

Supplementary Information for “Crystallisation controlled by the geometry of a surface” by Amanda J. Page and Richard P. Sear

1 Model

We study the crystallisation of Lennard-Jones (LJ) molecules in a wedge. The LJ potential is truncated at 2.5σ and shifted upwards so that it reaches 0 there. Thus it is zero at distances greater than 2.5σ and is continuous at that point. σ is the diameter of a molecule. The wall-molecule potential is not truncated. We work at reduced temperatures $T^* = kT/\epsilon$, where ϵ is the well depth of the LJ potential.

The wedge is made from two adjacent walls of a parallelepiped box where the angle between these two walls, β , is the opening angle of the wedge, see Figure S1. The wedge walls interact with the LJ molecules via the same potential used in earlier work¹ for a single wall,

$$U_{wall-p}(z) = \epsilon_{WS} \left(\left(\frac{\sigma}{z} \right)^9 - \left(\frac{\sigma}{z} \right)^3 \right), \quad (1)$$

with z the distance between the molecule and the wall, and ϵ_{WS} the strength of the wall-molecule interaction. The well depth for the attraction to the surface is $0.385\epsilon_{WS}$. Thus for $\epsilon_{WS}/\epsilon = 5$ the well depth for the wall-molecule attraction is approximately twice that of the molecule-molecule attraction.

The potential of equation (1) is completely smooth. This is reasonable for a system of colloidal particles at a wall but small molecules near a wall will experience a potential that is corrugated at least to some degree, due to the fact that the surface is composed of atoms. Experimental work on methane on graphite compares well with simulation work using smooth potentials¹⁻⁵ so for this system at least a smooth potential provides a good model for the molecule/surface interaction. However, templating the crystal using a regular crystalline lattice clearly has a strong effect, see for example the work of van Blaaderen and coworkers.^{6,7} Also recent work has shown that the roughness of an amorphous surface also has an effect.⁸ Here we focus on the effect of changing the geometry on a lengthscale much larger than that of an individual molecule. To understand the effect of smaller lengthscale corrugations will require additional work.

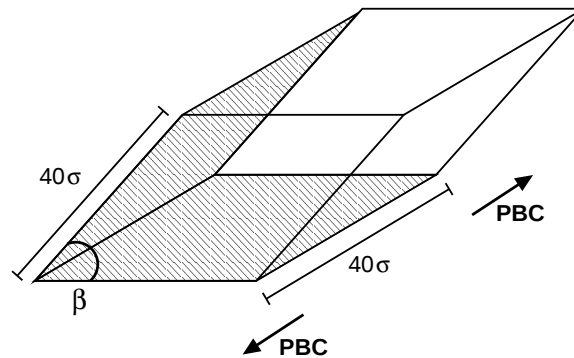


Figure S1 Diagram of the simulation box. Two adjacent sides of the parallelepiped box create the wedge geometry, these sides are shown as shaded in the diagram. The angle between these walls, and hence

the opening angle of the wedge, is β . Bounding the simulation in the other two directions are two soft repulsive walls. A wedge length of 40σ is simulated with periodic boundary conditions (PBC) along the axis of the wedge.

In a wedge there are two contributions to the wedge-molecule potential, $U_{wedge-p}$, one from each plane of the wedge,

$$U_{wedge-p} = U_{wall-p}(z_{left}) + U_{wall-p}(z_{right}), \quad (2)$$

where z_{left} and z_{right} are the perpendicular distances of the LJ molecule from the left and right walls of the wedge, respectively. The ratio ϵ_{WS}/ϵ controls the strength of the interaction between a wall and a molecule. All the results in this paper are for $\epsilon_{WS}/\epsilon = 5$.

The two walls of the wedge are shown as shaded in Figure S1. The two opposite sides (unshaded) of the simulation box are soft repulsive walls. All four walls are squares of side 40σ . Periodic boundary conditions are applied along the axis of the wedge.

2 Details of the computer simulations

All simulations are Metropolis Monte Carlo simulations⁹ in the canonical (NVT) ensemble. Initially the wedge is partially filled with the liquid phase coexisting with a vapour. By inspection, the contact angle the liquid/vapour interface makes with the wall is approximately 90° (for our surfaces with $\epsilon_{WS}/\epsilon = 5$). We varied the number of LJ molecules, N , so that for all wedge angles the liquid phase forms a sector of a cylinder with a radius of approximately 17σ . Keeping this radius approximately constant required increasing N from 4405 for $\beta = 45^\circ$, to 8810 for $\beta = 90^\circ$. To track the growth of the crystal phase we use bond order parameters. To calculate the nucleation rates in Figure 2 we used the Forward Flux Sampling (FFS) algorithm of Allen and coworkers,^{10,11} as we did in earlier work.^{1,12}

The crystals in Figure 1 were obtained by starting with a wedge filled with a droplet of the liquid phase and equilibrating at the triple-point temperature, $T^* = 0.65$. The liquid in the wedge was then cooled by dropping the reduced temperature by 0.025 every 10^5 cycles until it crystallised. The snapshots of Figures 1(A), 1(B) and 1(C) are all at $T^* = 0.55$, while 1(D) is the configuration of 1(C) quenched and subjected to our nearest-neighbour analysis.

2.1 Order parameters

As in this earlier work,^{1,12} we use bond order parameters to distinguish between molecules that are part of a crystal and molecules that in a liquid environment.¹²⁻¹⁵ The method starts by determining whether pairs of nearby molecules are nearest neighbours. The distance cutoff for a pair of molecules to be considered nearest neighbours is 1.5σ , and a crystal ‘link’ is taken to exist between neighbours i and j if the order-parameter product $\mathbf{q}_6(i) \cdot \mathbf{q}_6(j) \geq 0.65$. See references 12–14 for further details. The only difference between here and reference 12 is a change in how many crystal ‘links’ a molecule must have before it is counted as crystalline. In this change we follow the surface nucleation work of Mendez-Villuendas et. al.¹⁵ Instead of requiring that a molecule has 5 or more crystal ‘links’, we

require that these links exist between it and at least 55% of its nearest neighbours, and that it has at least 4 nearest neighbours. This is better able to distinguish crystalline and liquid molecules at a surface where the coordination number is lower than in the bulk.

2.2 Common Neighbour Analysis

Once a crystal has formed we wish to examine its structure. For this purpose we use common neighbour analysis (CNA). This technique was pioneered by Honeycutt and Andersen¹⁶ in their study of LJ clusters. It is now a standard technique for analysing the structure of crystalline phases. CNA is sensitive to thermal vibrations in the crystal. These can be reduced by quenching the structure into a local energy minimum. Quenching is done by running a simulation that only accepts moves that reduce the energy. Each quenching simulation run is run for 10^5 cycles. This is long enough that at the end of the run the energy is no longer decreasing by significant amounts, indicating that we are near a local minimum in the energy. The structure and the defects remain unchanged by the quenching procedure.

Different crystal structures are made up of molecules that are connected by unique combinations of bond types. In our CNA analysis a bond exists between molecules if the distance between the two molecules is less than 1.347σ . This lies approximately halfway between the nearest-neighbour distance, $2^{1/6}\sigma = 1.12\sigma$ and the next-nearest-neighbour distance $2^{1/2} \times 2^{1/6}\sigma = 1.78\sigma$. Thus we connect by bonds all nearest-neighbour pairs of molecules but exclude next-nearest-neighbour pairs.

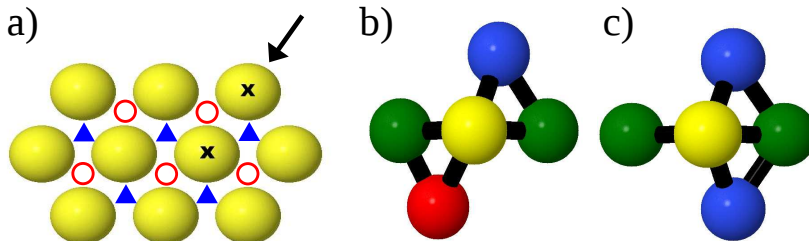


Figure S2 Figures showing the difference between the local environments in an fcc crystal and a hcp crystal. a) A single close-packed plane is shown from above, with the molecules shown as yellow spheres. Following the usual convention¹⁷ we call this layer A. The positions of the centres of molecules in layer B are shown as blue triangles, and the positions of molecules in a layer C are shown as red circles. b) and c) show the bonds around a pair of molecules in a close-packed layer. The pair are the two molecules marked by crosses in a). We are viewing them along the direction shown by the arrow in a). Therefore in b) and c) we can only see the nearer one of the two yellow molecules; the second molecule is directly behind the first and so is hidden. The bonds between the particles are shown as black lines. In both b) and c), the two green molecules are in layer A. They are the two molecules in layer A that are neighbours of both the two yellow molecules. The blue molecules are mutual nearest neighbours of the yellow pair that are in B layers. The red molecule is a mutual nearest neighbour in a C layer. Thus b) shows a type of bonding found in an fcc crystal (...CAB...) while c) shows bonding in a hcp crystal (...BAB...). b) is a [421] bond type in Honeycutt and Andersen's notation,¹⁶ and c) is a [422] bond type.

The fcc and hcp structures are both composed of stacks of close packed layers, the

{111} layers of the fcc lattice. A hcp lattice is a stack of layers in which the third layer is directly above the first, the fourth directly above the second etc. This is usually written as ABABAB... stacking.¹⁷ In an fcc lattice every plane is directly over the one two planes below, which is usually written as ABCABC... stacking. Every molecule in the hcp and fcc structures has 12 nearest neighbours and therefore 12 bonds.

If we consider one of these bonds we can determine how many molecules are neighbours of *both* of the two molecules joined by the bond. We call these the mutual nearest-neighbour (mnn) molecules. In both fcc and hcp lattices, there are always four mnn for each bond between a pair of nearest neighbours. Thus the number of mnn does not distinguish between the two lattices. However, in hcp lattice the lattice planes above and below a plane are directly above each other. This is not the case in an fcc lattice where an A layer has a B layer above and a C layer below. This means that the pattern of bonds in between the four mnn is different in the hcp and fcc lattices. In the hcp lattice one of the two mnn that is in the same close-packed plane as the two original molecules is a nearest neighbour of both the two out-of-plane mnn. In the fcc lattice each mnn is a neighbour of only other mnn. This is shown in Figure S2.

In the notation of Honeycutt and Andersen¹⁶ each of the (12 for a close-packed lattice) bonds of a molecule is characterised by three numbers in the form $[ijk]$. For a molecule with fcc ordering, all 12 bonds are $[421]$ bonds, whereas a molecule with hcp ordering has 6 $[421]$ and 6 $[422]$ bonds. In the sequence of numbers ijk , i is the number of mnn, j is the number of bonds between the mnn, and different values of k distinguish between different patterns of bonding between the mnn.¹⁶

The results of this analysis for a crystal in a wedge is shown in Figure 1D. It should be noted that as it is only possible to distinguish between fcc and hcp environments for a molecule that has close-packed planes above and below it. We cannot distinguish between the two environments for molecules in planes at the surface of the crystal. Thus there are two close-packed planes at the top-left and bottom-right surfaces of the crystal that are not shown in Figure 1D.

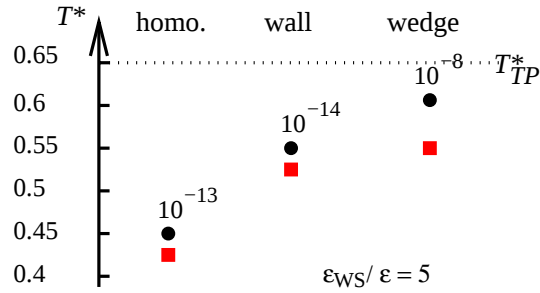


Figure S3 Schematic summarising nucleation of the crystal phase. From left to right, we have results for nucleation in the bulk; at a single wall with $\epsilon_{WS}/\epsilon = 5$; and in a 70.5° wedge with walls with $\epsilon_{WS}/\epsilon = 5$. The y -axis is temperature; $T_{TP}^* = 0.65$ is the triple-point temperature. In each column a black circle indicates the temperature at which we calculated the nucleation rate, and the number is the rate in units of $\sigma^{-3}\text{cycle}^{-1}$, $\sigma^{-2}\text{cycle}^{-1}$, $\sigma^{-1}\text{cycle}^{-1}$, for homogeneous nucleation, nucleation at a wall, and nucleation in a wedge, respectively. The red square indicates the temperature at which the nucleation barrier becomes small and nucleation rapid. These are located at $T^* = 0.425, 0.525$ and 0.55 for homogeneous nucleation, nucleation at a flat surface, and nucleation in a 70.5° wedge, respectively.

2.3 Nucleation rates

In earlier work¹² we calculated the rate of homogeneous nucleation (away from a surface) at the temperature $T^* = 0.45$. We found a rate of $10^{-13\pm1}\sigma^{-3}\text{cycle}^{-1}$. We have also calculated the rate of nucleation at a single planar surface with $\epsilon_{WS}/\epsilon = 5$. We found¹ a rate of $10^{-14\pm1}\sigma^{-2}\text{cycle}^{-1}$, at the higher temperature $T^* = 0.55$. Thus the rate of heterogeneous nucleation at a single wall at a supercooling of $T_{TP}^* - T^* = 0.1$ is close to the rate of homogeneous nucleation at twice this supercooling. Both these rates were calculated using FFS. In a wedge we halved the supercooling once more to $T_{TP}^* - T^* = 0.05$ and obtained nucleation rates. The highest rate we obtained at this temperature $T^* = 0.6$ was $10^{-8\pm1}\sigma^{-1}\text{cycle}^{-1}$ in a $\beta = 70.5^\circ$ wedge. So in this wedge we have a nucleation rate at one temperature that is faster than on a plane that is at twice the supercooling. Nucleation in wedges that are near the optimal angle for nucleation is much faster than that on planar surfaces. Nucleation on these planar surfaces although much slower than in a wedge is much faster than in the bulk. The nucleation behaviour in the bulk, at a flat wall and in a 70.5° wedge is summarised and the different rates compared, in Figure S3.

As the rates of homogeneous nucleation, nucleation on a plane, and in a wedge all have different units, strictly speaking they cannot be directly compared. When we compare rates we are comparing the rate in a molecular volume (σ^3) for homogeneous nucleation, with that on a molecular area (σ^2) for nucleation at a flat surface and that in a molecular length (σ) for nucleation in a wedge. In an experimental system the area in units of the molecular area is expected to be much larger than the length of any scratches in units of the molecular length. However, the nucleation rate in a wedge is so much larger than on a flat surface, that nucleation in a wedge still dominates. Classical nucleation theory predicts that nucleation rates should vary with supersaturation, $\Delta\mu$, as $\exp(-A/\Delta\mu^2) = 10^{(-A'/\Delta\mu^2)}$. Assuming¹ that $\Delta\mu$ varies linearly with T^* , this implies that if the nucleation rate on a flat surface is $10^{-14}\sigma^{-2}\text{cycle}^{-1}$ at $T^* = 0.55$ it is $10^{-14/(1/4)} = 10^{-56}\sigma^{-2}\text{cycle}^{-1}$ at $T^* = 0.6$. In the reduced molecular units, this is 48 orders of magnitude lower than in a 70.5° wedge.

The rates of heterogeneous nucleation above are all for surfaces with $\epsilon_{WS}/\epsilon = 5$. For $\epsilon_{WS}/\epsilon \gtrsim 7$ the crystal wets the surface/liquid interface¹ and for values of $\epsilon_{WS}/\epsilon \geq 11$ the barrier to nucleation on a single flat surface is abolished.¹ Thus for these strongly attractive surfaces there is no nucleation barrier even for a perfectly flat surface, and so scratching these surfaces should have little effect.

References

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Movie information

Movie 1 shows crystallisation occurring in a $\beta = 70.5^\circ$ wedge, at $T^* = 0.6$. The wedge is filled with a droplet of the liquid but in order to see the growing crystal nucleus, molecules that are determined as being liquid via our bond order parameters are not shown. Only those that are both crystalline and in the largest cluster of crystal molecules are shown. These molecules are shown in yellow and the walls of the wedge are shown in black. We are looking along the wedge. The movie is an animation of successive configurations at the FFS interfaces.¹⁰⁻¹² As our order parameter is the number of crystalline molecules in the largest cluster, configurations at successive interfaces have larger numbers of molecules. The animation starts with a small crystalline cluster and ends with a cluster that is far beyond the critical nucleus, i.e., the final configuration will with probability very close to one continue to grow until the entire system is crystalline.

Movie 2 shows crystallisation occurring in a $\beta = 45^\circ$ wedge, at $T^* = 0.55$. Details are as for Movie 1. The movie is obtained at a lower temperature than that for the 70.5° wedge because the nucleation rate in a 45° wedge is too low to be computed via FFS.

Both movies were made using Jmol (<http://jmol.sourceforge.net/>) to produce individual images of the molecules at successive interfaces. These images were then converted into a movie using ImageJ (<http://rsb.info.nih.gov/ij/>).