Epitaxy and polymorph selection in heterogeneous crystal nucleation

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Crystallisation and its initial stage of nucleation are of widespread interest in many areas of soft matter physics [1]. Here we investigate two generic phenomena that are important for everyone who needs to understand crystallisation—epitaxy and polymorph selection. We use computer simulations in order to access the dynamics of crystallisation at the molecular scale, something that is difficult to do in experiments.

Epitaxy occurs when a crystal nucleating on a surface always forms with a particular fixed orientation to the surface lattice. To investigate epitaxy, we consider nucleation on a crystalline surface of a different substance (see Figure 1). Sixty years ago, Turnbull and Vonnegut predicted that a crystalline surface is best at inducing nucleation of another crystal when there is a perfect match between the two bulk lattices. Our computer simulations show that this is not quite right. In fact, the crystal lattice of a finite nucleus is strained from that in the bulk, and nucleation is fastest when the surface matches this strained lattice [2, 3]. We show that epitaxy can be predicted from relatively simple energy calculations.

Most substances exhibit multiple crystal forms, a phenomenon known as polymorphism. Controlling which polymorph crystallises is often of crucial importance, especially in the pharmaceuticals industry [4]. We offer some insights into how and why different polymorphs form based on computer simulations of a simple model system (see Figure 2).

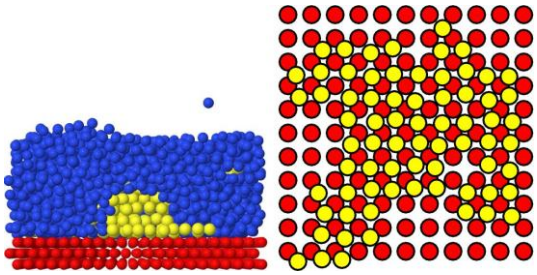

Figure 1: Nucleation on a crystalline surface. The surface is coloured red, the undercooled liquid blue, and the nucleus that has formed on the surface yellow. The left image is the simulation setup, the right image is a plan view with only the top layer of the surface and bottom layer of the nucleus shown. This is an example of epitaxy, where the orientation of the nucleus is fixed by the surface lattice.

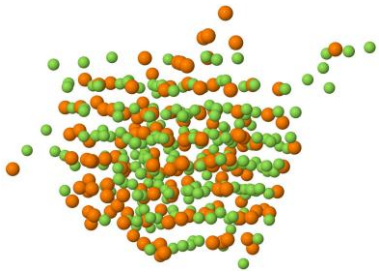

Figure 2: Competing polymorphs in crystal nucleation. The image shows a roughly 'critical' size nucleus, with some particles in a close-packed crystal environment (orange), and others in a body-centeredcubic environment (green). The image suggests that at the top of the nucleation barrier, the nucleus may not be one polymorph or the other, but a mixture.

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