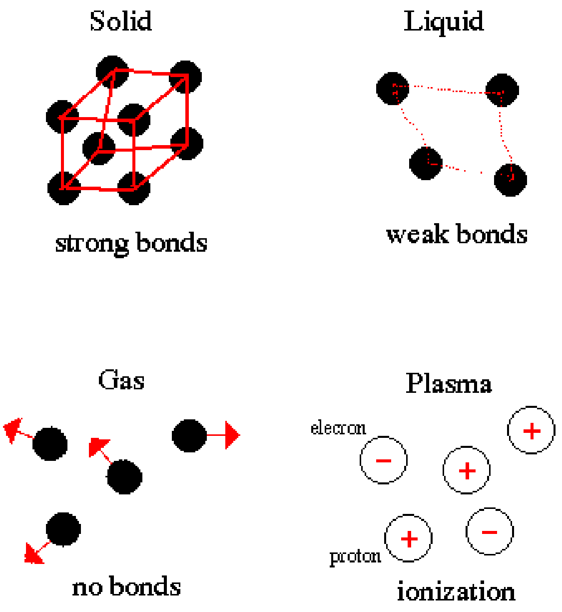
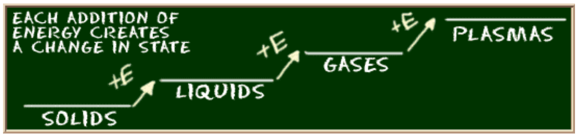
Crystallization and energy relations between states of matter

This text is meant as background information about how undercooling happens, and how the latent heat of crystallization has to be released and taken away somehow (conservation of energy; First Law of Thermodynamics), in order for i.e. a solid to crystallize from a fluid.

There are basically 4 states of matter: solid, liquid, gas, and plasma. We will here consider the three first of these states of matter.

Imagine a gas expanding into a vacuum. The gas molecules are free to move, because there are only very weak binding forces between gas molecules. The total energy of the gas will be distributed over the whole volume which the gas is filling. This form of energy is called **entropy** (denoted S), and is a measure for the degree of disorder in a system. Gas will therefore have a very high entropy, compared with a liquid, which has stronger binding forces (and better order) between its molecules. A solid will have even lower entropy (i.e. a very low degree of disorder), because the solid is made up of very well arranged molecules with very strong internal binding forces.





Therefore:

S (for gas) $>>$ S (for liquid) $>$ S (for solid)

The internal energy for all substances is denoted U.
A change in work is defined as: $\Delta W = P\,\Delta V$; where P is pressure and ΔV is change in volume.
A change in heat transfer is defined as $\Delta Q = T\,\Delta S$; where T is absolute temperature (Kelvin) and ΔS is change in entropy.
The relation between internal energy and entropy for a closed system is:
$\Delta U = \Delta Q - \Delta W = T\,\Delta S - P\,\Delta V$
For a multi-component system we may write:
$U = TS - PV + \sum \mu_i$, where μ is the chemical potential of the different components.

The chemical potential, μ, is the partial molar internal energy, and is identical to the molar Gibb's free energy, denoted G. The chemical potential is a critical parameter for the description of the proximity to equilibrium for multi-component systems.

At equilibrium for constant P and T:
$\Delta G = \Delta U - T\,\Delta S + P\,\Delta V = \Delta Q - T\,\Delta S = \Delta H - T\,\Delta S$
where ΔH is enthalpy = ΔQ (at constant pressure).

For a reversible chemical reaction at its equilibrium, $\Delta G = 0$.
A large negative ΔG means that the chemical reaction (as written) tends to go towards completion. A positive ΔG means that the reaction tends to go the opposite way.

If a solid (s) is dissolved in a liquid (l), $\Delta G = 0$ when the liquid is saturated. A large negative ΔG means undersaturation, i.e. more solid can be dissolved in the liquid. A positive ΔG for this system means oversaturation, that solids may start to crystallize.

The following diagram shows the relations for temperature (T) vs. chemical potential (μ) for the gas, liquid, and solid states of matter at constant pressure.

The stable state is the state which has the lowest value for the chemical potential at a given temperature.

If a fluid is present at a temperature under Tm (the melting point), i.e. at the point a, we see that the liquid's chemical potential μ_a is higher than the solid's (point b) chemical potential μ_b at this temperature. We say that the liquid then must be **undercooled**; the liquid is **metastable**. The liquid will now have a good chance of freezing spontaneously at this temperature, because such a change in the state of matter will lower the free energy (G) for the system. [And any system always tries to obtain the lowest possible free energy]. *But for the liquid to crystallize, the liquid has to get rid of the energy difference between the liquid and solid states of matter* ($\Delta\mu = \mu_a - \mu_b$), called ***the latent heat of crystallization***. This energy difference may in this isolated case of constant pressure be looked upon as the corresponding **enthalpy** (heat transfer), denoted H in the thermodynamics. (Here H = Q).

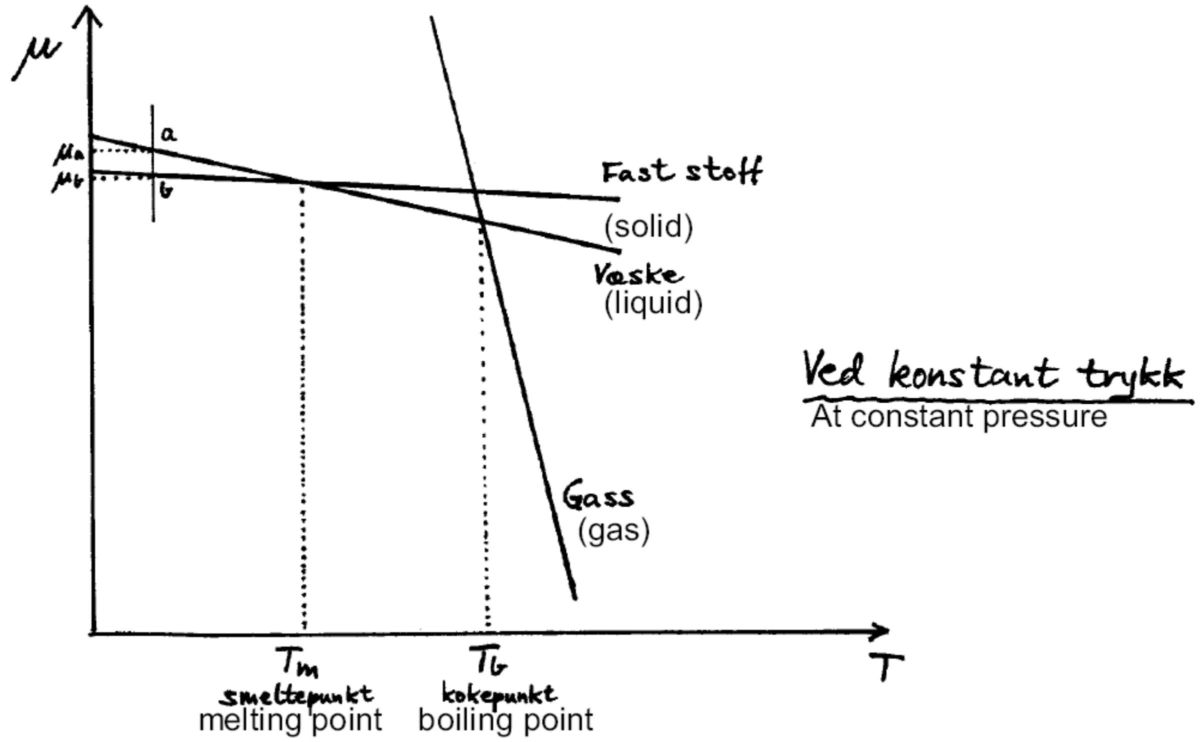


Diagram showing the temperature (T) -- chemical potential (μ) relations for gas, liquid, and solid at constant pressure.

CRYSTALLIZATION

Crystals are solids made up by atoms, ions or molecules in a regular pattern or system. The packing of the system is given from the way the atoms are packed, given by the internal size relations between the atoms. Elsewhere you will find descriptions about the rules that exist in nature for what symmetry and which forms are established from given size relations between the atoms (check textbooks in crystallography, mineralogy, or solid state chemistry or physics). The construction of atoms within crystals is mimicked in the crystals' forms of surface faces, edges, and corners.

The fundamental property for the atoms' construction of the crystals is *symmetry*. We may describe symmetry planes, symmetry axes, and symmetry centers. In 1830 the German crystallographer Hessel calculated that there could exist 32 different symmetry classes for crystals, each class characterized by a given combination of symmetry elements. These 32 classes may again be defined as belonging to 7 crystal systems: Cubic (isometric), tetragonal, hexagonal, trigonal, orthorhombic, monoclinic, and triclinic. Non-crystalline solids are called amorphous.

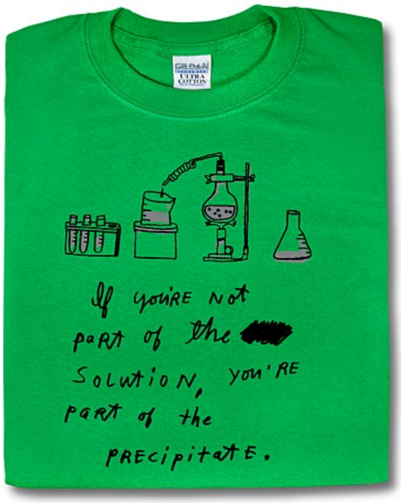
Crystals are described from what forms (faces) they have. The forms may be referred to from a coordinate system with help of so-called ”Miller indices”. The forms may also be visually expressed by plotting in a stereographic net. The crystals can also be described from reflections from an X-ray beam, so-called X-ray diffraction (XRD).

One complication is that crystals may form twins, i.e. intergrowth of crystals, according to defined crystal twin laws.

For a crystal to be formed, two processes must happen:
(1) Nucleation
(2) Crystal growth

Nucleation is that thee atoms, which will form a crystal, must come together in sufficient amounts and in correct proportions, to build thee first, atomic structure with a correct composition.

Only after this nucleation, will it be possible for the next atoms to make a new layer outside the first nucleus, to facilitate the growth of the crystal.



Crystals may form mainly in 4 settings:
(1) From liquid (precipitation from an aqueous solution)
(2) From melt (solidification)
(3) From gas (deposition)
(4) From another crystal
    (transformation, replacement, metamorphism)

To crystallize from a liquid, the liquid has to be at least saturated with respect to the substance which will crystallize. It is better if the liquid is *supersaturated*, i.e. it has more of the substance in the solution than is necessary to start the crystallization.

To crystallize from a melt, the melt has to have a temperature at least as high as the melting point of the substance to crystallize. It is better if the melt is *undercooled*, i.e. it has a lower temperature than necessary to start the crystallization.

To crystallize from a gas, the partial pressures of the gas species participating in the crystallization must be large; the larger, the better.

To transform a crystal, a change in temperature, pressure, and/or relevant species dissolved in the fluid will play significant roles.

Why do we often find many, small crystals, like in a basaltic lava?
Or other places we find few, but large crystals, like in a pegmatite?
What are the conditions to form such different occurrences?

At large degree of undercooling in a melt, and at large degree of oversaturation in a liquid, the nucleation speed is large, while the speed of crystallization is low. The result is that there will be created many nuclei, but that their crystal growth is slow: *we get many and small crystals.*

One example is when we're driving in a car in undercooled rain (temperature well under zero degrees C). When the undercooled rain hits the windshield window, there will instantly be formed numerous nuclei, but without any particular crystal growth. The result is what we call "steel ice", which is extraordinary hard because of all the small ice crystals. A geologic example is a lava, made up of many very small crystals, formed from a melt which quite suddenly solidified at a temperature far under its solidus (melting point).

At very small degree of undercooling in a melt, and at very small degree of oversaturation in a liquid, the nucleation speed will be low, while the speed of crystal growth will be high. The result is that few nuclei are formed, but that they will grow quite fast: *we get few and large crystals.*

One example is when there is water on the car hood, and the temperature decreases to right under zero degrees C. Now only a few nuclei will form, while at the same time the crystals grow fast. The result is few but large and long ice crystals on the hood of my car; see the photo to the right.

This particular crystal growth resembles trees, and we call such tree-like crystal growth for *dendritic* (dendro from Greek for tree). A geologic example is pegmatites, rocks where we find only some few crystals, each which may reach the size of houses.

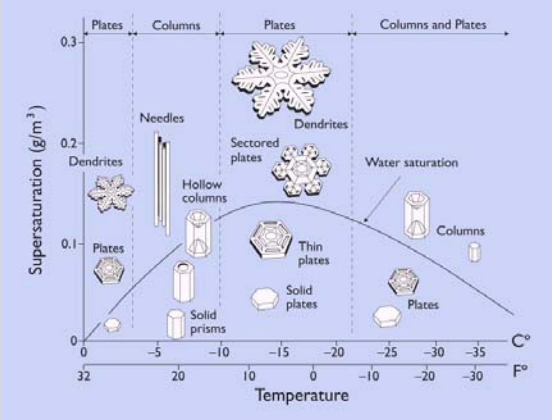
The major reason for all described above, is that solids have lower internal energy than liquids, which again has much lower internal energy than gases. For solids to melt, there must be a supply of energy, i.e. the temperature has to be increased.

If you want to melt an ice cube in your hand, you will feel that your hand gets cold. The reason is that the ice must take heat from your hand, in order for the ice to melt to water. We say that solids have a latent heat of crystallization. For ice this latent heat of crystallization is ca. 80 calories per gram. If you want to vaporize water in a pot, you must heat the water for a long time on a hot plate, in order to supply enough energy for the water to change its state to gas (water vapor).

Similarly, when you want to form a solid (crystals) from gas, melt or liquid. We will go from a high energy state of matter (gas, melt or liquid) to the low energy state of matter: solid. Now we have to get rid of the latent heat of crystallization, in order to form crystals in the solid. Therefore we get the phenomena undercooling and super saturation before crystals can form, because the atoms "work hard" to get rid of the latent heat of crystallization before crystals can form. This heat has to be released (and taken up by something else) before crystallization can happen.

Solids melt at their respective melting points. However, this point may be different if the substance contains impurities or solutions in the solid state (”solid solution”). Some substances contain substances which degas (i.e. water, carbon dioxide, sulfur compounds) at a lower temperature than the actual melting of the remaining parts of the solid. We have decomposition during heating of the compound before it melts.

Snow crystals are made according to the hexagonal crystal system. Fast growth during crystallization makes the snow crystals take many different forms, all as varieties within the hexagonal crystal system. Many books have been written about this. And check the Internet at www.its.caltech.edu/~atomic/snowcrystals/. One has found that the degree of undercooling is contributing for what crystal forms of snow and ice will form: prisms, plates, dendrites, sectored plates, hollow columns, needles, etc.; see the ice morphology diagram to the right.



We humans often copy the geometry of nature. See for example the frequently occurring snow crystal imitations in Norwegian knitwear! Although it is difficult to knit the hexagonal pattern, so the snow crystals often end up with 8 rather than 6 outgrowths (see picture). On the other side the real hexagonal crystals represent nature's efforts of attaining an equilibrium form characterized by minimum free energy. The hexagonal pencil shape is one such example, mimicking the ice crystals and quartz crystals, but also the bees' cells, drying fractures in soil, and columnar jointing in cooling lavas. Not just for mimicking, but the structure is one of optimum stability with minimum free energy.

Heat sinks for electronics mimic the dendritic crystal growth found in the snow crystals. Both appearances are maximized for heat transfer; cooling for the electronics; and release of the latent heat of crystallization for the snow crystals.

It is said that no snow crystals are alike. Mutual different crystal shapes of the same substance are made because fast crystal growth gives varying crystal forms. The degree of undercooling is found to give preferred crystal forms.

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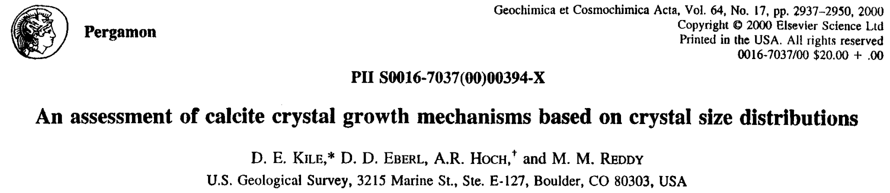
APPENDIX – Example of crystallization of calcite (trigonal calcium carbonate).



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An assessment of calcite crystal growth mechanisms based on crystal size distributions

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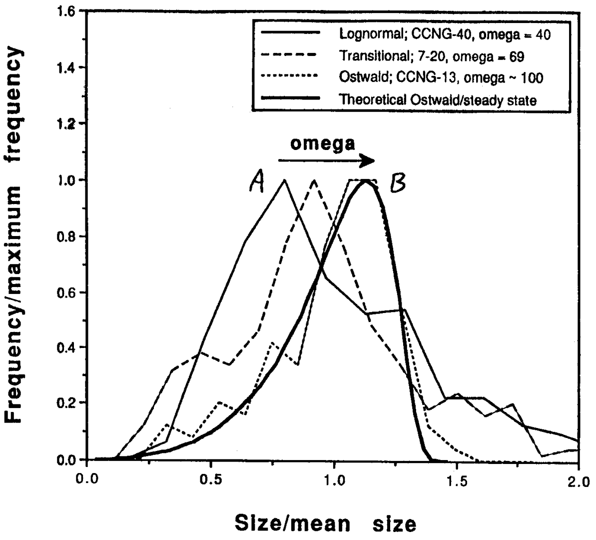

Fig. 6. Reduced plot of lognormal, transitional, and Ostwald CSDs showing a progressive shift with increasing Ω toward the theoretical Ostwald steady-state curve.

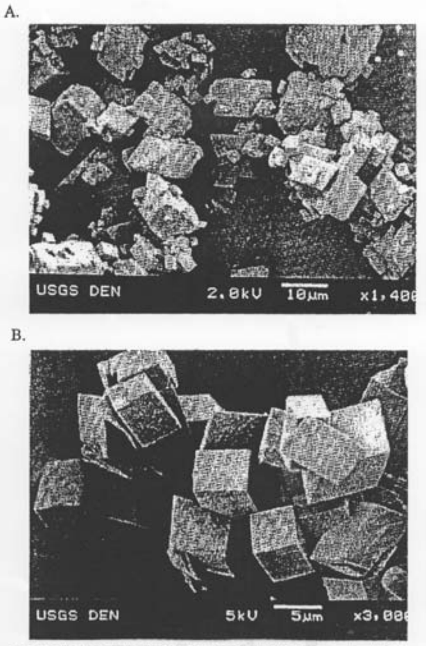

Fig. 8. (A) SEM photo of synthetic calcite (Baker) illustrating a lognormal CSD with large size variance ($\beta^2 = 0.52$). (B) SEM photo of synthetic calcite (CCNG-19) illustrating an Ostwald CSD with a small size variance ($\beta^2 = 0.09$).

When the degree of supersaturation (omega) increases, the crystals will obtain the critical size necessary for the crystals to grow. Photo A shows crystals of many different sizes, while Photo B shows that the critical size for crystal growth is reached by increasing degree of supersaturation in the liquid.

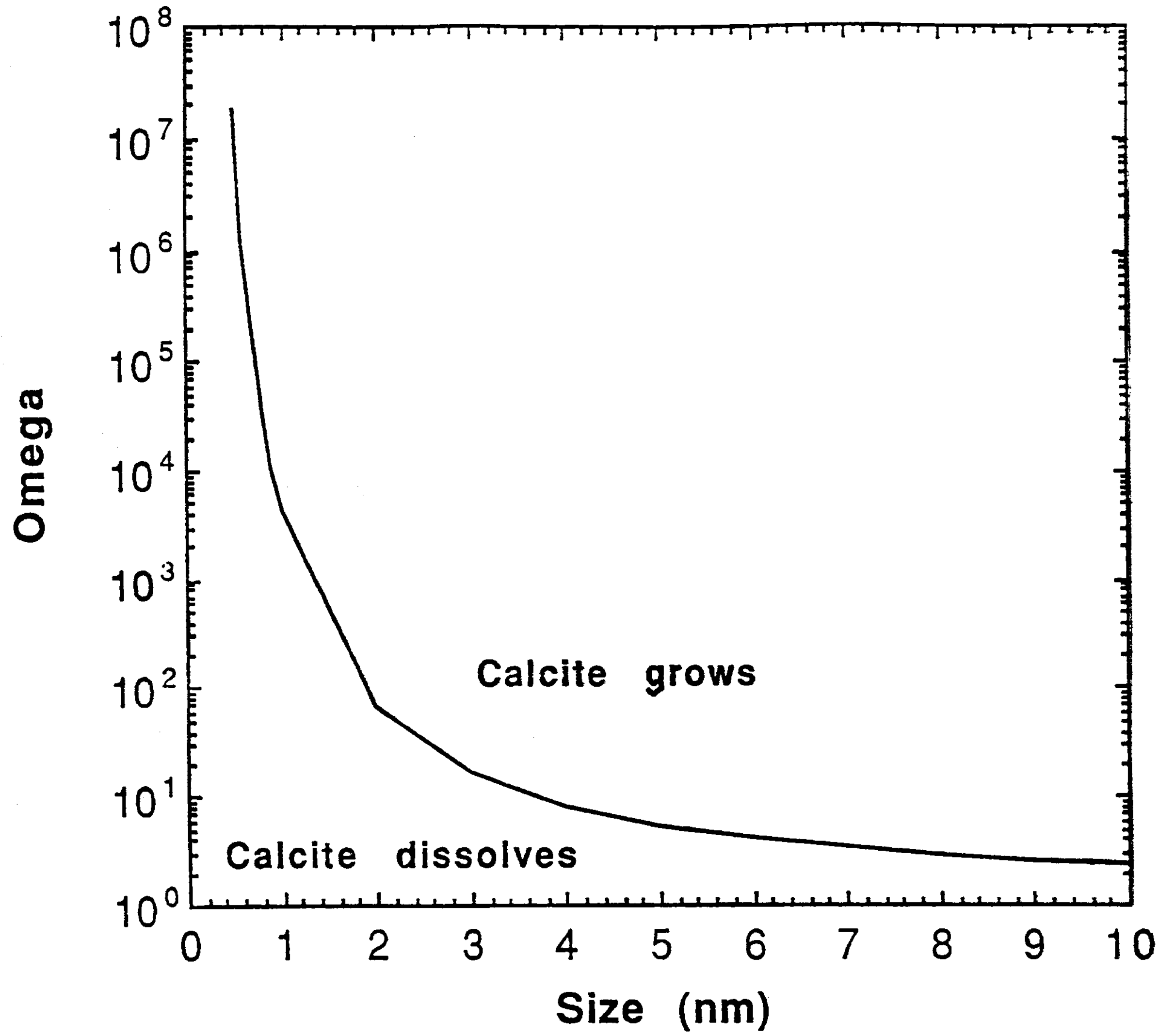

Fig. 10. Solubility of calcite vs. crystal size. The Ω axis is presented with respect to an infinitely large crystal, and the calculation for the curve includes the effects of surface-free energy on the calculation. The value for the surface-free energy for $CaCO_3$ used in the calculation is from Stumm (1992), and values for other free energies (see Eqn. 3) are from Garrels and Christ (1965).

Calcite crystal size as a function of degree of supersaturation (omega). The diagram shows that the crystals must reach a certain critical size (the curve) for the crystals to grow. Below the critical size the crystals will dissolve back into the liquid.