SOLIDIFICATION PRINCIPLES

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Course Content / Subject Headings

- **Liquid metals**
- **Nucleation**
  - Homogeneous and Heterogeneous
  - Dynamic nucleation
- **Growth**
  - The structure of the interface (in atomic scale)
- **Solidification of Single Phase Metals and Alloys**
  - Pure metals
  - Solute redistribution effects in alloys
  - Constitutional undercooling (super cooling) in alloys
  - Cellular and dendritic structures
  - Dendrite arm spacing (DAS)

- **Solidification of Multiphase Metals and Alloys**
  - Eutectics. Modification of eutectics (Cast iron and Al-Si alloys)
  - Pretectics, Monotectics
- **Particles and Inclusions in Melts**
- **Gasses in Melts**
  - Bifilm theory
- **The structure of Castings (Ingots)**
  - Macrostructure of fusion welds
- **Segregation**
  - Micro and Macro segregation
  - Segregation patterns in ingots
- **Cast Irons**
- **Aluminium Casting Alloys**

Liquid Metals

- The principal approaches to the study of liquids came from two directions. Liquids were considered as either dense gases or rather disordered solids. Also a geometrical concept in which the liquid is considered as a heap of atoms or molecules has been the subject of study.

Experimental Considerations

- ## The change in volume on melting

The change in volume on melting of some common metals

Metal	Lattice Structure	Melting Point ($^\circ$C)	Change in Volume (%)
Aluminium	f.c.c.	660	+6.0
Gold	f.c.c.	1063	+5.1
Zinc	h.c.p.	420	+4.2
Copper	f.c.c.	1083	+4.15
Magnesium	h.c.p.	650	+4.1
Cadmium	h.c.p.	321	+4.0
Iron	b.c.c./f.c.c.	1536	+3.0
Tin	b.c.t.	232	+2.3
Antimony	rhombohedral	631	- 0.95
Gallium	f.c. orthorhombic	30	-3.2
Bismuth	rhombohedral	271	-3.35
Germanium	dia. cubic	937	-5.0

- For close-packed metals, (hcp and fcc), melting causes a volume increase of 3.5-6 %. For most bcc metals the volume increase is 1-3%. Elements for which packing in the solids not dense (Si, Ge, Bi, Ga etc.) actually expand when they solidify.

- # The latent heat of melting (fusion)

Latent heats of melting and vaporisation of some common metals

Metal	Lattice structure	Melting point ($^{\circ}$C)	Latent heat* of melting (L_m)	Boiling Point ($^{\circ}$C)	Latent heat* of vaporisation (L_b)	$\dfrac{L_b}{L_m}$
Aluminium	f.c.c.	660	2.5	2480	69.6	27.8
Gold	f.c.c.	1063	3.06	2950	81.8	26.7
Copper	f.c.c.	1083	3.11	2575	72.8	23.4
Iron	b.c.c/f.c.c.	1536	3.63	3070	81.3	22.4
Zinc	h.c.p.	420	1.72	907	27.5	16.0
Cadmium	h.c.p.	321	1.53	765	23.8	15.6
Magnesium	h.c.p.	650	2.08	1103	32.0	15.4

*Latent heats in kcal/mol

- # The entropy of melting

Entropy changes during the heating of some common metals

Metal	Change in entropy[*] 298 °K to melting point ΔS	Entropy[*] of melting ΔS_m	$\dfrac{\Delta S_m}{\Delta S}$
Cadmium	4.53	2.46	0.54
Zinc	5.45	2.55	0.47
Aluminium	7.51	2.75	0.37
Magnesium	7.54	2.32	0.31
Copper	9.79	2.30	0.24
Gold	9.78	2.21	0.23
Iron	15.50	2.00	0.13

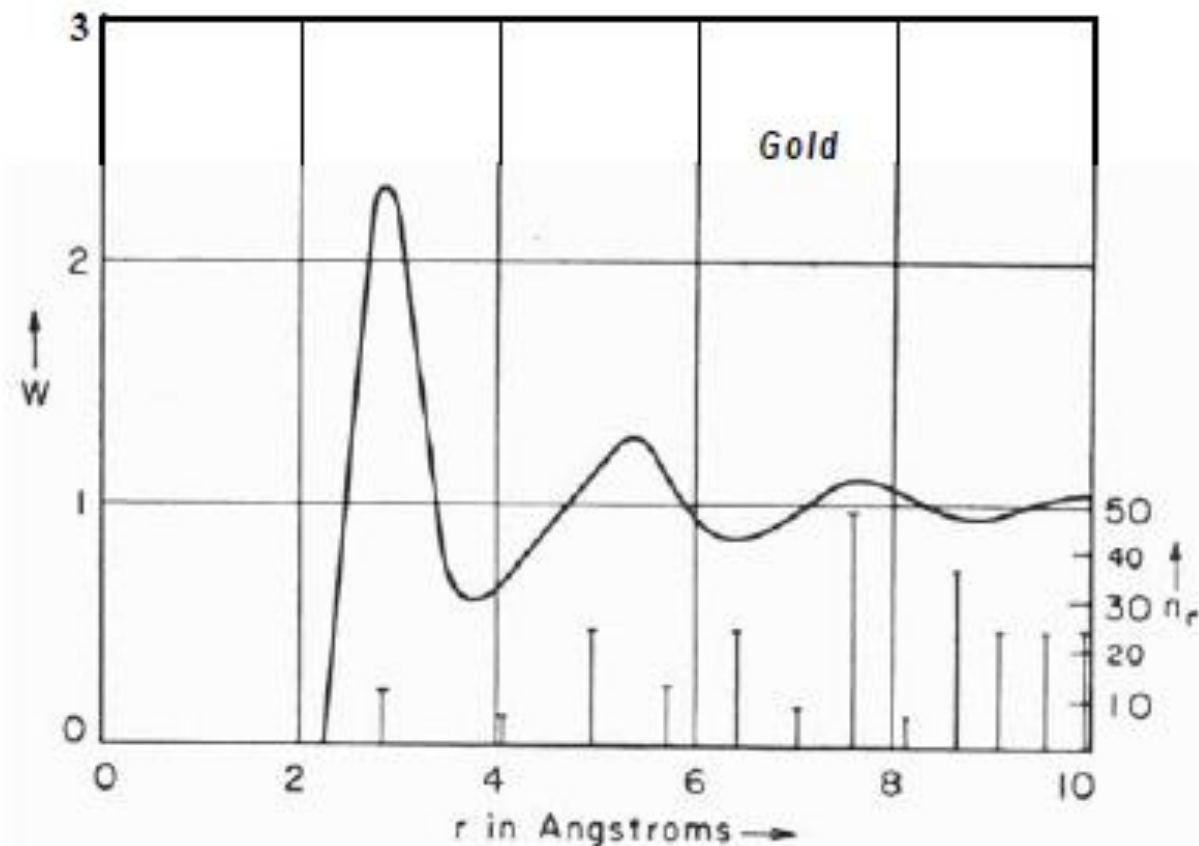[*] Entropies in cal/mol.K

- Diffraction studies of liquid structure
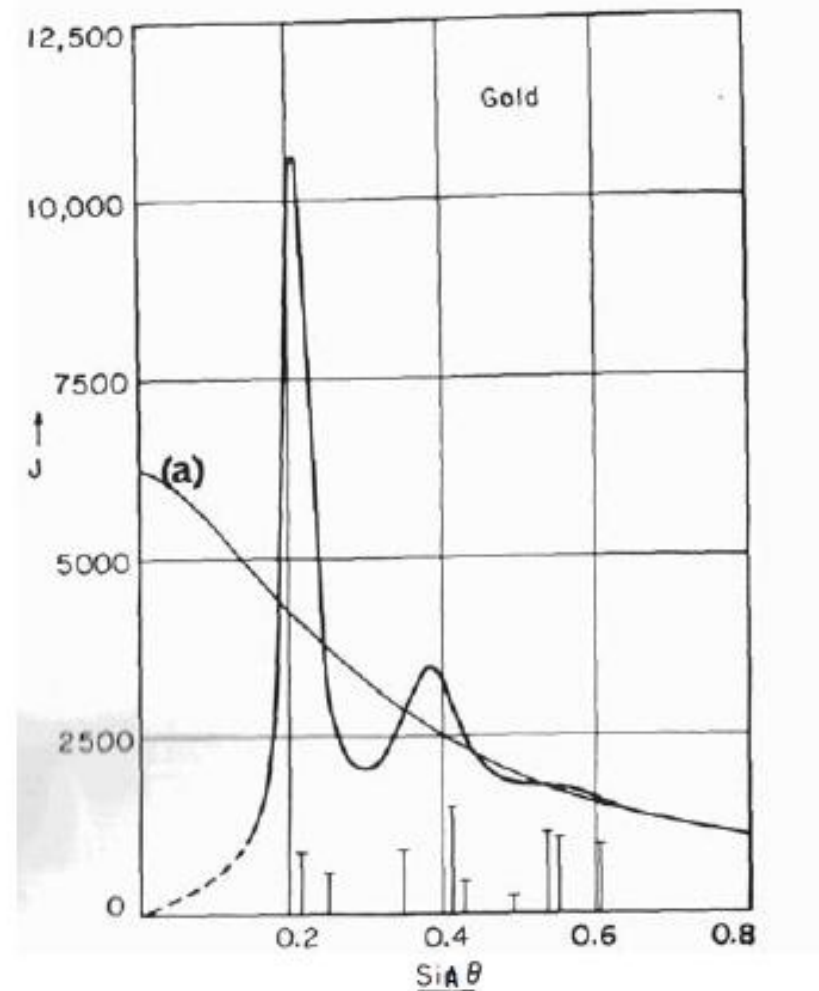
Fig. 1.1 X-ray diffraction intensity for liquid gold at 1100°C. Curve (a) is the square of the atomic structure factor. Lines in the powder pattern from crystalline gold are shown at the bottom of the figure (Vineyards after Hendus[b]).

Fig. 12 *Radial density function for liquid gold. W is the ratio of the radial distribution function density, ρ(r), to the bulk density, ρ₀. The radial density for crystalline gold is indicated by the vertical lines at the bottom of the figure (Vineyard[5] after Hendus[6]).*

COMPARISON OF STRUCTURAL DATA FOR LIQUID AND SOLID METALS OBTAINED BY DIFFRACTION

Metal	Liquid		Solid	
	atomic separation	co-ordination number	atomic separation	co-ordination number
Aluminium	2.96	10–11	2.86	12
Zinc	2.94	11	2.65	6
			2.94	6
Cadmium	3.06	8	2.97	6
			3.30	6
Gold	2.86	11	2.88	12

- Atomic spacing refers to the distance between the nuclei of atoms in a material.

According to diffraction studies:

- The average interatomic separation in the liquid is slightly greater than in the solid.

- The coordination number in the liquid is less than in the solid and usually in the range 8-11.

- These experimental considerations show that there is a relatively large increase in entropy on melting, particularly when the small change in coordination is taken into account This indicates that here is a considerable loss of order on melting without a large change in the separation of individual atoms or of the number of the neighbour atoms.

Theories of liquid structure

- Theories of liquid structure can be divided into those which consider the liquid as a dense gas (condensation theories) those which consider the liquid as disordered solid (lattice theories) and the geometrical theories)

- **Lattice theories**

These theories all use as a starting point a crystal lattice.

a) **The cell theory** in which melting is considered as a type of <u>order-disorder reaction</u> in which atom continue to be confined to the vicinity of a lattice site but are allowed to oscillate randomly and independently.

b) **The hole or free volume theory** which treated the liquid as a pseudo lattice which a large number of vacant sites.

c) **The significant structures theory** in which the liquid state involves partition between crystal like and gas like components

- **Geometrical theories**

The basic concept in this case is of a liquid as a heap of atoms or molecules.
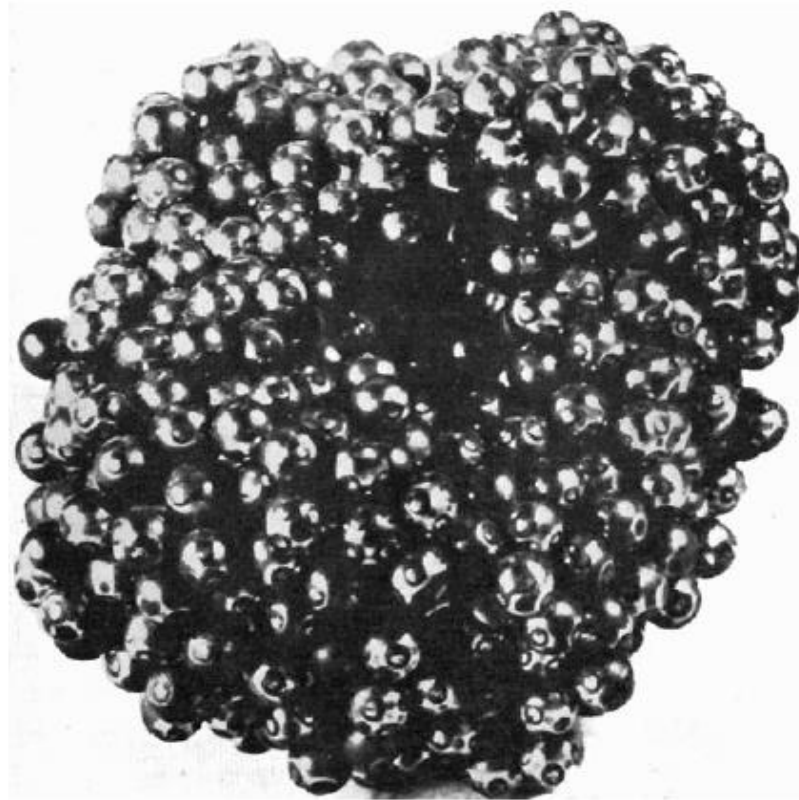
Fig. 1.3   A random close-packed heap of spheres (Bernal[20]).