

Glass Formation

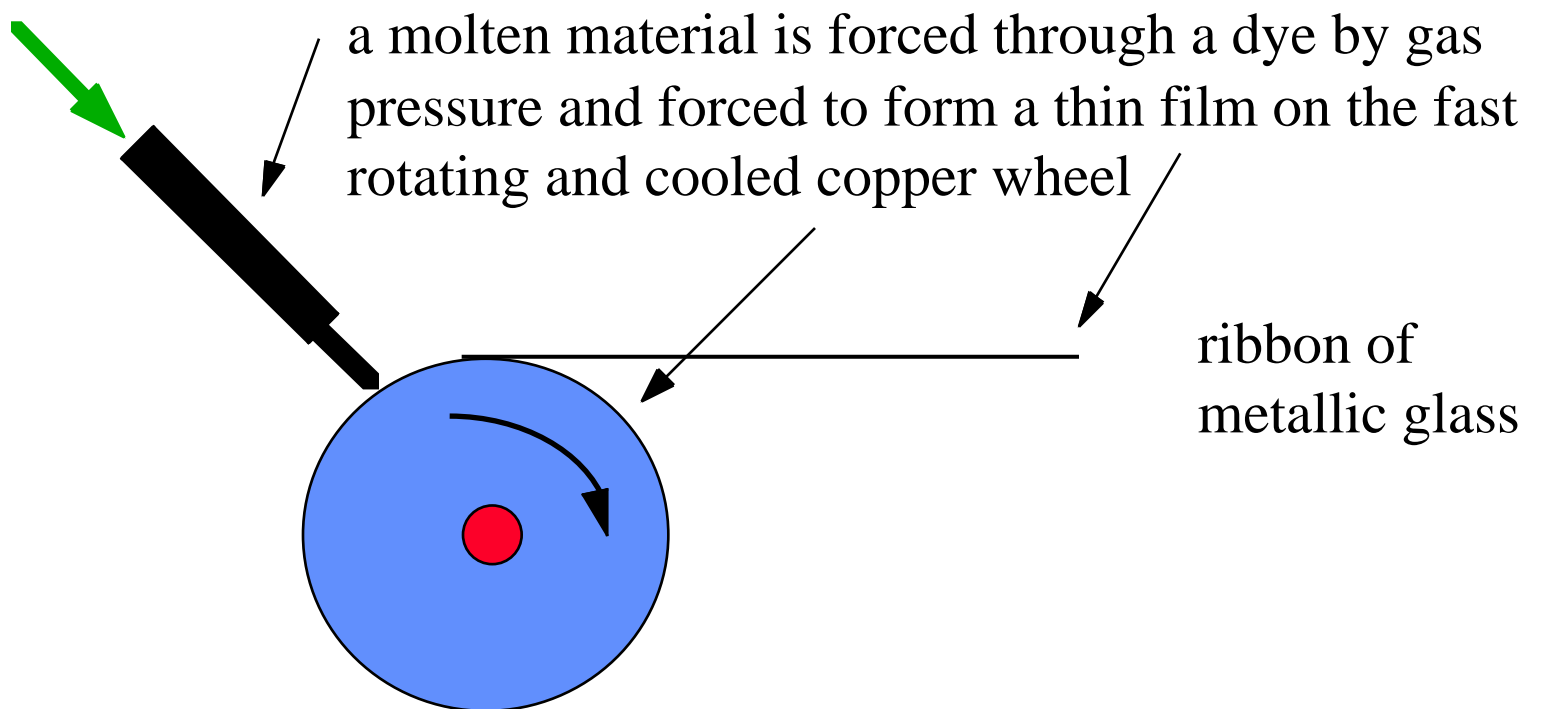
- Upon sufficiently fast cooling to a low enough temperature nearly any material can form a glass (D. Turnbull in Contemporary Physics 10, 473 (1969)).
- “low enough” to ensure that the sample is brought to $T < T_G$
- “sufficiently fast” to ensure that while traversing the T_M to T_G temperature range there is insufficient time to crystallize.
- Representative Solids and Their Glass Transition Temperatures:

Glass	Bonding	T_G (°K)
SiO ₂	Covalent	1430
Pd _{0.4} Ni _{0.4} P _{0.2}	Metallic	580
BeF ₂	Ionic	570
As ₂ S ₃	Covalent	470
Polystyrene	Polymer	370
Se	Polymeric	310
H ₂ O	Hydrogen Bonded	140
Isopentane	Van der Waals	65

From: R. Zallen, “The Physics of Amorphous Solids” John Wiley and Sons, 1983

Metallic Glass Formation

- Splat quenching techniques can achieve cooling rates of the order of 10^5 to 10^8 °K/sec. (Melt spinning see below is an example where 10^6 °K/sec can be easily reached °K in 1 millisecond). Note that laser glazing techniques yield even higher cooling rates of the order of ca. 10^{11} °K/sec.



- SiO_2 and As_2S_3 , at-Poly(styrene) are materials with very high glass forming tendencies: melts can be cooled down extremely slowly (10^{-4} to 10^{-1} °K/sec) without crystallizing.
- Ice-water bath quenching leads to quenching rates of the order of 10^{+1} to 10^{+2} °K/sec. Such rates are sufficient for the formation of Se, $\text{Pd}_{0.4}\text{Ni}_{0.4}\text{P}_{0.2}$, many organic and polymeric glasses.
- Vapor condensation techniques are used to prepare glasses that cannot be prepared by the melt quenching technique. These techniques yield the highest apparent cooling rates and construct the “glass” one atom at a time from the vapor phase. It relies on the fact that atoms, once vaporized and propelled on a cold substrate, do not have time to reach a crystallographic order. Ion bombardment, electron beam, plasma induced decomposition are used for this purpose. Used for the preparation of amorphous Si, Ge, H_2O , Fe, Co, Bi, ..

Applications of Glasses:

- **Practical Material Processing and Properties:**

Compare fused silica: SiO_2 (am) to quartz: SiO_2 (crystal)

The amorphous material can be easily prepared as a homogeneous material in large dimensions, the crystalline material of similar would have to be polycrystalline. Fused silica is isotropic, whereas quartz is birefringent !!

Fused silica is a good thermal insulator, quartz is not.

- **Uses:**

Oxide Glass: Window glass (SiO_2)

Oxide Glass: Fiber optics (SiO_2 , PMMA)

Organic and Inorganic Glasses: Structural materials

Amorphous Semiconductors: Solar cells, computer memory

Metallic glasses :Transformer cores

Structure of Liquids and Glasses

- Characterized by the Absence of Long Range Periodicity
- Atomic positions are NOT randomly distributed. In glasses, very much like in crystals there is considerable short range order. This short range order is at the source of the liquid cohesion (as opposed to the vapor state) and results from covalent, ionic, hydrogen, metallic and vanderwaals bonding.
- X-ray, Neutron and to some extent Electron Diffraction can provide some information about the average separation between species in the liquid or the glass. We will proceed using a result demonstrated in the section on diffraction. We wrote the scattering amplitude for a unit cell as:

$$A_{cell} = \sum_{j=1}^{N_{cell}} f_j \exp\left(-2\pi i \vec{S} \cdot \vec{r}_j\right)$$

By analogy, the scattering from an amorphous sample is written as:

$$A = \sum_{j=1}^N f_j \exp(-2\pi i \vec{S} \cdot \vec{r}_j)$$

where f_j is the atomic scattering factor for atom j in the material \vec{r}_j is the vector defining the position of atom j with respect to some fixed origin and \vec{S} is the scattering vector ($\mathbf{k}_S - \mathbf{k}$) of magnitude $2 \sin(\theta) / \lambda$. The scattered intensity at the scattering angle 2θ is then given by:

$$I = A \cdot A^* = \sum_{m=1}^N f_m \exp(-2\pi i \vec{S} \cdot \vec{r}_m) \sum_{n=1}^N f_n \exp(+2\pi i \vec{S} \cdot \vec{r}_n) \quad \text{or}$$

$$I = \sum_{m, n} f_m f_n \exp(-2\pi i \vec{S} \cdot [\vec{r}_m - \vec{r}_n])$$

If we now write the vector $\vec{r}_m - \vec{r}_n$ by \vec{r}_{mn} and denote by α the angle between \vec{S} and \vec{r}_{mn} , then:

$$I = \sum_{m, n} f_m f_n \exp(-2\pi i S r_{mn} \cos \alpha)$$

We have assumed that the relative atomic positions are fixed. We assume now that the object rotates in such a manner that all possible orientations with respect to the beam direction are equally probable. We assume also that this motion is sufficiently rapid so that one observes only the average scattered intensity. [Note that the above statement needs not be true in the actual experiment. It is only a mathematical procedure used to calculate the scattering. What we are implying is that the scattering arising from a collection of identical objects (elementary volume of material) with random orientations and positions is identical to the scattering of one of these elementary volumes averaged over time as this elementary volume is steadily and randomly rotated in space during the scattering experiment.]

Under these conditions, we have:

$$I = \sum_m \sum_n f_m f_n \langle \exp(-2\pi i S r_{mn} \cos \alpha) \rangle$$

where $\langle \rangle$ denotes the average over all possible orientations

$$\langle \exp(-2\pi i S r_{mn} \cos \alpha) \rangle = \langle \cos(-2\pi S r_{mn} \cos \alpha) \rangle + i \langle \sin(-2\pi S r_{mn} \cos \alpha) \rangle$$

$$\int_{\alpha=0}^{\alpha=\pi} \int_{\varphi=0}^{\varphi=2\pi} \cos(-2\pi S r_{mn} \cos \alpha) \sin \alpha d\alpha d\varphi$$

$$\langle \cos(-2\pi S r_{mn} \cos \alpha) \rangle = \frac{\int_{\alpha=0}^{\alpha=\pi} \int_{\varphi=0}^{\varphi=2\pi} \cos(-2\pi S r_{mn} \cos \alpha) \sin \alpha d\alpha d\varphi}{\int_{\alpha=0}^{\alpha=\pi} \int_{\varphi=0}^{\varphi=2\pi} \sin \alpha d\alpha d\varphi}$$

$$\langle \cos(-2\pi S r_{mn} \cos \alpha) \rangle = \frac{(2\pi) \int_{\alpha=0}^{\alpha=\pi} \cos(-2\pi S r_{mn} \cos \alpha) \sin \alpha d\alpha}{(4\pi)}$$

We then make the change of variable $X = -2 S r_{mn} \cos \alpha$ therefore:
 $\sin \alpha d\alpha = dX / (2 S r_{mn})$ and the limits of integration become $-2 S r_{mn}$
and $2 S r_{mn}$

$$\langle \cos(-2\pi S r_{mn} \cos \alpha) \rangle = \frac{\int_{X=-2\pi S r_{mn}}^{X=+2\pi S r_{mn}} \cos X dX}{2 \cdot 2\pi S r_{mn}} = \frac{\sin(2\pi S r_{mn}) - \sin(-2\pi S r_{mn})}{4\pi S r_{mn}}$$

$$\langle \cos(-2\pi S r_{mn} \cos \alpha) \rangle = \frac{\sin(2\pi S r_{mn})}{(2\pi S r_{mn})}$$

$$X = +2\pi S r_{mn}$$

$$\sin X dX$$

$$\langle \sin(-2\pi S r_{mn} \cos \alpha) \rangle = \frac{X = -2\pi S r_{mn}}{2 \cdot 2\pi S r_{mn}} = -\frac{\cos(2\pi S r_{mn}) - \cos(-2\pi S r_{mn})}{4\pi S r_{mn}} = 0$$

$$I = \sum_{m n} f_m f_n \frac{\sin(2\pi S r_{mn})}{(2\pi S r_{mn})}$$

which is known as the Debye function

Monoatomic Amorphous Materials

For a group of N identical atoms ($f_m = f_n = f$), we separate the contributions for $m = n$ from that arising when m differs from n

$$I = N f^2 \left[1 + \sum_{m n, m \neq n} \frac{\sin(2\pi S r_{mn})}{(2\pi S r_{mn})} \right]$$

If we define by $\rho(r)$ the concentration of atoms at distance r from a reference atom, we can write:

$$I = Nf^2 \int_0^R dr 4\pi r^2 \rho(r) \frac{\sin(2\pi Sr)}{(2\pi Sr)}$$

where R is the very large radius of the specimen assumed to be an isotropic sphere (not critical). If we denote by ρ_0 the average concentration, then the scattered intensity can be written as:

$$I = Nf^2 \int_0^R dr 4\pi r^2 [\rho(r) - \rho_0] \frac{\sin(2\pi Sr)}{(2\pi Sr)} + \int_0^R dr 4\pi r^2 \rho_0 \frac{\sin(2\pi Sr)}{(2\pi Sr)}$$

The second integral corresponds to the scattering of a sphere of radius R of constant and uniform concentration, it will only be significant at very, very small scattering angles and will be zero (i.e. can be neglected) in the range of S vectors considered here. This last integral reduces to a δ function at the origin for infinite R .

The Radial Distribution Function:

At this point we define the liquid structure factor by the function S_L :

$$S_L = I/Nf^2$$

$$S_L = 1 + \int_{r=0}^{\infty} dr 4\pi r^2 [\rho(r) - \rho_0] \frac{\sin(2\pi Sr)}{(2\pi Sr)}$$

We define the **Radial Distribution Function** $g(r)$ by $g(r) = \rho(r) / \rho_0$

$$S_L = 1 + 4\pi\rho_0 \int_{r=0}^{\infty} dr [g(r) - 1] r^2 \frac{\sin(2\pi Sr)}{(2\pi Sr)}$$

$$S_L = 1 + \rho_0 \int_{r=0}^{\infty} dr [g(r) - 1] \exp(-2\pi i \vec{S} \cdot \vec{r})$$

Since the above equation is a Fourier Integral, it can therefore be inverted to yield:

$$g(r) - 1 = \frac{1}{8\pi^3 \rho_0} \int d\vec{S} (S_L - 1) \exp(+2\pi i \vec{S} \cdot \vec{r}) = \frac{1}{2\pi^2 \rho_0 r} \int dS (S_L - 1) S \sin(2\pi Sr)$$

Crystal, Glass vs Gas Structure vs. RDF (from R. Zallen)

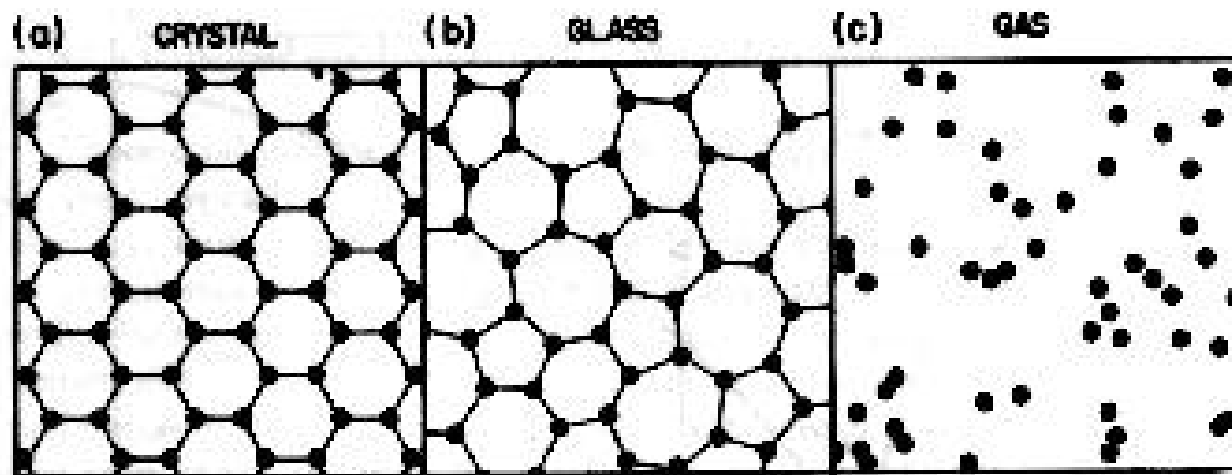


Figure 1.6 Schematic sketches of the atomic arrangements in (a) a crystalline solid, (b) an amorphous solid, and (c) a gas.

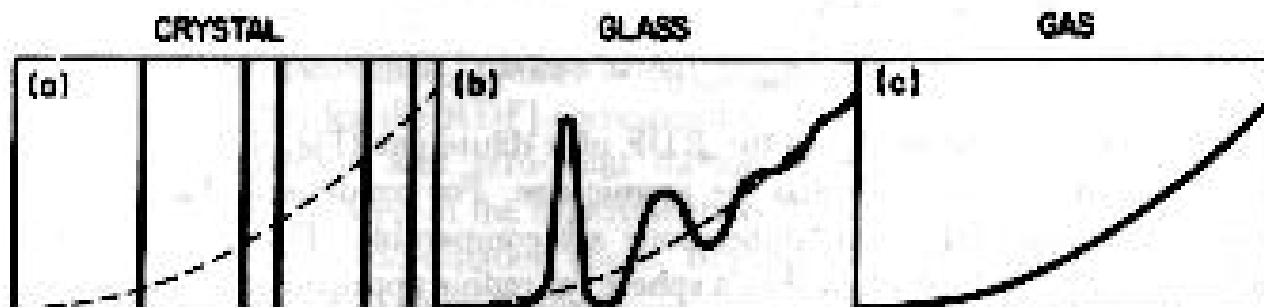
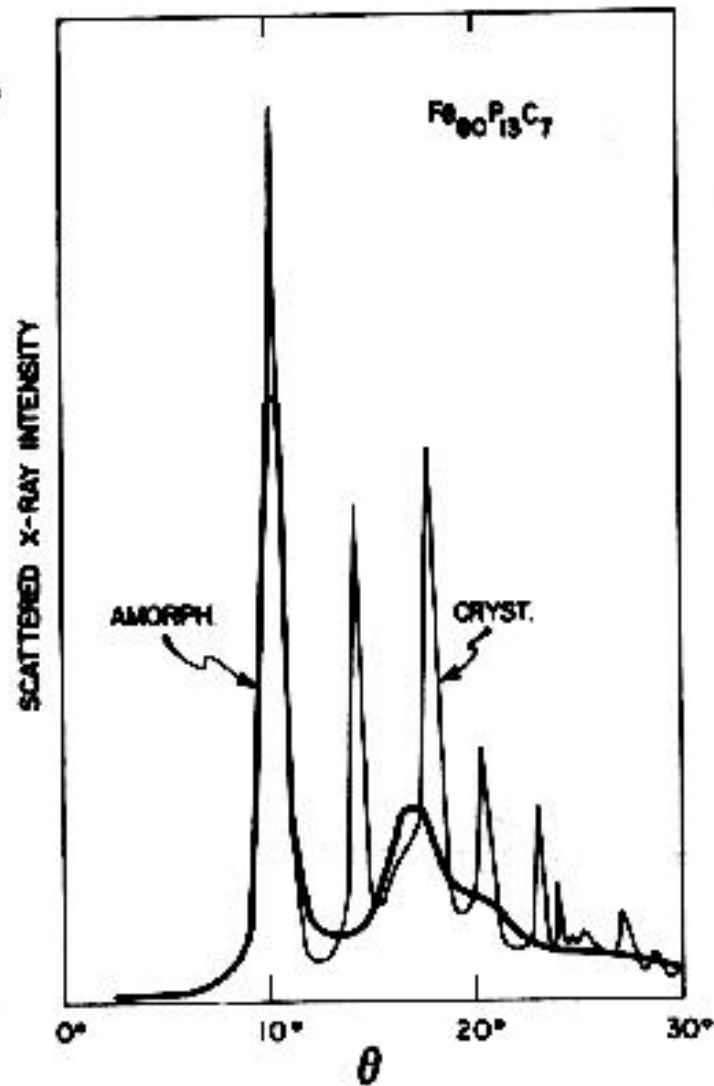
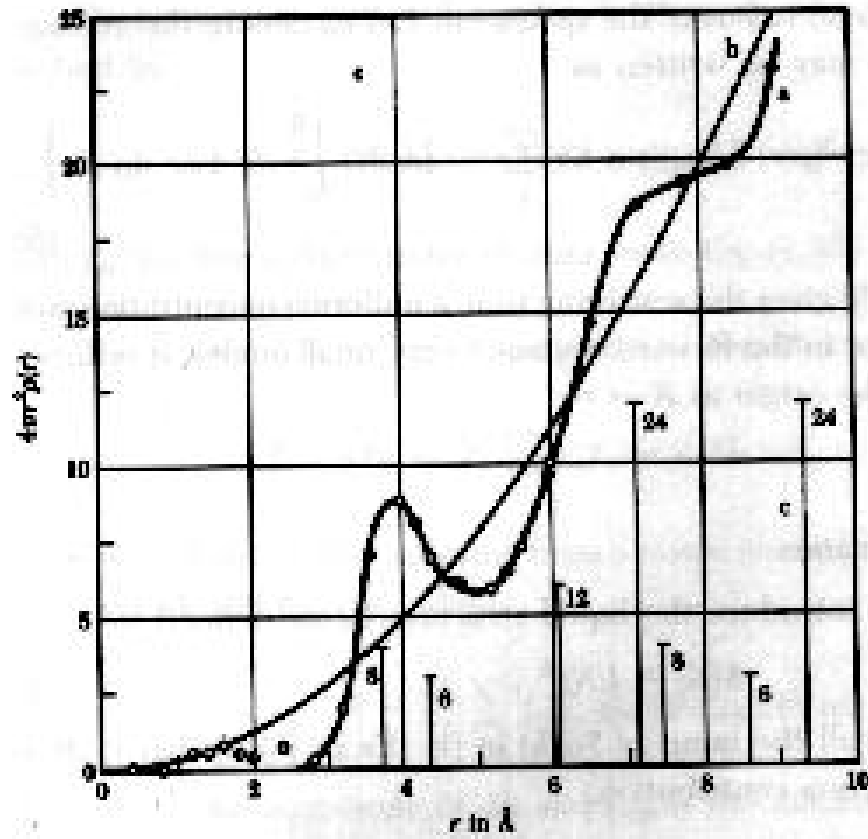


Figure 2.3 Schematic sketches of the radial distribution functions for (a) a crystalline solid, (b) an amorphous solid, and (c) a gas. These distributions schematically correspond to the atomic arrangements sketched in Fig. 1.6.

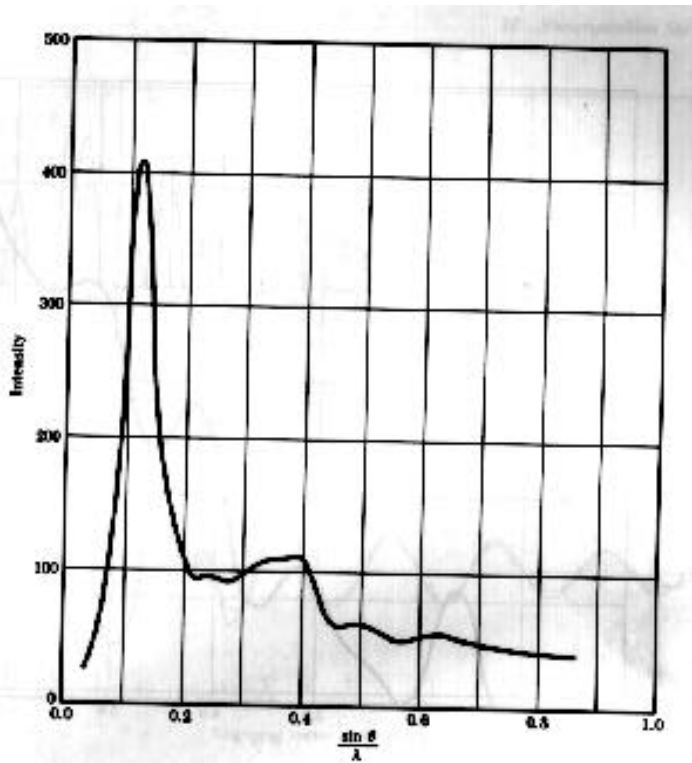
Metallic Glass vs. Crystal (from R. Zallen)



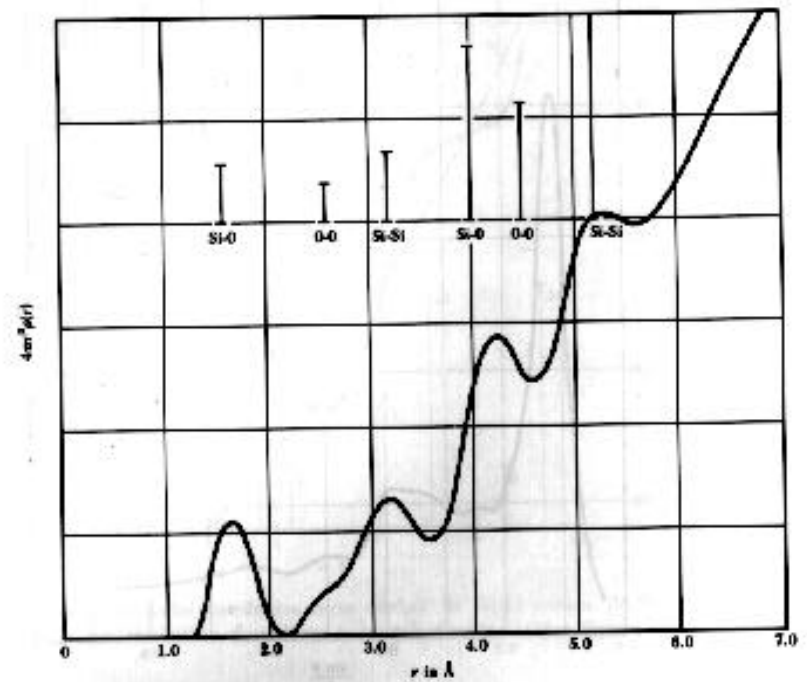
Radial Distribution Function for Sodium Liquid



Structure of Vitreous SiO₂



Scattered X-ray Intensity vs S



Radial Distribution Function