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Crystallization

Basic Concepts and Industrial Applications
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1 Crystallization: Introduction

Wolfgang Beckmann

The beauty of crystals can be found in both the naturally appearing minerals such as diamonds or quartzite crystals and the industrial products such as sugar crystals. Crystals that are bound by flat faces intersecting at well-defined angels are characteristic of the substance and give the crop a reproducible appearance. This regular appearance is due to the long-range order of the building blocks of the crystal, be it either atoms or molecules. For example, in sodium chloride, the sodium and chlorine atoms are arranged in a cubic lattice (Figure 1.1). This arrangement maximizes the attractive interactions between the building blocks and thus minimizes the energetic state. The long-range order of its building blocks makes the crystalline state distinct from the gaseous and liquid as well as the amorphous solid state. The long-range order is also the root cause of a number of well-defined properties of the crystals, so these properties can be tailored through the crystallization process.

A further consequence of the well-defined arrangement of the building blocks is the outer shape of the crystals; crystals are limited by flat faces that intersect under well-defined angles determined by the lattice. This can be easily observed for the large crystals of rock sugar (Figure 1.2). For a given substance, ordering is a characteristic. Consequently, the faces and their angles are characteristics of a given substance. All crystals grown under similar conditions will exhibit the same faces and partitioning of the faces.

Though the lattice is characteristic of a given substance, a large number of substances can crystallize following more than one ordering motive, leading to polymorphism. Carbon, for example, can crystallize in two different lattices, as diamond and as graphite. In diamond, the carbon atoms are arranged in two face-centered cubic lattices; in graphite, the carbon atoms are arranged in layers in which the atoms have a hexagonal symmetry (Figure 1.3). With respect to energy and stability, graphite is more stable than diamond at room temperature and ambient pressure, though the barrier for transformation is extremely high.

A further equally important consequence of packing is the well-known purification during crystallization; only molecules of one type are incorporated, while most other molecules are rejected by the growing interface. This is for geometric as well as...
Figure 1.1  Arrangement of the sodium and chlorine atoms in the simple cubic lattice of sodium chloride.

Figure 1.2  Crystals of rock sugar with large well-developed flat faces, which intersect under certain angels characteristic of the substance; note that the apparent roughness of the faces arises not from the crystallization process, but from the downstream processes like washing.
for energetic reasons as it is energetically favorable to incorporate a proper building block instead of an impurity molecule.

Crystallization belongs to the oldest unit operations known to mankind. Namely, the crystallization of salts can be found through the ages. Early civilizations in coastal areas used large open ponds, salines, to crystallize out the salt, which could then be easily handled, stored, transported, traded, and finally used (Figure 1.4). Salines around the seaport of Ostia are said to have facilitated the development of Roma and the Roman Empire.

However, salt obtained by evaporation of seawater had a number of drawbacks; the purity was limited, mainly due to the high content of inclusions of mother liquor that entrained impurities. Hence, industrial techniques have developed over the time for the industrial crystallization of salt, resulting in the modern continuous vacuum crystallization apparatus.

Today, crystalline products can be found in every aspect of life. Relevant product properties are determined by crystal properties and thus tailored via crystallization. Three examples are shown in Figure 1.5. Sucrose, sugar, is extracted from
plants and crystallized to meet a certain particle size distribution, typically in the range of 700–800 μm, to be free of fines, which allows a free-flowing product that does not agglomerate. Finally, the process arrives at purities of >99.5% in an essentially single-step process of a seeded batch crystallization. Table salt also is required to be free flowing and not to agglomerate even in the high relative humidity environment of a kitchen. Here, additives can be employed during the crystallization, which is usually continuously operated evaporation crystallization. Finally, one of the main components of chocolate, cocoa fat has to be crystallized in a certain crystal modification or polymorph to achieve the special mouth taste of chocolate. This modification is unstable at room temperature and achieved via melt crystallization, where the crystals of the desired modification are generated and grown via a temperature program. In addition, additives can be used to stabilize the required modification. The unstable modification of the fatty acid ester can recrystallize to a more stable one, resulting in undesired changes in the appearance of the product.

In a number of cases, mother liquor is the desired product of the crystallization process. The crystallization of ice from aqueous solutions can be used for freeze concentration of aqueous solutions. One example of everyday life is orange
juice that can be freeze concentrated at low temperatures gently and in an energy-efficient way. The concentration of waste from effluent waters is another application.

The application of crystallization in industry ranges from the isolation of the few milligrams of a substance newly synthesized in the laboratory – where a well-defined melting point is used to both achieve and prove a decent purity of the crop and as an identity check – to a mass crystallization carried out in very diverse industries; some products are listed with their annual production volume in Table 1.1.

The equipment used in the industrial crystallization varies widely, from multi-purpose batch vessels in the life science industry to highly sophisticated dedicated equipment used for some large volume products.

In the following chapters, the basic concepts of the modern understanding of crystallization will be discussed, such as the internal structure of the crystals and their growth mechanisms or the phase diagrams. Attention will be directed to the purification by crystallization and to effects of polymorphism. Next, the basic methods to carry out a crystallization, from both the solution and the melt, are discussed. Finally, the concepts of mass crystallization in continuously operated crystallizers will be shown.

<table>
<thead>
<tr>
<th>Product</th>
<th>Produced in</th>
<th>Production (t/a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium chloride</td>
<td>2001 in the EU</td>
<td>38 350 000</td>
</tr>
<tr>
<td>Sugar</td>
<td>2001 in the EU</td>
<td>15 000 000</td>
</tr>
<tr>
<td>Caprolactam</td>
<td>2002 worldwide</td>
<td>3 500 000</td>
</tr>
<tr>
<td>Ascorbic acid</td>
<td>2009 worldwide</td>
<td>110 000</td>
</tr>
<tr>
<td>Acetylsalicylic acid</td>
<td>2008 worldwide</td>
<td>35 000</td>
</tr>
</tbody>
</table>
2
Mechanisms of Crystallization

Wolfgang Beckmann

One of the most important features of crystals is the long-range order of their building blocks and symmetry of their arrangement. This arrangement maximizes the interaction between the building blocks, stabilizing the crystal. Most macroscopic properties of crystals, such as their shape or the purification during crystallization, are a direct consequence of this arrangement. Thus, the discussion of the mechanisms of crystallizations has first to deal with the symmetry and long-range order in crystals. In the second part, the nucleation and growth mechanisms of crystals are discussed. In both cases, a supersaturated mother phase or a deviation from saturation is necessary. The dependence of the processes on supersaturation and other parameters has to be discussed. The discussion of crystal nucleation has two goals: first, to determine the mechanisms and thus also the prerequisites for nucleation; second, to derive expressions for the dependence on supersaturation.

2.1
Crystal Lattice

2.1.1
Arrangement of Building Blocks and Symmetries

Crystallization is a phase transformation for which the free enthalpy $\Delta_{tr} G$ has to be negative (Equation 2.1). The crystal will be stabilized by minimizing the enthalpy term $\Delta_{tr} H$, which is determined by the interaction of the building blocks. Interactive forces might either be van der Waals or electrostatic forces. In molecular crystals, hydrogen bonding also plays an important role.

The van der Waals forces do have a relatively short-range order, a typical potential is given by $\Phi = (A/r^{12}) - (B/r^6)$, where $r$ is the distance between the interaction bodies. The potential is shown in Figure 2.1. The interaction potential of electrostatic forces decreases via $\Phi = C/r$.

$$\Delta_{tr} G = \Delta_{tr} H - T \Delta_{tr} S.$$  (2.1)
Due to the rapid decrease of the potential with distance, the nearest-neighbor interactions determine the energetics of the arrangement. Consequently, only well-defined symmetries in the arrangement of the building blocks of a crystal are allowed. This is visualized for a two-dimensional lattice by packing units with different symmetries (Figure 2.2). In part (a), objects with a two-, four-, and sixfold symmetry are packed; in part (b), the units have a five- and sixfold symmetry. The former set of objects allows packing, maximizing the pair interaction of building blocks, while the latter ones lead to suboptimal packing that is subsequently not found in crystals.

The considerations can be applied to the three-dimensional lattice. The packing of spheres in a plane is optimal for a hexagonal arrangement, as shown in Figure 2.3.

![Figure 2.1 Trend of the pair interaction potential of van der Waals forces. Note that the minimum in the pair interaction at $r_{\text{min}}$ is slightly different from the equilibrium distance in a crystal. It is apparent that the interaction is mainly determined by the first nearest neighbors.](image)

**Figure 2.2** Construction of a 2D lattice by packing units with different symmetries. In part (a), objects with a two-, four-, and sixfold symmetry are packed; in part (b), the units have a five- and sixfold symmetry. While the former set of objects maximizes the interaction between building blocks, the latter ones can only be arranged in a suboptimal packing.
Between three building blocks, a concave cavity is formed. In successive layers, the building blocks are also hexagonally arranged. The building blocks of the second layer reside in the cavities formed between the blocks of the first layer. For the packing of the third layer, two possibilities exist. This layer can reside in a different cavity, as shown in Figure 2.3. This leads to the cubic closest-packed lattice, which is a face centred lattice as will be shown later. Alternatively, the layer can be arranged like the first, leading to the hexagonally closest packing. The space filling in both cases is 74%.

In the following, only the face-centered cubic lattice (fcc) will be discussed. For this lattice, a ball-and-stick model is shown in Figure 2.4. The bottom view shows the stacking arrangement in the two different cavities, while the side view shows the ABCABC . . . stacking. Some building blocks have been color coded to indicate the unit cell to be discussed in Section 2.1.2.

2.1.2
Unit Cell

The arrangement of the building blocks in the lattice can be reduced to the smallest unit, the unit cell, from which the lattice can be built by simple displacements in

![Figure 2.3](image3.png)

*Figure 2.3* Optimized packing of spheres in (a) in one dimension, followed by the addition of further layers of hexagonally arranged building blocks (b and c). Here, only the case of the cubic closest packing is shown.

![Figure 2.4](image4.png)

*Figure 2.4* Lattice model for the closest packing of spheres. The bottom view in (a) can be compared with the packing shown in Figure 2.3. Part (b) shows that this packing leads to the ABCABC . . . stacking.
three dimensions. Figure 2.5 shows such a unit cell and the construction of the lattice by adding successive cells. The unit cell has the dimensions $a$, $b$, and $c$. The vectors of the unit cell are orthogonal, but not necessarily perpendicular; $\alpha$ is the angle between the $y$- and $z$-axes, $\beta$ is the angle between the $x$- and $z$-axes; and $\gamma$ is the angle between the $x$- and $y$-axes.

As described for a two-dimensional lattice (Figure 2.2), only certain symmetry operations are allowed to build the crystal lattice. These are the seven crystal systems listed in Figure 2.6. For the cubic and monoclinic lattices, the unit cells are also shown.

In certain of the seven crystal systems, the unit cells can contain face- or body-centered building blocks. For the cubic lattice, the body- and face-centered unit cell is shown in Figure 2.7.

For the body-centered cubic lattice (bcc), the addition of a building block is equal to a linear displacement by half a lattice constant in the three lattice directions. For building blocks that do not have a rotational symmetry, an additional rotation of the building blocks can occur; one of the most prominent being a rotation by $180^\circ$. This combined displacement and rotation by $180^\circ$ appears like the movement of a screw.

<table>
<thead>
<tr>
<th>Crystal System</th>
<th>$a - b - c$</th>
<th>$\alpha - \beta - \gamma$ or $90^\circ$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cubic</td>
<td>$a - b - c$</td>
<td>$\alpha - \beta - \gamma - 90^\circ$</td>
</tr>
<tr>
<td>Tetragonal</td>
<td>$a - b - c$</td>
<td>$\alpha - \beta - \gamma - 90^\circ$</td>
</tr>
<tr>
<td>Monoclinic</td>
<td>$a - b - c$</td>
<td>$\alpha - \gamma - 90^\circ, \beta - 90^\circ$</td>
</tr>
<tr>
<td>Triclinic</td>
<td>$a - b - c$</td>
<td>$\alpha - \beta - \gamma - 90^\circ$</td>
</tr>
<tr>
<td>Orthorhombic</td>
<td>$a - b - c$</td>
<td>$\alpha - \beta - \gamma - 90^\circ$</td>
</tr>
<tr>
<td>Trigonal</td>
<td>$a - b - c$</td>
<td>$\alpha - \beta - \gamma - 90^\circ$</td>
</tr>
<tr>
<td>Hexagonal</td>
<td>$a - b - c$</td>
<td>$\alpha - \beta - 90^\circ, \gamma - 120^\circ$</td>
</tr>
</tbody>
</table>

Figure 2.6  Relation of the lattice constants and angles for the seven crystal systems that are allowed. The simple cubic and monoclinic lattices are drawn.
The lattice of closely packed spheres (Figure 2.3) can be reduced to a cubic unit cell with face-centered building blocks, as shown in Figure 2.8.

2.1.3 Miller Indices to Describe Crystal Faces

The well-defined flat faces limiting a crystal are described by Miller indices. They are denoted $hkl$ and are independent of the size of the crystal. Using the three axes of the unit cell, a face will intersect these axes at certain distances, for example, for the $y$-axis at $2b$ (Figure 2.9). By referring the intersection to the length of the unit cell in this direction, one arrives at certain multiples for the intersection, that is, $n_y = y / b$. The Miller indices $hkl$ are defined as the reciprocal of the three intersections (Equation 2.2). It is required that $hkl$ are integers:

$$h : k : l = \frac{a}{x} : \frac{b}{y} : \frac{c}{z} = \frac{1}{n_x} : \frac{1}{n_y} : \frac{1}{n_z}.$$

Figure 2.7 Cubic unit cell with $a = b = c$ and $\alpha = \beta = \gamma = 90^\circ$. The simple cubic cell (a) and the body-centered (b) and face-centered (c) cubic unit cells are to be distinguished.

Figure 2.8 Comparison of the lattice model of closest-packed spheres with the ABCAB . . . stacking with the fcc lattice.

The lattice of closely packed spheres (Figure 2.3) can be reduced to a cubic unit cell with face-centered building blocks, as shown in Figure 2.8.

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$$h : k : l = \frac{a}{x} : \frac{b}{y} : \frac{c}{z} = \frac{1}{n_x} : \frac{1}{n_y} : \frac{1}{n_z}.$$

The calculation of the indices is shown in Figure 2.9 for a face at two different growth stages, the small dark face and the larger gray face. Both indices are the same.
The indices of the three lowest indexed faces of a cubic lattice are shown in Figure 2.10. It should be noted that in a cubic system, all six faces of the cube are identical, so the indices (001), (010), and (001) describe the same faces and can be used arbitrarily. By definition, \((hkl)\) describe a certain face, while \(\{hkl\}\) describe symmetrically equivalent faces.

2.1.4
Lattice Defects

The perfect lattice just described will not be found for real crystals, not even for crystals grown with extreme care. Instead, the crystals will contain a variety of lattice defects with different density. These defects determine the properties of the crystals such as mechanical strength or electric conductivity. Lattice defects also play an
important role in the growth of the crystals, namely, the screw dislocation (see Section 2.3.3).

Lattice defects are characterized by their dimensionality $D$ with which they extend into the lattice. This will be explained by often encountered defects (Table 2.1).

Figure 2.11 shows a two-dimensional lattice with two different defects, a vacancy and an interstitial atom. Both defects are confined to a point and do not extend into the lattice, so their dimensionality is $D = 0$.

Screw dislocations are one example for line defects and can be generated by a shearing of the crystal (Figure 2.12). This defect extends in one dimension along the line shown, so that $D = 1$.

Twinning is the most prominent example of faults with $D = 2$. The fault extends through an entire plane in the crystal (Figure 2.13). For a fcc lattice, twinning can occur by stacking faults; the order of ABCABC . . . is reversed at a certain point to ABCBAC . . . . For the outer shape of the crystal, twinning will appear as an inflection, or forming of a mirror image, a twin. Figure 2.13 also shows a twin of a silver halide crystal. The twin plane is clearly seen.

Finally, volume defects $D = 3$ can be formed by the inclusion of mother liquor (Figure 2.14). It is interesting to note that the liquid inclusions can be confined by well-expressed low-indexed (negative) faces. Liquid inclusions, for example, occur under high growth rates, for example, for precipitations.

**Table 2.1** Lattice defects ordered by their dimensionality $D$.

<table>
<thead>
<tr>
<th>Defect</th>
<th>$D$</th>
<th>Example</th>
</tr>
</thead>
<tbody>
<tr>
<td>Point</td>
<td>0</td>
<td>Vacancy, interstitial atom</td>
</tr>
<tr>
<td>Line</td>
<td>1</td>
<td>Step dislocation, screw dislocation</td>
</tr>
<tr>
<td>Surface</td>
<td>2</td>
<td>Twin, small-angle grain/tilt boundary</td>
</tr>
<tr>
<td>Volume</td>
<td>3</td>
<td>Inclusion</td>
</tr>
</tbody>
</table>

Figure 2.11 Vacancy and interstitial atoms in a two-dimensional lattice. These lattice defects are confined to a point; thus, $D = 0$. 
2.1.5 Equilibrium, Growth, and Dissolution Form of Crystals

The discussion of crystal shapes has to distinguish between the equilibrium form, which is governed by thermodynamics, and the growth and dissolution form, which is governed by the kinetics of the growth process.