

Liquids and Melts

Books

D Tabor – Gases, Liquids and Solids CUP 1991
(3rd edition)

JN Murrell and AD Jenkins Properties of
Liquids and Solutions

We have already seen how to characterise the structure of amorphous materials experimentally using different types of scattering.

At this level of structure, liquids are essentially the same as glasses – it is in their dynamics that they differ.

So the simplest model of a liquid assumes 'hard sphere' interactions – i.e. repulsive forces dominate.

As with glasses, computer simulations are often used to model structure.

Density of 'random close-packed' structure – i.e. the structure in which there are no spaces large enough to fit another atom – is 0.638 compared with 0.7405 for cubic close packing.

The density of a liquid is therefore only ~10% different from a crystalline solid – **little volume change on melting.**

Properties of Liquids

- **Unable to withstand shear stresses** – liquids flow, but they may exhibit instantaneous shear modulus if they take a finite time to respond.
- Have a **critical point**, when liquid and gas phase are indistinguishable.
- Can **withstand negative pressures**, although ultimately will cavitate.
- Have **well defined volumes**, and relatively strong interatomic cohesive forces.
- Nearest neighbour organisation not very different from solid, and coordination number only drops by ~10% , say from 12 to 10, upon melting.

Melting Transition

1st order phase change, with associated latent heat and change in entropy.

Magnitude of changes at T_m quite small, compared with gas-liquid transition, except for change in fluidity.

There are various approaches to the melting transition, but it is not well understood.

Lindemann Criterion:

(An early, simple and widely used criterion to predict melting points).

Assumes solid melts when rms amplitude of vibration exceeds critical fraction of lattice spacing.

[Note that melting cannot be explained simply by the interatomic potential, which can only predict solids and gases.]

$$\langle u^2 \rangle^{1/2} = f a_0$$

where f appears to depend on lattice.

Solid	T_m calculated (K)	T_m experimental(K)
Lead	400	600
Silver	1100	1270
Iron	1800	1800
Tungsten	4200	3650
Sodium chloride	1200	1070
Quartz	1900	2000

Dislocation Theories of Melting

We have seen how around dislocation cores, the packing of a crystal is severely disrupted.

This model assumes that **in the liquid every atom is situated within a dislocation core** – to give non-regular packing overall.

Thus the liquid is imagined to be saturated with dislocations.

Note that the stored energy of dislocations in a heavily cold-worked material with high dislocation density can start to approach the latent heat of melting.

Must have an **energy penalty for dislocation creation which decreases** as the number of dislocations already present increases.

This can occur because dislocation dipoles can be formed with screening of long range fields.

If dipole separation comparable with core diameter

Total energy/pair ~ 2 x core energy

Using the fraction c of dislocations present as a parameter ($c=1$ fully saturated) **find lowest free energy state for**

$c=0$ at $T < T_m$

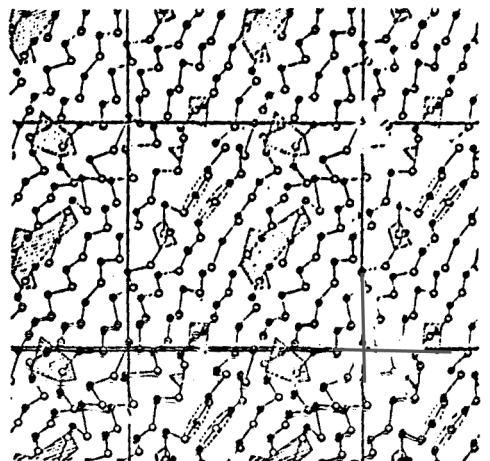
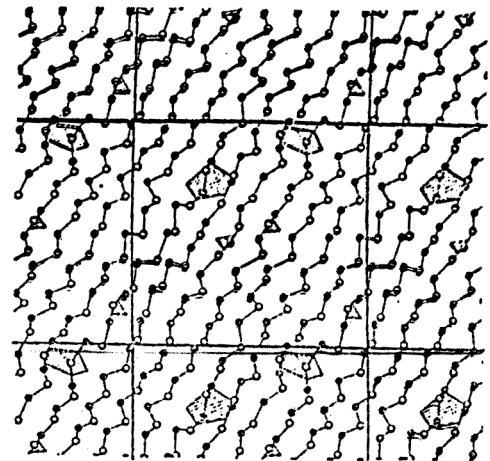
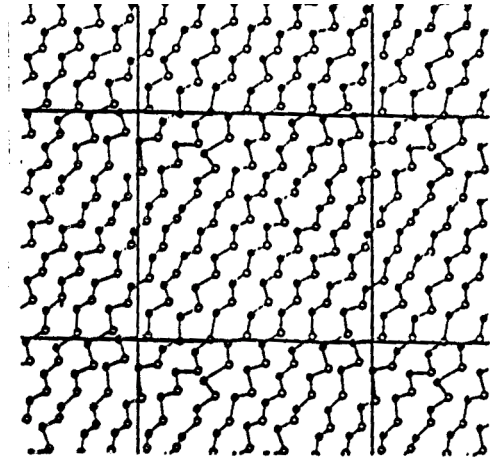
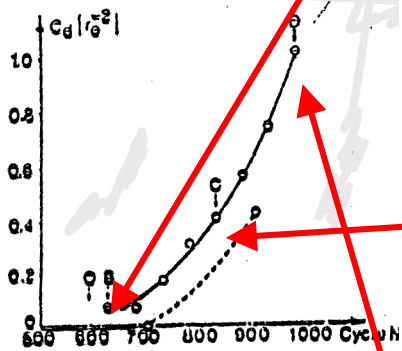
and $c=1$ for $T > T_m$

As dislocations proliferate, solid loses its rigidity.

This can be studied by computer simulation, including using a molecular dynamics approach to study how the crystal structure changes with annealing.

However in practice surfaces (grain boundaries, free surface etc) may also matter – melting tends to initiate there and spread into the bulk.

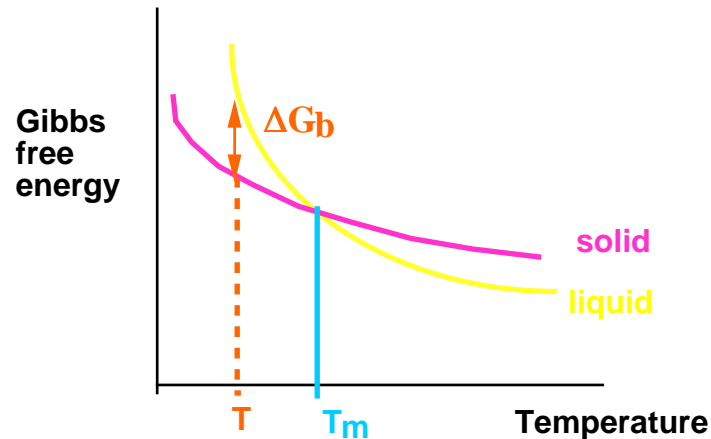
Computer Simulation of Melting



At late stage of melting, many dislocations present and crystal structure not really visible

Kinetics of Crystallisation

Will now look at a more general version of what we first considered for polymer crystallisation.



T_m occurs when Gibbs free energy of solid and liquid are identical.

This neglects any specific crystallography associated with crystal nucleus.

For now we will consider only homogeneous nucleation ie ignore the role of surfaces and seeds.

On solidifying the entropy changes by an amount ΔS_m .

$$\Delta S_m = \left(\frac{\partial G_S}{\partial T} \right)_p - \left(\frac{\partial G_L}{\partial T} \right)_p = \frac{\Delta H_m}{T_m}$$

where ΔH_m is the latent heat of fusion released upon crystallisation and is measurable by experiment.

In general there is a **degree of supercooling**, but if this is small we can integrate the equation for ΔS_m to yield

$$\Delta G_b \sim -\frac{\Delta H_m}{T_m} \Delta T$$

(This assumes the derivatives of free energy in solid and liquid phase don't change much with temperature, so that they can be approximated by straight lines.)

If you create a spherical droplet of a crystal (ignoring crystallography) of radius r in the liquid melt we can work out the total free energy change.

It will involve two terms

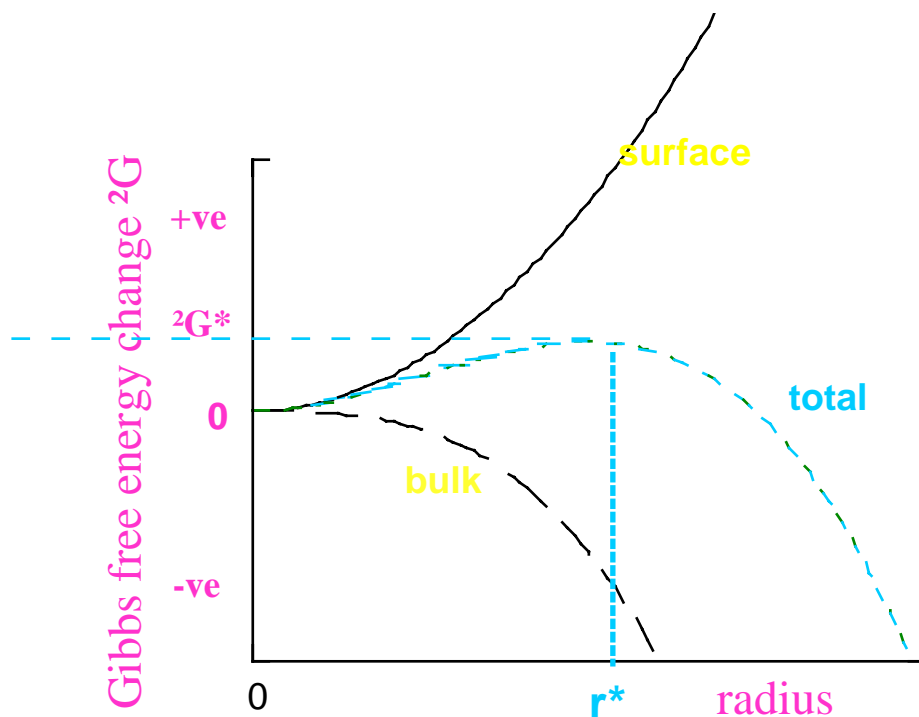
- **bulk**, associated with change in free energy $\Delta G_b(\Delta T)$
- **surface** – associated with the interface.

$$\Delta G = -\frac{4}{3} \pi r^3 \frac{\Delta H_m}{T_m} \Delta T + 4\pi r^2 \gamma_{SL}$$

bulk term **surface term**

γ_{SL} is the interfacial energy of solid/liquid interface

The dependence of the total free energy change on droplet radius can be plotted.



A critical nucleus size r^* exists when $\frac{\partial \Delta G}{\partial r} = 0$

This occurs when

$$4\pi r^{*2} \frac{\Delta H_m}{T_m} \Delta T = 8\pi r^* \gamma_{SL}$$

$$\Rightarrow \boxed{r^* = \frac{2\gamma_{SL}T_m}{\Delta H_m\Delta T}}$$

Droplets smaller than this are energetically unfavourable, shrink and disappear.

For these the energy gain on the formation of small droplets is insufficient to offset the interfacial energy cost.

Larger droplets grow.

ΔG^* is effectively an energy barrier to droplet formation

$$\boxed{\Delta G^* = \frac{16\pi}{3} \gamma_{SL}^3 \left(\frac{T_m}{\Delta H_m} \right)^2 \frac{1}{\Delta T^2}}$$

r^* is largest at $T \sim T_m$ - as the supercooling increases smaller droplets are stable.

One can evaluate the probability of a droplet of radius r forming in terms of the activation barrier.

$$P(r) \sim \exp -\Delta G(r)/kT$$

Number of critical clusters per N atoms is

$$N^* = N \exp -\Delta G^*/kT$$

Experiments to test these ideas are very difficult to do – in general heterogeneous rather than homogeneous nucleation will occur.

Classical experiments looked at very small particles nucleating in the melt.

In classical experiments small particles nucleating in the melt were looked at, in the belief that some of these would have nucleated homogeneously.

The rate $R = K \exp - \Delta G^*/kT$

The prefactor K takes into account the necessary diffusive processes required to allow a droplet to grow.

In general the rate will be determined by the exponential, but there are some systems where the necessary diffusion becomes kinetically limited e.g when the viscosity of the liquid becomes very high, following the Vogel-Fulcher law we discussed before.

$$\text{If } \eta \propto \exp \frac{B}{T - T_o}$$

As T_o approached $\eta \rightarrow \infty$.

Then nucleation will become kinetically inhibited and it is favourable for a glass to form.

Example – Tin

Melting point	505.7K
γ_{SL}	$54.5 \times 10^{-3} \text{ J m}^{-2}$
ΔH_m	$4.4 \times 10^8 \text{ J m}^{-3}$

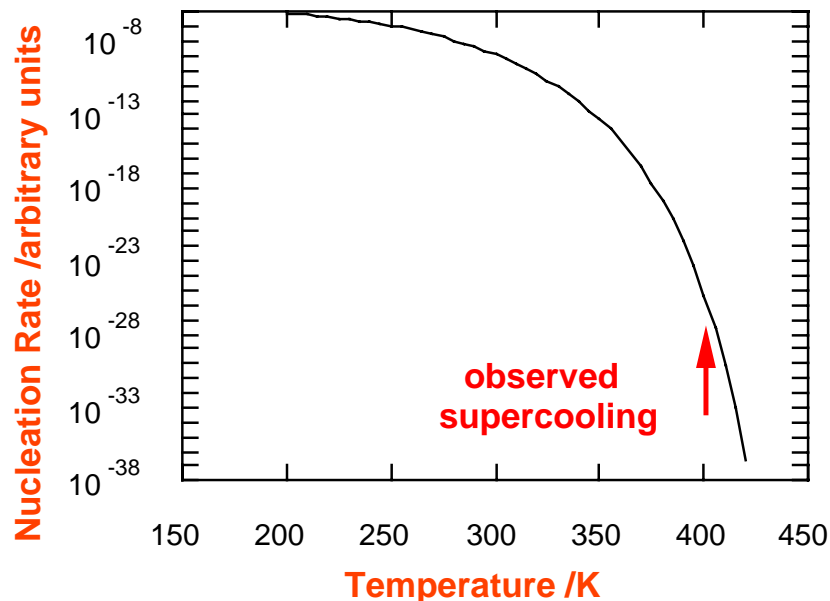
$$\Rightarrow \Delta G^* = \frac{16}{3} \gamma_{SL}^3 \left(\frac{T_m}{\Delta H_m} \right)^2 \frac{1}{\Delta T^2} = \frac{3.58 \times 10^{-15}}{\Delta T^2} \text{ JK}^{-2}$$

$$\therefore \frac{\Delta G^*}{kT} = \frac{2.6 \times 10^8}{\Delta T^2 T}$$

This can be plotted to show how rate depends on temperature.

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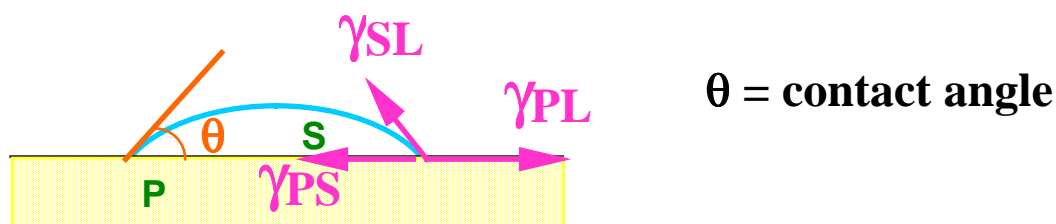
Nucleation Rate for Tin



Heterogeneous Nucleation

For heterogeneous nucleation have to correct this theory, to allow for change in energy penalty when we nucleate on a surface.

On a particle surface P, a droplet nucleus (S) may form.



Young's equation defines contact angle by balancing the different interfacial energy terms.

(Recall surface tension \equiv line tension/unit length.)

$$\gamma_{SL} \cos \theta = \gamma_{PL} - \gamma_{PS}$$

[Note the condition for complete wetting is that $\gamma_{SL} < \gamma_{PL} - \gamma_{PS}$ so that there is no real solution for θ ; then the drop completely wets the surface. These ideas hold for liquids wetting a surface too.]

In order to calculate the energy cost of nucleation we need to know the volume and surface area of such a spherical cap.

For a cap formed from a sphere of radius r

$$V = \frac{1}{3} \pi r^3 (1 - \cos\theta)^2 (2 + \cos\theta)$$

$$S_{PS} = \pi r^2 \sin^2\theta$$

$$S_{SL} = 2\pi r^2 (1 - \cos\theta)$$

[These equations reduce to the previous ones when $\theta = 180^\circ$, ie for homogeneous nucleation of a spherical drop.]

When such a spherical cap is created, change in free energy becomes

$$-\frac{1}{3} \pi r^3 (1 - \cos\theta)^2 (2 + \cos\theta) \frac{\Delta H_m}{T_m} \Delta T + \gamma_{SL} 2\pi r^2 (1 - \cos\theta) + \gamma_{PS} \pi r^2 \sin^2\theta - \gamma_{PL} \pi r^2 \sin^2\theta$$

new PS interface PL interface lost

Last two terms can be rewritten as $\gamma_{SL} \cos\theta \pi r^2 \sin^2\theta$ from Young's equation.

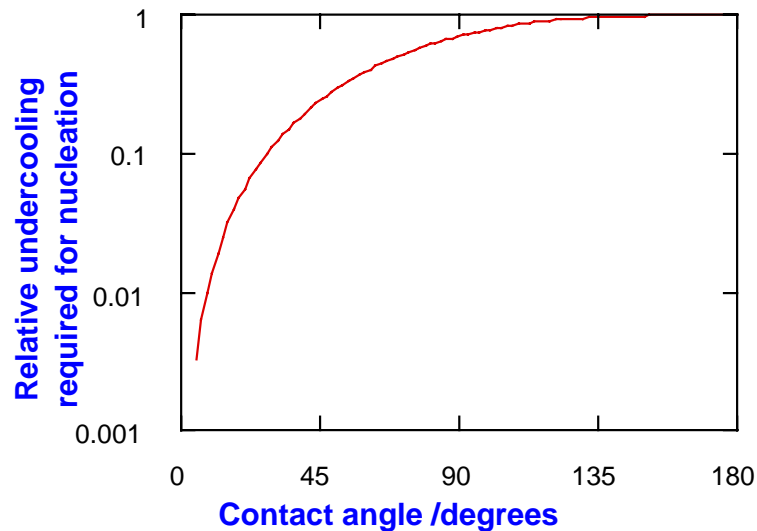
Differentiating to solve for r^* and rearranging, can show that all terms involving θ disappear and

$$r^* = \frac{2\gamma_{SL}T_m}{\Delta H_m \Delta T} \quad \text{as before}$$

and

$$\Delta G^* = \frac{16\pi}{3} \gamma_{SL}^3 \left(\frac{T_m}{\Delta H_m} \right)^2 \frac{1}{\Delta T^2} \frac{(1 - \cos \theta)^2 (2 + \cos \theta)}{4}$$

For contact angles $< 90^\circ$ this leads to a **substantial reduction in ΔG^*** , and hence in the supercooling necessary for nucleation.



This is why surfaces and dust particles can be so effective at favouring solidification.

When the particle is a seed crystal of the same material as the melt $\gamma_{PS}=0$ and $\gamma_{SL}=\gamma_{PL}$ (no interface)
 $\Rightarrow \cos\theta = 1$ and the contact angle is zero.

Then $\Delta G^* = 0$ and no activation energy is required.

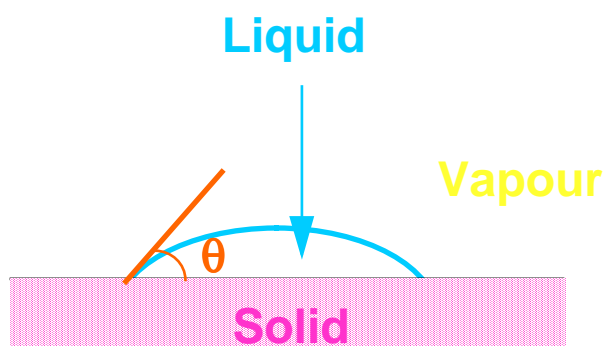
Melting

Supercooling is the rule when observing crystal nuclei forming from the melt.

This is not the case when crystals are heated to their melting point.

In general you cannot superheat a solid – why?

Consider a liquid droplet forming as it melts on a solid surface with vapour above.



Contact angle given by the same type of equation as previously, but now known as the Young-Dupré equation.

$$\gamma_{SV} - \gamma_{SL} = \gamma_{VL} \cos\theta$$

Uniform wetting of the surface occurs when the contact angle goes to zero

$$\gamma_{SV} - \gamma_{SL} > \gamma_{VL}$$

If this inequality holds at the triple point, the solid will be covered by a thin layer of its own melt.

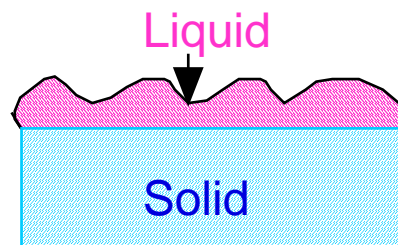
In general this inequality is found to be true for most solid/liquid pairs.

The solid and liquid are chemically identical (and number of nearest neighbours not very different) so that γ_{SL} is usually small.

Liquid surface energies (ie with the vapour phase) are usually less than solid surface energies because the fluidity of the former allows more rearrangements to occur.

Premelting usually occurs as the solid is heated towards T_m .

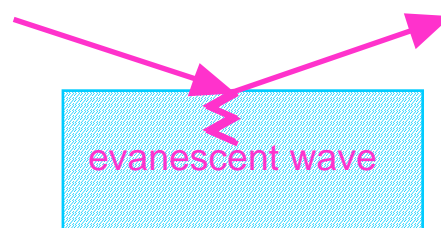
A thin layer of liquid forms on the surface below T_m and then increases to ∞ at T_m .



Can be studied experimentally:

- **Grazing angle X-ray diffraction**
- **Ion beam channelling.**

Grazing Angle X-ray Diffraction

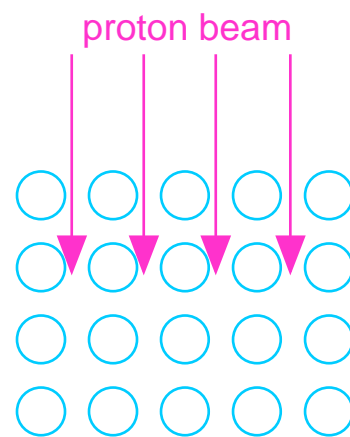


For sufficiently low angles of incidence very little penetration into the material (evanescent wave does not propagate far).

Only near surface structure seen.

Diffraction spots near the surface disappear below T_m : surface melting occurs.

Ion Beam Channelling



Ions/protons directed along lattice planes are not likely to be backscattered when the structure is regular; when disorder introduced into the surface by melting, backscattered yield increases.

Melting always starts at the surface, and becomes a bulk phenomena at T_m .

Examples of premelting phenomena:

- **Formation of ice from snow to give glaciers.**
- **Powder sintering below T_m .**