

Crystalline Solids

Books

There are many good texts on crystalline solids which cover the defects we will be covering here, many of which will already be familiar to you from Solid State.

e.g

Kittel

Ashcroft and Mermin

Rosenberg

More specialist texts:

Hull and Bacon – Introduction to Dislocations

Ashby and Jones – Engineering Materials

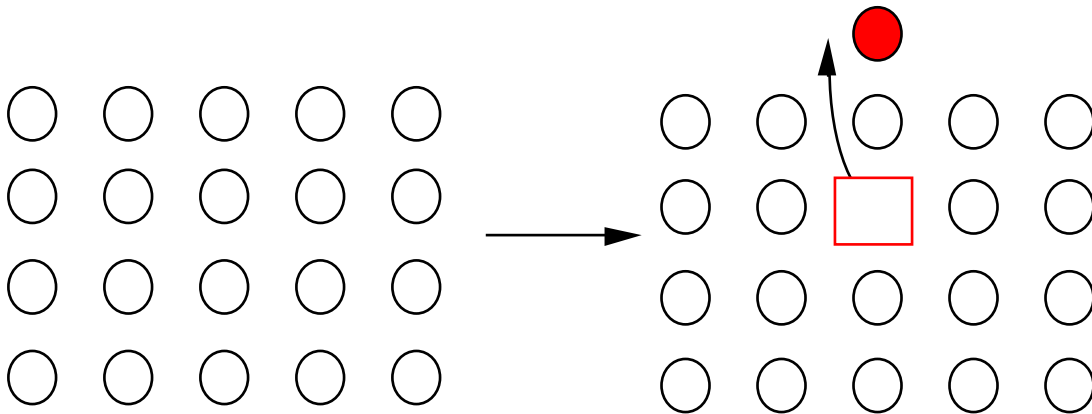
Defects

Three basic (geometric) types:

- **Point** – vacancy, interstitial, substitutional
- **Line** – dislocations
- **Plane** – grain boundaries

Point Defects

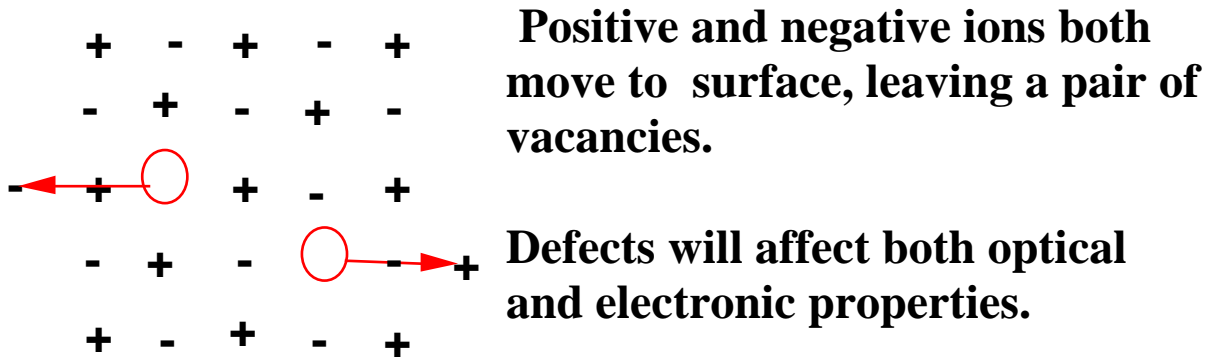
1. Vacancy or Schottky Defect



Perfect Crystal
Free energy G_0

Defect Crystal
Free energy G

More complicated in ionic crystals, where still need to maintain charge neutrality in the bulk.

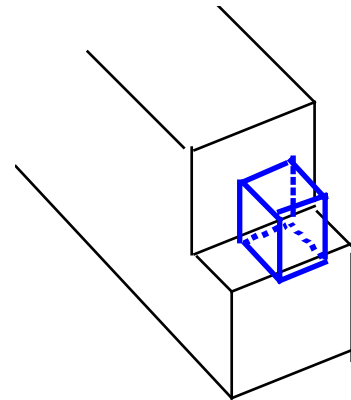


In general, the energy of formation E_v depends on site to which atom moved.

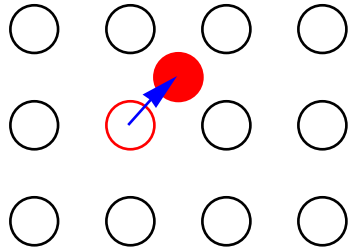
E_v lower if transferred to kink site (crystal ledge) than perfect surface.

On average E_v corresponds to net breaking of $\sim 1/2$ neighbouring bonds
 $\sim 1/2$ latent heat of sublimation/atom

$$E_v \sim 1\text{eV}$$



2) Interstitial vacancy – Frenkel defect



Ionic crystal – 2 types



More likely since cations tend to be smaller than anions
⇒ lower associated strain energy.

Energy due to strain (non-ionic case)

Strain energy = $1/2$ elastic constant \times strain² /vol

Define shear modulus $G = \frac{\text{stress}}{\text{strain}} = \frac{\tau}{\gamma}$

Strain energy = $1/2 G \gamma^2$ (or equivalently $1/2 \tau\gamma$)

If b = lattice parameter

Volume $\sim b^3$

Strain ~ 1

\Rightarrow Strain energy = $1/2 G b^3$

hence $E_{\text{Frenkel}} \sim 5\text{-}6\text{eV}$

Much larger than E_{Schottky} and also $E_{\text{Frenkel}} > k_B T$

In general not thermodynamically stable, and won't be discussed further.

Equilibrium number of vacancies in monatomic crystal

(For complete discussion see Waldram, Theory of Thermodynamics)

Compute F for crystal with N atoms, n vacancies on $N+n$ sites.

3 contributions to total entropy

- S_c determined by density of states etc for given configuration of atoms.
- $S_b \propto$ number of bulk configurations
- $S_s \propto$ number of surface arrangements

And

$$S_c = k_B \ln g_c(E)$$
$$S_b = k_B \ln W_b$$
$$S_s = k_B \ln W_s$$

At equilibrium

$$dF = dF_c - TdS_b - TdS_s = 0$$

where $dF_c = dE - TdS_c - TdS_s$, the change in free energy when we move an atom from a particular bulk site to a particular surface site, without allowing lattice rearrangements to occur.

$DF_c \sim 6$ nearest neighbour bond energies (since break on average 1/2 the bonds in the surface)

Now $W_b = \frac{(N+n)!}{N!n!}$

If 1 vacancy added W_b multiplied by

$$\frac{N + n + 1}{n + 1} \sim \frac{N + n}{n}$$

$$\therefore dS_b = k_B \ln\left(\frac{N + n}{n}\right)$$

For large crystals $dS_s \ll dS_b$

$$\therefore dF \sim dF_c - k_B T \ln\left(\frac{N + n}{n}\right) = 0$$

$$\therefore n \sim N \exp -dF_c/k_B T$$

This is generally quite small, but can become appreciable towards the melting point.

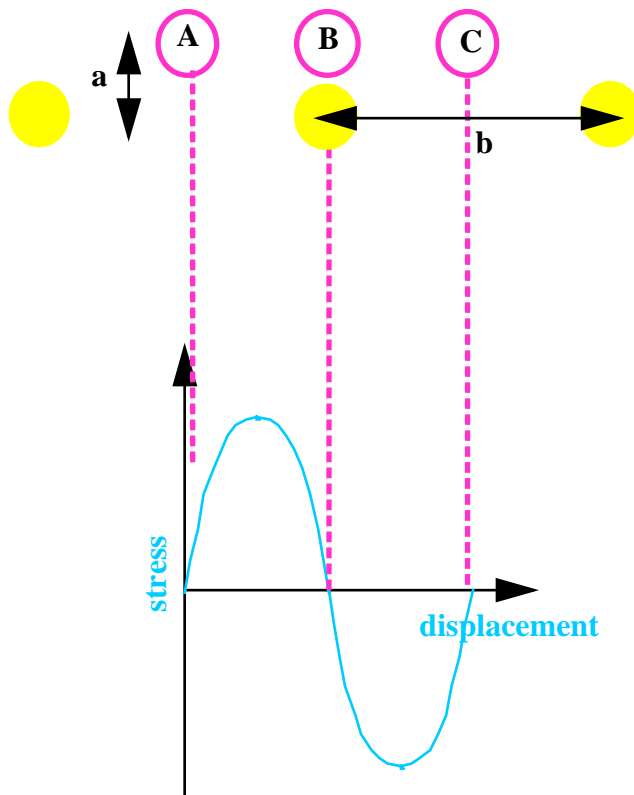
We will see later how vacancies are important for creep and diffusion

Dislocations – Line Defects

Dislocations were originally invoked to explain the discrepancy between theoretical shear stress and that experimentally determined, long before a dislocation was directly seen.

Theoretical Shear Stress

As two atom planes move past one another, the stress must increase and then decrease.



Assume a sinusoidal form for the variation of shear stress τ with displacement x .

Shear stress $\tau = k \sin \frac{2\pi x}{b}$ with $k = \text{const}$

Near origin, slope is measure of elastic shear modulus G .

Hence, within this linear regime $d\tau = G \frac{dx}{a}$ and

$$d\tau]_{x=0} = \frac{2\pi k}{b} \cos\left(\frac{2\pi x}{b}\right) dx]_{x=0} \sim \frac{2\pi k}{b} dx$$

$$\Rightarrow \frac{2\pi k}{b} = \frac{G}{a} \quad \text{and therefore} \quad k = \frac{Gb}{2\pi a}$$

$$\therefore \tau = \frac{Gb}{2\pi a} \sin\left(\frac{2\pi x}{b}\right)$$

Maximum shear stress τ_0 is given by

$$\tau_0 = \frac{Gb}{2\pi a} \sim \frac{G}{2\pi}$$

Better models give $\tau_0 \sim G/30$

Experiment shows this is far too high

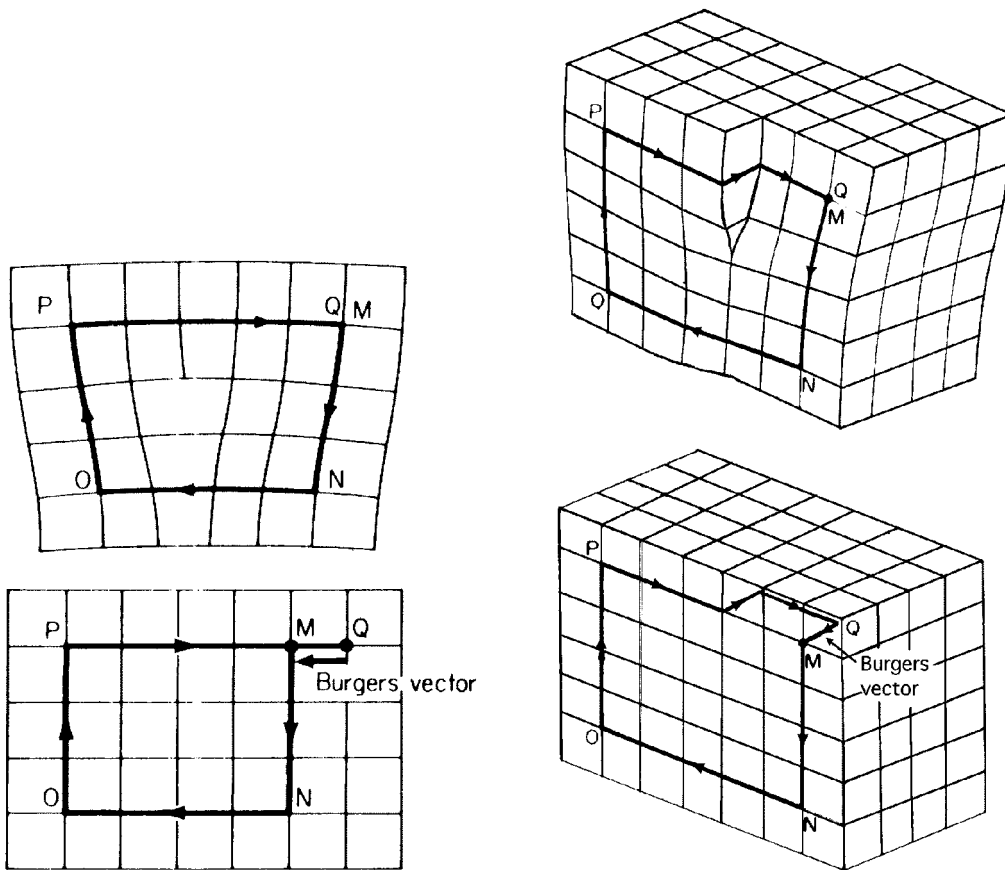
e.g Copper $G=4.6 \text{ GN m}^{-2} \Rightarrow \tau_0 = 0.72 \text{ GN m}^{-2}$

Experimentally a good single crystal gives τ_0 100 kN m^{-2}

Dislocations

The origin of the discrepancy between theory and experiment lies in the existence of dislocations.

Dislocations are characterised by their **Burger's vectors**. These represent the 'failure closure' in a Burger's circuit in imperfect (top) and perfect (bottom) crystal.



Edge

Vectors describing dislocation line and Burger's vector are **Perpendicular**

Screw

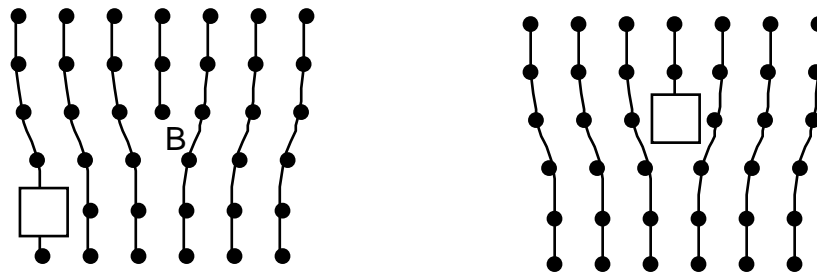
Parallel

Many objects can impede dislocation motion:

- Other dislocations
- Precipitates
- Grain boundaries

Climb – Diffusion-Controlled Creep

Dislocation climb allows dislocations to climb round obstacles which are impeding their glide, thus allowing slip to continue.



A vacancy diffuses to the position of atom B, causing the dislocation to climb one lattice vector.

Diffusion can occur either through the bulk of the crystal - as shown ('**lattice diffusion**') - or along the dislocation core ('**pipe diffusion**').

This non-conservative dislocation mechanism gives rise to high temperature **creep** deformation.

It only occurs at **comparatively high temperatures** because of the temperature dependence of the diffusion. It is a means of unpinning sessile dislocations.

Planar Defects – Grain Boundaries

In practice, metals (and indeed semiconductors) are **polycrystalline** and contain grain boundaries.

Lattice planes are not continuous across a grain boundary, and **dislocation glide is impeded**.

Grain size therefore affects the strength of a metal.

Larger grains mean softer material.

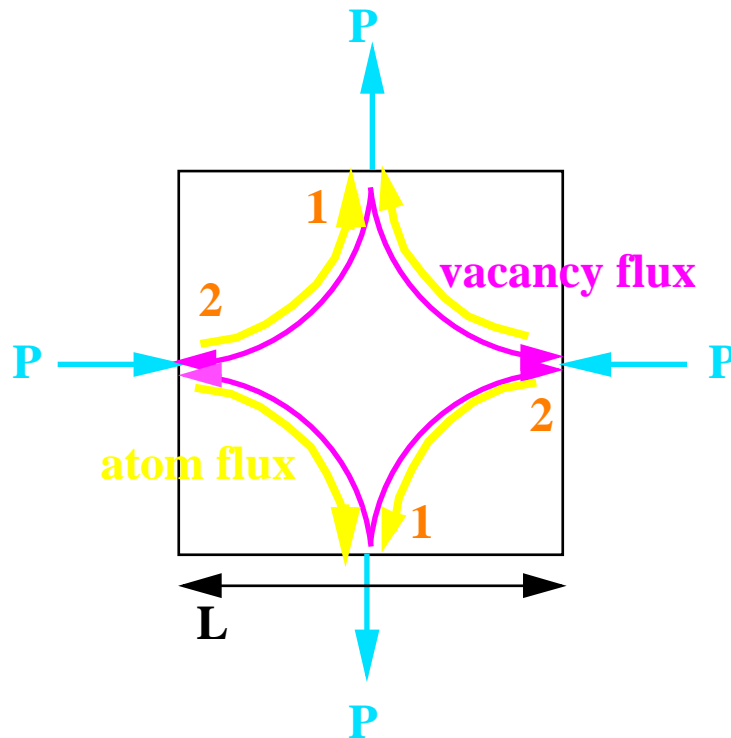
Grain boundaries are regions of poor packing, and hence are easy sites for vacancy diffusion to occur.

Diffusion will happen here more than in the bulk at low temperatures.

Can therefore identify two regimes of creep due to vacancy diffusion alone.

2. **Coble creep at low temperatures; grain boundary diffusion.**
3. **Nabarro-Herring creep at high temperatures; bulk diffusion of vacancies.**

Diffusion and Flow in Crystals



Model for bulk diffusion:

Imagine a cubic grain with population of vacancies under shear stress τ , or equivalently stresses P shown.

No net change in volume.

Atomic volume = Ω

Change in $G_v = P\Omega$

At sites labelled 1 have net increase in vacancies and at 2 have decrease

$$n_1 = n_{eq} e^{P\Omega/kT} \qquad n_2 = n_{eq} e^{-P\Omega/kT}$$

Differences in populations lead to net flux of vacancies from 1 to 2 to remove gradient, and equivalently net flux of atoms from 2 to 1.

Concentration gradient $\sim \frac{n_1 - n_2}{L}$

Flux J = Flow rate/unit area/unit time $= D_v \frac{(n_1 - n_2)}{L}$

In unit time cube increases in thickness by $J\Omega$

\therefore **strain rate** $\dot{\epsilon} = \frac{J\Omega}{L} = \frac{D_v(n_1 - n_2)}{L^2} \Omega$

Now $n_1 - n_2 \sim n_{eq} 2P\Omega/kT$ for $P\Omega/kT \ll 1$

\therefore
$$\dot{\epsilon} = \frac{D_v n_{eq} 2P\Omega^2}{kTL^2}$$

**Now bulk diffusion coefficient $D = D_v \times n_{eq}/N$
where n_{eq}/N is probability of vacancy site and $1/N = \Omega$**

\therefore
$$\dot{\epsilon} = \frac{2P\Omega D}{kTL^2}$$

Other models give other prefactors.

$$\text{Effective viscosity} = \frac{\text{shear stress}}{\text{shear strain}} = \frac{P}{\dot{\epsilon}}$$

$$\bullet \quad \eta = \frac{kTL^2}{2D\Omega}$$

and is strongly grain size dependent.

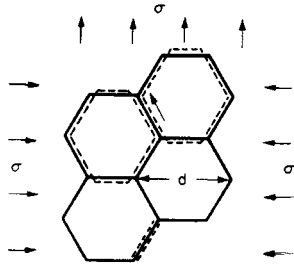
e.g. for lead (M Pt ~600K)

Viscosity η in poises

T/K	L=1cm	L=10 ⁻³ cm (polyXtal)
300	10 ²³	10 ¹⁷
595	10 ¹⁷	10 ¹¹

(1poise = 0.1 Pa s)

Grain Boundary or Coble Creep



In practice there must always be flow of grain boundaries to accommodate shape changes.

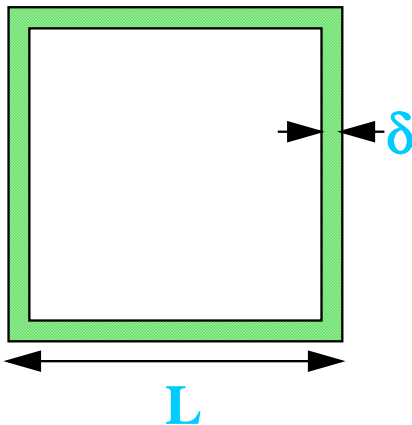
Because grain boundaries more disordered than bulk

$$D_{gb} \gg D_{bulk}$$

Typically $D_{gb} \sim 10^6 D_{bulk}$ (although very hard to measure).

Contribution to creep from grain boundary will be

$$\sim \frac{\delta}{L} D_{gb}$$



$\delta \sim 1\text{nm}$ (ie few atoms layers are disordered); so for 1mm grain size $\delta/L \sim 10^{-6}$.

Contributions from N-H and Coble creep similar.

As grain size decreases Coble creep becomes more important.

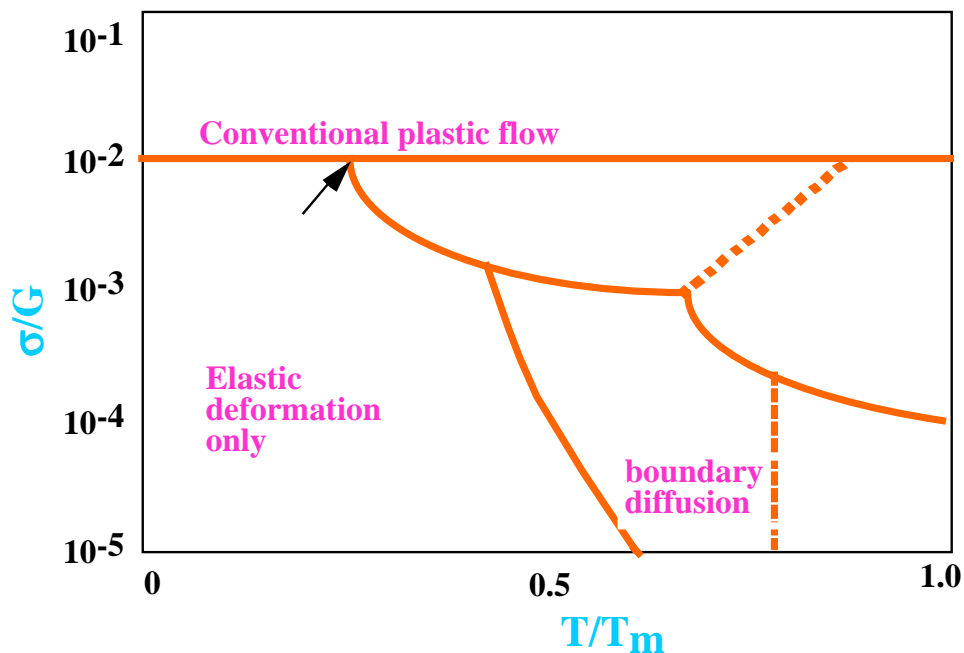
Also true at low temperature when activation energy to create vacancies becomes an obstacle.

Ashby Deformation Map

These are a way of pulling all the ideas so far discussed together, taking into account the different regimes of behaviour.

Axes are normalised

Boundaries between different regimes will depend on strain rate and grain size.



Fracture

Book e.g JF Knott Fundamentals of Fracture Mechanics

All materials show some elasticity.

Metals and many polymers also exhibit significant plasticity.

Fracture may occur with or without plasticity.

Brittle fracture is usually associated with rapid crack propagation **without plastic deformation.**

Ductile behaviour does **have associated plastic deformation.**

Arguments similar to those used to arrive at the concept of dislocations, show that the theoretical failure stress is much higher than that experimentally observed.

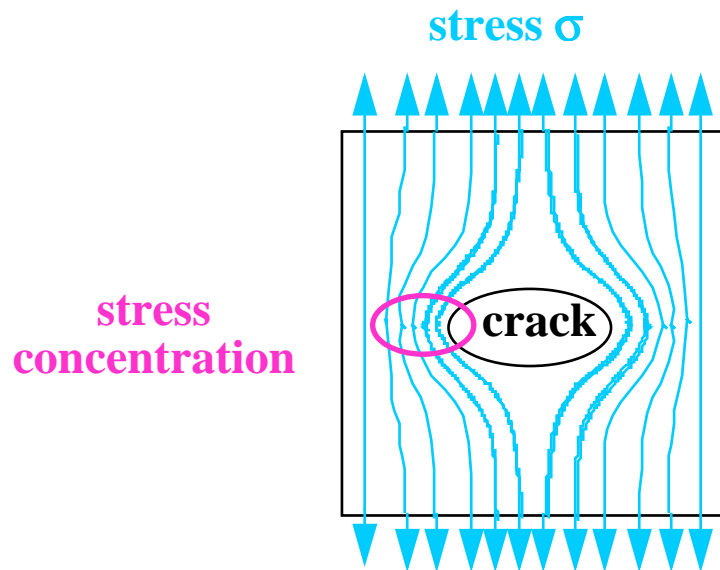
As before this is attributed to the presence **of flaws: pre-existing cracks and stress concentrations.**

Stress Concentrations at Notches and Cracks

Inglis (1913) and Kolosoff (1914)

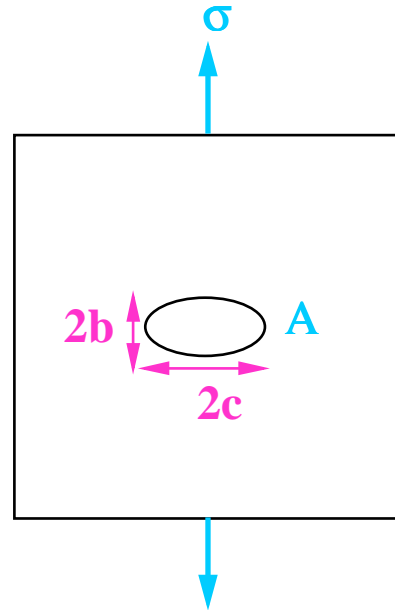
Imagine lines of force around a crack

Since crack cannot bear load, the lines of force become concentrated around the tips of the crack leading to a **stress concentration**.



Consider elliptical hole in plate under uniform tension σ .

Crack tip radius
 $\rho = b^2/c$



Stress concentration a maximum at A, and can be

shown to be $\sigma_A = \sigma \left(1 + \frac{2c}{b}\right) = \sigma \left(1 + 2\sqrt{\frac{c}{\rho}}\right)$

Usually have $c \gg \rho$; then

$$\sigma_A \sim 2\sigma \sqrt{\frac{c}{\rho}}$$

For circular hole $b=c$ and $\sigma_A = 3\sigma$ acting tangentially.

As ρ decreases (ie crack gets sharper), stress concentration increases.

eg $c=10\mu\text{m}$, $\rho = 0.5\text{nm}$ (ie atomically sharp)

$$\sigma_A/\sigma \sim 300$$

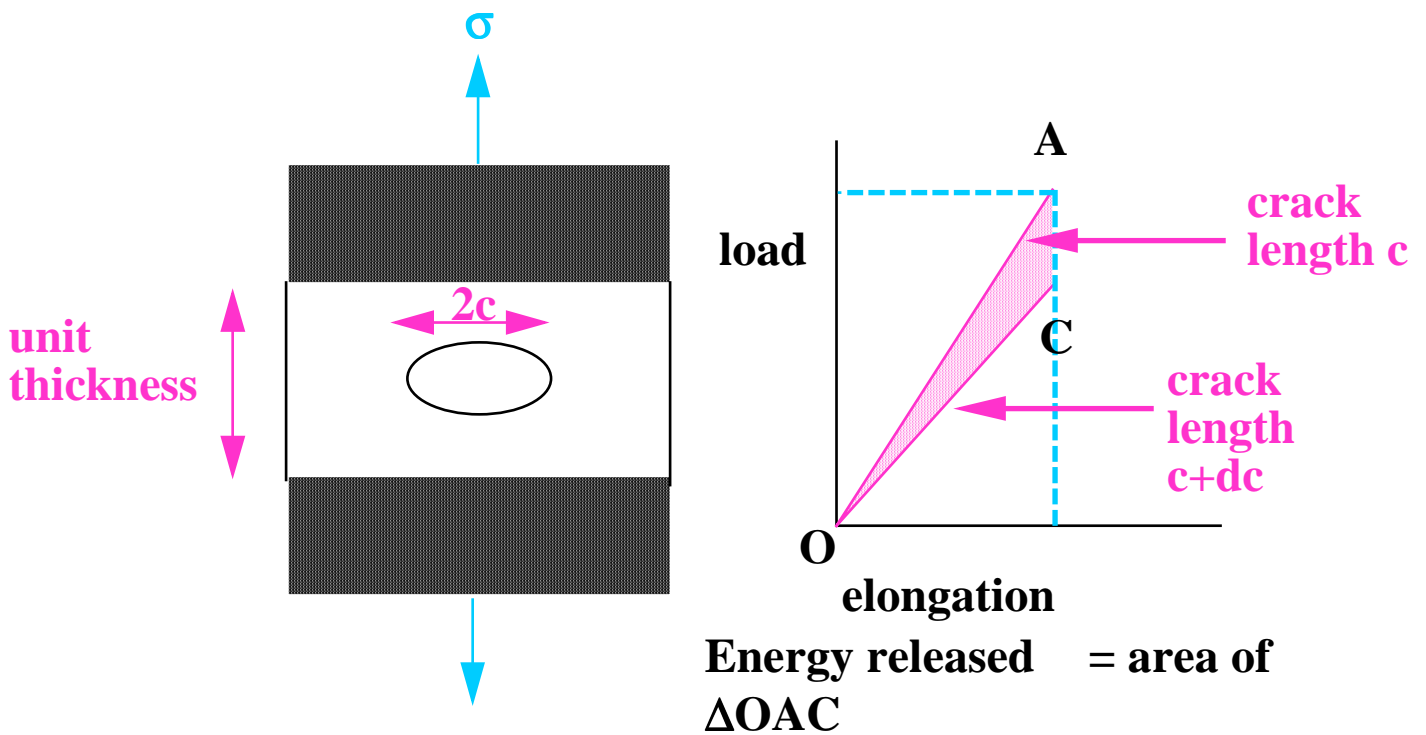
Stress falls off very fast ahead of crack tip within distance $\sim c$.

Crack can be surface notch or step (in which case c is the total notch length).

Griffith Criterion

This criterion expresses when a pre-existing crack is likely to lead to crack propagation and hence fracture.

It is an argument based on energy balance.

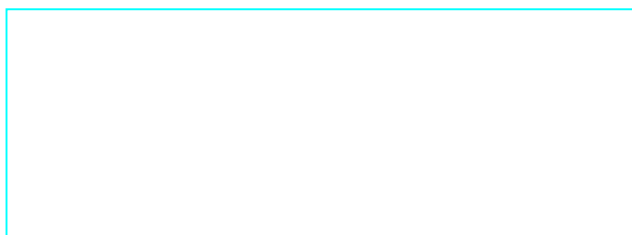


$$\sim \frac{1}{2} \sigma \times \frac{\sigma}{E} \times \pi c^2 \quad \text{for unit thickness}$$

↑
strain

(approx for sphere)

More accurate calculations lead to



$$\text{Energy } U = \frac{\pi\sigma^2 c^2}{E}$$

As crack grows $\frac{dU}{dc} = \frac{2\pi\sigma^2 c}{E}$

Griffith criterion says the crack will advance catastrophically if more energy is released than that absorbed by crack growth (W) due to creation of new surface

$$W = 2c \cdot 2\gamma = 4c\gamma$$

i.e. $\frac{2\pi\sigma^2 c}{E} > 4\gamma$

$$\Rightarrow \sigma_c = \sqrt{\frac{2E\gamma}{\pi c}}$$

Griffith criterion

Can also be expressed in terms of

G = elastic energy release rate, or crack driving force (where the use of the word rate means per increment of crack length not time)

G has dimensions of energy/unit plate thickness/unit crack extension

Two crack tips

$$2G = dU/dc = dW/dc = 4\gamma$$

$$\Rightarrow \sigma_c = \sqrt{\frac{EG}{\pi c}}$$

**Strong materials have high E and γ , and small c.
But strong is not the same as tough.**

Tough materials imply large energy absorption as crack advances i.e. large G or dW/dc or γ .

Note energy released $\propto c^2$

But energy absorbed $\propto c$

Critical condition must always be met for large enough crack, but may not be for small specimen with small cracks.

Fracture Mechanics

When a block containing a crack is stressed, there is a stress concentration at the crack tip which falls off with distance.

The stress at any point (away from the actual crack tip where a singularity would be implied) can be written

$$\sigma_{ij} = \frac{K}{\sqrt{2\pi r}} f_{ij}(\theta)$$

$\theta =$ azimuthal angle
 $r =$ distance ahead of tip

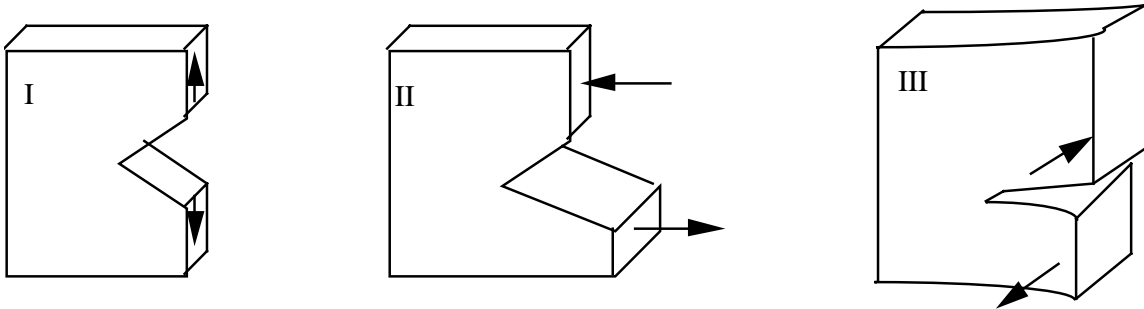
K is the stress intensity factor – it depends on crack length, applied stress and specimen geometry.

$$K = Y\sigma\sqrt{c}$$

↑
specimen geometry dependent term

K is a link between detailed stress field around crack and 'macroscopic' quantities such as applied stress and crack length.

Modes of Loading



For the simple case of mode I loading of crack of length $2c$

$$K = \sigma\sqrt{\pi c} \quad \text{i.e. } Y = \sqrt{\pi}$$

Recalling $\sigma_c = \sqrt{\frac{2E\gamma}{\pi c}}$

$$K_{Ic} = \sqrt{2E\gamma} = \sqrt{EG}$$

Critical stress intensity factor
For mode I loading

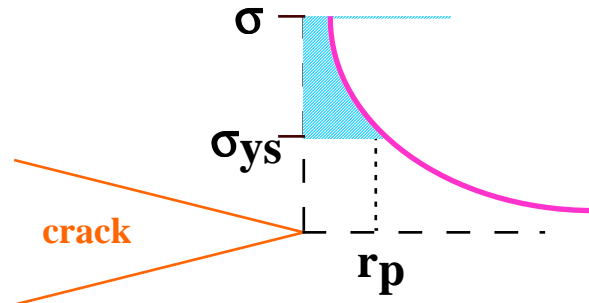
Note this provides a way to measure γ for brittle material, by finding the value of K_{Ic} ie introduce notch of known length c , and find critical stress.

However many materials do not simply show brittle failure, and there may be extensive crack tip plasticity.

Existence of this plasticity removes the stress singularity at the crack tip.

Energy absorption is then much greater, and appropriate γ will not simply be surface energy.

Simplest model assumes deformed zone of radius r_p ahead



of crack tip within which stress = yield stress σ_{ys}

$$\sigma = \frac{K_I}{\sqrt{2\pi r_p}} = \sigma_{ys} \quad \Rightarrow \quad r_p = \frac{K_I^2}{2\pi\sigma_{ys}^2} \quad \text{and} \quad K_I = \sigma\sqrt{\pi c}$$

$$r_p = \frac{c\sigma^2}{2\sigma_{ys}^2}$$

In fact this is underestimate, since load indicated by shaded area must still be supported and hence stress beyond circular zone pushed up so more deforms.