

for N atomic crystal,

$$A(q) = \sum_j f_j \exp(-i\vec{q} \cdot \vec{r}_j) \sum_n \exp(-i\vec{q} \cdot \vec{R}_n)$$

unit cell structure factor

lattice sum

Position determination

$$\vec{q} \cdot \vec{R}_n = 2\pi \times \text{integer}$$

since  $\sum_n \exp(-i\vec{q} \cdot \vec{R}_n) \sim N$

otherwise,  $\sum_n \exp(-i\vec{q} \cdot \vec{R}_n) \sim 1$

## Real and inverse lattice

$$\vec{r} \cdot \vec{q} = 2\pi \times \text{integer}$$

(Laue condition ~ Bragg Law)

$$\vec{r} = u_1 \vec{a}_1 + u_2 \vec{a}_2 + u_3 \vec{a}_3$$

$$\vec{q} = v_1 \vec{b}_1 + v_2 \vec{b}_2 + v_3 \vec{b}_3$$

$$b_1 = 2\pi \frac{a_2 \times a_3}{a_2 \cdot a_3 \times a_1}$$


$$b_2 = 2\pi \frac{a_3 \times a_1}{a_3 \cdot a_1 \times a_2}$$

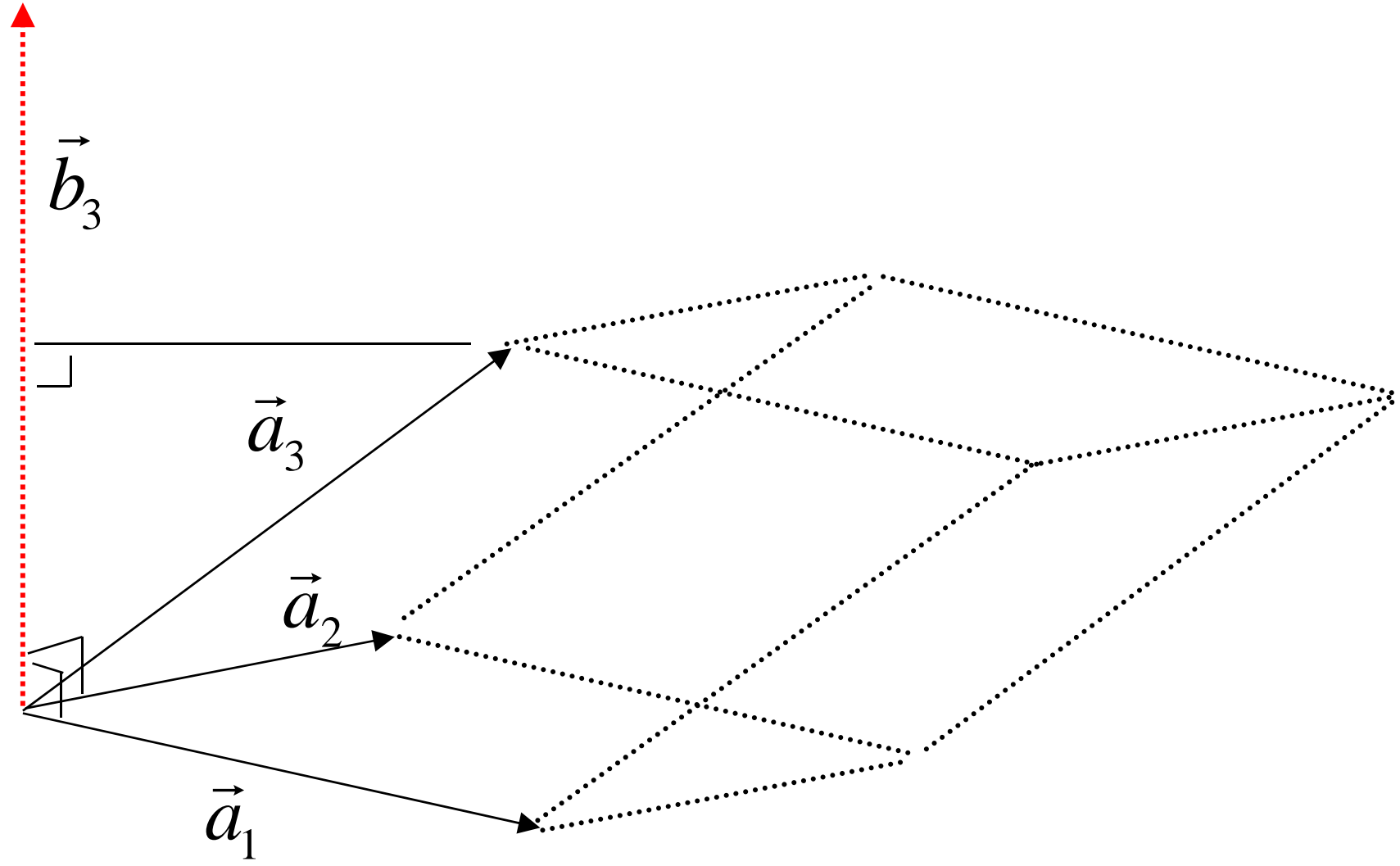
$$b_3 = 2\pi \frac{a_1 \times a_2}{a_1 \cdot a_2 \times a_3}$$

$$b_i \cdot a_j = 2\pi \delta_{ij}$$

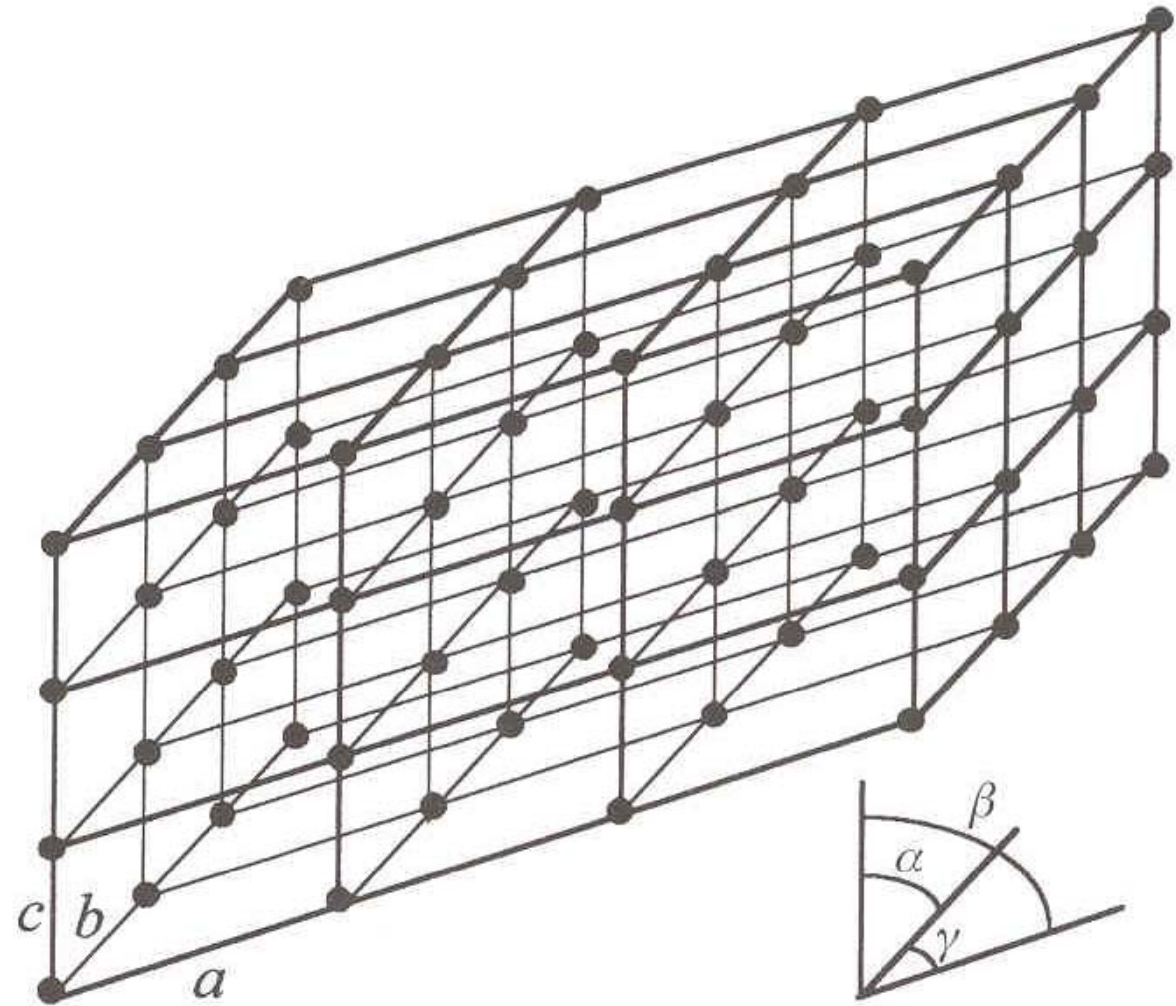
when  $i \neq j$ , 0

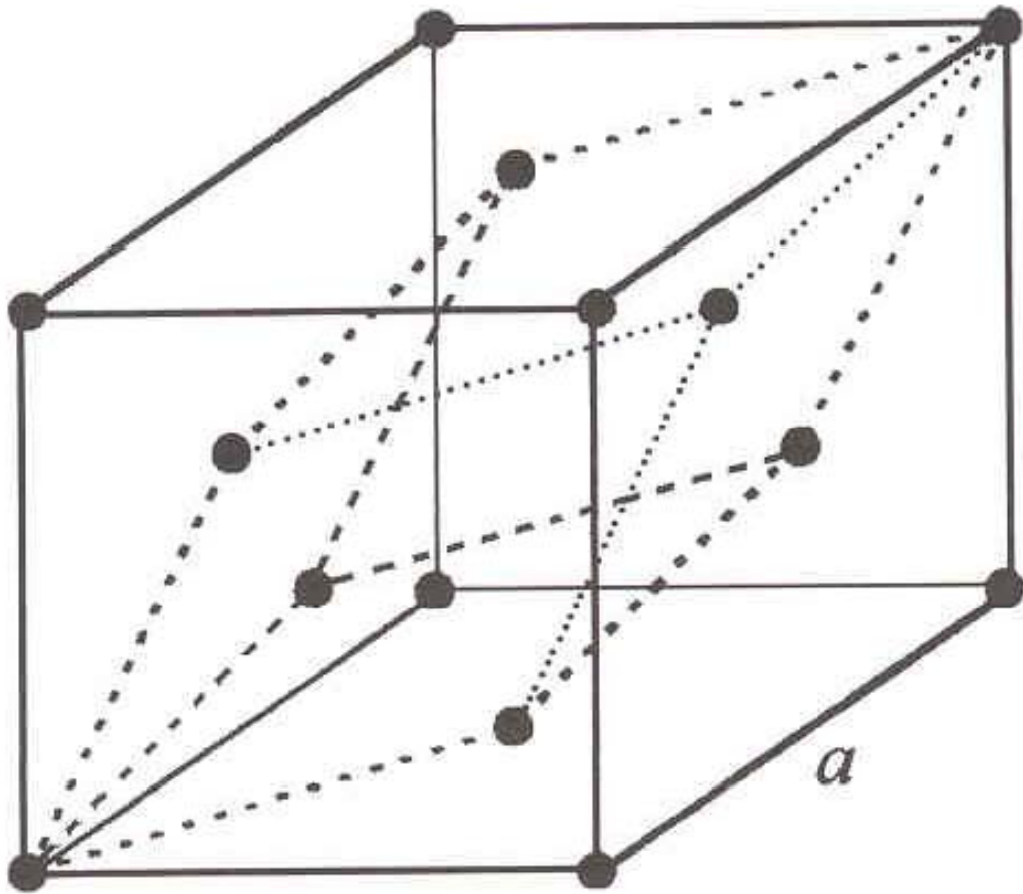
when  $i = j$ ,  $2\pi$


$$\vec{r} \cdot \vec{q} = 2\pi \times (u_1 v_1 + u_2 v_2 + u_3 v_3)$$

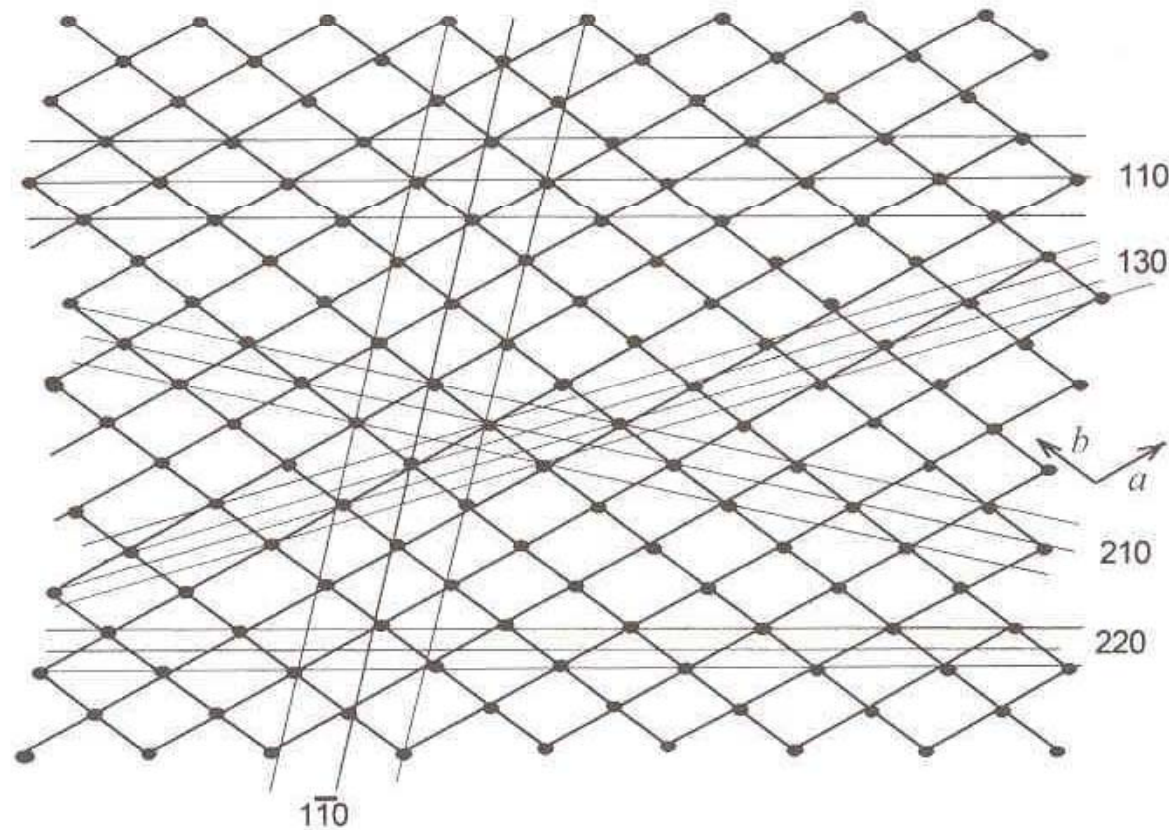


**Fig. 2.5** A general three-dimensional lattice, showing the definitions of  $a$ ,  $b$  and  $c$  and  $\alpha$ ,  $\beta$  and  $\gamma$ . The lines represent the intersections of two lattice planes and the filled circles represent the intersections of three lattice planes, the lattice points.

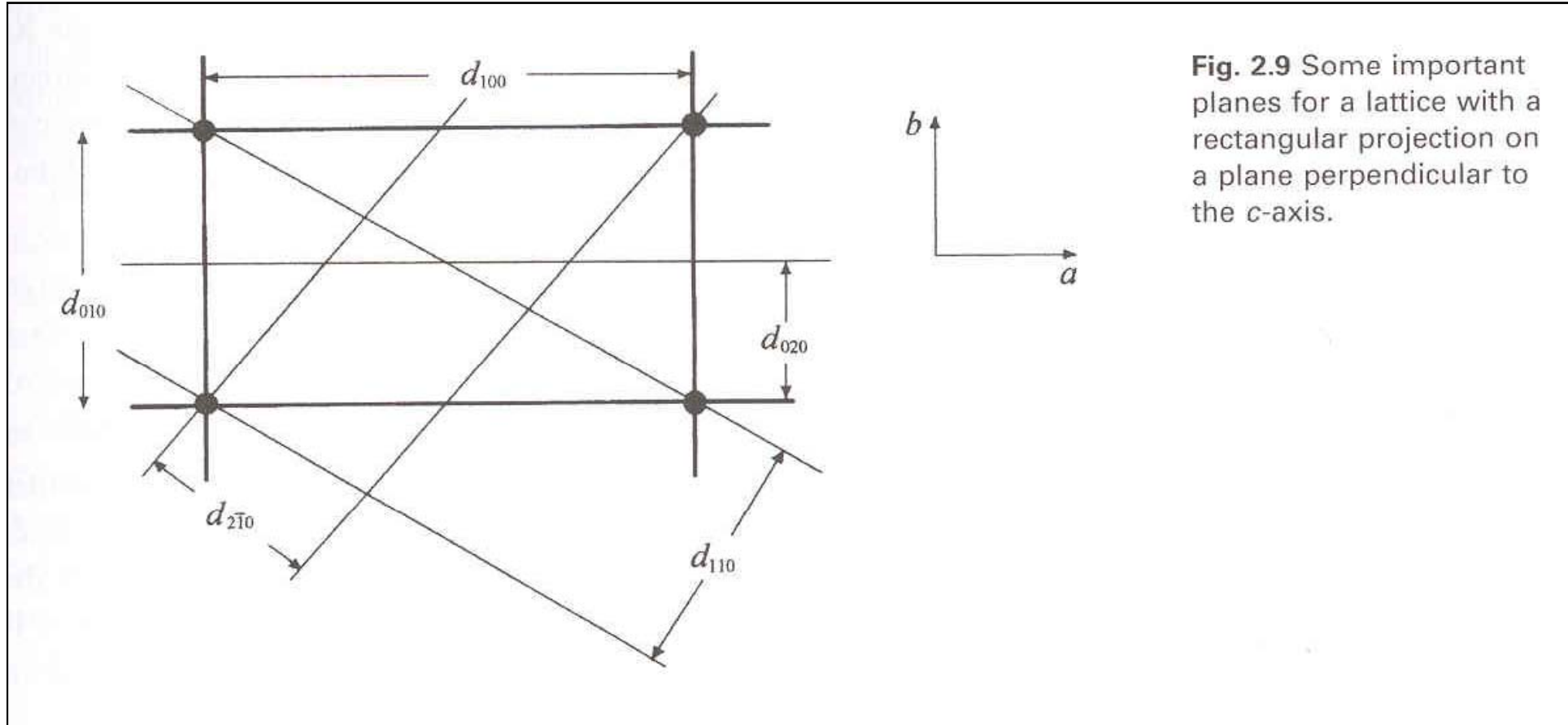




**Fig. 2.6** The face-centred cubic unit cube, showing also the rhombohedral primitive cell.

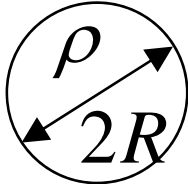


**Fig. 2.8** Crystal plane indices. All the planes shown are assumed to be parallel to the  $c$ -axis, which is normal to the plane of the page. A bar over an integer indicates that, if any particular lattice point on a starting plane of a given set is taken as the origin, it is necessary to move in the negative direction of the corresponding axis to find the adjacent plane for which the intersections with the other two axes lie on their positive directions. Note that the  $(\bar{1}\bar{1}0)$  planes could equally well be labelled the  $(\bar{1}10)$  planes.



**Fig. 2.9** Some important planes for a lattice with a rectangular projection on a plane perpendicular to the  $c$ -axis.

# Structure factor for a uniform sphere

$$P(q) \sim [F(q)]^2$$
$$2\pi\vec{s} = \vec{q}$$
$$\rho \sim 0$$
A diagram of a sphere with a radius vector labeled  $\rho$  and a diameter vector labeled  $2R$ .

$$F(q) = \int \rho(\vec{r}) \exp(-i\vec{q} \cdot \vec{r}) d\vec{r}$$

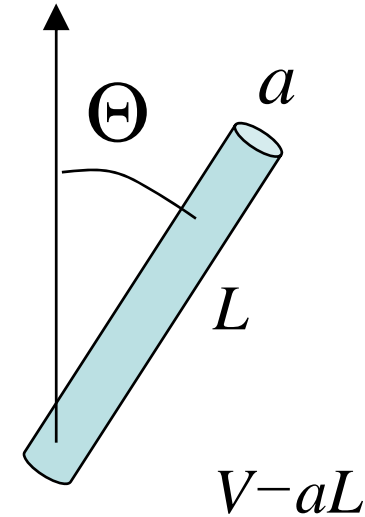


# Structure factors for several structures

Thin rod

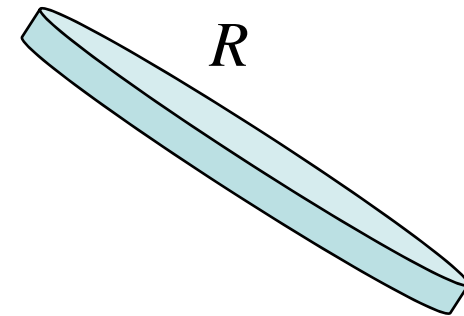
At a certain orientations,

$$F(q) = \frac{4}{qL \cos \Theta} \sin\left(\frac{qL \cos \Theta}{2}\right)$$



Circular disk

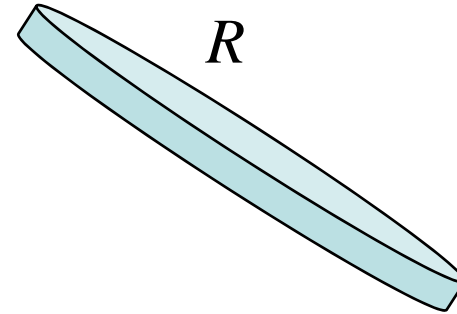
$$F(q) = \frac{2}{q^2 R^2} \left[ 1 - \frac{J_1(2qR)}{qR} \right]$$



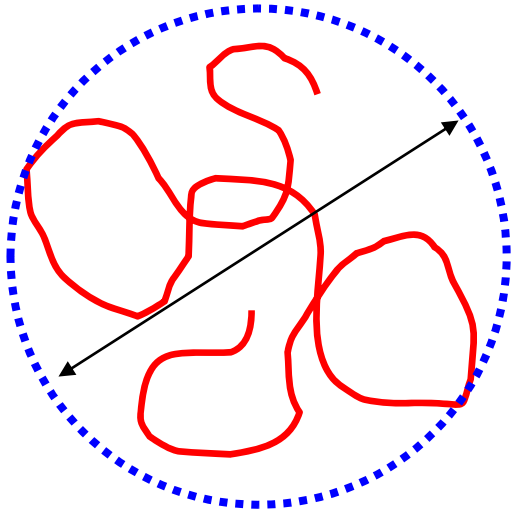
# Structure factors for several structures

Circular disk

$$P(q) = \frac{2}{q^2 R^2} \left[ 1 - \frac{J_1(2qR)}{qR} \right]$$

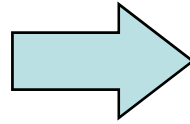


## How about this?



Random coil  
Or Gaussian coil

-synthetic polymer, DNA, protein...



$$P(q) \sim [F(q)]^2$$

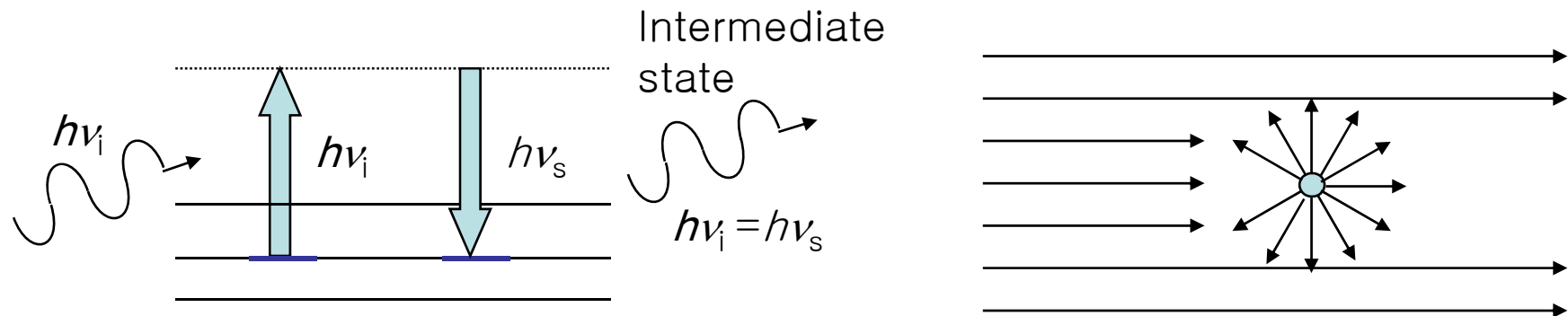
constant form factor?

$$P(q) \sim 2 \frac{\exp(-q^2 R_g^2) - 1 + q^2 R_g^2}{q^4 R_g^4}$$

[http://www.ncnr.nist.gov/programs/sans/pdf/polymer\\_tut.pdf](http://www.ncnr.nist.gov/programs/sans/pdf/polymer_tut.pdf)

# Light Scattering

- Definition
  - Spreading out of wave when it meets impurities in the continuous medium
  - Ground scattering or non-resonant scattering
  - Light can drive oscillation of electron cloud.
  - Electron cloud immediately radiates same frequency of incident light in random direction.



# Static Light Scattering

- Elastic light scattering, classical light scattering
- Rayleigh scattering
- Intensity of light scattered by one small particle, non polarized light

$$I_{\theta} = \frac{8\pi^4 \alpha^2}{r^2 \lambda^4} I_0 (1 + \cos^2 \theta)$$

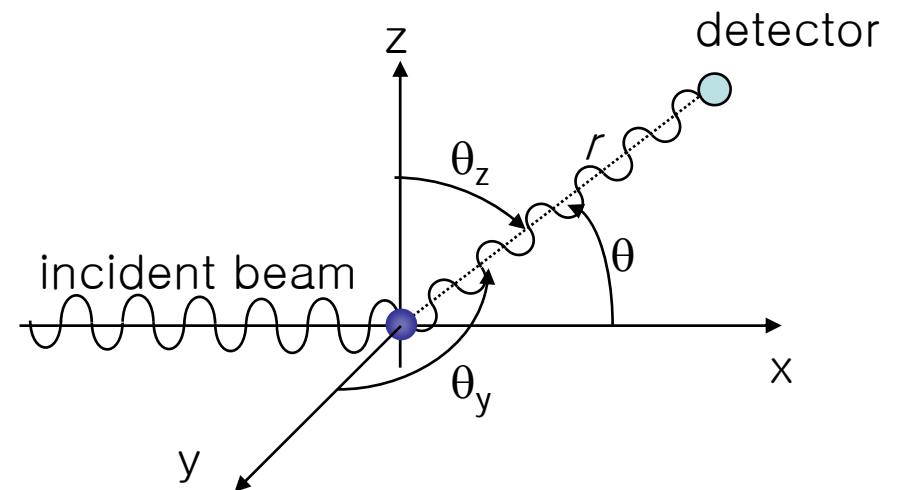
$I_{\theta}$  : Scattering light intensity at  $\theta$

$I_0$  : Incident light intensity

$\alpha$  : Polarizability

$r$  : Distance between detector and sample

$\lambda$  : Wavelength of incident light



- Light scattering in ensembles of small molecules

- For a dilute ideal gas

$$\alpha = \left( \frac{n^2 - n_0^2}{n_0^2} \right) \frac{1}{4\pi\nu} = \frac{M}{2\pi N_A} \left( \frac{dn}{dc} \right),$$

}

$M$  : Molar mass

$N_A$  : Avogadro constant

$(dn/dc)$  : Specific refractive index increment

$N_V$  : Total # of molecule in a volume  $V$

$c$  : Concentration

$$N_V / V = cN_A / M$$

$$I_\theta = I_0 (1 + \cos^2 \theta) \frac{2\pi^2 (dn/dc)^2}{r^2 \lambda^4 N_A} Mc$$

- For solution (ideal, small particle)

$$I_\theta = I_0 (1 + \cos^2 \theta) \frac{2\pi^2 n_0^2 (dn/dc)^2}{r^2 \lambda_0^4 N_A} Mc$$

$\lambda = \lambda_0 / n_0$

}

$\lambda_0$  : wavelength in vacuo

$n_0$  : refractive index of solvent

- In macromolecular solution of small particle
  - Increase in scattering intensity from a solution
  - **Fluctuations** in **solute concentration** in small volume  
Fluctuations considered as the source of light scattering
  - Chemical potential of polymer solution ( $\mu$ )
 
$$\left( \frac{\partial \mu_1}{\partial c} \right)_{T,P} = \text{constant} (1/M + 2A_2c + 3A_3c^2 + \dots)$$
  - $A_2, A_3, \dots$  : virial coefficients
  - For polymer solution of small macromolecules

$$I_\theta = I_0 (1 + \cos^2 \theta) \frac{2\pi^2 n_0^2 (dn/dc)^2}{r^2 \lambda_0^4 N_A} c \frac{1}{1/M + 2A_2c + 3A_3c^2 + \dots}$$

- For dilute polymer solution of large particle
  - The beams scattered from different point of particle are coherent, capable of interference.

– Rayleigh ratio ( $R_\theta$ )

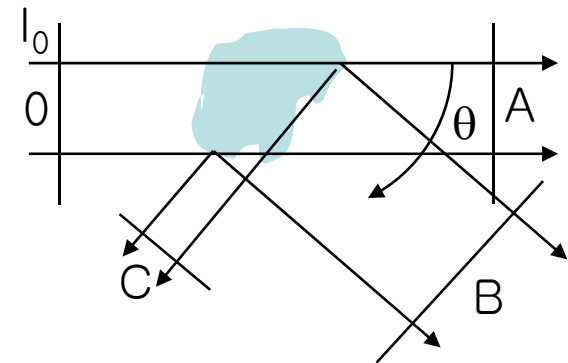
$$R_\theta = \frac{r^2 I_\theta}{I_0 (1 + \cos^2 \theta)} = \frac{Kc}{1/M + 2A_2C + 3A_3C^2 + \dots},$$

$$K = \frac{2\pi^2 n_0^2 (dn/dc)^2}{\lambda_0^4 N_A}$$

– Particle scattering function ( $P_\theta$ )

$$P_\theta = \frac{R_\theta(\text{experimental})}{R_\theta(\text{without interference})}$$

$$P_\theta = 1 - \frac{q^2 \langle R_g^2 \rangle}{3} = 1 - \frac{16\pi^2}{3\lambda^2} \langle R_g^2 \rangle \sin^2(\theta/2)$$





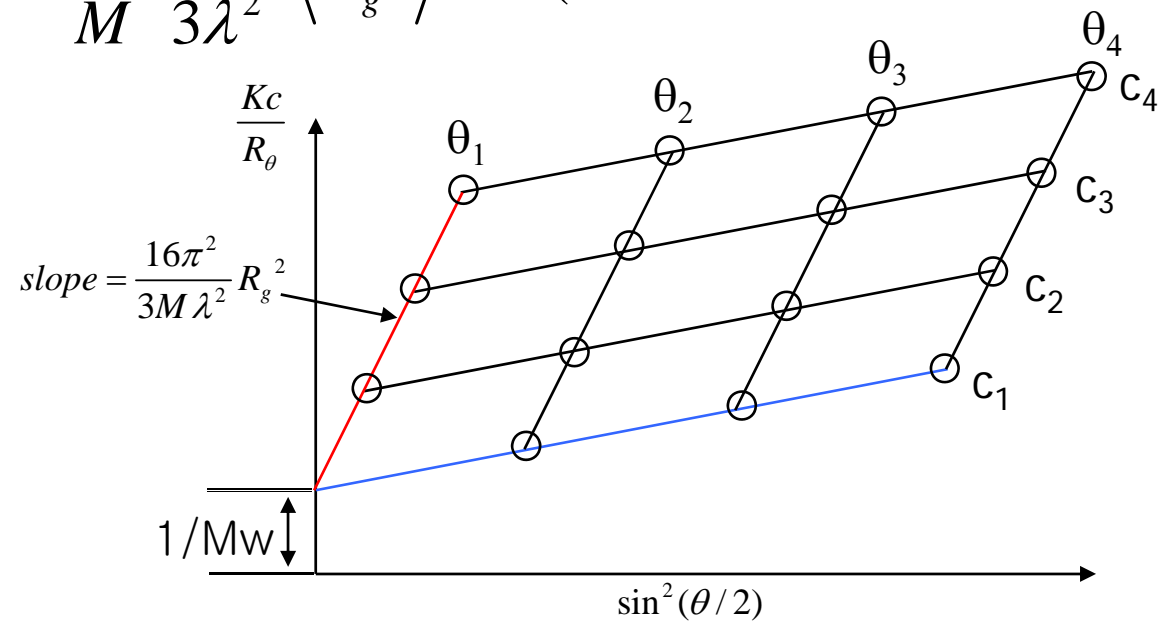
- Zimm plot
  - For the large enough polymer sol'n
  - At low concentration

$$\begin{aligned}
 \left. \frac{Kc}{R_\theta} \right|_{\substack{c \rightarrow 0 \\ \theta \rightarrow 0}} &= \left( \frac{1}{M} + 2A_2c + 3A_3c^2 + \dots \right) \frac{1}{P_\theta} \\
 &\approx \left( \frac{1}{M} + 2A_2c + 3A_3c^2 + \dots \right) \left( 1 + \frac{16\pi^2}{3\lambda^2} \langle R_g^2 \rangle \sin^2(\theta) \right) \\
 &\approx \frac{1}{M} \left( 1 + \frac{q^2 \langle R_g \rangle^2}{3} \right) + 2A_2c \quad q = \frac{4\pi \sin(\theta)}{\lambda}
 \end{aligned}$$

- Zimm plot

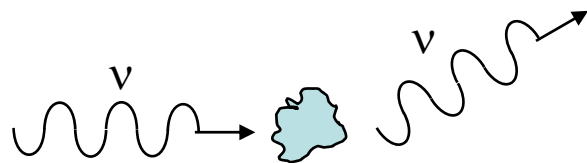
$$\lim_{\theta \rightarrow 0} \frac{Kc}{R_\theta} = \frac{1}{M} + 2A_2c$$

$$\lim_{c \rightarrow 0} \frac{Kc}{R_\theta} = \frac{1}{M} + \frac{1}{M} \frac{16\pi^2}{3\lambda^2} \langle R_g^2 \rangle \sin^2(\theta)$$

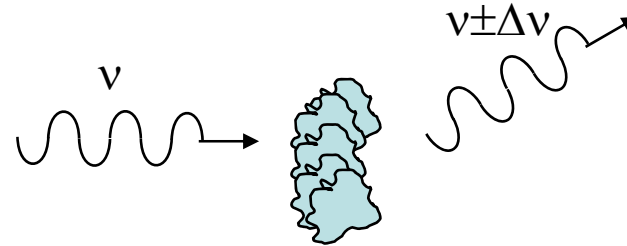


# Dynamic Light Scattering

- Quasi-elastic light scattering, photon correlation spectroscopy
- Scattered waves interfere constructively or destructively at different time (fluctuation)
- Determination of diffusional characterization of macromolecule
- Measurement of diffusion coefficients and hydrodynamic radius



Fixed scatter



Moving scatter  
Doppler effect

- Autocorrelation function in DLS

- Correlation function of electric field

$$G^{(1)}(\tau) = \langle E_s(t)E_s(t + \tau) \rangle$$

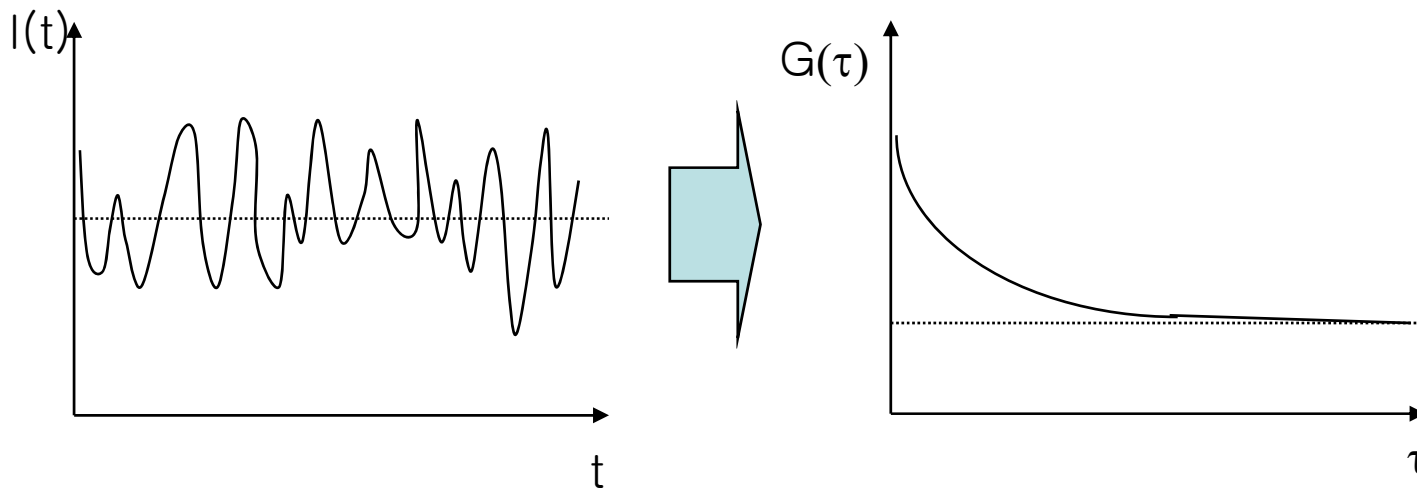
- Correlation function of scattered intensity of light

$$G^{(2)}(\tau) = \langle I_s(t)I_s(t + \tau) \rangle$$

- Siegert relation

(in normalized form)

$$g^{(2)}(\tau) = \frac{\langle E^*(\tau)E(t)E^*(t + \tau)E(t + \tau) \rangle}{\langle I \rangle^2} = 1 + |g^{(1)}(\tau)|^2$$



- **Translational diffusion constant (D)**

- Spherical identical scatters undergoing Brownian motion

$$g^{(1)}(\tau) = e^{-Dq^2\tau} e^{i\omega_0 t}$$

- From Siegert relation

$$g^{(2)}(\tau) = 1 + e^{-2Dq^2\tau}$$

$$\left( \begin{array}{l} g^{(2)}(t) : \text{normalized field ACF, } g^{(2)}(t) = \frac{G^{(2)}(t)}{\langle I_s \rangle^2} \\ D : \text{translational diffusion constant} \\ q : \text{scattering factor} \\ q = \frac{4\pi}{\lambda} \sin(\theta/2) \end{array} \right)$$

- **Hydrodynamic radius ( $R_h$ )**

- Stokes-Einstein equation (for a spherical molecule)

$$D = \frac{k_B T}{6\pi\eta R_h}$$

$$\left( \begin{array}{l} k_B : \text{Boltzman constant} \\ T : \text{absolute temperature} \\ \eta : \text{viscosity of solvent} \\ R_h : \text{hydrodynamic radius} \end{array} \right)$$

- Experimental data analysis

