

# Estrutura de líquidos

espalhamento de radiação e-m

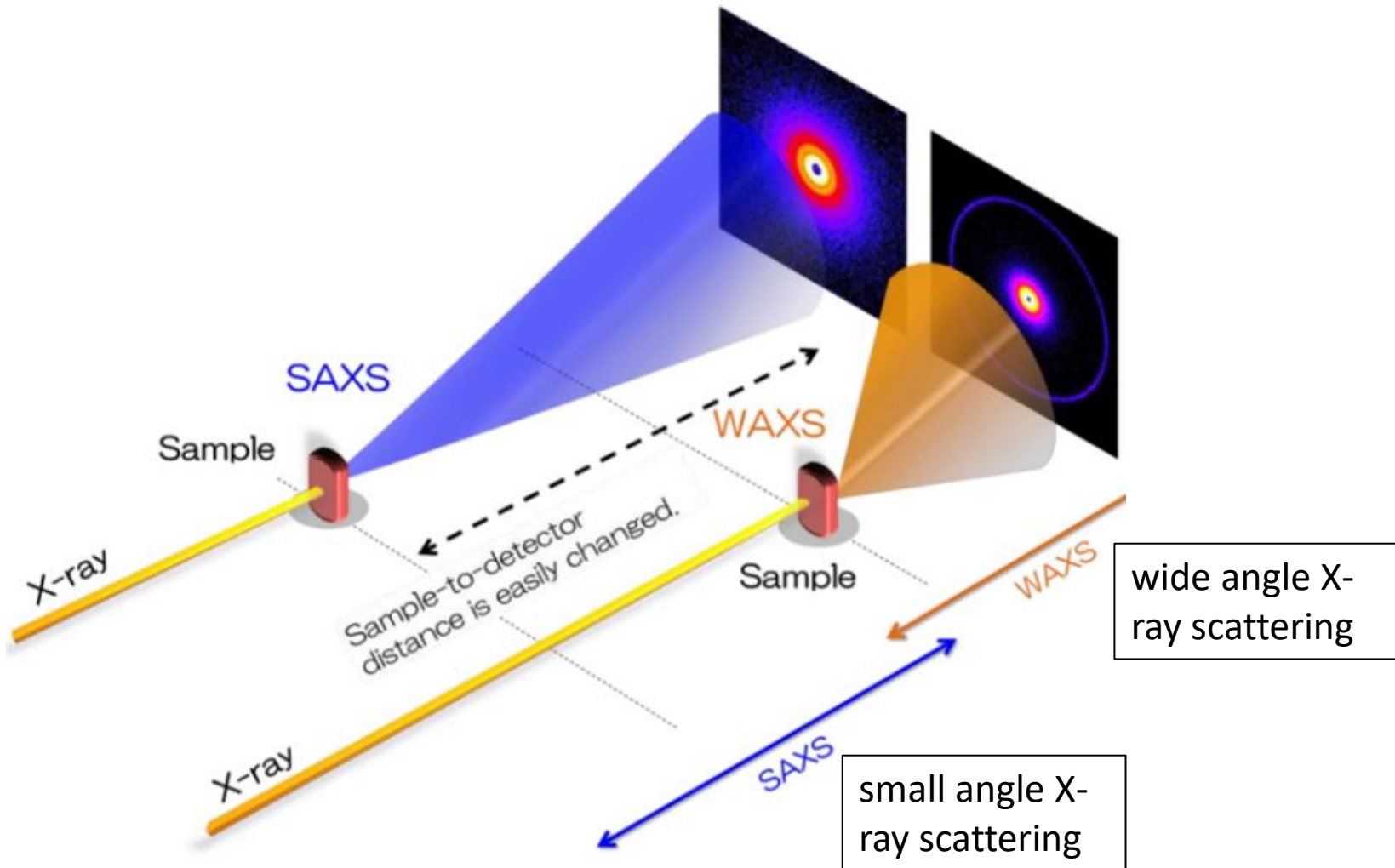
Vera Bohomoletz Henriques

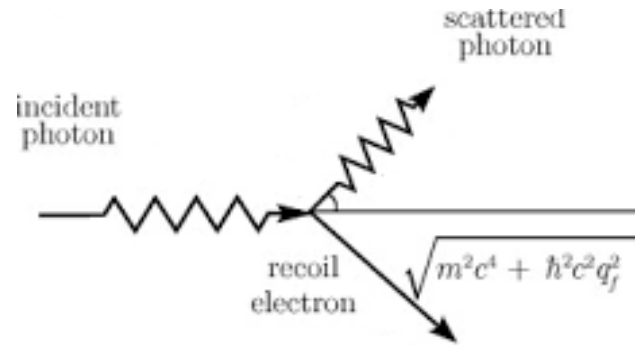
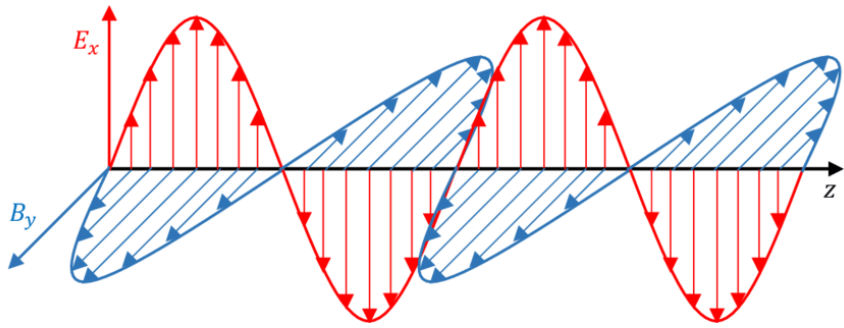
*BioLat group*

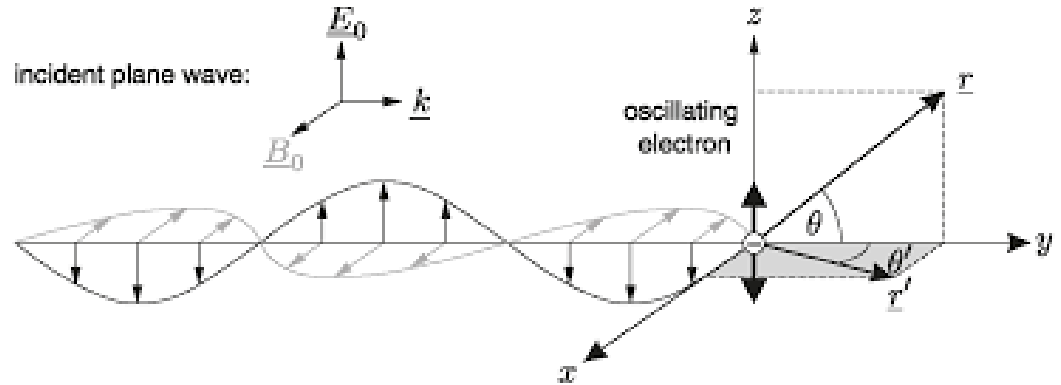
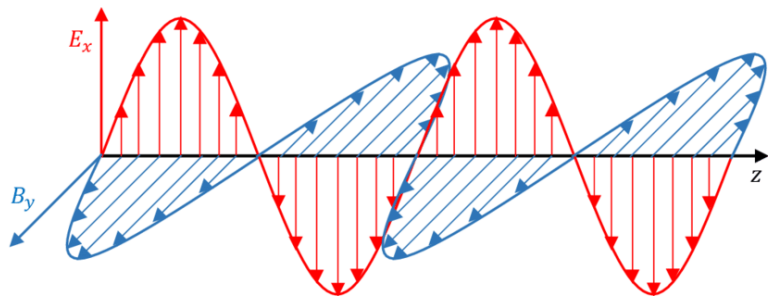
Instituto de Física USP

29 de abril de 2022

# Experimento: espalhamento (elástico) de raio X por elétrons da amostra



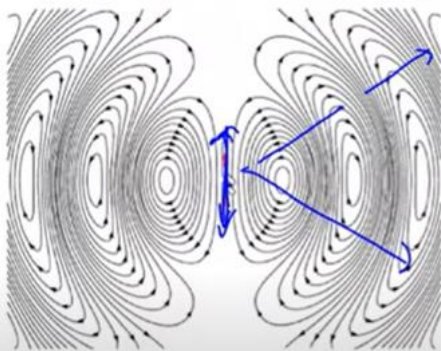




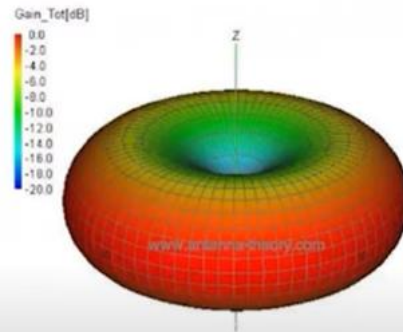
### Oscillating electric charge emits polarized light

Optical / electromagnetic emission of oscillating charge is polarized:

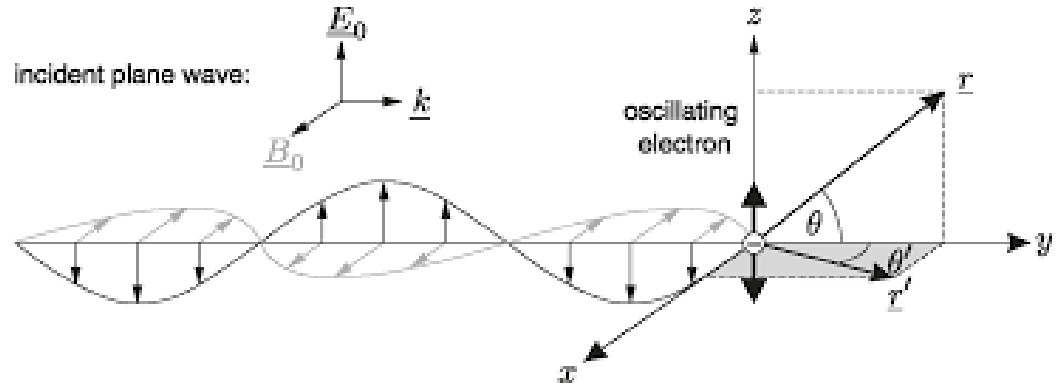
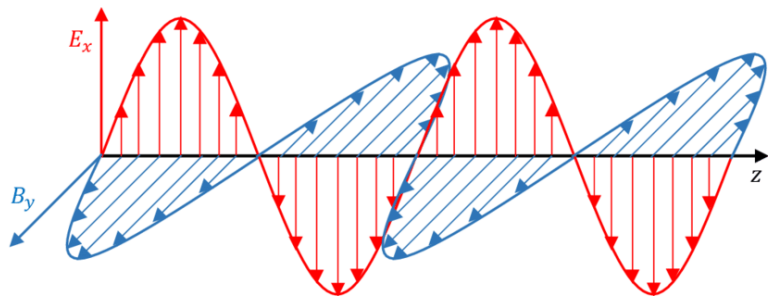
- no component of E-field  $\perp$  to oscillating charge
- Small source (size  $\ll \lambda$ ) emits dipole radiation:  $E_{\parallel} \propto \cos \theta$  (see Fig.)



Arrows indicate E-field



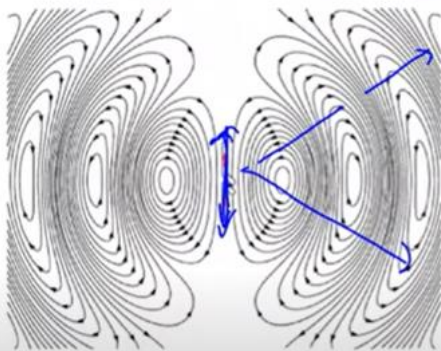
Intensity emitted in different directions



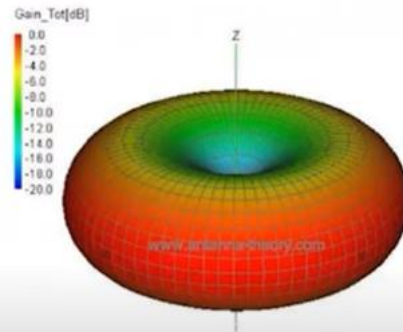
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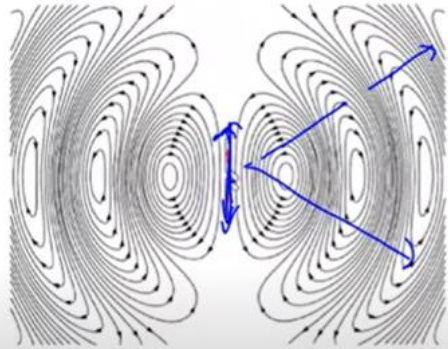


Intensity emitted in different directions

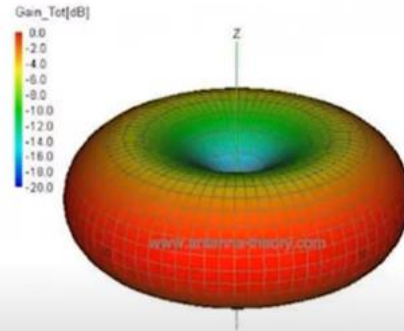
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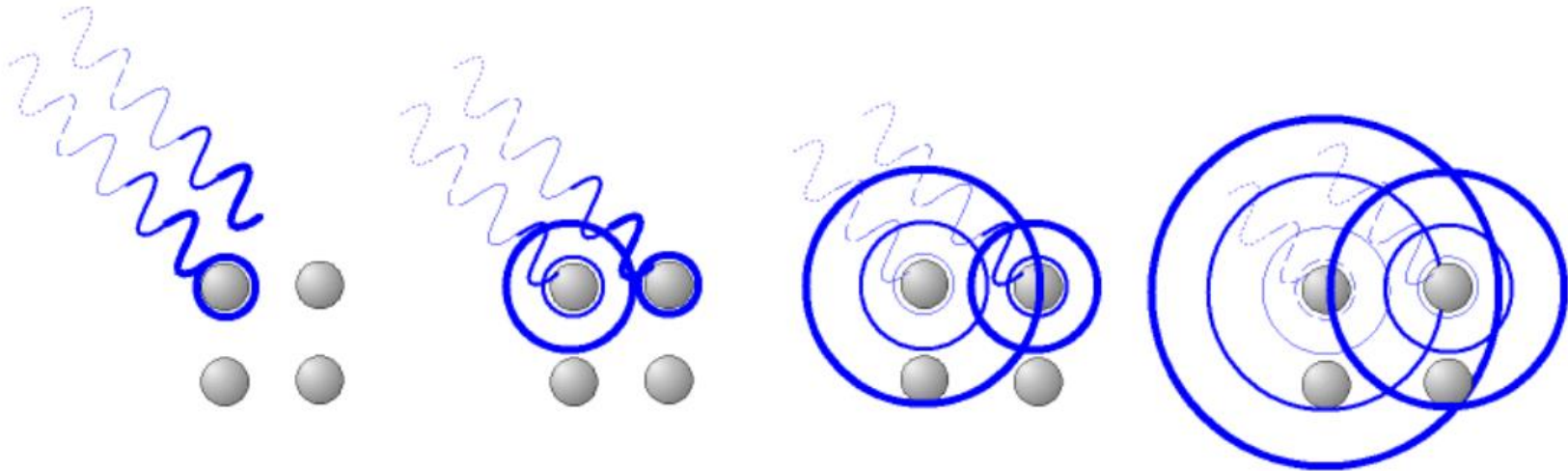
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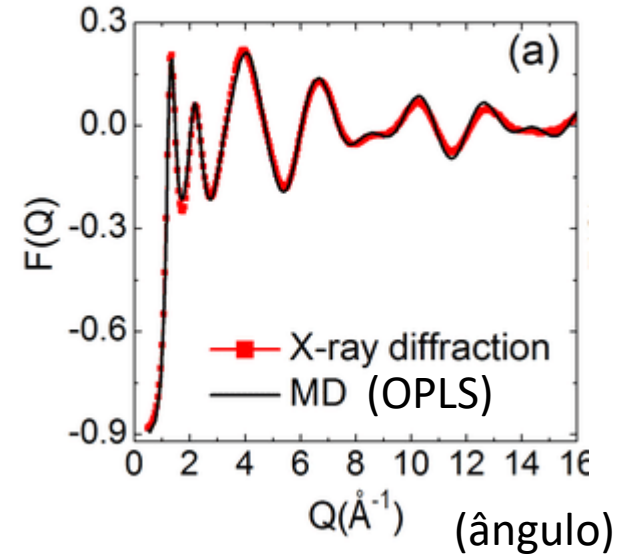
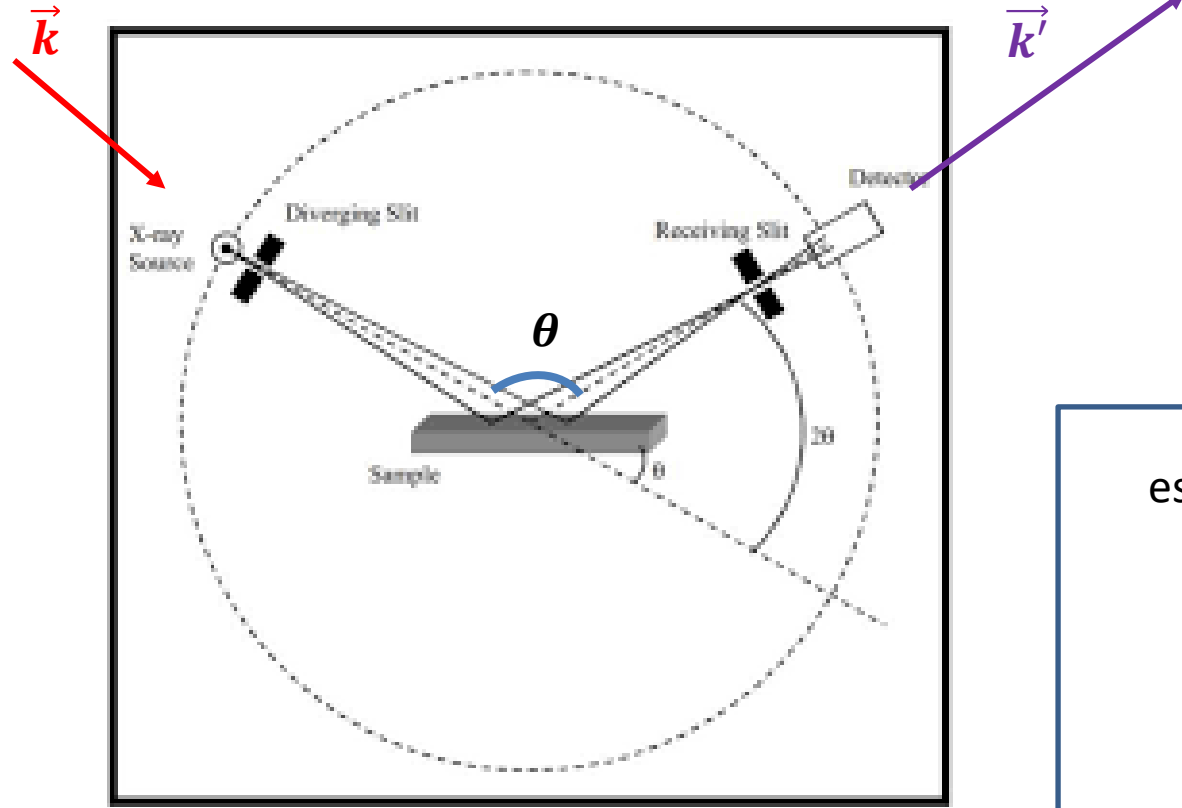


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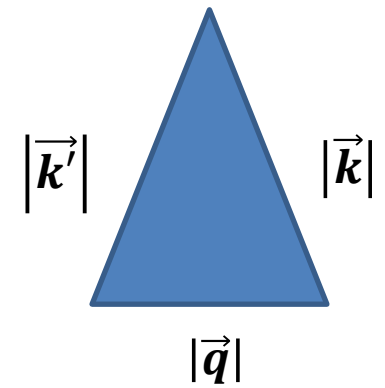


\*X-ray scattering structure factors of liquid  $PCl_3$

$$\vec{k} - \vec{k}' \equiv \vec{q}$$



espalhamento "elástico"  $|\vec{k}| \cong |\vec{k}'|$



$$|\vec{q}| = 2|\vec{k}| \text{sen} \left( \frac{\theta}{2} \right)$$

\*[https://www.researchgate.net/figure/a-and-b-X-ray-scattering-structure-factors-of-liquid-PCl-3-d-and-e-X-ray\\_fig7\\_260150880](https://www.researchgate.net/figure/a-and-b-X-ray-scattering-structure-factors-of-liquid-PCl-3-d-and-e-X-ray_fig7_260150880)

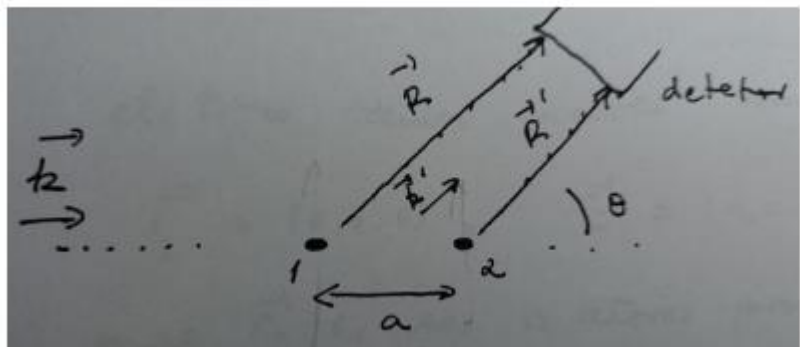
## Superposição da onda eletromagnética espalhada pelos elétrons

$$E(\theta, \omega, t) = \frac{e \pi(\theta) a(t - R/c)}{4\pi\epsilon_0 c^2 R}$$

$$a\left(t - \frac{R}{c}\right) = \frac{e}{m} \frac{\omega^2 E_0}{\omega^2 - \omega_0^2 + i\omega\Gamma}$$

$$E(\theta, R, t; \omega) = \sum_{i=1}^N E_i = \sum_{i=1}^N A_i(\theta, \omega) \frac{e^{ik'R_i}}{R_i} e^{i\omega(t + \frac{d_i}{c})}.$$





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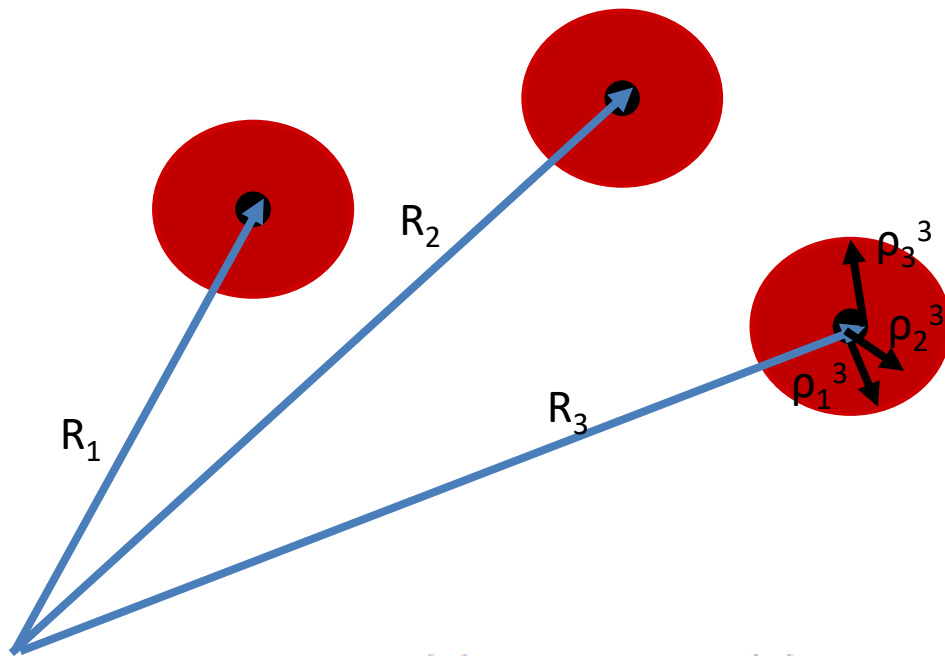
$$\sum_{i=1}^N e^{i(\vec{k} - \vec{k}') \cdot \vec{r}_i}$$

$$E(\theta, R, t; \omega) = A(\theta) \frac{e^{ik'R}}{R} e^{i\omega t} \sum_{i=1}^N e^{i\vec{q} \cdot \vec{r}_i}$$

$$E(\theta, R, t; \omega) = A(\theta) \frac{e^{ik'R}}{R} e^{i\omega t} \sum_{i=1}^N e^{i\vec{q} \cdot \vec{r}_i},$$

$$I(\theta, R, t; \omega) = \varepsilon_0 c \frac{\overline{A^2}(\theta, \omega)}{R^2} \sum_{i=1}^N \sum_{j=1}^N e^{i\vec{q} \cdot (\vec{r}_i - \vec{r}_j)},$$

$$I(\theta, R, t; \omega) = \varepsilon_0 c \frac{\overline{A^2}(\theta, \omega)}{R^2} \sum_{i=1}^N \sum_{j=1}^N e^{i\vec{q} \cdot (\vec{r}_i - \vec{r}_j)},$$



N é o número total de elétrons no sistema, distribuídos entre os diferentes átomos

$$\vec{r}_i^{(n)} = \vec{R}_i + \vec{\rho}_i^{(n)},$$

$$\sum_{\text{cargas } \mu} e^{i\vec{q} \cdot \vec{r}_\mu} = \sum_{\text{átomos } i=1}^N e^{i\vec{q} \cdot \vec{R}_i} \sum_{\text{elétron } n=1}^Z e^{i\vec{q} \cdot \vec{\rho}_i^{(n)}}.$$

Questão: como são as expressões de P e Q na última expressão da intensidade da luz espalhada?

$$I(\theta, R, t; \omega) = \varepsilon_0 c \frac{\overline{A^2}(\theta, \omega)}{R^2} \sum_{i=1}^N \sum_{j=1}^N e^{i\vec{q} \cdot (\vec{r}_i - \vec{r}_j)},$$

$$\sum_{\text{cargas } \mu} e^{i\vec{q} \cdot \vec{r}_\mu} = \sum_{\text{átomos } i=1}^N e^{i\vec{q} \cdot \vec{R}_i} \sum_{\text{elétron } n=1}^Z e^{i\vec{q} \cdot \vec{\rho}_i^{(n)}}.$$

$$I(\theta, R, t; \omega) = \varepsilon_0 c \frac{\overline{A^2}(\theta, \omega)}{R^2} [F(q)F^*(q)][P(q)P^*(q)],$$

Contribuições  
dos elétrons no  
mesmo átomos

Contribuições  
dos elétrons  
em átomos  
diferentes

**Exemplo** sólido unidimensional:  $N$  átomos localizados em posições  $\vec{r}_i = i\vec{a}, i = 0, 1, \dots, N - 1$ , fixas. Nuvem eletrônica de cada átomo com geometria esférica, densidade de carga uniforme.

(i) Fator de estrutura: interferência da radiação espalhada por diferentes átomos

Da expressão para o fator de estrutura, temos,

$$P(q) \propto \left| \sum_{l=0}^{N-1} e^{i\vec{q} \cdot l\vec{a}} \right|^2 = \left| \frac{1 - e^{iN\vec{q} \cdot \vec{a}}}{1 - e^{i\vec{q} \cdot \vec{a}}} \right|^2 = \frac{\text{sen}^2 \left( \frac{N}{2} \vec{q} \cdot \vec{a} \right)}{\text{sen}^2 \left( \frac{1}{2} \vec{q} \cdot \vec{a} \right)}.$$

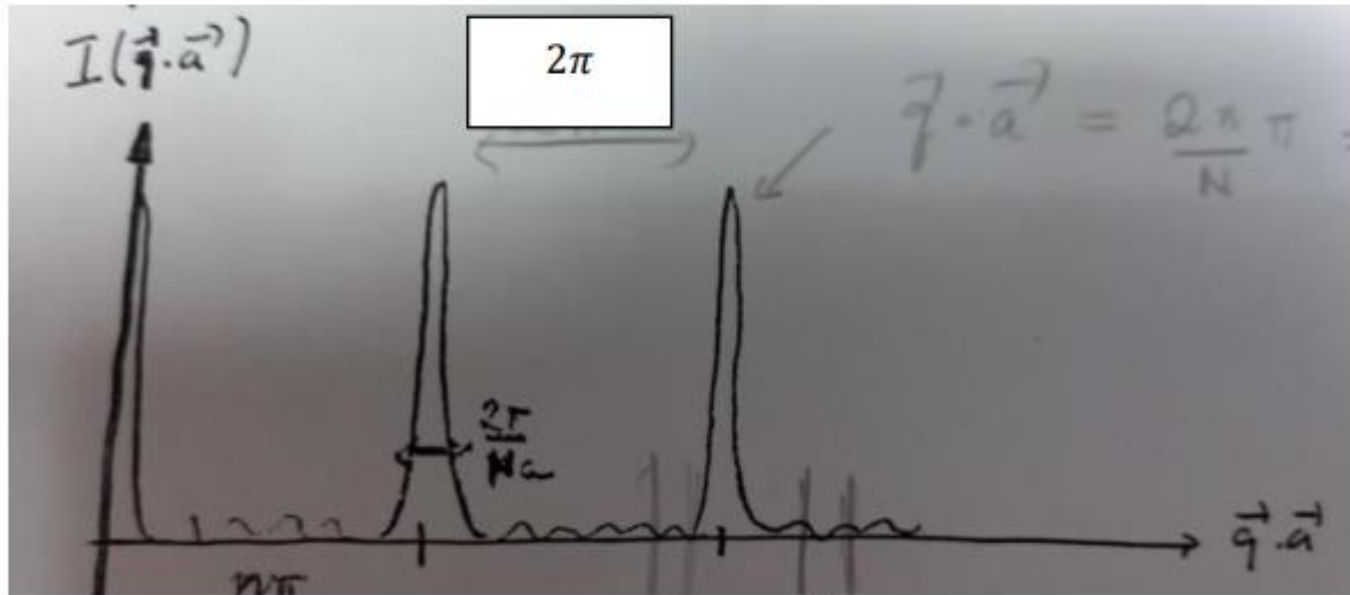
A intensidade tem mínimos para

$$\frac{N}{2} \vec{q} \cdot \vec{a} = n\pi$$

e máximos “especiais” (quando numerador e denominador se anulam) para

$$\frac{1}{2} \vec{q} \cdot \vec{a} = m\pi,$$

com  $P(q) \propto N^2$ .



$$2\pi/N$$

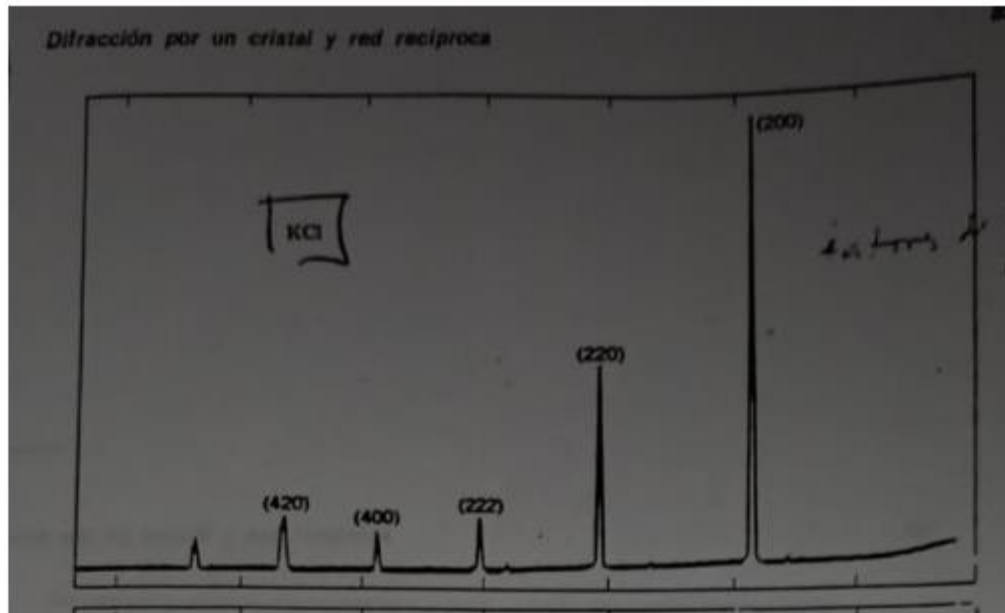
Essa condição que encontramos é a *condição de Laue* para os máximos de difração de um sólido unidimensional (ver Kittel, cap. 2, Eq. 22)

$$\vec{q} \cdot \vec{a} = 2m\pi.$$

Lembrando que  $\vec{q} \equiv \vec{k}' - \vec{k}$ , o vetor diferença entre os vetores de onda da onda emitida e onda espalhada, podemos verificar que essa condição se reduz, para  $\vec{q} \parallel \vec{a}$ , à *condição de Bragg* (ver Kittel, cap. 2, Eq. 4)

$$2k \sin\left(\frac{\theta}{2}\right) a = 2m\pi, \quad \text{ou} \quad 2a \sin\left(\frac{\theta}{2}\right) = m\lambda.$$

Para um cristal real, tridimensional, o quadro é semelhante, como pode se ver na figura experimental de difração de pó de cristal de KCl e KBr, retirada de Kittel (Fig. 31).



(ii) Fator de forma: interferência da radiação espalhada pela distribuição espacial da carga eletrônica no átomo.

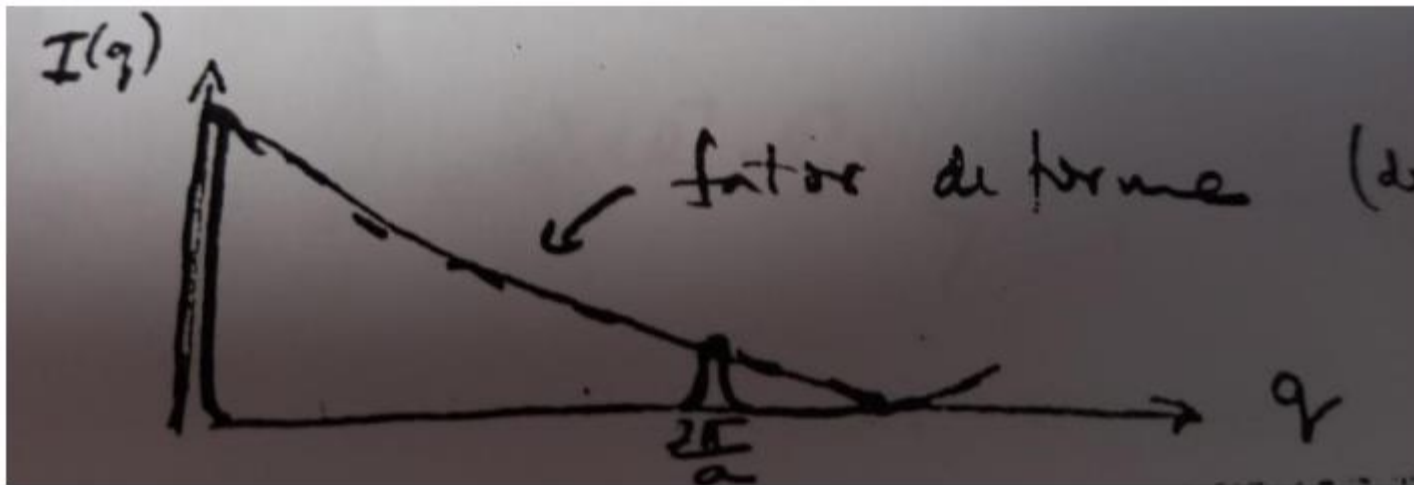
$$\begin{aligned}
 F(\vec{q}) &\equiv \sum_{\text{el\u00e9tron } n=1}^z e^{i\vec{q}\cdot\vec{\rho}_i^{(n)}} \rightarrow \int_{\text{nuvem eletr\u00f4nica}} d^3\rho \, qn(\vec{r}) e^{i\vec{q}\cdot\vec{\rho}} \\
 &= qn2\pi \int_0^\pi \text{sen}\theta \, d\theta \int_0^{R_0} \rho^2 d\rho \, e^{iq\rho\cos\theta},
 \end{aligned}$$

se tomamos o eixo  $z$  das coordenadas polares paralelo ao vetor  $e^{i\vec{q}\cdot\vec{\rho}}$ . Invertendo a ordem da integra\u00e7\u00e3o e efetuando a segunda integral por partes, obtemos

$$F(\vec{q}) = \frac{4\pi n}{q^3} \{ \text{sen}(qR_0) - qR_0 \cos(qR_0) \}.$$

Ent\u00e3o,  $F(0) = \frac{4\pi}{3} nR_0^3$ , e  $F(\vec{q}) = 0$ , para  $qR_0 \approx \frac{\pi}{2}$  (verifique graficamente). Para raio at\u00f4mico  $R_0$  da ordem de um quarto do espa\u00e7amento da rede  $a$ , ter\u00edamos um envelope do fator de forma que pode “esconder” o fator de estrutura. Veja na figura:





Observe que quanto menor a dimensão que se quer o ângulo de espalhamento necessário.

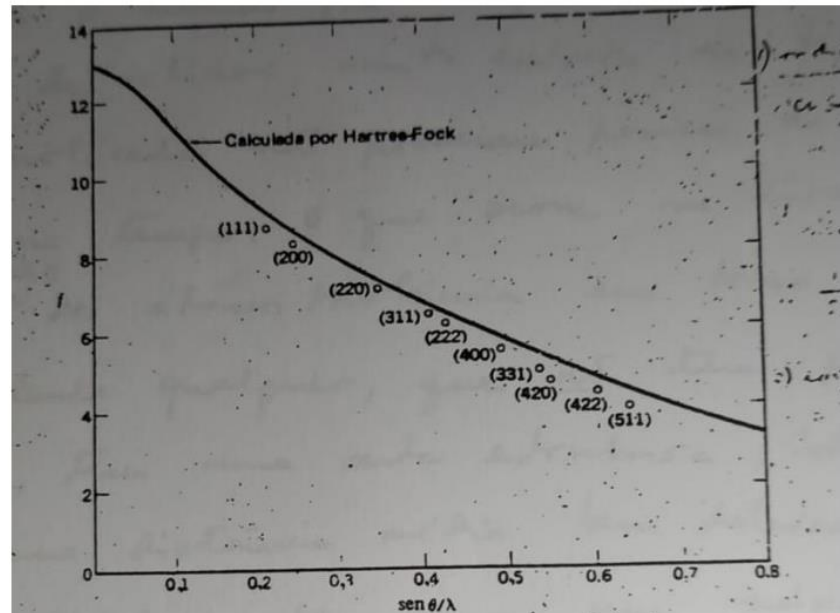


Figura 32. Factores absolutos de difusão atômica del aluminio según Batterman, Chipman, y DeMarco. Se ha marcado cada reflexión observada. La radiación incidente fue  $\text{MoK}\alpha$  con  $\lambda = 0,709 \text{ \AA}$ . Obsérvese que no aparecen reflexiones cuando los índices son parcialmente pares o impares, que es lo esperado, de acuerdo con (63), para un cristal fcc.

## O fator de estrutura de líquidos: lidando com as flutuações térmicas de posição

No caso dos líquidos, os átomos não possuem posições de equilíbrio bem definidas, portanto, para obter a interferência da radiação espalhada pelos mesmos é necessário tomar a média térmica sobre o espaço de configurações de posição. Nesse caso, a intensidade da luz espalhada é dada por

$$\langle I(\theta, R, t; \omega) \rangle = \epsilon_0 c \frac{\overline{A^2}(\theta, \omega)}{R^2} \langle |F(q)|^2 \sum_{i=1}^N \sum_{j=1}^N e^{i\vec{q} \cdot (\vec{R}_i - \vec{R}_j)} \rangle,$$

$$\langle I(\theta, R, t; \omega) \rangle = \epsilon_0 c \frac{\overline{A^2}(\theta, \omega)}{R^2} NP(q)S(q),$$

com o fator de forma definido por

$$P(q) \equiv |F(q)|^2,$$

e o fator de estrutura por

$$S(q) \equiv \frac{1}{N} \langle \sum_{i=1}^N \sum_{j=1}^N e^{i\vec{q} \cdot (\vec{R}_i - \vec{R}_j)} \rangle.$$

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$$S(q) = \frac{1}{N} \left\{ N + \left\langle \sum_{i=1, i \neq j}^N \sum_{j=1}^N e^{i\vec{q} \cdot (\vec{R}_i - \vec{R}_j)} \right\rangle \right\}$$

$$= \frac{1}{N} \left\{ N + \sum_{i=1, i \neq j}^N \sum_{j=1}^N \left\langle \int_V d\vec{r} \delta(\vec{r} - \vec{R}_i + \vec{R}_j) e^{i\vec{q} \cdot \vec{r}} \right\rangle \right\}$$

$$= 1 + \int_V d\vec{r} e^{i\vec{q} \cdot \vec{r}} \left\langle \frac{1}{N} \delta(\vec{r} - \vec{R}_i + \vec{R}_j) \right\rangle.$$

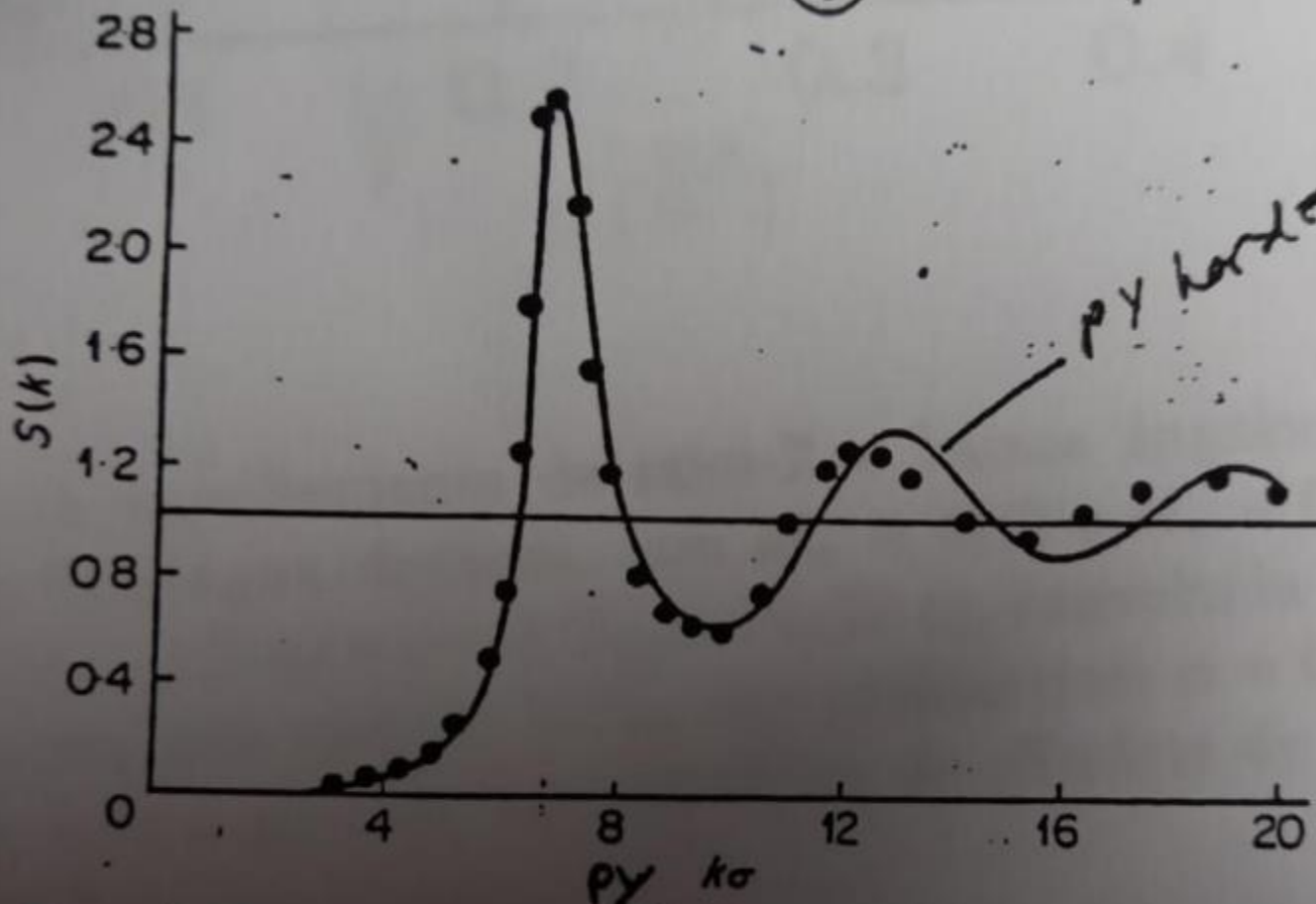
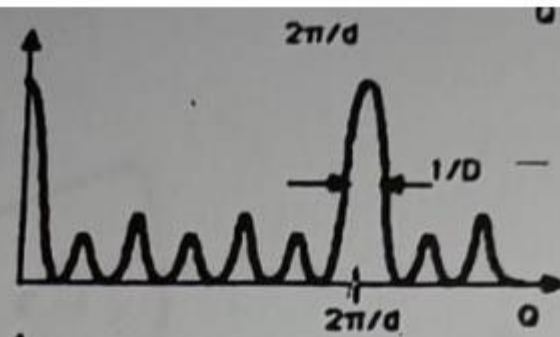
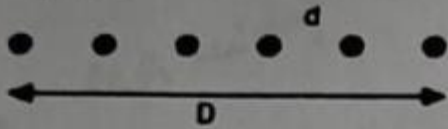
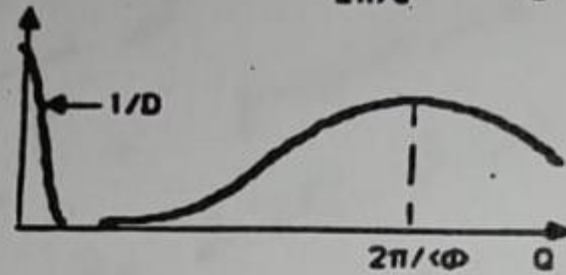
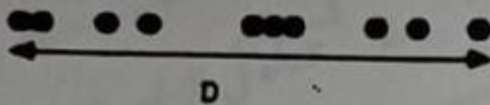


Figure 3.19 The hard-sphere (and liquid-Rb ( $40^\circ\text{C}$ )) structure factor in the vicinity of the melting point. The principal structural features are seen to be reproduced by the hard-sphere curve

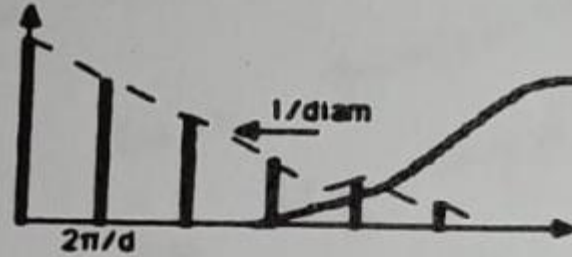
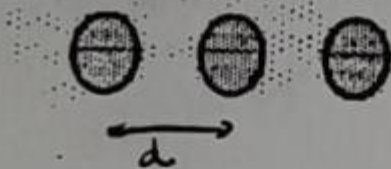
N points



N points, no long range order



Large scale heterogeneities (periodic)



(pseudoperiodic)

