

Chapter 1

CRYSTAL–AMBIENT PHASE EQUILIBRIUM

1.1. Equilibrium of Infinitely Large Phases

The equilibrium between two infinitely large phases α and β is determined by the equality of their chemical potentials μ_α and μ_β . The latter represent the derivatives of the Gibbs free energies with respect to the number of particles in the system at constant pressure P and temperature T , $\mu = (\partial G/\partial n)_{P,T}$, or in other words, the work which has to be done in order to change the number of particles in the phase by unity. In the simplest case of a single component system we have

$$\mu_\alpha(P, T) = \mu_\beta(P, T). \quad (1.1)$$

The above equation means that the pressures and the temperatures in both phases are equal. The requirement $P_\alpha = P_\beta = P$ is equivalent to the condition that the boundary dividing both phases is flat or, in other words, that the phases are infinitely large. This question will be clarified in the next section where the equilibrium of phases with finite sizes will be considered.

Let us assume now that the pressure and the temperature are infinitesimally changed in such a way that the two phases remain in equilibrium, i.e.

$$\mu_\alpha + d\mu_\alpha = \mu_\beta + d\mu_\beta. \quad (1.2)$$

It follows from (1.1) and (1.2) that

$$d\mu_\alpha(P, T) = d\mu_\beta(P, T). \quad (1.3)$$

Recalling the properties of the Gibbs free energy ($dG = VdP - SdT$) we can rewrite (1.3) in the form

$$-s_\alpha dT + v_\alpha dP = -s_\beta dT + v_\beta dP, \quad (1.4)$$

where s_α and s_β are the molar entropies, and v_α and v_β are the molar volumes of the two phases in equilibrium with each other.

Rearranging (1.4) gives the well-known equation of *Clapeyron*

$$\frac{dP}{dT} = \frac{\Delta s}{\Delta v} = \frac{\Delta h}{T\Delta v}, \quad (1.5)$$

where $\Delta s = s_\alpha - s_\beta$, $\Delta v = v_\alpha - v_\beta$, and $\Delta h = h_\alpha - h_\beta$ is the enthalpy of the corresponding phase transition.

Let us consider first the case when the phase β is one of the condensed phases, say, the liquid phase and the phase α is the vapor phase. Then the enthalpy change Δh will be the enthalpy of evaporation $\Delta h_{\text{ev}} = h_v - h_l$ and v_l and v_v will be the molar volumes of the liquid and the vapor phases, respectively. The enthalpy of evaporation is always positive and the molar volume of the vapor v_v is usually much greater than that of liquid v_l . In other words the slope dP/dT will be positive. We can neglect the molar volume of the crystal with respect to that of the vapor and to assume that the vapor behaves as an ideal gas, i.e. $P = RT/v_v$. Then Eq. (1.5) attains the form

$$\frac{d \ln P}{dT} = \frac{\Delta h_{\text{ev}}}{RT^2}, \quad (1.6)$$

which is well-known as the equation of *Clapeyron–Clausius*. Replacing Δh_{ev} with the enthalpy of sublimation Δh_{sub} we obtain the equation which describes the crystal–vapor equilibrium.

Assuming Δh_{ev} (or Δh_{sub}) does not depend on the temperature, Eq. (1.6) can be easily integrated to

$$\frac{P}{P_0} = \exp \left[-\frac{\Delta h_{\text{ev}}}{R} \left(\frac{1}{T} - \frac{1}{T_0} \right) \right], \quad (1.7)$$

where P_0 is the equilibrium pressure at some temperature T_0 .

In the case of the crystal–melt equilibrium the enthalpy Δh is equal to the enthalpy of melting Δh_m which is always positive and the equilibrium temperature is the melting point T_m .

As a result of the above considerations we can construct the phase diagram of our single component system in co-ordinates P and T (Fig. 1.1). The enthalpy of sublimation of crystals Δh_{sub} is greater than the enthalpy of evaporation Δh_{ev} of liquid and hence the slope of the curve in the phase diagram giving the crystal–vapor equilibrium is greater than the slope of the curve of the liquid–vapor equilibrium. On the other hand the molar volume v_l of the liquid phase is usually greater than that of the crystal phase v_c (with some very rare but important exceptions, for example, in the cases of water and bismuth), but the difference is small so that the slope dP/dT is great, in fact, much greater than that of the other two cases and is also positive with the exception of the cases mentioned above. Thus the $P - T$ space is divided into three parts. The crystal phase is

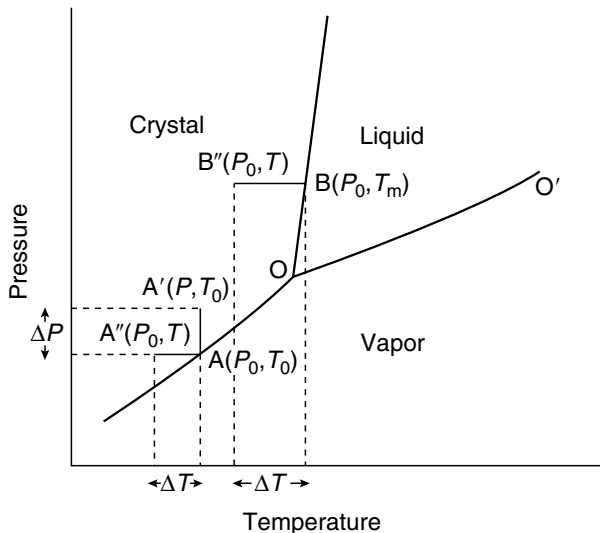


Fig. 1.1. Phase diagram of a single component system in $P - T$ coordinates. O and O' denote the triple point and the critical point, respectively. The vapor phase becomes supersaturated or undercooled with respect to the crystalline phase if one moves along the line AA' or AA'' . The liquid phase becomes undercooled with respect to the crystalline phase if one moves along the line BB'' . ΔP and ΔT are the supersaturation and undercooling.

thermodynamically favored at high pressures and low temperatures. The liquid phase is stable at high temperatures and high pressures and the vapor phase is stable at high temperatures and low pressures. Two phases are in equilibrium along the lines and the three phases are simultaneously in equilibrium in the so-called triple point 0. The liquid–vapor line terminates at the so-called critical point 0' beyond which the liquid phase does not exist any more because the surface energy of the liquid becomes equal to zero and the phase boundary between both phases disappears.

1.2. Supersaturation

When moving along the dividing lines the corresponding phases are in equilibrium, i.e. Eq. (1.1) is strictly fulfilled. If the pressure or the temperature is changed in such a way that we deviate from the lines of the phase equilibrium one or another phase becomes stable. This means that its chemical potential becomes smaller than the chemical potentials of the phases in the other regions. Any change of the temperature and/or pressure which leads to change of the region of stability leads in turn to transition from one phase to another. Thus the decrease of the temperature or the increase of the pressure leads to crystallization or liquefaction of the vapor, the decrease of the temperature leads to solidification of the liquids. Figure 1.2 shows the variation of the chemical potentials of the crystal and vapor phases with the pressure at a constant temperature. The chemical potential of the vapor increases with the pressure following the logarithmic law which corresponds to a shift along the line AA' in Fig. 1.1. At the same time the chemical potential of the crystal phase is a linear function of the pressure its slope being given by the molecular volume v_c . Both curves intersect at the equilibrium pressure P_0 . At pressures smaller than P_0 the chemical potential of the crystal is greater than that of the vapor and the crystal should sublime. In the opposite case $P > P_0$ the vapor should crystallize. The difference of the chemical potentials, which is a function of the pressure, represents the thermodynamic driving force for crystallization to occur.

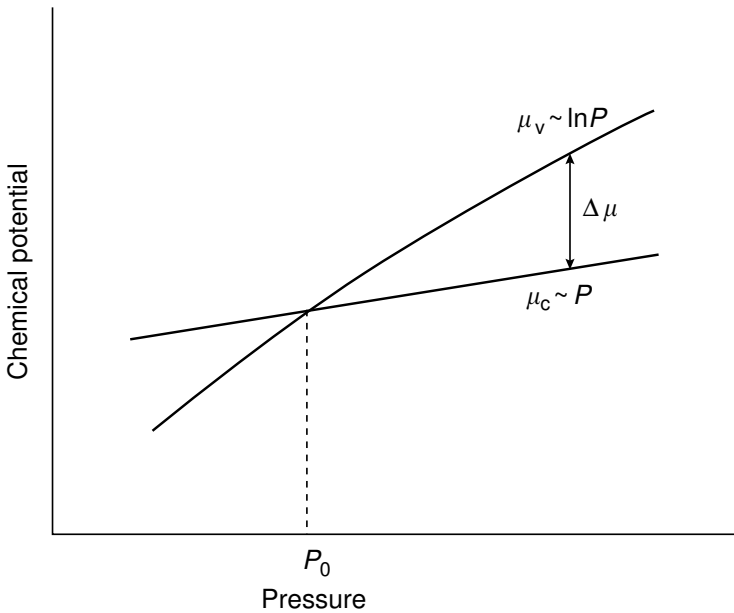


Fig. 1.2. Dependence of the chemical potentials of the vapor, μ_v , and the crystal, μ_c on the pressure when one moves along the line AA' in Fig. 1.1. P_0 denotes the equilibrium pressure.

It is called a *supersaturation* and is defined as the *difference of the chemical potentials $\Delta\mu$ of the infinitely large mother and new phases* at the particular value of the temperature. In other words we have (Fig. 1.2)

$$\Delta\mu = \mu_v(P) - \mu_c(P). \quad (1.8)$$

As written above the expression for the supersaturation is incorrect. The correct way of writing it is just the opposite. The supersaturation should be equal to the chemical potential of the new phase relative to the chemical potential of the mother phase, i.e. $\Delta\mu = \mu_c(P) - \mu_v(P)$. However, we have to remember that the chemical potentials are always negative quantities and smaller chemical potential means more negative chemical potential. This is clearly seen in Eq. (1.58) where the chemical potential of the infinitely large crystal (at 0 K) is equal to the energy required to evaporate an atom

(which is a positive quantity) taken with a negative sign. Then the difference $\mu_c - \mu_v$ will be negative. To avoid confusion with signs we usually define $\Delta\mu$ as in Eq. (1.8). That is why when writing the expression for the work for nucleus formation (Eq. (2.3)) we put a minus sign before the term that includes the supersaturation.

Bearing in mind Eq. (1.1), or $\mu_v(P_0) = \mu_c(P_0)$, we can rewrite Eq. (1.8) in the form

$$\Delta\mu = [\mu_v(P) - \mu_v(P_0)] - [\mu_c(P) - \mu_c(P_0)].$$

For small deviations from equilibrium the above equation turns into

$$\Delta\mu \cong \int_{P_0}^P \frac{\partial\mu_v}{\partial P} dP - \int_{P_0}^P \frac{\partial\mu_c}{\partial P} dP = \int_{P_0}^P (v_v - v_c) dP \cong \int_{P_0}^P v_v dP.$$

Treating the vapor as an ideal gas ($v_v = kT/P$) we obtain upon integration

$$\Delta\mu = kT \ln \frac{P}{P_0}, \quad (1.9)$$

where P_0 is the equilibrium vapor pressure of the infinitely large crystal phase at the given temperature.

Without going into details we can write an expression for the supersaturation in the case of crystallization from solution, when the solution is treated as ideal, in the form

$$\Delta\mu = kT \ln \frac{C}{C_0}, \quad (1.10)$$

where C and C_0 are, respectively, the real and the equilibrium concentrations of the solute. In fact a more rigorous treatment requires the consideration of multicomponent systems. For more details see Chernov [1980].

Figure 1.3 shows the variation of the chemical potentials of the crystal and liquid phases with the temperature at a constant pressure (the line BB'' in Fig. 1.1). The supersaturation which in this case is frequently called *undercooling* is again defined as the difference of the chemical potentials of the infinitely large liquid and crystal phases,

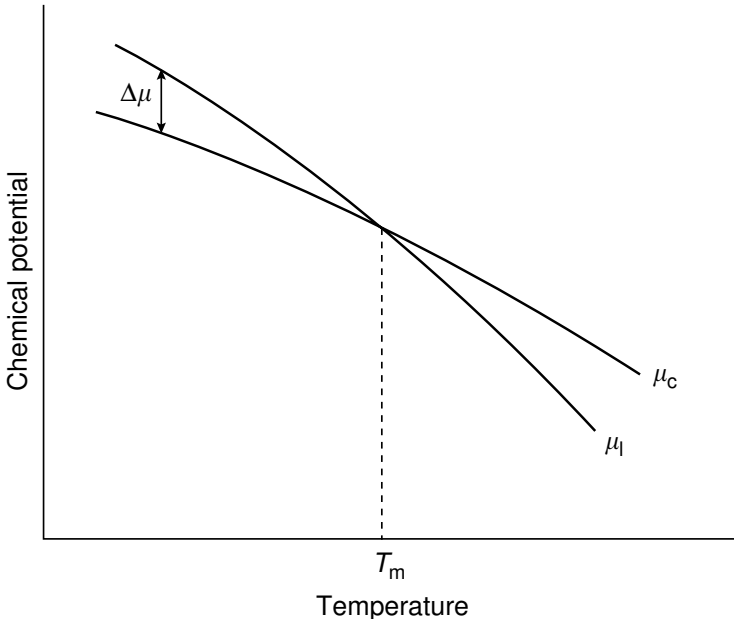


Fig. 1.3. Dependence of the chemical potentials of the liquid phase, μ_l , and the crystal phase, μ_c , on the temperature when one moves along the line BB'' in Fig. 1.1. The melting point is denoted by T_m .

μ_l and μ_c , respectively, at a given temperature

$$\Delta\mu = \mu_l(T) - \mu_c(T). \quad (1.11)$$

Following the same procedure as above we obtain

$$\begin{aligned} \Delta\mu &= [\mu_l(T) - \mu_l(T_m)] - [\mu_c(T) - \mu_c(T_m)] \\ &\cong \int_{T_m}^T \frac{\partial\mu_l}{\partial T} dT - \int_{T_m}^T \frac{\partial\mu_c}{\partial T} dT = \int_T^{T_m} \Delta s_m dT. \end{aligned}$$

Assuming the entropy of melting $\Delta s_m = s_l - s_c$ is independent of the temperature one obtains after integration

$$\Delta\mu = \Delta s_m (T_m - T) = \frac{\Delta h_m}{T_m} \Delta T. \quad (1.12)$$

Obviously, equation (1.12) is also applicable to the case of crystallization of undercooled vapor after the enthalpy of melting is replaced by the enthalpy of sublimation (the line AA'' in Fig. 1.1).

Finally, in the particular case of electrocrystallization of metals the supersaturation is given by

$$\Delta\mu = ze\eta, \quad (1.13)$$

where z denotes the valence of the neutralizing ions, $e = 1.60219 \times 10^{-19} \text{C}$ is the elementary electric charge and $\eta = E - E_0$ is the so-called *overvoltage or overpotential* given by the difference of the equilibrium potential E_0 of the deposited metal in the solution and the electrical potential E applied from outside [Kaischew 1946/1947].

Let us now compare the supersaturation for growth from vapor and the undercooling for growth from melt of such a “simple” crystal as Si. The Si vapor consists of Si, Si₂ and Si₃, but the concentration of the monomer is many orders of magnitude larger than that of polymer molecules and the latter can be neglected. The growth from vapor very often takes place at a temperature of about 600 K and the atom arrival rate \mathfrak{R} is usually of order of one monolayer (ML) per minute or approximately $1.1 \times 10^{13} \text{ cm}^{-2}\text{s}^{-1}$ [Voigtländer 2001]. The equilibrium vapor pressure of Si at 600 K is $P_e = 1.3 \times 10^{-32} \text{ atm}$ or $1.3 \times 10^{-27} \text{ N/m}^2$. The flux of atoms which arrive per second on unit area of 1 cm^2 is given by $\mathfrak{R}_e = P_e(2\pi mkT)^{-1/2}$ (see Eq. (2.56)) where $m \approx 4.66 \times 10^{-26} \text{ kg}$ is the mass of a single atom, $k = 1.38 \times 10^{-23} \text{ J/K}$ is the Boltzmann constant. Then $\mathfrak{R}_e \approx 6.5 \times 10^{-8} \text{ cm}^{-2}\text{s}^{-1}$ and $\Delta\mu = kT \ln(\mathfrak{R}/\mathfrak{R}_e) \approx 2.5 \text{ eV}$. Repeating the same calculations at higher temperatures (the equilibrium vapor pressure increases exponentially with temperature, see Eq. (1.58)) we find that $\Delta\mu = 1.2 \text{ eV}$ at 1000 K and becomes negative $\Delta\mu = -0.2 \text{ eV}$ at 1400 K. In other words, at about 1300 K the Si crystal begins to evaporate rather than to grow at the above atom arrival rate. We calculate now the undercooling in Si melt. With $\Delta s_m = 30 \text{ J/mol}$ [Hultgren *et al.* 1973] we find $\Delta\mu \approx 3 \text{ meV}$ ($\Delta T = 10 \text{ K}$). Comparing both estimates we reach the following very important conclusion. Under typical conditions (comparatively low temperatures in vapor growth and close to the melting point in growth from melts) the growth from vapor takes place very far from equilibrium compared with the growth from melt.

It was Max Volmer [1939] who introduced the term “Überschreitung” or “step across” for both the supersaturation

and the undercooling to denote the transition through the line of co-existence of the two phases. Thus, the difference of the chemical potentials of the infinitely large new and mother phases appears as a measure of deviation from the phase equilibrium and determines the rate of the transition from one phase to another.

1.3. Equilibrium of Finite Phases

In the previous section we considered the equilibrium of two phases in a single component system assuming that the phases are sufficiently (or infinitely) large or, in other words, the phase boundary between them is flat. This is not obviously the case at the beginning of the process of phase transition which is of interest to us. Thus, in the cases of transition from vapor to crystal, from vapor to liquid or from liquid to vapor phases, the process of formation of the new phase always goes through the formation of small crystallites, droplets or bubbles. In this section we will clarify two questions: (i) the mechanical equilibrium of small particles with their ambient phase or, in other words, the interrelation of the pressures in the two phases when the phase boundary is not flat, and (ii) the thermodynamic equilibrium of small particles or their equilibrium vapor pressure as a function of their size. In fact we will derive and interpret the equations of Laplace and Thomson–Gibbs.

1.3.1. Equation of Laplace

We consider a vessel with a constant volume V containing vapor with pressure P_v and a liquid droplet with a radius r and an inner pressure P_l both at one and the same constant temperature T . The condition for equilibrium is given by the minimization of the Helmholtz free energy of the system $F(V, T)$

$$dF = -P_v dV_v - P_l dV_l + \sigma dS = 0, \quad (1.14)$$

where V_v and V_l are the volumes of the vapor phase and the droplet, σ is the surface tension of the liquid and S is the droplet surface area. The value of the surface tension of the infinitely large liquid phase

is usually taken for σ . As $V = V_v + V_l = \text{const}$ and $dV_v = -dV_l$, Eq. (1.14) can be rewritten after rearrangement in the form

$$P_l - P_v = \sigma \frac{dS}{dV_l}.$$

Bearing in mind that $S = 4\pi r^2$ and $V_l = 4\pi r^3/3$,

$$\frac{dS}{dV_l} = \frac{d(4\pi r^2)}{d\left(\frac{4\pi r^3}{3}\right)} = \frac{2}{r},$$

and the above equation turns into

$$P_l - P_v = \frac{2\sigma}{r}, \quad (1.15)$$

which is known as the *Laplace* equation. The latter states that the pressure in a small droplet is always higher than the pressure of the surrounding vapor. The difference $2\sigma/r$ is called the *Laplace* or *capillary pressure* and is equal to zero when the phase boundary is flat ($r \rightarrow \infty$). Then $P_l = P_v = P_\infty$ as stated in Sec. 1.1. Here the notation P_∞ for the equilibrium pressure is used instead of P_0 to emphasize the fact that the dividing surface is flat, i.e. it has an infinite radius of curvature.

The physical meaning of Eq. (1.15) becomes more clear if we derive it from the balance of forces. The overall force exerted on the droplet from outside is a sum of the force $4\pi r^2 P_v$ exerted from the vapor phase and the force $8\pi r\sigma$ due to the surface tension. It is equal to the force due to the internal pressure $4\pi r^2 P_l$, i.e.

$$4\pi r^2 P_v + 8\pi r\sigma = 4\pi r^2 P_l,$$

and Eq. (1.15) results. Thus the Laplace pressure is clearly due to the surface tension of the small droplet.

In the case of arbitrary surface with principal radii of curvature r_1 and r_2 , Eq. (1.15) reads

$$P_l - P_v = \sigma \left(\frac{1}{r_1} + \frac{1}{r_2} \right). \quad (1.16)$$

Let us estimate as an example the pressure in a water droplet in a fog. The typical size of the droplets is about $1 \mu\text{m} = 1 \times 10^{-6} \text{ m}$. The surface tension of the water is $75 \text{ erg cm}^{-2} = 0.075 \text{ J m}^{-2}$. Then $2\sigma/r = 150,000 \text{ N m}^{-2} = 1.5 \text{ atm}$. If the outside pressure is 1 atm we obtain that the inner pressure is 2.5 times higher than the outer pressure.

1.3.2. Equation of Thomson–Gibbs

In order to solve the problem of the thermodynamic equilibrium we consider the same system as before at constant pressure P and temperature T . In this case the variation of the Gibbs free energy $G(P, T, n_v, n_l, S)$ of the system reads ($dP = dT = 0$)

$$\Delta G = \mu_v dn_v + \mu_l dn_l + \sigma dS = 0, \quad (1.17)$$

where n_v and n_l are the number of moles in the vapor and liquid phases, respectively.

When writing the expression for the Gibbs free energy we take for the chemical potential of the atoms in the small droplet the value which is valid for the bulk phase and compensate the difference between the bulk liquid and the small droplet by the surface energy σS . Besides, we again ascribe to the surface tension its bulk value. As the system is closed $n_v + n_l = \text{const}$ and $dn_v + dn_l = 0$. Solving (1.17) together with $dn_v = -dn_l$ gives

$$\mu_v - \mu_l = \sigma \frac{dS}{dn_l}.$$

With $n_l = 4\pi r^3/3v_l$ it turns into the famous equation of *Thomson–Gibbs*

$$\mu_v - \mu_l = \frac{2\sigma v_l}{r}. \quad (1.18)$$

Comparing Eqs. (1.15) and (1.18) it becomes immediately clear that the product $(P_l - P_v)V_l = n\Delta\mu$ is just equal to the work gained when a liquid droplet is formed from the unstable vapor phase or, in other words, when $n = V_l/v_l$ atoms or molecules are transferred from

the vapor phase with higher chemical potential to the liquid phase with lower chemical potential [Gibbs 1928].

As μ_l is the chemical potential of the bulk liquid phase the difference $\mu_v - \mu_l$ is just equal to the supersaturation $\Delta\mu$ (see Eq. (1.9)) and

$$P_r = P_\infty \exp\left(\frac{2\sigma v_l}{rkT}\right). \quad (1.19)$$

The latter states that the equilibrium vapor pressure of a small liquid droplet with a radius r is higher than that of the infinitely large liquid with a flat surface. The physical reason is easy to understand if we imagine that an atom on a curved convex surface is more weakly bound to the remaining atoms than in the case of an atom on a flat surface.

Obviously, we have the opposite case when considering a vapor bubble with a radius r in an overheated liquid. Following a similar procedure we find

$$P_r = P_\infty \exp\left(-\frac{2\sigma v_l}{rkT}\right). \quad (1.20)$$

The dependence of the equilibrium vapor pressures of a liquid droplet and a gas bubble on their size is shown in Fig. 1.4.

In order to derive an analogous equation for a small crystallite we have to know its equilibrium shape. The latter is defined as the shape at which the crystal has a minimal surface energy at a given constant volume. For a liquid droplet the equilibrium shape is obviously a sphere. We will accept by now that Eq. (1.19) is valid for small crystallites with the only exception that the radius of the droplet is replaced by the radius of the sphere inscribed in the crystallite.

Let us now evaluate the effect of the droplet size on the equilibrium vapor pressure. We consider again a small water droplet with a radius of $1 \mu\text{m}$. Such a droplet contains 1.4×10^{11} molecules ($v_l = 3 \times 10^{-23} \text{ cm}^3$). For such a large droplet we can take again the surface tension of the infinitely large liquid phase $\sigma = 75 \text{ dyne/cm}$. Then Eq. (1.19) yields $P_r/P_\infty = 1.001$ and the Thomson–Gibbs effect can be neglected. However, for smaller droplets with a radius of

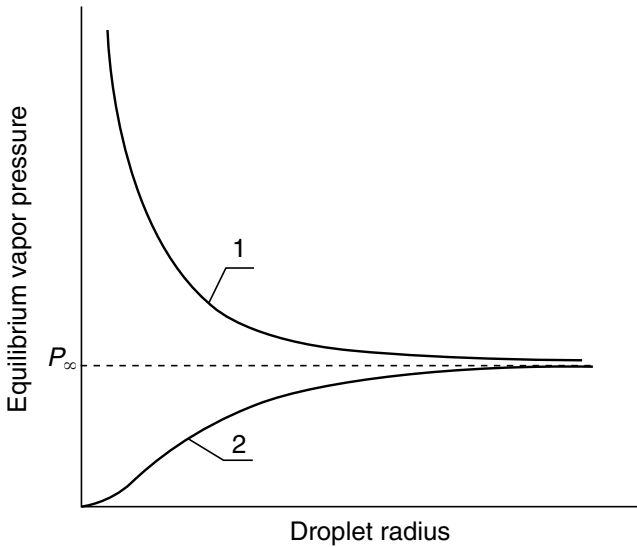


Fig. 1.4. Dependence of the equilibrium vapor pressures of a small liquid droplet (curve 1, Eq. (1.19)) and in a vapor bubble in an overheated liquid (curve 2, Eq. (1.20)). P_∞ denotes the equilibrium vapor pressure of the infinitely large liquid phase.

the order of 10 \AA , which contain 140 molecules, $P_r/P_\infty = 3.3$. We point out that for such small droplets the surface tension should be smaller than that of the infinitely large liquid phase as suggested by Kirkwood and Buff [1949] and by Tolman [1949]. It is of interest to estimate the temperature of melting of small crystallite by using Eqs. (1.12) and (1.18). We consider as an example a small Ge crystal with a radius of 10 \AA and containing about 200 atoms in its melt. With the values for the surface energy at the crystal–melt boundary $\sigma = 250 \text{ erg/cm}^2$ [Skripov 1977], the entropy of melting $\Delta s_m = 30.55 \text{ J/K mol}$ and $v_c = 2.3 \times 10^{-23} \text{ cm}^3$ we obtain $T_m - T = 220 \text{ K}$. The latter means that whereas the bulk Ge melts at 1210 K the small Ge crystallite melts below 1000 K . As seen from the above, we can introduce a crystal size, which is usually called a Thomson–Gibbs size, under which the Thomson–Gibbs effects play a significant role. As will be shown below this characteristic size differs for three-dimensional (3D) and two-dimensional (2D) crystals.

1.4. Equilibrium Shape of Crystals

When considering the equilibrium of a small crystal with its ambient phase (vapor, solution or melt) there exists obviously a shape which is the most favorable from a thermodynamic point of view in the sense that the work of formation of such a crystal is the minimal one at the given crystal volume. The work of formation of a small crystal consists of two parts: a volume part $(P_c - P_v)V_c = n(\mu_v - \mu_c)$ which is gained when transferring n atoms or molecules from the ambient (vapor) phase with chemical potential μ_v to the crystal phase with lower bulk chemical potential μ_c when the crystal phase is the stable one ($\mu_c < \mu_v$), and a surface part σS which is spent to create a new phase-dividing surface. The volume part depends obviously only on the volume of the crystal or on the number of the atoms transferred. At a constant volume the surface part depends only on the crystal shape. Then the condition for minimum of the Gibbs free energy change connected with the crystal formation at a constant volume which determines the equilibrium shape is reduced to the minimum of the surface energy. The equilibrium shape of a liquid droplet is evidently a sphere. The case of a crystal is more complicated as the latter is confined by crystal faces with different crystallographic orientations and, respectively, different specific surface energies. This means that the surface energy depends on the crystallographic orientation and in that sense it is anisotropic.

In general there are three ways to create a new surface. In the first one two homogeneous phases are cut (or cleaved) into two parts each and then the different halves are put into contact. New surface can be formed also by transfer of atoms from one phase to another forming convex (during growth) or concave (during evaporation or dissolution) form. Finally new surface can be created by stretching out an old one (by stretching out the bulk crystal). When two liquid phases are involved the above three methods do not differ. The work spent to create reversibly and isothermally a unit area of a new surface is called *specific surface free energy*. When a new surface is formed by the two first methods chemical bonds are broken or created. Thus the work for creation of a new surface or, in other words,

the specific surface free energy, is equal as a first approximation to the sum of the energies of the broken bonds per unit area. When applying the third method the number of the broken bonds remains unchanged but the surface area per dangling bond is changed which in turn leads to a change of the surface energy.

It follows from the above that the more closely packed the given crystal face the smaller is the density of the unsaturated bonds and thus its specific surface free energy. Let us consider for example the specific surface free energies of the faces of a crystal with a simple cubic lattice. The latter does not exist in nature, with the only exception being one of the crystal modifications of the metal polonium, but is widely used in theoretical considerations. It is well-known under the name *Kossel crystal*. When determining the specific surface energy we will take into account the bonds between first, second and third nearest neighbor atoms. The procedure of determination of σ of the face (hkl) involves a construction of a column in the shape of a prism with a form of the base which follows, for convenience, the symmetry of the crystal face, i.e. square on (100), hexagonal on (111) faces of cubic crystals, etc. [Honnigmann 1958]. Then the energy necessary for detachment of this column from the crystal face Ψ_{hkl} is divided by the doubled area Σ_{hkl} of the contact because two surfaces are involved. Thus $\sigma_{hkl} = \Psi_{hkl}/2\Sigma_{hkl}$. Following Fig. 1.5(a) a column of atoms with a square base is detached from the (100) face of a Kossel crystal and two surfaces are created. The value of the surface energy is then

$$\sigma_{100} = \frac{\psi_1 + 4\psi_2 + 4\psi_3}{2b^2} = \frac{1}{b^2} \left(\frac{1}{2}\psi_1 + 2\psi_2 + 2\psi_3 \right),$$

where ψ_1, ψ_2 and ψ_3 are the works required to break the bonds between first, second and third neighbors, respectively, and b^2 is the area per atom, b being the interatomic distance.

For the rhombohedral face (110) (see Fig. 1.5(b)) the column has a rectangular base and

$$\sigma_{110} = \frac{2\psi_1 + 6\psi_2 + 4\psi_3}{2b^2\sqrt{2}} = \frac{1}{b^2} \left(\frac{1}{\sqrt{2}}\psi_1 + \frac{3}{\sqrt{2}}\psi_2 + \sqrt{2}\psi_3 \right).$$

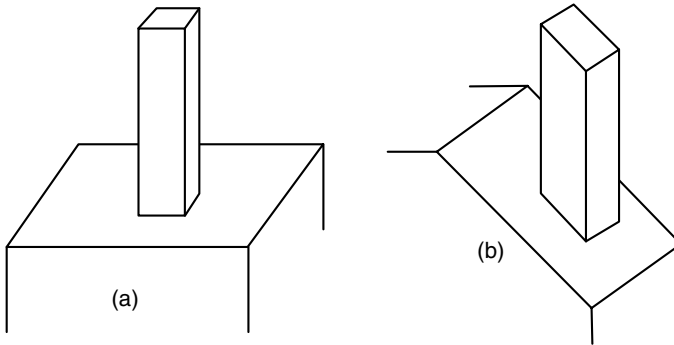


Fig. 1.5. For the determination of the specific surface energies σ_{hkl} of the faces (a) (100) and (b) (110) of a crystal with simple cubic lattice.

The shortest first neighbor bonds have the greatest contribution to the energy. The energies of the second neighbor bonds are probably not greater than 10% of the energies of the first neighbor bonds for metallic and covalent bonds. The contribution of the third neighbor bonds could be neglected. It follows from above that $\sigma_{100} < \sigma_{110}$. Performing the same calculations for the faces (111) and (211) we will find that $\sigma_{100} < \sigma_{110} < \sigma_{111} < \sigma_{211}$, etc.

1.4.1. Theorem of Gibbs–Curie–Wulff

1.4.1.1. Crystal in a three-dimensional medium

We consider first the simpler case of a crystal in a three-dimensional homogeneous medium (vapor, solution or melt). Following Gibbs [1878] and Curie [1885] we derive an expression for the equilibrium shape of a single crystal proceeding from the general condition of the minimum of the Helmholtz free energy of the system at $T = \text{const}$ and $V = \text{const}$:

$$dF = 0, \quad dV = 0. \quad (1.21)$$

We assume first that the crystal is a polyhedron confined by a limited number of different crystal faces with areas Σ_n to which a series of *discrete* values of the specific surface energies σ_n correspond.

Then the equilibrium condition (1.21) reads

$$dF = -P_v dV_v - P_c dV_c + \sum_n \sigma_n d\Sigma_n = 0, \quad (1.22)$$

where P_c is the inner pressure of the crystal and P_v is the pressure of the vapor phase, and V_v and V_c are the volumes of the vapor phase and the crystal, respectively.

Bearing in mind that $V = V_v + V_c = \text{const}$ or $dV_v = -dV_c$ the above equation is reduced to

$$-(P_c - P_v)dV_c + \sum_n \sigma_n d\Sigma_n = 0. \quad (1.23)$$

The volume of the crystal can be considered as a sum of the volumes of pyramids constructed on the crystal faces with a common apex in an arbitrary point within the crystal. Then

$$V_c = \frac{1}{3} \sum_n h_n \Sigma_n,$$

and

$$dV_c = \frac{1}{3} \sum_n (\Sigma_n dh_n + h_n d\Sigma_n),$$

where h_n are the heights of the pyramids.

On the other hand every change of the volume with accuracy to infinitesimals of second order is equal to the shift of the surfaces Σ_n by a distance dh_n so that

$$dV_c = \sum_n \Sigma_n dh_n.$$

Combining the last two equations gives

$$dV_c = \frac{1}{2} \sum_n h_n d\Sigma_n. \quad (1.24)$$

Substituting (1.24) in (1.23) gives

$$\sum_n \left[\sigma_n - \frac{1}{2}(P_c - P_v)h_n \right] d\Sigma_n = 0.$$

As the changes $d\Sigma_n$ are independent from each other every term in the brackets is equal to zero and

$$P_c - P_v = 2 \frac{\sigma_n}{h_n}. \quad (1.25)$$

The difference $P_c - P_v$ does not depend on the crystallographic orientation and for the equilibrium shape one obtains

$$\frac{\sigma_n}{h_n} = \text{const}, \quad (1.26a)$$

or

$$\sigma_1 : \sigma_2 : \sigma_3 \cdots = h_1 : h_2 : h_3 \cdots. \quad (1.26b)$$

The relationship (1.26a) expresses the geometrical interpretation given later by Wulff [1901] known as the *Wulff's rule* or *Gibbs–Curie–Wulff's theorem*. It states that *in equilibrium the distances of the crystal faces from a point within the crystal (called a Wulff's point) are proportional to the corresponding specific surface energies of these faces*. According to this rule we can construct the equilibrium shape by the following procedure: We draw vectors normal to all possible crystallographic faces from an arbitrary point. Then distances proportional to the corresponding values of the specific surface energies σ_n are marked on the vectors and planes normal to the vectors are constructed through the marks. The resulting closed polyhedron is the equilibrium shape. Crystal faces with the lowest surface energies belong to it. Crystal faces which only touch the apexes of this polyhedron or are situated even further do not belong to the equilibrium form.

The proportionality constant in (1.26a) is determined by the difference of the pressures in both phases. As shown in the previous section, $(P_c - P_v)v_c = \Delta\mu$ where $v_c = V_c/n_c$ is the molar volume of the crystal phase. The condition $P_c - P_v = \text{const}$ is thus equivalent to the statement that the difference of the chemical potentials, or in other words, the supersaturation $\Delta\mu = \mu_v - \mu_c$ has one and the same value all over the crystal surface. Then

$$\Delta\mu = \frac{2\sigma_n v_c}{h_n} \quad (1.27)$$

and hence the supersaturation determines the scale or the size of the crystal. As seen Eq. (1.27) has the familiar form of the Thomson–Gibbs equation. As the Wulff’s point has been arbitrarily chosen we can take it in the centre of the crystal.

1.4.1.2. Crystal on a surface

In the same way we can derive the Gibbs–Curie–Wulff’s theorem for a crystal formed on a foreign substrate (Fig. 1.7). [Kaischew 1950, 1951, 1960]. In this case the crystal lies with one of its faces with specific surface energy σ_m on the substrate, the latter having a specific surface energy σ_s . An interfacial boundary is formed between the crystal and the substrate. In order to find its specific energy we will perform the following imaginary experiment.

1.4.1.2.1. Relation of Dupré

We consider two crystals A (substrate) and B (deposit) of equal dimensions (Fig. 1.6) [Kern *et al.* 1979]. We cleave them reversibly and isothermally and produce two surfaces of A, each one with area Σ_A , and two surfaces of B, each one with area $\Sigma_B = \Sigma_A$. In doing

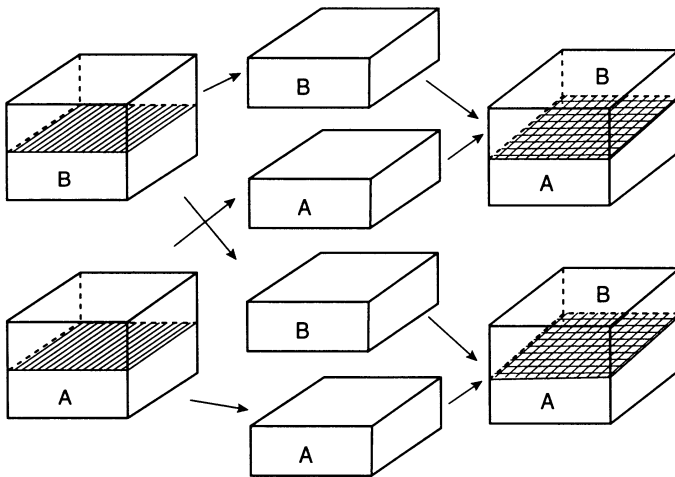


Fig. 1.6. For the determination of the specific energy of the interface between two isomorphic crystals A and B (after Kern *et al.* [1979]).

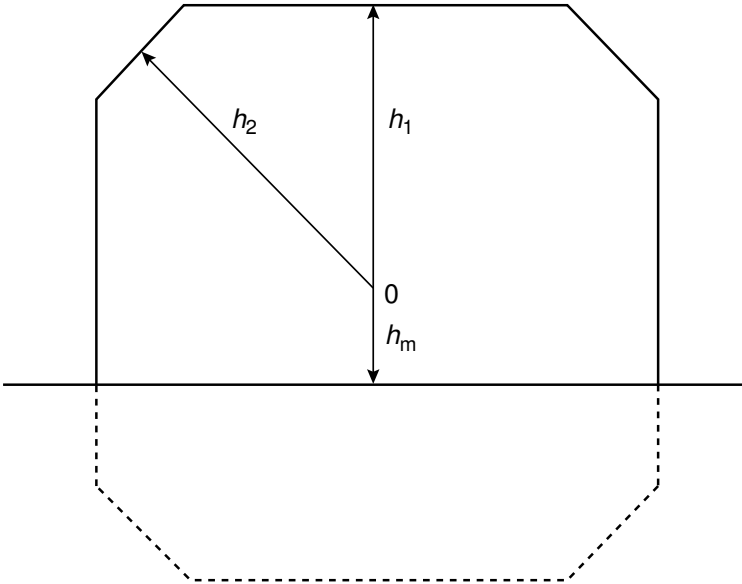


Fig. 1.7. Equilibrium shape of a crystal on a foreign substrate. The Wulff's point is denoted by 0. The distance from the Wulff's point to the contact plane is denoted by h_m . The distances h_1 and h_2 to the free surfaces remain the same as in a free polyhedron. The equilibrium shape in the absence of a foreign substrate is shown by the additional dashed line.

so, we expend energies U_{AA} and U_{BB} . We then put the two halves of A in contact with the two halves of B and produce two interfacial boundaries AB , each one with area $\Sigma_{AB} = \Sigma_B = \Sigma_A$. The work gained is $-2U_{AB}$. The excess energy of the boundary AB required to balance the energy change accompanying the above process is $2U_i$. Thus we have

$$2U_i = U_{AA} + U_{BB} - 2U_{AB}.$$

Clearly when the two crystals are undistinguishable from each other, $U_{AA} = U_{BB} = U_{AB}$ and the excess energy $U_i = 0$. Using the definition of the specific surface energy ($\sigma_{hkl} = U_{hkl}/2\Sigma_{hkl}$) one obtains the well-known relation of Dupré [1869]:

$$\sigma_i = \sigma_A + \sigma_B - \beta, \quad (1.28)$$

where the specific interfacial energy $\sigma_i = U_i/\Sigma_{AB}$ is defined as the excess energy of the boundary per unit area, and the specific adhesion energy $\beta = U_{AB}/\Sigma_{AB}$ is defined as the energy per unit area to disjoin two different crystals. Note that β accounts for the binding between the two crystals and does not depend on the lattice misfit. The latter will be taken into account when considering the epitaxial growth of thin films.

1.4.1.2.2. Equilibrium shape

When a crystal is formed on a foreign substrate a surface energy $\sigma_s\Sigma_m$ is lost and surface energy $\sigma_i\Sigma_m$ is gained, Σ_m being the area of the contact. Then instead of (1.22) one has to write

$$dF = -P_v dV_v - P_c dV_c + \sum_{n \neq m} \sigma_n d\Sigma_n + (\sigma_i - \sigma_s) d\Sigma_m = 0. \quad (1.29)$$

Following the same procedure as above we find the relation known in the literature as Wulff–Kaischew theorem [Kaischew 1950; Müller and Kern 2000]

$$\frac{\sigma_n}{h_n} = \frac{\sigma_m - \beta}{h_m} = \text{const} \quad (1.30a)$$

or

$$\sigma_1 : \sigma_2 : \sigma_3 \cdots \sigma_m - \beta = h_1 : h_2 : h_3 \cdots h_m, \quad (1.30b)$$

where h_m is the distance from the Wulff point to the contact plane (Fig. 1.7).

It follows that the distance h_m from the Wulff's point to the contact plane is proportional to the difference of the corresponding specific surface energy and the specific adhesion energy. Obviously, when the substrate catalytic potency is equal to zero, $\beta = 0$, the distance h_m will have its “homogeneous” value in the absence of a substrate. In this case we speak of *complete non-wetting*. At the other extreme $\beta = \sigma_A + \sigma_B = 2\sigma$ ($\sigma_A = \sigma_B = \sigma$) we have the case of *complete wetting* and the crystal will be reduced to a two-dimensional monolayer island. In all intermediate cases $0 < \beta < 2\sigma$

we have *incomplete wetting* and the height of the crystal will be smaller than its lateral size.

1.4.2. Polar diagram of the surface energy

We have considered by now a crystal confined by discrete faces with small Miller indices. Let us now imagine a crystal face which is slightly deviated (by a small angle θ) from one of the small index faces, say, the cubic one (100) of a Kossel crystal as shown in Fig. 1.8(a). Such a face is called *vicinal*. It is clear for geometrical reasons that it consists of terraces and steps. For simplicity we accept that the steps are monoatomic and equidistant. The specific surface energy of such a face is a sum of the surface energy of the terraces σ_0 and of the energy of the steps or the edge energy $\varkappa \cong b\sigma_0$ which can be evaluated in the same way as the surface energy just by counting the number of the broken bonds per unit length. If one neglects the interaction between the steps as a first approximation for the specific

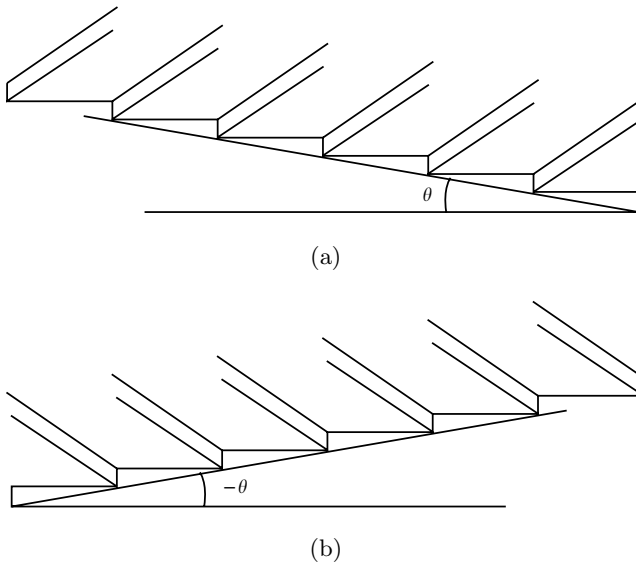


Fig. 1.8. Vicinal surfaces deviated by an angle (a) θ and (b) $-\theta$ from a small index (singular) face.

surface energy of such a vicinal face one obtains [Landau 1969]

$$\sigma(\theta) = \frac{\varkappa}{b} \sin(\theta) + \sigma_0 \cos(\theta). \quad (1.31)$$

We consider now a vicinal face which is symmetric to the first one, i.e. tilted by an angle of $-\theta$ (Fig. 1.8(b)). Its surface energy is

$$\sigma(-\theta) = -\frac{\varkappa}{b} \sin(\theta) + \sigma_0 \cos(\theta). \quad (1.32)$$

Graphic representations of the $\sigma(\theta)$ functions (1.31) and (1.32) are given in Fig. 1.9(a). As seen they are continuous everywhere with the exception of the point $\theta = 0$, where $(d\sigma/d\theta)_{\theta \geq 0} = \varkappa/b$ and $(d\sigma/d\theta)_{\theta \leq 0} = -\varkappa/b$. In other words the $\sigma(\theta)$ dependence has a *singular point* at $\theta = 0$ its derivative making a jump of $2\varkappa/b$. The same singular points exist at $\theta = \pm\pi/2, \pm\pi$, etc. In Fig. 1.9(b) the same

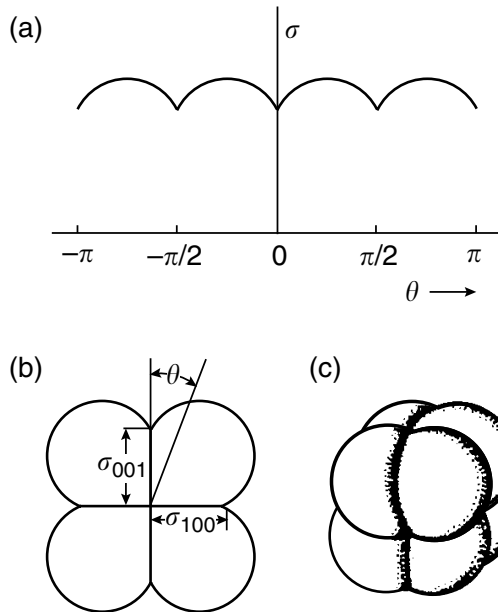


Fig. 1.9. Polar diagram of the specific surface energy — dependence of the surface energy on angle θ in (a) orthogonal coordinates, (b) polar coordinates (two-dimensional representation) and (c) spherical coordinates (three dimensional representation). First neighbor interactions only are taken into account (after Chernov [1984]).

functions are plotted in polar co-ordinates. A contour consisting of circular segments and possessing singular points at $\theta = 0, \pi/2,$ and $3\pi/2$ results. In the three-dimensional case (Fig. 1.9(c)) a body is obtained which consists of 8 spherical segments and has 6 sharp singular points. This plot is called a *polar diagram* of the surface energy.

When constructing the above polar diagram only the bonds between the first neighbor atoms have been taken into account. The bonds between the second neighbors in the Kossel crystal are directed at angle $\pi/4$ with respect to the first neighbor bonds. We can perform the same considerations as above [Chernov 1984] accounting for the second neighbor bonds only. Thus a polar diagram which is inscribed in the first one (the second neighbor bonds are much weaker than the first neighbor ones) and is rotated at an angle of $\pi/4$ with respect to the latter is obtained (Fig. 1.10). The sum of the two curves gives

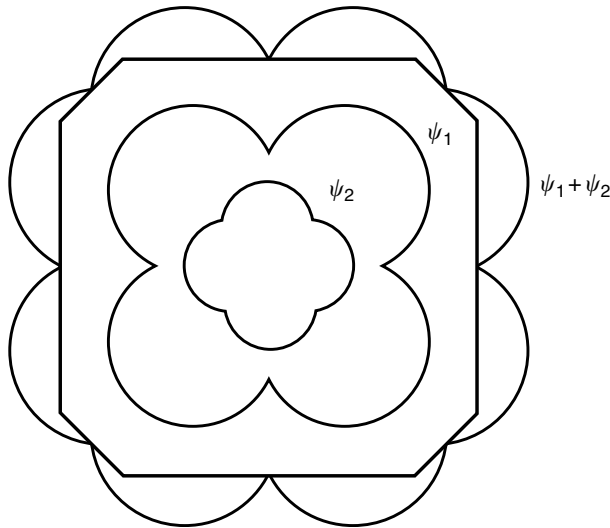


Fig. 1.10. Polar diagram of the specific surface energy (the outermost contour denoted by $\Psi_1 + \Psi_2$, (two-dimensional representation) taking into account the first (Ψ_1) and second (Ψ_2) nearest neighbor interactions. The contours denoted by Ψ_1 and Ψ_2 give the polar diagrams as calculated by taking into account separately the first and the second nearest neighbors. The closed contour consisting of straight lines drawn through the singular points of the contour $\Psi_1 + \Psi_2$ gives the equilibrium shape of the crystal.

the polar diagram when accounting simultaneously for both the first and the second neighbors. As seen new shallower minima appear which correspond to faces which are analogous to the (110) faces in the three-dimensional Kossel crystal. The contribution of the third neighbor bonds is insignificant and will not affect considerably the shape of the polar diagram. In any case accounting for the more distant neighbors always leads to more complicated polar diagrams and equilibrium shapes.

1.4.3. Herring's formula

Let us now derive the condition for the equilibrium shape of the crystal accounting for the anisotropy of the surface energy, or in other words, the $\sigma(\theta)$ dependence. This is a question of utmost importance as it is unambiguously connected with the problem of the equilibrium structure (the roughness) of the crystal surfaces. The three-dimensional problem is somewhat complicated from mathematical point of view and for this reason we will consider the simpler case of a "two-dimensional" crystal which represents a cross-section of the three-dimensional one. On the other hand the 2D case is very important for understanding of the two-dimensional nucleation and in turn of the layer growth of smooth crystal faces.

When treating the problem we will follow exactly the approach of Burton, Cabrera and Frank [1951]. The crystal volume V_c will be replaced by the crystal surface area S_c and the specific surface energy $\sigma(\theta)$ by the specific edge energy $\varkappa(\theta)$. Then, instead of (1.21) we write

$$\Phi = \min, \quad S_c = \text{const}, \quad (1.33)$$

where

$$\Phi = \int_L \varkappa(\theta) dl \quad (1.34)$$

is the edge energy of the “two-dimensional crystal” the integration being carried out over the whole periphery L of the latter, and

$$S_c = \int_S ds \quad (1.35)$$

is the surface area of the crystal where ds is the surface area of a curvilinear sector.

Let r and φ be the polar co-ordinates of a point M of the crystal boundary L (Fig. 1.11) and let x and y be the corresponding orthogonal co-ordinates. We construct a tangent T to the crystal boundary L at the point M and a perpendicular ON with length n from the origin O to the tangent. The latter makes an angle θ with the abscissa. The line element of the crystal boundary in a

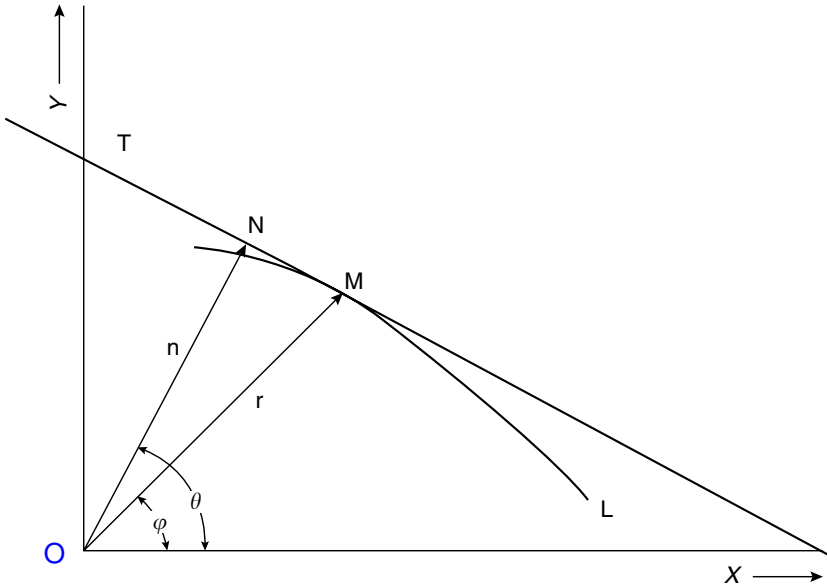


Fig. 1.11. The derivation of the Herring’s formula in the two-dimensional case. L and T denote the crystal boundary and the tangent to it at a point M , r and φ are the polar coordinates of a point M of the crystal surface, and n and θ are the polar coordinates of the point N belonging to the polar diagram $\varkappa(\theta)$ (after Burton, Cabrera and Frank [1951]).

parametric form $x = x(t)$ and $y = y(t)$ reads

$$dl = (x'^2 + y'^2)^{1/2} dt,$$

where $x' = dx/dt$ and $y' = dy/dt$.

By the same way the area of the curvilinear sector ds is

$$ds = \frac{1}{2}(xy' - yx')dt.$$

If we choose the angle θ as the parameter the integrals (1.34) and (1.35) can then be rewritten in the form

$$\Phi = \int_0^{2\pi} \varkappa(\theta)(x'^2 + y'^2)^{1/2} d\theta, \quad (1.36)$$

$$S_c = \frac{1}{2} \int_0^{2\pi} (xy' - yx') d\theta. \quad (1.37)$$

From Fig. 1.11 we find that the perpendicular n from the origin to the tangent T is given by

$$n = x \cos \theta + y \sin \theta.$$

Then we can find the point N for any point M of the crystal boundary. Conversely, making use of the transformations

$$x = n \cos \theta - n' \sin \theta, \quad (1.38a)$$

$$y = n \sin \theta + n' \cos \theta, \quad (1.38b)$$

we can construct the crystal contour if we know $n(\theta)$, ($n' = dn/d\theta$).

Then Eqs. (1.36) and (1.37) can be written in terms of $n(\theta)$

$$\Phi = \int_0^{2\pi} \varkappa(\theta)(n + n'') d\theta = \min, \quad (1.39)$$

$$S_c = \frac{1}{2} \int_0^{2\pi} n(n + n'') d\theta = \text{const}, \quad (1.40)$$

where $n'' = d^2n/d\theta^2$.

Following the method of Lagrange we multiply Eq. (1.40) by an indefinite scalar λ and sum up both equations to obtain

$$\int_0^{2\pi} \left[\varkappa(\theta)(n + n'') - \frac{1}{2} \lambda n(n + n'') \right] d\theta = \min . \quad (1.41)$$

The condition for minimum is still preserved as we multiplied it by a constant and added a constant. The solution of (1.41) will give us a function $n = n(\theta)$ which satisfies both conditions $\Phi = \min$ and $S_c = \text{const}$. To solve the problem we will use the method of Euler for finding of an extremum [Zeldovich and Myshkis 1967; Arfken 1973]. It states that if we have a functional of the kind

$$\int_a^b F(x, y, y', y'') dx = \min ,$$

where $y = y(x)$, $y' = dy/dx$, $y'' = d^2y/dx^2$, the equation which satisfies it has the form

$$\frac{\partial F}{\partial y} - \frac{\partial}{\partial x} \left(\frac{\partial F}{\partial y'} \right) + \frac{\partial^2}{\partial x^2} \left(\frac{\partial F}{\partial y''} \right) = 0 ,$$

where the functions y , y' and y'' are taken upon differentiation as independent variables without accounting for their dependence on x .

Applying the above method from (1.41) one obtains

$$\frac{\partial^2}{\partial \theta^2} [\varkappa(\theta) - \lambda n(\theta)] + [\varkappa(\theta) - \lambda n(\theta)] = 0 . \quad (1.42)$$

Thus the equilibrium shape of the crystal is governed by a nonlinear equation of second order which satisfies the conditions $\Phi = \min$ and $S_c = \text{const}$. Its solution $n(\theta)$ will give us the rule for constructing the equilibrium shape of our two-dimensional crystal (the crystal contour) on the base of the polar diagram of the edge energy and making use of Eqs. (1.38a). In fact we have to solve the much simpler linear differential equation of second order. With the substitution $u = \varkappa(\theta) - \lambda n(\theta)$, Eq. (1.42) turns into $u'' + u = 0$. Its solution reads [Kamke 1959]

$$u = C \sin(x - \phi)$$

or

$$n(\theta) = \frac{1}{\lambda} \varkappa(\theta) - C \sin(\theta - \phi),$$

where C and ϕ are constants. The second term in the right-hand side is a periodic function with a period 2π . However, different crystals have different symmetry and thus different period. For example, cubic crystals have period of $\pi/2$, hexagonal crystals have a period $\pi/3$, etc. In order to get rid of this restriction we put $C = 0$ and obtain

$$n(\theta) = \frac{1}{\lambda} \varkappa(\theta). \quad (1.43)$$

By analogy with the previous case the proportionality constant which multiplies the crystal volume $\lambda = \Delta\mu/s_c$ where s_c is the area of an atom in the two-dimensional crystal and

$$\Delta\mu = \frac{\varkappa(\theta)s_c}{n(\theta)}. \quad (1.44)$$

Equation (1.44) which appears as a generalized Thomson–Gibbs equation is the Gibbs–Curie–Wulff’s theorem for two-dimensional crystals in which $n(\theta)$ is the radius-vector of the polar diagram $\varkappa(\theta)$.

Carrying out the differentiation in Eq. (1.42) gives

$$n + n'' = \frac{1}{\lambda} [\varkappa(\theta) + \varkappa''(\theta)],$$

where $\varkappa''(\theta) = d^2\varkappa(\theta)/d\theta^2$.

Realizing that

$$n + n'' = \frac{(x'^2 + y'^2)^{3/2}}{x'y'' - y'x''} = R$$

is in fact the principal radius of the curvature of the crystal contour, R , then with $\lambda = \Delta\mu/s_c$ one obtains

$$\Delta\mu = \frac{s_c}{R} \left[\varkappa(\theta) + \frac{d^2\varkappa(\theta)}{d\theta^2} \right].$$

By analogy, for a three-dimensional crystal with principal radii of curvature R_1 and R_2 and polar angles θ_1 and θ_2 , for the equilibrium shape one obtains an expression with (s_c and $\varkappa(\theta)$) respectively

replaced by v_c and $\sigma(\theta)$ (for more rigorous derivation see Chernov [1984]) which is known as the formula of *Herring* [Herring 1951, 1953]

$$\Delta\mu = \frac{v_c}{R_1} \left(\sigma + \frac{d^2\sigma}{d\theta_1^2} \right) + \frac{v_c}{R_2} \left(\sigma + \frac{d^2\sigma}{d\theta_2^2} \right). \quad (1.45)$$

In the same way the generalized Gibbs–Curie–Wulff’s theorem for the three-dimensional crystals reads

$$\Delta\mu = \frac{2\sigma(\theta)v_c}{n(\theta)}. \quad (1.46)$$

Equations (1.44) and (1.46) give us the practical rule for construction of the equilibrium shape. First, we ascribe a particular value to the scale parameter $\Delta\mu/2v_c$ which determines the size of the crystal. Then we draw the radius vector $n(\theta)$ from the central point at an arbitrary selected crystallographic direction θ and find the cross-sectional point with the polar diagram (Fig. 1.12). We then construct through it a plane normal to $n(\theta)$ and repeat this procedure for the whole contour of the diagram. A family of planes results and its inner envelope is in fact the equilibrium shape of the crystal.

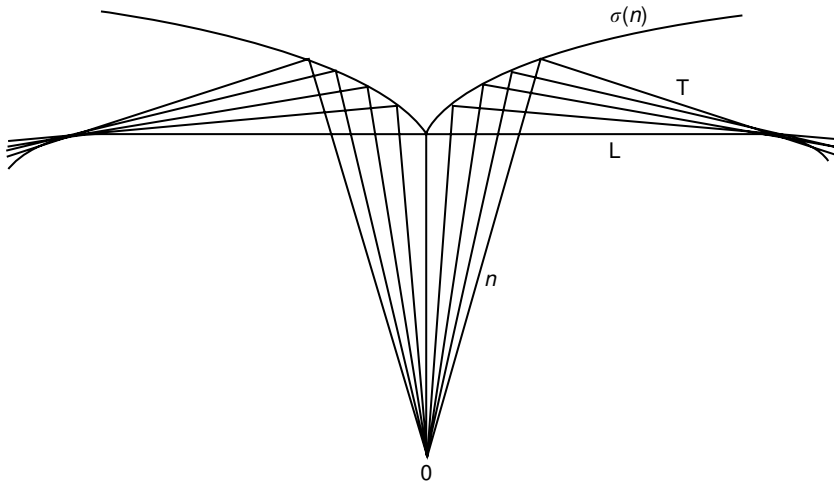


Fig. 1.12. Construction of the equilibrium shape based on the polar diagram of the surface energy following Eq. (1.46).

Let us go back to the Herring's formula (1.45) and consider more closely the quantity $\sigma_n^* = \sigma + d^2\sigma/d\theta_n^2$ ($n = 1, 2$) which is usually called the *surface stiffness*. At the singular points the first derivatives of σ with respect to θ experiences a jump (equal to $2\kappa/b$ in the above oversimplified case). Hence, the second derivatives and in turn the surface stiffnesses σ_n^* have infinitely large values. The left-hand side of Eq. (1.45) has a finite value and obviously the condition the right-hand side to have a finite value is the principal radii R_1 and R_2 to be infinitely large. Hence at the singular points the curvature of the corresponding crystal faces will be equal to zero or, in other words, the crystal faces will be flat. This is the reason the flat faces are often called *singular faces*. Immediately aside of the singular points the second derivatives of σ and in turn the surface stiffnesses σ_n^* acquire finite positive values and hence also do the radii R_1 and R_2 . Therefore, the crystal surface will be rounded. It will consist of terraces and steps or, in other words, it will be atomically rough. Finally, there are regions where $\sigma_n^* = 0$ and so are the radii R_1 and R_2 (the ratios σ_n^*/R_n again having finite values). These are obviously the edges and the apexes of the crystal. Negative values of the surfaces stiffnesses have no physical meaning as this means negative radii R_1 and R_2 and hence concave regions which cannot exist on the equilibrium shape.

As discussed above the supersaturation must have one and the same value over every point of the surface of a crystal with an equilibrium shape. It follows that the supersaturation around a crystal without an equilibrium shape will differ from one point to another. Facets with areas smaller then required by the equilibrium condition will have larger chemical potential and hence the supersaturation over them will be lower than the current one in the system and *vice versa*. If such a crystal is immersed into a supersaturated ambient phase and given enough time to equilibrate, smaller facets will dissolve to become larger facets, and larger facets will grow to become smaller facets up to the moment the supersaturation attains one and the same value all over the crystal surface and the equilibrium shape is reached. As will be shown below the above conclusion is valid for crystallites sufficiently small ($kTR_n/\sigma_n^*v_c \ll 1$) so that

the supersaturation difference which is the driving force for the equilibration to be reached is sufficiently large.

Finally, Eq. (1.45) can be expressed in the form

$$\Delta\mu = v_c \left(\frac{\sigma_1^*}{R_1} + \frac{\sigma_2^*}{R_2} \right) \quad (1.47)$$

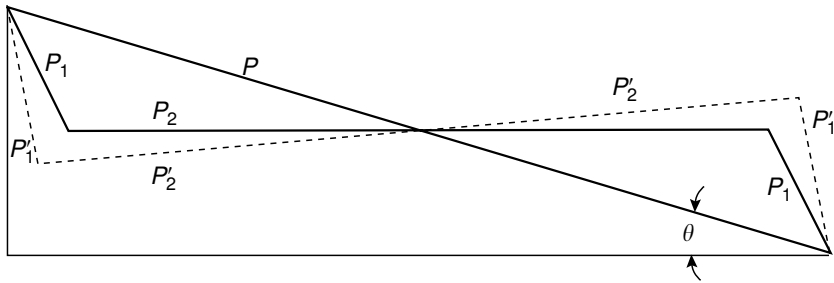
or

$$P_c - P_v = \frac{\sigma_1^*}{R_1} + \frac{\sigma_2^*}{R_2}. \quad (1.48)$$

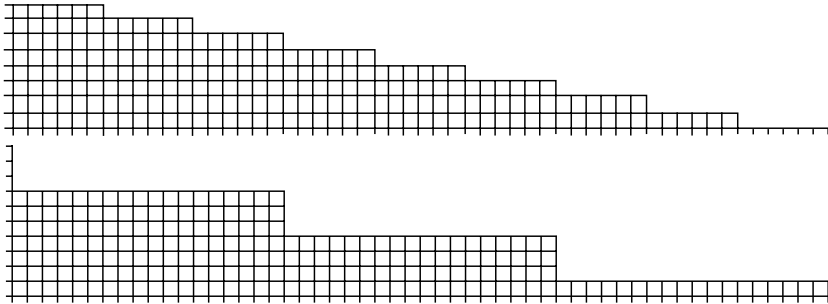
We conclude that the Herring's formula is a generalization for finite crystallites of Laplace's equation (1.16) which relates the liquid surface tension to the pressure difference on both sides of the curved liquid surface. The Laplace pressure is determined in this case by the surface stiffnesses which govern the crystal curvature rather than by the specific surface energies. Thus Eq. (1.48) explains the term surface stiffness. It is a measure of resistivity of the crystal faces against bending (roughening) when a pressure (force per unit area) is applied on them. Flat facets require infinitely high pressures in order to be "bent".

1.4.4. *Stability of crystal surfaces*

In fact we have just concluded that the structure of a given crystal surface is determined by the corresponding value of the surface stiffness. When the latter is infinite the corresponding crystal face is flat and atomically smooth. When the surface stiffness has some finite positive value the crystal surfaces are rounded and in the near vicinity of the singular faces should consist of terraces divided by steps. We accepted that the steps are of monomolecular height. The width of the terraces or the density of the steps depends on the value of the polar angle. However, we can have different structures of a vicinal face at one and the same value of the polar angle. Thus if the steps are with double height the terraces should be twice as wide, when the steps have a triple height the terraces will have a triple width, etc., at one and the same value of the polar angle (Fig. 1.13(b)). So one cannot determine unambiguously the real structure of the



(a)



(b)

Fig. 1.13. A scheme illustrating the stability of a vicinal crystal surface against faceting: (a) Schematic view in terms of the slope $p = \tan \theta$ of the original vicinal face which breaks down into facets with slopes $p_1 = \tan \theta_1$ and $p_2 = \tan \theta_2$. The dashed lines with slopes p'_1 and p'_2 give possible deviations from the faceted surface with slopes p_1 and p_2 , respectively (see text). (b) Side view of a vicinal surface of a Kossel crystal whose slope is accommodated either by single height steps or by facets (after Cabrera and Coleman [1963]).

corresponding vicinal surface on geometrical reasons only. Moreover, under real conditions the surface energy and in turn the surface stiffness can change their values. This is usually the case when some impurity atoms are adsorbed on the crystal surface. The impurity atoms saturate the unsaturated dangling bonds on the crystal surface and decrease the surface energy. The larger the concentration of the impurity atoms the smaller will be the specific energy of a particular crystal surface [Szyszkowski 1908; Moelwin-Hughes 1961; Mutaftschiev 2001]. Another reason for changing of the surface

energy is the surface reconstruction [Mönch 1979]. As a result the structure of the crystal surface should change. So our next task is to find the real structure of the crystal surfaces or in other words the condition of the stability of a given crystal surface. The problem of the stability of the crystal surfaces was first considered by Chernov [1961] and discussed later by Cabrera and Coleman [1963]. In this chapter we follow the presentation of the latter.

We consider an infinite vicinal crystal surface inclined to the nearest singular face by an angle θ (Fig. 1.13) and consisting of terraces and monomolecular steps. It is easy to realize such a face bearing in mind that single crystal wafers which are cut and polished under the crystallographic orientation of one of the singular faces are always inclined to the latter at some very small angle. In general such a face can be represented by $z = z(x, y)$ where $z = 0$ determines the singular face. Then the orientation at a point (x, y) will be determined by two independent components $p = -dz/dx$ and $q = -dz/dy$. We consider for simplicity the case in which the steps are parallel to the y axis (which is thus normal to the surface of the sheet), i.e. $q = 0$ and the vicinal face is described by $z = z_0 - px$ where $p = \tan \theta$. Let the face area be denoted by Σ_0 . Then the area of the reference singular face is $\Sigma = \Sigma_0 \cos \theta$.

The surface energy of the face Σ_0 is $\Phi_0 = \sigma(\theta)\Sigma_0$. In terms of the component p it can be written as

$$\Phi_0 = \sigma(\theta)\Sigma_0 = \sigma(p)(1 + p^2)^{1/2}\Sigma = \xi(p)\Sigma, \quad (1.49)$$

where $(1 + p^2)^{1/2} = 1/\cos \theta$ and $\xi(p) = \sigma(p)(1 + p^2)^{1/2}$.

Let us now assume that two new faces with slightly different orientations

$$p_1 = p + \delta p_1 \quad \text{and} \quad p_2 = p + \delta p_2 \quad (1.50)$$

are formed. The total projected areas of these faces are Σ_1 and Σ_2 , respectively. If the face Σ_0 is the stable one its surface energy Φ_0 should be smaller than the surface energy of the newly formed profile $\Phi = \xi(p_1)\Sigma_1 + \xi(p_2)\Sigma_2$ at constant volume. In other words, the condition $\Delta\Phi = \Phi - \Phi_0 > 0$ should be fulfilled. The condition of constant volume is reduced in our case to that of a constant area

of the cross-section shown in Fig. 1.13(a). It can be easily obtained from $\Delta S = S_1 - S_2 = 0$, where S_1 and S_2 are the areas under the profiles, with slopes p and p_1 and p_2 , respectively. One obtains

$$p_1 \Sigma_1 + p_2 \Sigma_2 = p \Sigma. \quad (1.51)$$

Substituting (1.50) in (1.51) and making use of the relation

$$\Sigma_1 + \Sigma_2 = \Sigma, \quad (1.52)$$

the condition for constant volume $\Delta S = 0$ turns into

$$\Sigma_1 \delta p_1 + \Sigma_2 \delta p_2 = 0. \quad (1.53)$$

The functions $\xi(p_i)$ ($i = 1, 2$) can be expanded in Taylor series up to the parabolic terms

$$\xi(p_i) = \xi(p) + \xi'(p) \delta p_i + \frac{1}{2} \xi''(p) (\delta p_i)^2, \quad (1.54)$$

where $\xi'(p) = d\xi/dp$ and $\xi''(p) = d^2\xi/dp^2$.

Substituting (1.54) in the expression for $\Delta\Phi$ and making use of (1.52) and (1.53) give

$$\Delta\Phi = \frac{1}{2} \xi''(p) [\Sigma_1 (\delta p_1)^2 + \Sigma_2 (\delta p_2)^2]. \quad (1.55)$$

The term in the square brackets is always positive and the condition $\Delta\Phi > 0$ is satisfied when

$$\xi''(p) > 0. \quad (1.56a)$$

Bearing in mind that $d\sigma/dp = (d\sigma/d\theta)(d\theta/dp)$, $\theta = \tan^{-1}(p)$, $d\theta/dp = -1/(1+p^2)$, and $\xi''(p) = \sigma^*/(1+p^2)^{3/2}$, the condition (1.56a) reduces to

$$\sigma^* = \sigma + \frac{d^2\sigma}{d\theta^2} > 0. \quad (1.56b)$$

It follows that when the surface stiffness of the original vicinal face which consists of terraces divided by monomolecular steps is positive it will be stable. Otherwise, it will break down into terraces divided by macrosteps, or in the limiting case, into separate crystal

faces preserving the overall slope of the original face with respect to the singular face.

A schematic plot of $\xi(p)$ is given in Fig. 1.14. We have in principle three possibilities. In the first one (Fig. 1.14(a)) the second derivative of $\xi(p)$ is everywhere positive between the singular minima at $p = 0$ and $p = p_0$. This means that all possible surfaces between $p = 0$ and $p = p_0$ will be stable and will not break into facets as long as there are no species adsorbed on them. In the second case (Fig. 1.14(b)) the second derivative of $\xi(p)$ is everywhere negative. This means that only the singular surfaces with the orientations p and p_0 will be stable. If a surface with orientation p such that $0 < p < p_0$ is formed it will break down into facets with the orientations $p = 0$ and $p = p_0$. In the general case (Fig. 1.14(c)) in between 0 and p_0 there are regions with $\xi''(p) > 0$ and $\xi''(p) < 0$. It follows that only the surfaces at the singular minima whose orientations are between p_1 and p_2 , where the condition $\xi''(p) > 0$ is fulfilled, can exist on the crystal surface. All others are not stable and should break down into facets.

The physical meaning of this result is simple. If the new crystal surfaces with orientations p_1 and p_2 have smaller specific surface energies than the original face with orientation p and a decrease of the surface energy overcompensates the increase of the surface area

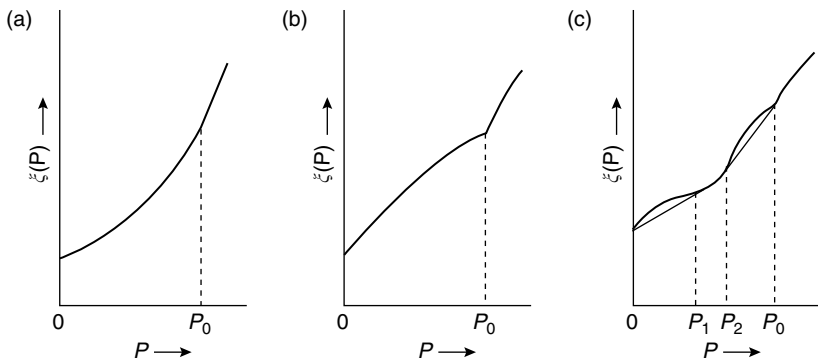


Fig. 1.14. Schematic plot of the parameter $\xi(p) = \sigma(p)(1 + p^2)^{1/2}$ vs the slope p : (a) $\xi''(p) > 0$, (b) $\xi''(p) < 0$, (c) $\xi''(p) > 0$ between p_1 and p_2 and $\xi''(p) < 0$ between 0 and p_1 and between p_2 and p_0 (after Cabrera and Coleman [1963]).

the crystal surface will break down into facets. In the reverse case it will be stable.

The stability of the facets can be examined by the same way as for the original surface. In this case we allow two new surfaces with orientations $p'_1 = p_1 + \delta p_1$ and $p'_2 = p_2 + \delta p_2$ to form (Fig. 1.13(a)). From the condition of the positive change of the surface energy at constant volume we find that the facets will be stable when the corresponding surface stiffnesses σ_1^* and σ_2^* of the facets are positive. Thus an unstable smooth surface with negative surface stiffness should break down into facets with positive surface stiffnesses.

Faceting of crystal surfaces was observed long ago. Early works are reviewed by Moore [Moore 1963]. In principle, faceting could be caused by any reason which diminish the specific surface energy. In particular, this is the adsorption of surface active species. Thus the adsorption of Ag on stepped Ge(111) surfaces leads to formation of (544) and (111) facets at Ag coverage of about 0.2 monolayers at $T \cong 400^\circ\text{C}$ [Suliga and Henzler 1983]. At increased coverage of Ag greater than 0.7 monolayers (211) facets are formed. The above results were refined in a later paper [Henzler, Busch and Friese 1990]. A Ge crystal has been cut and polished with 3° misorientation ($p = 0.0524$) with respect to the (111) surface. Vicinal surfaces with monoatomic steps and 18 atomic spacings wide terraces were obtained which can be described by Miller indices (19, 17, 17). Silver was then deposited at room temperature and the crystal was annealed at 400°C for 10 min. After cooling down to room temperature again the following changes were observed. At a coverage of the Ag atoms of 1/4 monolayer (with respect to the surface coverage of Ge(111)) the initial (19, 17, 17) surface broke down to facets (13, 11, 11) with greater slopes and narrower terraces and flat wider portions with (111) orientation. The fractions of the overall surface of both facets were estimated to be 0.75 and 0.25, respectively. At Ag coverage of 1/2 monolayer half of the surface was found to have (10, 8, 8) orientation and the other half has (111) orientation. After desorption of the silver and annealing of the Ge crystal the initial orientation (19, 17, 17) was recovered.

Clean Si(100) surfaces misoriented by 5° in the [011] direction contain steps of average spacing 29 Å and height 2.7 Å (double steps). After a deposition of As beyond a critical surface coverage of 0.38 monolayers which is independent of the temperature the terraces become about 100 Å wide and the steps are 9 Å (6 monolayers) high [Ohno and Williams 1989(a)]. The process is reversible. After desorption of the arsenic the surface recovers its initial structure. The same is observed for Si(111) surfaces misoriented by 6° in the $[\bar{1}10]$, $[2\bar{1}\bar{1}]$ and $[\bar{2}11]$ directions. At coverages of As higher than a critical one of 0.16 monolayers the single steps turn into double steps [Ohno and Williams 1989b].

Besides, it was found that Si(112) surfaces are stable when heated up to 800°C regardless of carbon contamination and break down to (111), (113), (525) and (255) surfaces when heated between $950\text{--}1150^\circ\text{C}$ in the presence of carbon on the crystal surface. The extent of faceting increases if carbon is introduced before heating beyond 950°C . Annealing at 1250°C removes the carbon and restores the initial surface structure [Yang and Williams 1989].

It is worth noting that the As-induced faceting of Si(100) and (111) surfaces takes place at As_2 pressures comparable to those used when GaAs is grown on Si single crystal wafers. It is thus unsafe to assume that the surface of the substrate preserves its stepped structure under the conditions of the experiment. The same is valid when the necessary precautions to lower the carbon contaminations in the vacuum chamber are not taken into account. Works on faceting of metal surfaces are summarized by Somorjai and van Hove [1989].

1.5. Atomistic Views on Crystal Growth

1.5.1. *Equilibrium of infinitely large crystal with the ambient phase — The concept of half-crystal position*

The above considerations were purely macroscopic in the sense that thermodynamic macroquantities have been used for description of the equilibrium between different phases. Moreover, the elementary processes of attachment and detachment of individual building units