

Crystallisation controlled by the geometry of a surface

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For many years scientists have scratched surfaces in order to promote crystallisationⁱ. Crystals are observed to nucleate along the scratches. Despite the popularity of this technique, our understanding of why crystals nucleate in scratches is very limited. There is some theory for nucleation in grooves^{ii,iii,iv,v}, and this does predict that nucleation in a groove should be faster than on a smooth surface. However the theories are highly approximate, in particular they completely neglect the effect of the crystal lattice. To our knowledge, there have been no quantitative measurements of the nucleation rate in a groove, and there is no data on the microscopic details of how the nucleation occurs here. Here we study, via computer simulation, the heterogeneous nucleation of a crystal in a wedge-shaped groove. In agreement with experiment, we find that nucleation in these grooves is indeed many orders of magnitude faster than on a flat surface. We also find that there is a competition between the angle of the wedge, and the angles that are intrinsic to the lattice of the crystal. This competition results in a wedge angle at which the nucleation rate goes through a maximum, a phenomenon that is not seen in the nucleation of liquids. It also potentially allows us to use carefully engineered wedges to control the crystal form (polymorph) that nucleates.

As we are interested in the generic features of nucleation in grooves we study crystallisation in a simple model: the Lennard-Jones (LJ) model of noble gases and methane. We studied crystallisation in the liquid phase coexisting with the vapour, and

hence at low pressure. There the liquid phase is the equilibrium phase down to a reduced temperature of $T^*=0.65$; below this temperature the liquid is metastable and the crystal is the equilibrium phase^{vi}. The reduced temperature $T^*=kT/\epsilon$, where kT is the thermal energy and ϵ is the well-depth of the LJ potential. For the LJ model the face centered cubic (fcc) and hexagonal close packed (hcp) crystals are almost equally stable^{vii}, so it can potentially crystallise into either polymorph.

Our groove consists of two smooth planes that meet along a line, forming a wedge with internal angle β , see Figure 1. These planes interact with the LJ molecules via the potential^{viii} $u(z) = \epsilon_{WS}((\sigma/z)^9 - (\sigma/z)^3)$, where σ is the diameter of the LJ molecules and z is the distance between the LJ molecule and the plane. Thus the parameter ϵ_{WS} controls the strength of the interaction between the planes and the LJ molecules. All our results here are for $\epsilon_{WS}/\epsilon = 5$. This value of ϵ_{WS}/ϵ is large enough for the planes to create a potential well for the particles at the wall. This potential well favours the crystal phase at the wall because the crystal is denser than the fluid, and so the number of molecules in the potential well of the wall increases when crystallisation occurs at the wall. However, for $\epsilon_{WS}/\epsilon = 5$ the potential well is not large enough to cause the crystal phase to wet the wall/liquid interface at the triple point^{viii}. Our simulations of the model are Monte Carlo simulations. See the Supporting Information for details.

In Figure 2 we have plotted the nucleation rate in a wedge, as a function of wedge angle. At this temperature, $T^*=0.6$, the rate on a flat plane ($\beta = 180^\circ$) is too low to be computed. However, if we extrapolate from a rate obtained at a lower temperature^{viii} we obtain a rate of $10^{56}\sigma^2\text{cycle}^{-1}$ (see Supporting Information). Here a cycle is a unit of time, it is one attempted Monte Carlo move per molecule. The nucleation rate on a smooth plane only becomes comparable to the rates in Figure 2 at twice the super-cooling, at $T^* = 0.55$ ^{viii}. Thus, the rate of nucleation in wedges is many orders of magnitude higher than on a planar surface. On a scratched surface, nucleation will occur at the scratches, and scratching the surface will approximately halve the super-cooling required to see crystallisation.

In Figure 2, the dependence of the nucleation rate on the wedge angle β is clearly non-monotonic. As β decreases from 180° the nucleation rate increases rapidly until it reaches a maximum for β around 70° . Further decreasing β actually decreases the nucleation rate. As far as we are aware, this finding of a maximum is novel, and it is only found for the nucleation of a crystal. For the nucleation of a new fluid phase, the nucleation rate increases rapidly and monotonically as the wedge angle β decreases^{ii,iii,iv}.

To understand why there is a maximum in the nucleation rate we examined crystallisation in detail for a number of wedge angles. First we considered nucleation at an angle $\beta = 70.5^\circ$ near the maximum in the rate. Movie 1 in the Supporting Information is an animation of a growing nucleus in a wedge with this angle; the inset in Figure 2 shows the nucleus near the top of the

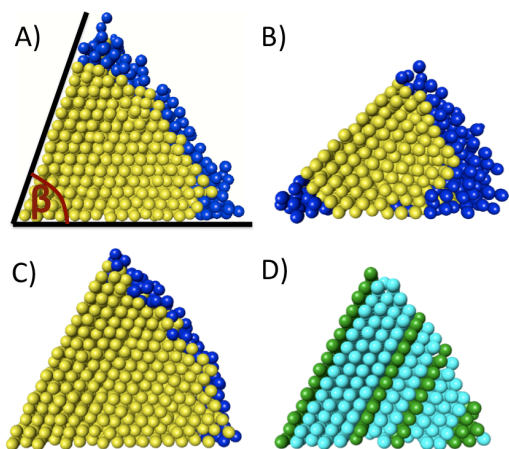


Figure 1. Simulation configurations of crystals in wedges. In each case we see a cross section of the final crystal found after the liquid droplet has completely crystallised. We are looking along the axis of the wedge, and the point of the wedge is at the bottom left. The surfaces of the wedge are shown schematically as black lines in (A) only. (A), (B) and (C) are snapshots of crystals in wedges of angles $\beta = 70.5^\circ$, 45° and 62° , respectively. The molecules in a locally crystalline environment are shown in yellow while those in a fluid environment are shown in dark blue. The temperature $T^* = 0.55$, and $\epsilon_{WS}/\epsilon = 5$. (D) is same crystal as (C) but here we have analysed the crystal to distinguish between fcc and hcp. Particles in a locally fcc environment are dark green and those in a locally hcp environment are cyan; the fluid molecules are not shown.

nucleation barrier, and Figure 1(A) shows the final crystal. In Movie 1 we see that as the nucleus of the crystal phase grows, close-packed, $\{111\}$, planes of a face-centered-cubic (fcc) lattice grow along *both* sides of the wedge. This is possible because in a defect-free, unstrained, fcc lattice the angle between close-packed planes is 70.5° . These are the densest planes, and so maximise the interaction between the growing crystal and the attractive surfaces of the wedge. Once crystallisation in the wedge is complete we obtain a defect-free fcc crystal, see Figure 1(A). The final crystal has a liquid surface layer (the blue molecules) because the LJ crystal surface melts^{vi,ix,x}.

Thus we see that in a wedge of angle 70.5° , an fcc crystal can grow in the wedge without strain or defects and with dense planes along both sides of the wedge. These dense planes mean a large number of molecules in the potential well of the wall. This large number in the potential well means that the growing nucleus has a large and negative contribution to its energy from the interaction with the walls, and this reduces the free energy barrier to nucleation.

The situation is very different in narrow wedges. Movie 2 shows a growing nucleus in a 45° wedge; the final crystal is shown in Figure 1(B). In Figure 1(B) we see that crystallisation is incomplete both in the corner of the wedge and along one side (the top side). In Movie 2 we see that that crystal nucleus forms in contact with only the top side of the wedge. It is not possible to have two close-packed planes at an angle of 45° to each other. So the crystal is forced to form with a close-packed plane along only one wedge surface; along the other surface the crystal packing is irregular resulting in incomplete crystallisation here (note the blue molecules along the bottom surface of the crystal in Figure 1(B)).

Thus we see that the nucleation rate has a maximum near 70° because there the crystal fits perfectly into the wedge, with the maximally dense $\{111\}$ planes in contact with both wedge surfaces. At other angles this is not possible as the angle between the close-packed planes is fixed by the geometry of the fcc lattice. A detailed understanding of nucleation as a function of β requires the study of the patterns of defects in crystals in wedges. We defer this study to a future publication.

We have shown that the nucleation rate of the fcc crystal is largest for wedge angles near where it fits perfectly into the wedge. This perfect angle will vary from one polymorph to another as it is set by the crystal lattice. This suggests that we could favour a specific polymorph by setting β equal to the angle between two dense planes in the required polymorph.

In the other polymorph of LJ, the hcp crystal, close packed planes and the dense $\{10\bar{1}1\}$ planes are at angle of 62° to each other. This is far from an optimal angle for the fcc phase and so a wedge with this angle should favour the hcp over the fcc polymorph. The crystal we obtained in a $\beta = 62^\circ$ wedge is shown in Figure 1(C) and (D). It is mostly hcp but it is not perfect, there are stacking faults (sheets of green molecules). By stacking faults, we mean that the crystal is a stack of close-packed planes but that the stacking is not the ABABAB... stacking of a perfect hcp lattice but in parts it is ABABCAB...

Stacking faults are known to be very cheap defects in hard-spheres^{xi}, which also have fcc and hcp polymorphs. It is possible that in close-packed lattices (fcc and hcp) this small free-energy cost of stacking faults^{xi} makes a perfect hcp crystal hard to achieve. In other systems where defects have higher costs, it may be easier to obtain different pure polymorphs in wedges of different angles. Both Ha *et al.*^{xii} and Beiner *et al.*^{xiii} have found experimentally that confining a liquid in nano-sized pores changes

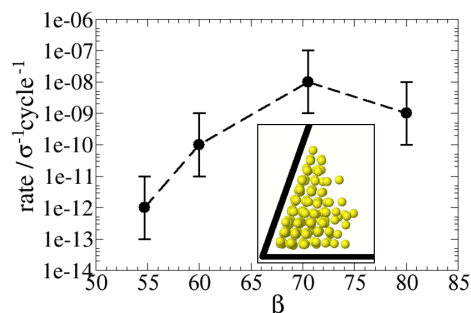


Figure 2. The nucleation rate as a function of wedge angle β . The temperature $T^* = 0.6$, and $\epsilon_{ws} / \epsilon = 5$. Inset is a nucleus near the top of the barrier in a 70.5° wedge. It has 209 crystalline molecules.

crystal polymorph that formed. So, there is also experimental evidence that changing a geometrical feature can change the polymorph produced.

In conclusion, we have studied the nucleation of crystal phases in wedges. We find that if the wedge angle is optimal then the rate of nucleation is orders of magnitude higher in the wedge than on flat surfaces. Therefore, generically we expect crystallisation to start in grooves or pits in surfaces, not on the flat parts of surfaces. This expectation is consistent with the common observation that crystallisation readily occurs on a scratched surfaceⁱ. Here, we have used simulation to see for the first time how the crystal nucleus grows in a groove. We found that nucleation is highly sensitive to the wedge angle β . This is because there are angles that are intrinsic to crystals, such as the 70.5° angle between the close-packed planes in an fcc lattice. As this effect is a direct consequence of the crystal lattice we expect it to be a general feature of crystallisation, even with more complex molecules, for example proteins. Nucleation is faster when the wedge angle is such that a defect-free unstrained piece of the crystal fits perfectly into the wedge. As different crystal polymorphs have different intrinsic angles, this may provide a way to control the polymorph that nucleates. A wedge into which the desired polymorph fits perfectly, but which has the wrong angle for other polymorphs, will favour nucleation only of the desired polymorph.

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Supporting Information Available: Details of the simulations, 2 movies of nucleation.

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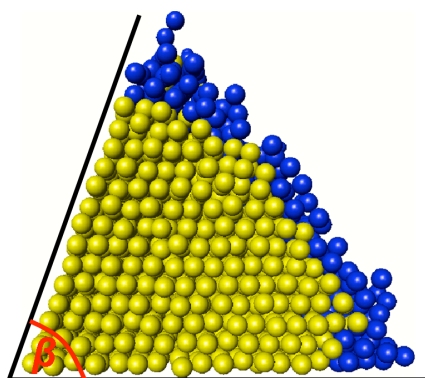
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ABSTRACT FOR WEB PUBLICATION

Crystallisation is of great importance in fields as diverse as atmospheric chemistry and the pharmaceutical industry. It starts with nucleation, the formation of a microscopic crystal. Here we study, via computer simulation, the heterogeneous nucleation of a crystal in wedge-shaped grooves in a surface. We find that nucleation in these grooves is many orders of magnitude faster than on a flat surface. We also find that there is an optimum wedge angle at which nucleation is fastest. Our observation that nucleation in grooves dominates that on flat surfaces not only explains the effectiveness of scratching a surface to induce crystallisation, it allows us to see the microscopic behaviour that underlies this common technique. We also show how it may also be possible to control the crystal form, the polymorph, by controlling the groove geometry to favour nucleation of the desired polymorph.
