions. This is not intended to be a realistic model of the configuration of the outermost layer. From the experiments, that clearly consists of a series of (10 $\bar{1}4$) facets, which presumably neutralize the dipole by absorption of charged ions. For computational purposes, we require a configuration that neutralizes the dipole. Since we are interested in the interfacial energy between the monolayer and the crystal and not the interface between the outer crystal layer and the water, the details of the latter are not important, provided the gross electrostatics are correct. The incommensurate (01 $\bar{1}2$)/SAM interface is more complicated. Previously, we introduced surface defects to reduce the crystal surface charge density to match that of the monolayer. Here, we take an alternative approach and increase the monolayer charge by inserting bicarbonate ions between the headgroups of the monolayer. The side view of one such monolayer is shown in Figure 1.

The simulations were carried out using the general-purpose molecular dynamics program DL_POLY.³ A time step of 1 fs and a NVT ensemble with a Nosé–Hoover thermostat, with a thermostat relaxation time of 100 fs, were used. The DL_POLY code imposes periodic boundary conditions in all three dimensions. We follow the usual practice for simulating surfaces or interfaces whereby each simulation cell consists of a slab (chosen to be thick enough that the effects of any extra interfaces created are negligible), followed by a vacuum layer wide enough to ensure minimal interaction between the slab and its periodic images in the direction of the interface normal. Such a configuration can completely relax in the direction of the interface normal. The repeat distances in the lateral directions are chosen to minimize the in-plane stresses. Further details of the construction of the slab are given below. The Coulomb interactions are calculated using the Ewald summation method. The interatomic potentials used for calcite were derived by Pavese et al.,⁴ and the parameters of Moller et al.⁵ were used for the SAM with the CHARMM22 parameters⁶ for the headgroups. The TIP3P potential⁷ was used for water.

These were chosen as robust potential models that have been used with success in a large number of simulations. Both their advantages and their shortcomings are thus well-known. The interaction potentials between the SAM and calcite and water and calcite were derived using the methods of Schroder et al.⁸ and validated by comparison with *ab initio* methods, as described in our earlier publication.⁹ The sensitivity of the simulation to the model is discussed there in some detail. The essential point is that it is not sufficient to construct an interface potential using the standard Lorenz–Berthelot mixing rules.¹⁰ These give interfacial energies that are much too large when compared with those of *ab initio* calculations. The bicarbonate ion was modeled

by adding an H atom, charge $0.4e$, to one of the carbonate O atoms and increasing the charge on the O atom by $0.6e$. The O–H bond length is 0.96 \AA , and the C–O–H bond angle is 115° . These parameters are consistent with the C–O–H group of the carboxylic acid headgroup used in earlier simulations.¹¹

Two types of SAM substrates were used to match the two crystal surfaces. The SAM for the interface with the (0001) surface was a hexagonal array with lattice spacing of 4.97 \AA and the $\sqrt{3} \times \sqrt{3}R30^\circ$ structure. The tilt angles used for the initial conformations were the experimental values. Since an interface between the SAM and the (01 $\bar{1}2$) calcite surface is incommensurate, we must introduce misfit defects. In previous work,² we used line defects, analogous to misfit dislocations. Here, we propose to investigate whether the presence of bicarbonate at the interface can reduce the energy cost of these misfit defects. We therefore introduce bicarbonate ions into the monolayer within the line defects. This was carried out by distorting the monolayer using the Coulomb interaction with an array of Ca^{2+} ions. A regular array of ions corresponding to half the lattice sites of the (01 $\bar{1}2$) surface were placed over the SAM. A row of Ca^{2+} ions was then removed, resulting in a zero total charge for the system. The Ca^{2+} ions were fixed in position, and the SAM was relaxed during a 40 ps, low temperature (2 K) simulation, resulting in a distorted monolayer with a linear gap between the molecules. This gap was subsequently filled with a double row of bicarbonate ions (Figure 1), giving a monolayer with a charge density equal to half that of the (01 $\bar{1}2$) surface, as required to quench the surface dipole. Clearly, this is not the only way in which bicarbonate ions could be introduced to reduce the misfit between SAM and calcite. However, previous results (and some trials) suggest that it is a good candidate for a low-energy configuration.

Interfaces with one, two, three, and four crystal layers, in an aqueous environment, were modeled to investigate the effect of the different headgroup orientations of MHA and MPA on thin calcite films. The surface dipole is canceled by two methods, by terminating the crystal slab with a full layer of bicarbonate ions and by terminating the crystal slab with a half-layer of carbonate ions. The initial conformations were calculated by relaxing the crystal slab onto the frozen SAM at low temperature (2 K) for 40 ps. The relaxed conformations for the four-layer simulations of the MPA/(01 $\bar{1}2$) bicarbonate-terminated interface and the MHA/(0001) carbonate-terminated interface are shown in Figure 2. Water was subsequently added by equilibrating a water lattice at 300 K over the frozen SAM and crystal. (See ref 9 for a more extended discussion of the protocol.) The final conformation from this simulation was used as a starting conformation for a 400 ps simulation in which all of the atoms in the SAM, the crystal, and the water layer were mobile. The lower C atom of the monolayer was fixed in each case to represent the attachment to the Au substrate. The energy was calculated from the average of configuration energy sampled every picosecond of the final 300 ps of the simulation. The protocol we have described cannot *guarantee* that the final configuration is the equilibrium configuration. A system of this complexity could easily contain metastable states with deep minima. The purpose of the extended protocol is to ensure that the system has had the opportunity to investigate a large volume of configuration space so that it can find a low-energy starting point. Subsequent monitoring of the energy of the system suggests that our simulations are long enough to ensure that (at the very worst) we are in a deep minimum from which the system would not escape in any realistic simulation time. This stability also shows that the free water surface, where present, is in equilibrium (i.e., not evaporating into the vacuum space).

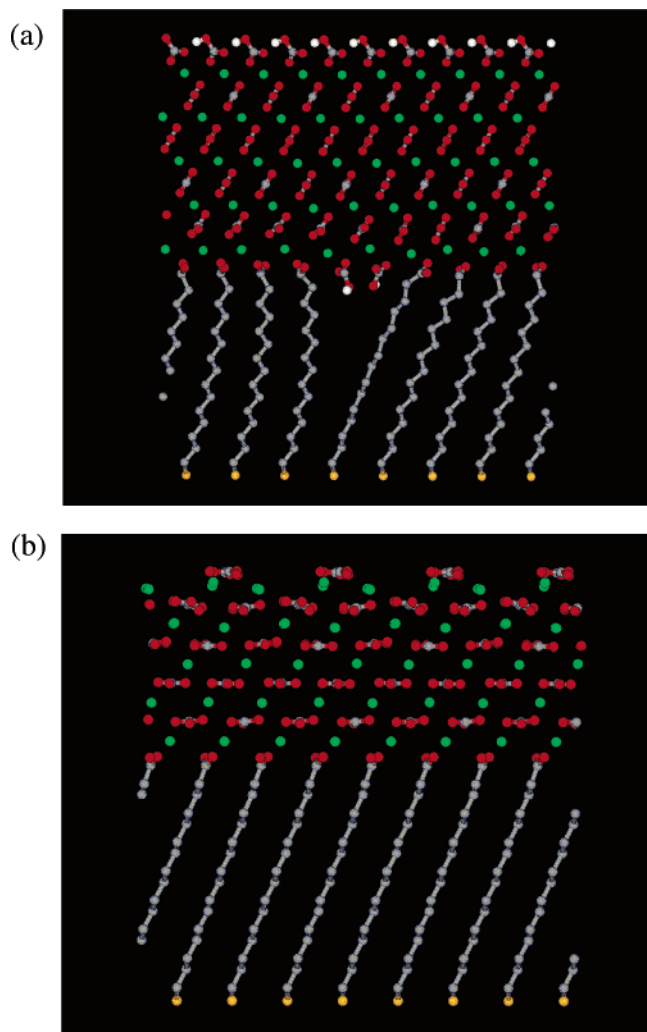


Figure 2. Initial conformations of (a) the MHA/(0112) bicarbonate-terminated interface and (b) the MPA/(0001) carbonate-terminated interface. The C atoms are colored gray, O atoms red, H atoms white, Ca ions green, and S atoms yellow.

The interfacial energies for the two crystal orientations were calculated using the method outlined previously. The intrinsic two-dimensional nature of monolayers and SAMs means that great care must be taken when defining the interfacial energy. In an earlier publication, we demonstrated that the equivalent of the Gibbs interfacial energy could be calculated for monolayers if we consider the reference state to be a monolayer on water, neutralized with a half-layer of Ca^{2+} ions, and a perfect crystal block. The final state is the monolayer on the crystal and a water block. Thus, the interfacial energy is given by⁹

$$\gamma_{\text{cm}} = \left(E_{\text{cm}} + \frac{1}{2} E_{\text{w}} - E_{\text{mw}} - \frac{1}{2} E_{\text{c}} \right) / A \quad (1)$$

Here, E_{cm} is the (configurational) energy of a half-block of crystal on a SAM; similarly, E_{w} is the energy of a water block, E_{mw} is the energy of a SAM on a half-block of water, and E_{c} is the energy of a crystal block. A is the surface area of the simulation block. The calculation is shown schematically in Figure 3a. It is important to note that the definition of γ_{cm} in ref 9 is with respect to the bulk crystal and the monolayer/water interface. In most treatments of heterogeneous nucleation, one defines the interfacial energy with respect to a bulk substrate. In the case of calcite growth on SAMs, there is no bulk substrate available, so we use the definition of ref 9. There

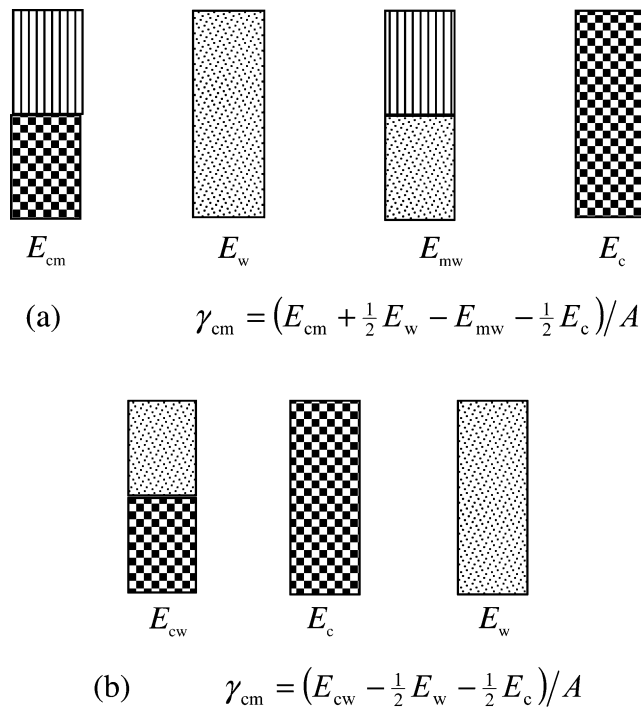


Figure 3. Schematic representation of (a) the crystal/monolayer interfacial energy and (b) the crystal/water interfacial energy. The checkerboard pattern represents a crystal block, the lines represent the monolayer, and the dots represent a water block.

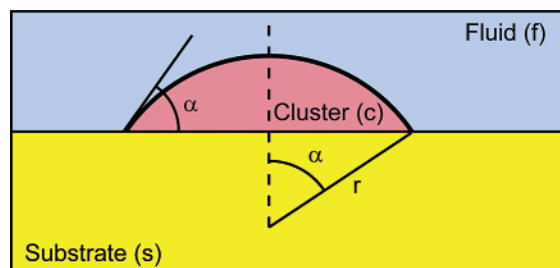


Figure 4. Schematic drawing of a spherical nucleus on a flat substrate. Through the use of the contact angle approach, the ratio between the interfacial energy and the surface energy ($m \approx \cos(\alpha)$) determines the volume, the interfacial area, and the surface area of the cluster.

is an additional complication in the case of the (0112) interface as the crystal/SAM interface includes bicarbonate ions. The bicarbonate ions are placed at the monolayer/calcite interface as shown, for example, in Figure 1. In the previous case, the reference state for the SAM was the undistorted monolayer, neutralized with a half-layer of Ca^{2+} ions. We now add an extra row of Ca^{2+} ions (so that it is charged) and also add bicarbonate ions in the water close to the extra Ca^{2+} ions to neutralize the simulation cell. This is the most stable configuration for the reference system containing bicarbonate ions since it minimizes the Coulombic term.

The relationship between the homogeneous nucleation barrier ΔG^*_{hom} and the heterogeneous nucleation barrier ΔG^*_{hetr} can be calculated by using the method outlined by Liu et al.¹² There are two essential differences between the two cases. First, the shape of the nucleus in heterogeneous nucleation will not be spherical. In the simplest case, it will be a sphere cut off by the surface. Second, the surface-energy term contains a contribution from a nucleus/substrate interface as well as the nucleus/fluid interface. Both these effects are related to the contact angle between nucleus and substrate, α (defined in Figure 4). Liu et al describe heterogeneous nucleation on a flat substrate, incorporating these effects with a multiplicative function $f(m)$

$$\Delta G_{\text{het}}^* = f(m)\Delta G_{\text{hom}}^* \quad (2)$$

where m is the ratio of the distance above the center of the nucleus where the surface cuts the nucleus to the radius of the nucleus itself (as shown in Figure 4). For a spherical nucleus, $m \approx \cos(\alpha)$. For $m \leq 0.25$, the behavior of $f(m)$ for a faceted nucleus is indistinguishable from that of a spherical one. As we shall see, our values for m are within this range. With the help of the goniometric equations for the surface area, the interfacial area, and the volume of such a spherical cluster, the following equation for $f(m)$ can be obtained

$$f(m) = \frac{m^3 - 3m + 2}{4} \quad (3)$$

with

$$m = -\frac{\gamma_{\text{cm}}}{\gamma_{\text{cw}}} \approx \cos(\alpha) \quad (4)$$

$$-1 \leq m \leq 1$$

where $\gamma_{\text{cw}} = (E_{\text{cw}} - \frac{1}{2}E_{\text{w}} - \frac{1}{2}E_{\text{c}})/A$ is the crystal/water interfacial energy. (See Figure 3b for a schematic of the

calculation.) Young's equation¹³ is used to describe the "contact angle" α (and hence m) as a function of the surface and interfacial energy. We note that the use of configurational energies from our simulations implies that the interfacial energies we are using are based on internal energies and not on free energies. The calculation of the interfacial free energies for so complex a system would be a prohibitive task. Since the interfacial energies are obtained from differences between the configurational energies, the entropy terms will tend to cancel. Moreover, we do not require an absolute value but only a ratio to determine m . For this purpose, the internal energy should therefore be a reasonable estimate of the free energy. Given this and through the use of the calculated values for the interfacial and surface energies, the influence of the substrate on the nucleation barrier can be calculated.

Results and Discussion

Snapshots of the simulations for the one-layer bicarbonate- and carbonate-terminated (0001)/MHA interfaces are shown in Figures 5a and 5b, and the (01 $\bar{1}2$)/MHA one-layer interfaces are shown in Figures 5c and 5d. Snapshots for the equivalent simulations for the four-layer interfaces are shown in Figure 6. It is clear that, although there is significant disorder in the very

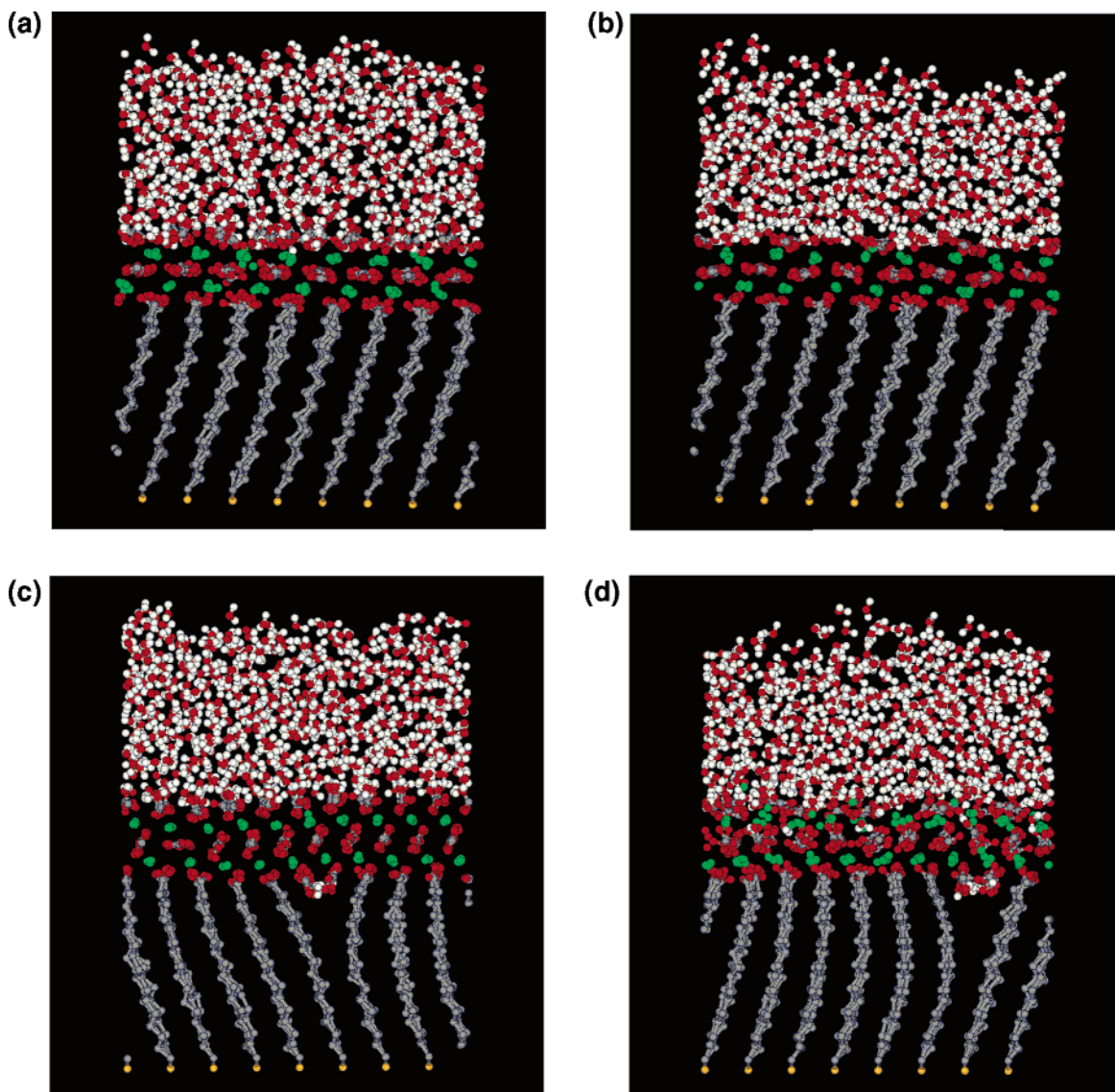


Figure 5. Snapshots of the 300 K simulations of (a) (0001)-oriented, bicarbonate-terminated, (b) (0001)-oriented, carbonate-terminated, (c) (01 $\bar{1}2$)-oriented, bicarbonate-terminated, and (d) (01 $\bar{1}2$)-oriented, carbonate-terminated one-layer calcite films on MHA.

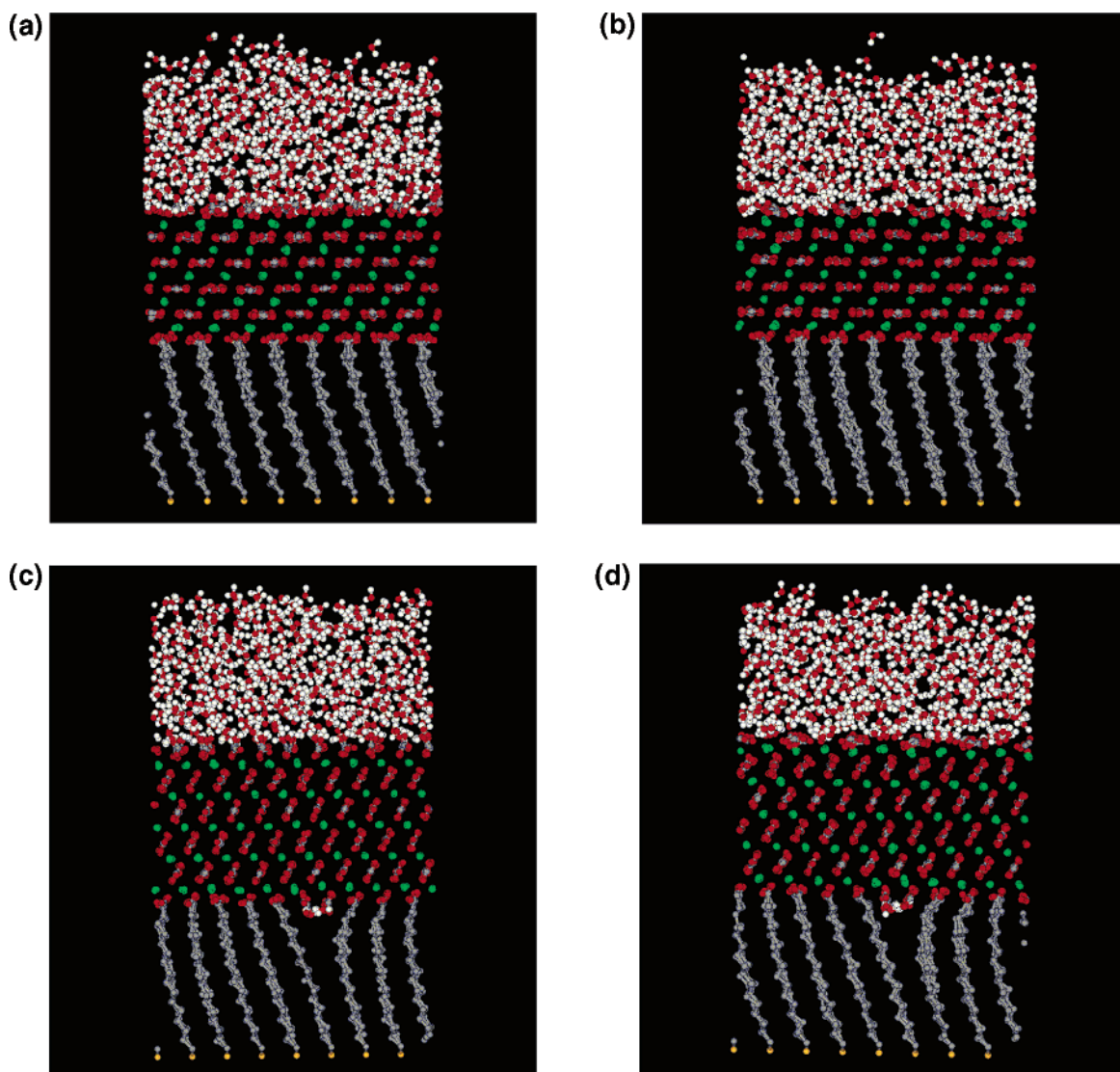


Figure 6. Snapshots of the 300 K simulations of (a) (0001)-oriented, bicarbonate-terminated, (b) (0001)-oriented, carbonate-terminated, (c) (0112)-oriented, bicarbonate-terminated, and (d) (0112)-oriented, carbonate-terminated four-layer calcite films on MHA.

TABLE 1: Mean Order Parameters of the (0001) and (0112) Thin Films, with One, Two, Three, and Four Crystal Layers, on Odd (MPA) and Even (MHA) SAMs, Terminated by HCO_3^- and CO_3^{2-} Ions^a

	(0001)				(0112)			
	HCO_3^- terminated		CO_3^{2-} terminated		HCO_3^- terminated		CO_3^{2-} terminated	
	odd	even	odd	even	odd	even	odd	even
1 layer	0.92	0.91	0.66	0.87	0.98	0.92	0.64	0.66
2 layer	0.96	0.96	0.92	0.93	0.98	0.98	0.85	0.85
3 layer	0.97	0.97	0.96	0.95	0.98	0.98	0.88	0.90
4 layer	0.97	0.97	0.95	0.95	0.99	0.98	0.91	0.91
energy (kJ mol^{-1})	3	3	8	9	6	3	8	9

^a The last row gives the mean excess energy per CaCO_3 unit with respect to the crystal energy.

thin (one-layer) crystal, the four-layer crystals are stable in both orientations and match the SAM structures very well.

We can quantify the order in the thin crystal films by defining an order parameter $\sigma = \frac{1}{2} \langle 3 \cos^2 \theta - 1 \rangle$, where the angled brackets represent the average over the final 300 ps of the simulations. In the case of the (0001) orientation, the angle θ is defined as the angle between the surface normal and the normal to the plane of the carbonate ion. For the (0112) orientation, θ is defined as the angle between the surface normal and the normal to the plane of the carbonate ion minus 63° . The carbonate ions orient at 27° to the surface normal in the (0112) surface. The order parameters are summarized in Table 1 for

all the simulations. The carbonate-terminated films have a lower order than the bicarbonate-terminated films, mainly because the terminating half-layer of carbonate ions is less ordered than the full lattice planes, particularly for the (0112) orientation. The bicarbonate-terminated films display a high degree of order for each thickness, and there is no evidence that the MHA SAMs induce a higher degree of order than MPA SAMs.

Also included in the table are the differences between the average energies of the CaCO_3 units in the thin films and the average energy in a bulk crystal. The unit energy of the films are calculated by subtracting the mean simulation energy for a zero-layer film (SAM, compensating Ca^{2+} and bicarbonate ions, and

TABLE 2: Interfacial Energy of the (0001) and (01 $\bar{1}2$) Interfaces with Odd (MPA) and Even (MHA) SAMs and the Corresponding Values of m and $f(m)$ as defined in Eqs 3 and 4

	(0001)			(01 $\bar{1}2$)		
	γ_{cm} (J m $^{-2}$)	m	$f(m)$	γ_{cm} (J m $^{-2}$)	m	$f(m)$
even (MHA)	0.081	−0.62	0.90	0.074	−0.57	0.88
odd (MPA)	0.086	−0.66	0.92	0.095	−0.73	0.95

water) from the mean simulation energy for the four-layer film and dividing by the difference between the number of CaCO₃ units in the two simulations. In all cases, the value is slightly higher than the equivalent lattice energy for a bulk crystal calculated for a bulk crystal using the same potentials and simulation conditions. The excess energies are small; however, the carbonate-terminated films have higher energies than the bicarbonate-terminated films in all cases, which implies that the presence of bicarbonate ions in solution lowers the nucleation barrier. There is no significant difference between the odd and even substrates or between the (0001) and (01 $\bar{1}2$) orientations.

The interfacial energies for the four interfaces were calculated from the energies of the simulations using eq 1. The reference state was a crystal block, with eight crystal layers terminated with bicarbonate ions, and a monolayer with 48 molecules and 24 Ca²⁺ ions on a water slab with 495 molecules. In the case of the (01 $\bar{1}2$) interface, the monolayer has an additional 6 Ca²⁺ ions and 12 bicarbonate ions. The final state has a monolayer with 48 molecules on a bicarbonate-terminated crystal with 4 layers and a water block of 990 molecules. Again, the (01 $\bar{1}2$) crystal monolayer interface had 12 bicarbonate ions in the monolayer to compensate for the higher charge density of the (01 $\bar{1}2$) planes. All interfacial energy simulations were carried out at 300 K for 400 ps. The calculated interfacial energies are summarized in Table 2. We note that both the lowest and the highest interfacial energies were obtained for the (01 $\bar{1}2$) orientation on MHA. The (0001) orientations had intermediate values. These results seem to correlate well with experimental observations. However, in view of the small differences and the uncertainties introduced by calculating interfacial energies from the difference between large simulation energies, they should be treated with caution. The results support the argument that the molecules of the MPA SAM need to distort more from the most favorable orientation to fit the (01 $\bar{1}2$) surface.

The values for the ratio of interfacial energies, m , and the heterogeneous/homogeneous nucleation barrier ratio, $f(m)$, can be obtained from the calculated interfacial energy using eqs 3 and 4. We use the value of 0.13 J m $^{-2}$ for the crystal/water interfacial energy.² The results are shown in Table 2. The barrier for nucleation on the (01 $\bar{1}2$) face is 7% smaller for SAMs of thiols with even chain length than that for SAMs of thiols with odd chain length. The difference between the nucleation barriers for the (01 $\bar{1}2$) and the (0001) orientation is rather small (2–4%) but not negligible since the nucleation rate depends exponentially on the nucleation barrier. However, in the calculation of the nucleation barrier, kinetic effects have not been taken into account. It is possible that the preferred (01 $\bar{1}2$) orientation is caused by a kinetic preference for this orientation. Simulations of bicarbonate ions on top of the calcium/SAM interface have shown that they tend to be close-packed in a rather upright orientation.¹⁴ This orientation of the bicarbonate ions is closer to the orientation of the carbonate ions in the (01 $\bar{1}2$) orientation than that in the (0001) orientation. The reorientation of the bicarbonate ions, after they have lost their proton, might be a kinetic barrier that is sufficiently high to prevent the formation of (0001)-oriented calcite crystals.

Conclusions

We have modeled interfaces between SAMs and the polar faces of calcite to investigate the prevalence of the nucleation of (01 $\bar{1}2$)-oriented crystals on SAM substrates and the observed odd–even effect. We added bicarbonate ions between the monolayer molecules to compensate for the lattice mismatch between the (01 $\bar{1}2$) calcite surface and the SAM. The bicarbonate ions also helped to cancel the dipole moment induced by the charged planes. We found that, in contrast to earlier simulations in which the lattice mismatch between the SAM and the (01 $\bar{1}2$) calcite face was accommodated with surface defects,² the (01 $\bar{1}2$) MHA interface had a lower energy than that of the (0001) MHA interface. It also had a lower interfacial energy than that of the (01 $\bar{1}2$) MPA interface, which would account for the observed odd–even effect. The differences between the interfacial energies are small, and they should, therefore, be treated with some caution; nevertheless, they are in good agreement with experimental observations, although a kinetic preference for the (01 $\bar{1}2$) orientation cannot be excluded.

The models of thin films on the SAMs displayed no significant difference between the order or the energy of the films on the different substrates. A difference was observed, however, between films terminated with bicarbonate ions and those terminated with carbonate ions, with the bicarbonate-terminated films displaying both increased order and lower energy. This result suggests that the presence of bicarbonate ions in solution enhances the nucleation of both (01 $\bar{1}2$)- and (0001)-oriented crystals.

In summary, our simulations indicate that the presence of bicarbonate ions in the supersaturated solution not only enhances the nucleation rate but may also influence the orientation of the nucleated crystals. The (01 $\bar{1}2$) face of calcite nucleates on a range of substrates, some of which would seem to have very poor lattice matching. The mechanism we outline in this paper, where bicarbonate ions compensate for the charge mismatch between the calcite surface and the substrate, could account for the observed (01 $\bar{1}2$) nucleation on other charged substrates.¹⁵

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