Equilibrium in Polycrystalline Materials

- No torque at grain boundary
  
  If the boundary energy is independent of orientation, the torque term is zero and the grain boundary behaves like a soap film. The boundary tensions $\gamma_{12}$, $\gamma_{23}$ and $\gamma_{13}$ must balance.

  $$\gamma_{13} \sin(180^\circ - \theta_3) = \gamma_{12} \sin(180^\circ - \theta_2)$$

  $$\Rightarrow \gamma_{13} \sin \theta_3 = \gamma_{12} \sin \theta_2 \Rightarrow \frac{\gamma_{13}}{\sin \theta_2} = \frac{\gamma_{12}}{\sin \theta_3}$$

  $$\therefore \gamma_{23} = \gamma_{12} \cos(180^\circ - \theta_2) + \gamma_{13} \cos(180^\circ - \theta_3)$$

  $$\Rightarrow \gamma_{23} = -\gamma_{12} \cos \theta_2 - \gamma_{13} \cos \theta_3$$

  $$\Rightarrow \gamma_{23} = -\gamma_{12} \cos \theta_2 \left(\frac{\sin \theta_2}{\sin \theta_3}\right) \cos \theta_3$$

  $$\Rightarrow \gamma_{23} = -\left(\frac{\gamma_{12}}{\sin \theta_3}\right) \left(\cos \theta_2 \sin \theta_3 + \sin \theta_2 \cos \theta_3\right)$$

  $$\Rightarrow \gamma_{23} = -\left(\frac{\gamma_{12}}{\sin \theta_3}\right) \sin(\theta_2 + \theta_3) = -\left(\frac{\gamma_{12}}{\sin \theta_3}\right) \sin(360^\circ - \theta_1)$$

  $$\Rightarrow \gamma_{23} = \left(\frac{\gamma_{12}}{\sin \theta_3}\right) \sin \theta_1 \Rightarrow \frac{\gamma_{23}}{\sin \theta_1} = \frac{\gamma_{12}}{\sin \theta_3}$$

  $$\Rightarrow \frac{\gamma_{23}}{\sin \theta_1} = \frac{\gamma_{13}}{\sin \theta_2} = \frac{\gamma_{12}}{\sin \theta_3}$$

Fig. 3.17 The balance of grain boundary tensions for a grain boundary intersection in metastable equilibrium.

$$\Rightarrow \frac{\gamma_{23}}{\sin \theta_1} = \frac{\gamma_{13}}{\sin \theta_2} = \frac{\gamma_{12}}{\sin \theta_3}$$
Equilibrium in Polycrystalline Materials

- **Measuring grain-boundary energy**
  - One method of measuring grain-boundary energy is to anneal a specimen at a high temperature and then measure the angle at the intersection of the surface with the boundary, Fig. 3.18.

  - In this case, the presence of any torque terms has been neglected, though an approximation may introduce large errors. If the solid-vapor energy \( (\gamma_{SV}) \) is the same for both grains, balancing the interfacial tensions gives

    \[
    2\gamma_{SV} \cos \left( \frac{\theta}{2} \right) = \gamma_b
    \]  

    (3.14)

    Therefore if \( \gamma_{SV} \) is known, \( \gamma_b \) can be calculated.

![Diagram](image)

**Fig. 3.18** The balance of surface and grain boundary tensions at the intersection of a grain boundary with a free surface.
Interphase interfaces

Boundaries between different solid phases, i.e. where the two adjoining crystals can have different crystal structures and/or compositions.

Interphase boundaries in solids can be divided on the basis of their atomic structure into three classes: coherent, semicoherent and incoherent.

Strain-free coherent interfaces. (a) Each crystal has a different chemical composition but the same crystal structure. (b) The two phases have different lattices.
A coherent interface arises when the two crystals match perfectly at the interface plane so that the two lattices are continuous across the interface.

This can only be achieved if, disregarding chemical species, the interfacial plane has the same atomic configuration in both phases, and this requires the two crystals to be oriented relative to each other in a special way.

For example, such an interface is formed between the hcp silicon-rich K phase and the fcc copper-rich α-matrix in Cu-Si alloys. The lattice parameters of these two phases are such that the (111) fcc plane is identical to the (0001) hcp plane.
The requirement that the close-packed planes and directions are parallel produces an orientation relationship between the two phases such that

\[(111)_α/\langle 0001\rangle_κ\]
\[[\bar{1}10]_α/\langle 1\bar{1}20\rangle_κ\]

Within the bulk of each phase every atom has an optimum arrangement of nearest neighbours that produces a low energy.

At the interface, however, there is usually a change in composition so that each atom is partly bonded to wrong neighbours across the interface.

This increases the energy of the interfacial atoms and leads to a chemical contribution to the interfacial energy \(γ_{ch}\).

For a coherent interface this is the only contribution, i.e. \(γ(\text{coherent}) = γ_{ch}\).

In the case of the \(α-K\) interface in Cu-Si alloys the interfacial energy has been estimated to be as low as 1 mJ m\(^{-2}\). In general coherent interfacial energies range up to about 200 mJ m\(^{-2}\).
In the case of a hcp-fcc interface there is only one plane that can form a coherent interface: no other plane is identical in both crystal lattices.

If, however, the two adjoining phases have the same crystal structure and lattice parameter then, apart from differences in composition, all lattice planes are identical.

When the distance between the atoms in the interface is not identical it is still possible to maintain coherency by straining one or both of the two lattices (Coherency strains).
The strains associated with a coherent interface raise the total energy of the system, and for sufficiently large atomic misfit, or interfacial area, it becomes energetically more favourable to replace the coherent interface with a *semicoherent* interface in which the disregistry is periodically taken up by *misfit dislocations*.

If $d_\alpha$ and $d_\beta$ are the unstressed interplanar spacings of matching planes in the $\alpha$ and $\beta$ phases respectively, the disregistry, or misfit between the two lattices ($\delta$) is defined by

$$\delta = \frac{d_\beta - d_\alpha}{d_\alpha}$$

in one dimension the lattice misfit can be completely accommodated without any long-range strain fields by a set of edge dislocations with a spacing $D$

$$D = \frac{b}{\delta}$$

The matching in the interface is now almost perfect except around the dislocation cores where the structure is highly distorted and the lattice planes are discontinuous.
The interfacial energy of a semicoherent interface can be approximately considered as the sum of two parts: (a) a chemical contribution, \( Y_{ch} \) as for a fully coherent interface, and (b) a structural term \( Y_{st} \), which is the extra energy due to the structural distortions caused by the misfit dislocations.

As the misfit \( \delta \) increases the dislocation spacing diminishes. For small values of the \( \delta \) structural contribution to the interfacial energy is approximately proportional to the density of dislocations in the interface.

However \( Y_{st} \) increases less rapidly as \( \delta \) becomes larger and it levels out when \( \delta = 0.25 \).

As the misfit dislocation spacing decreases the associated strain fields increasingly overlap and annul each other. The energies of semicoherent interfaces are generally in the range 200-500 mJ m\(^{-2}\).

When \( \delta > 0.25 \), i.e. one dislocation every four interplanar spacings, the regions of poor fit around the dislocation cores overlap and the interface cannot be considered as coherent, i.e. it is incoherent.
When the interfacial plane has a very different atomic configuration in the two adjoining phases there is no possibility of good matching across the interface.

The pattern of atoms may either be very different in the two phases or, if it is similar, the interatomic distances may differ by more than 25%.

In general, incoherent interfaces result when two randomly oriented crystals are joined across any interfacial plane.

Very little is known about the detailed atomic structure of incoherent interfaces, but they have many features in common with high-angle grain boundaries. They are characterized by a high energy (500-1000 mJ m\(^{-2}\)) which is relatively insensitive to the orientation of the interfacial plane.
FCC and BCC crystals often appear with the closest-packed planes in each phase, (111)fcc and (110) bcc, almost parallel to each other.

Two variants of this relationship are found: the so-called Nishiyama- Wasserman (N-W) relationship:

\[(110)_{\text{bcc}}// (111)_{\text{fcc}}, [001]_{\text{bcc}}// [\bar{1}01]_{\text{fcc}}\]

and the so-called Kurdjumov–Sachs (K–S) relationship:

\[(110)_{\text{bcc}}// (111)_{\text{fcc}}, [\bar{1}11]_{\text{bcc}}// [0\bar{1}1]_{\text{fcc}}\]

Atomic matching across a (111)fcc // (110)bcc interface bearing the NW orientation relationship for lattice parameters closely corresponding to the case of fcc and bcc iron
Second-Phase Shape: Interfacial Energy Effects

In a two-phase microstructure one of the phases is often dispersed within the other, for example $\beta$-precipitates in an $\alpha$-matrix.

Such a system will have a minimum free energy when the shape of the precipitate and its orientation relationship to the matrix are optimized to give the lowest total interfacial free energy.

This situation arises during the early stages of many precipitation hardening heat treatments, and the $\beta$ phase is then termed a *fully coherent precipitate* or a *GP zone*.

Thus a $\gamma$-plot of the $\alpha/\beta$ interfacial energy would be largely spherical and, ignoring coherency strains, the equilibrium shape of a zone should be a sphere.

The zones are a silver-rich fcc region within the aluminium-rich fcc matrix. Since the atomic diameters of aluminium and silver differ by only 0.7% the coherency strains make a negligible contribution to the total free energy of the alloy.

In other systems such as Al-Cu where the atomic size difference is much larger strain energy is found to be more important than interfacial energy in determining the equilibrium shape of the zone.
Electron micrograph of Ag-rich zones in an Al-4 atomic % Ag alloy
Coherency strain contract
Semi-coherent precipitates

From an interfacial energy standpoint it is favourable for a precipitate to be surrounded by low-energy coherent interfaces.

However, when the precipitate and matrix have different crystal structures it is usually difficult to find a lattice plane that is common to both phases.

The Wulff theorem would then predict the equilibrium shape to be a disc with a thickness/diameter ratio of $\gamma_c/\gamma_i$ where $\gamma_c$ and $\gamma_i$ are the energies of the (semi-) coherent and incoherent interfaces.

The above construction only predicts the equilibrium shape if misfit strain energy effects can be ignored.

Disc-shaped precipitates may be much wider than the equilibrium shape if the incoherent edges grow faster than the broad faces.
The tetragonal \( \theta' \) phase in aged Al-4 wt% Cu alloys are plate-shaped.

The unit cell of the \( \theta' \) precipitate in Al-Cu alloys. (b) The unit cell of the matrix.
Electron micrograph showing the Widmanstätten morphology of "V' precipitates in an Al-4 atomic % Ag alloy
Incoherent Precipitates

Electron micrograph showing incoherent particles of in an Al-Cu alloy.
Precipitates on Grain Boundaries

When a second-phase particle is located on a grain boundary as it is necessary to consider the formation of interfaces with two differently oriented grains.

The precipitate can have

(i) incoherent interfaces with both grains,
(ii) a coherent or semicoherent interface with one grain and an incoherent interface with the other,
(iii) it can have a coherent or semicoherent interface with both grains.
An precipitate at a grain boundary triple point in an (αβ- Cu-In alloy. Interfaces A and B are incoherent while C is semicoherent.
**ANTI-PHASE BOUNDARIES**

Fig. 3: Dislocation cutting through an ordered precipitate forming an APB

- Additional energy is required to create an APB

\[
\Delta \tau_{APB} = \frac{\pi}{2b} \gamma_{APB} \frac{r}{L} = \frac{\pi}{2b} \gamma_{APB} V_f
\]

[Diagram showing anti-phase domains and boundaries]
PRECIPITATION HARDENING

- Contributions to Precipitation Hardening
  - Anti-Phase Boundaries
  - Interfaces
  - Coherency Strains
  - Modulus Effect

\[ \Delta \tau_{tot} = \Delta \tau_{APB} + \Delta \tau_{int} + \Delta \tau_{coh} + \Delta \tau_{mod} \]

Fig. 4: Schematic of a sheared precipitate
Complexions

Grain boundaries can be considered as quasi-two-dimensional “phases” that may undergo phase like transitions in which their structure and chemistry changes abruptly at critical values of thermodynamic parameters.

The grain boundary properties most strongly affected by these transitions will be the non-equilibrium properties, such as mobility, diffusivity, intergranular cohesive strength and grain boundary sliding resistance.

If a significant fraction of the grain boundaries in a polycrystalline material undergo a transition, the cumulative effect can be a dramatic and rather sudden change in macroscopic properties.

Grain boundary complexion transitions have traditionally been called grain boundary “phase transitions”, in analogy to bulk phase transitions.

Equilibrium interfacial states do not satisfy the Gibbs definition of a phase because they are inhomogeneous and may have gradients of structure, composition, properties and other order parameters.

A complexion, concisely defined, is interfacial material or strata that is in thermodynamic equilibrium with the abutting phase(s) and has a stable, finite thickness that is typically on the order of 0.2–2 nm.
The grain boundary energy, $c$, is always a continuous function of one of the thermodynamic parameters (e.g. $T$, $P$, $\mu_i$, $R$ or $n^\gamma$) for a complexion transition that occurs under equilibrium conditions.

This implies that two (or more) complexions may coexist at equilibrium in a manner analogous to the coexistence of bulk phases at solidus and liquidus lines on phase diagrams.

A second-order (or higher-order) complexion transition occurs when there is a discontinuity in a second (or higher-order) derivative of $\gamma$

complexion transitions are not limited to changes in the atomic structure or thickness of the grain boundary core (which are sometimes called “structural transitions”) but may also include transitions in composition, chemical bonding, roughening, atomic reconstructions of the grain boundary core even if they do not result in a thickness change.
Fig. 2. A schematic illustration of grain boundary excess free energy $\gamma$ in a pure material as a function of (a) pressure and (b) temperature for two "competing" complexion: $\alpha$ (blue line) and $\beta$ (red line). Solid lines represent the stable complexion and dashed lines represent the metastable complexion. A first-order grain boundary complexion transition occurs at the vertical dotted black lines and is recognizable by the discontinuity in the slope of $\gamma$. (a) Complexion $\beta$ has a larger excess specific volume than $\alpha$ (and hence a larger slope, $(\partial \gamma/\partial P)_T$), and is therefore the stable complexion at low pressure. (b) Complexion $\beta$ has a larger excess specific entropy than $\alpha$ (and hence a larger negative slope, $(\partial \gamma/\partial T)_P$), and is therefore the stable complexion at high temperature. Hart referred to $\beta$, which has larger excess specific volume and larger excess specific entropy, as the "high temperature phase (H-phase)", and $\alpha$ was referred to as the "low temperature phase (L-phase)" [5]. Adapted from Hart [5]. (For interpre-
Figure 4. (a) HAADF-STEM (I-III) and HRTEM (IV-VI) images of different grain boundary complexionions in alumina (top), and representative schematics of each boundary type (bottom). (b) Experimentally measured reduced grain boundary mobilities ($M_r$) for each complexion type (I–VI) versus inverse temperature for doped aluminas displaying normal and abnormal grain growth with different morphologies. Note the reduced mobility is the mobility times the grain boundary energy ($\gamma$), which is the parameter that is directly measurable from grain growth. Reprinted from Reference 31 with permission from Elsevier.