Advanced Topics in Condensed Matter

Lecture 5: Inelastic scattering

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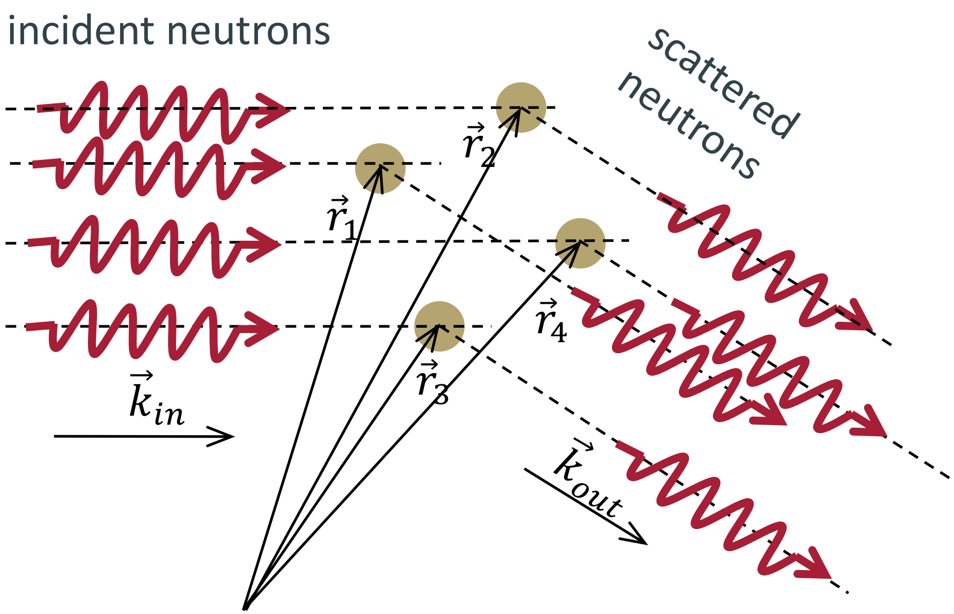
Reminder

$$I(\vec{q}) \propto \frac{\sigma_{coh}}{4\pi} N \cdot S(\vec{q}) + \frac{\sigma_{inc}}{4\pi} N$$ - scattered intensity



$$\vec{q} = \vec{k}_{out} - \vec{k}_{in}$$

$$S(\vec{q}) = \frac{1}{N}\left\langle \sum_{n,m=1}^{N} e^{-i\vec{q}(\vec{r}_n - \vec{r}_m)} \right\rangle$$

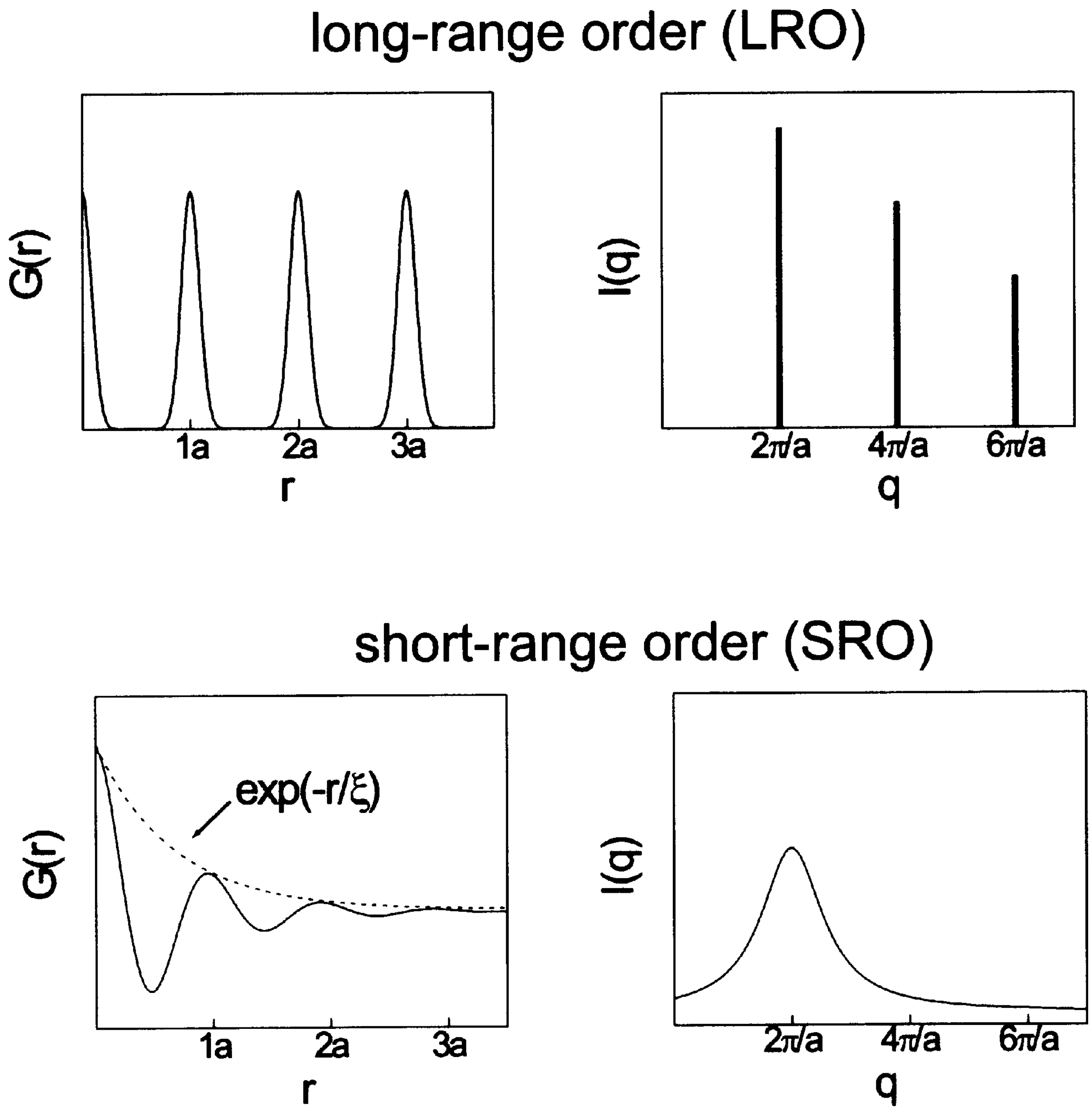
- static structure factor

$$S(\vec{q}) = \int G(\vec{r}) e^{-i\vec{q}\vec{r}} d\vec{r}$$

$$G(\vec{r}) = \frac{1}{N}\left\langle \sum_{n,m=1}^{N} \delta\left(r - \left((\vec{r}_n - \vec{r}_m)\right)\right) \right\rangle$$

- correlation function

Correlation function G(r) and structure factor S(q)



Pair Distribution Function

$$G(\vec{r}) = \frac{1}{N}\left\langle \sum_{\alpha\alpha'} \delta\big(\vec{r} - (\vec{r}_{\alpha'} - \vec{r}_\alpha)\big) \right\rangle = \frac{1}{N}\left\langle \sum_{\alpha=\alpha'} \delta\big(\vec{r} - (\vec{r}_{\alpha'} - \vec{r}_\alpha)\big) + \sum_{\alpha\neq\alpha'} \delta\big(\vec{r} - (\vec{r}_{\alpha'} - \vec{r}_\alpha)\big) \right\rangle =$$

$$= \frac{1}{N}\left\langle N\delta(\vec{r}) + \sum_{\alpha\neq\alpha'} \delta\big(\vec{r} - (\vec{r}_{\alpha'} - \vec{r}_\alpha)\big) \right\rangle =$$

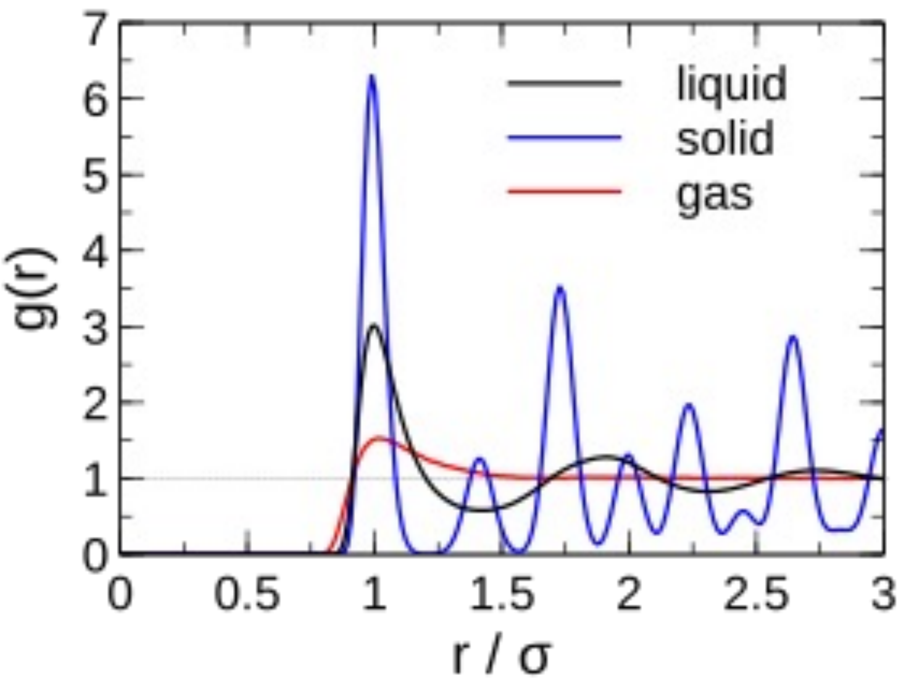
$$= \delta(\vec{r}) + \left\langle \frac{1}{N} \sum_{\alpha\neq\alpha'} \delta\big(\vec{r} - (\vec{r}_{\alpha'} - \vec{r}_\alpha)\big) \right\rangle =$$

$$= \delta(\vec{r}) + \left\langle \frac{N}{N} \sum_{\alpha'\neq 0} \delta\big(\vec{r} - (\vec{r}_{\alpha'} - \vec{r}_0)\big) \right\rangle =$$

$$= \delta(\vec{r}) + \left\langle \sum_{\alpha\neq 0} \delta\big(\vec{r} - (\vec{r}_{\alpha} - \vec{r}_0)\big) \right\rangle =$$

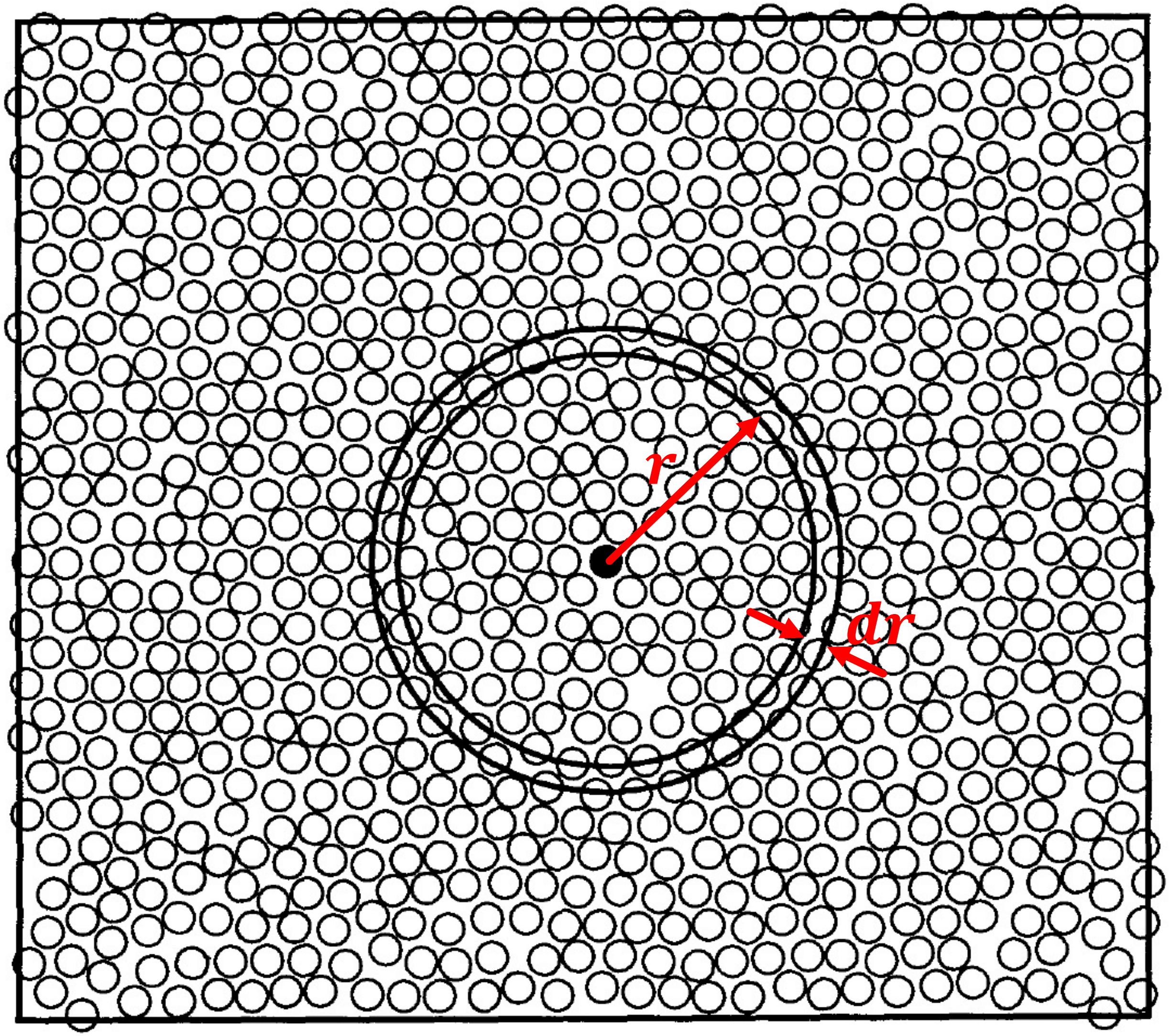
$$= \delta(\vec{r}) + \langle n\rangle g(\vec{r}), \quad \text{where}$$

PDF $$g(\vec{r}) = \frac{1}{\langle n\rangle}\left\langle \sum_{\alpha\neq 0} \delta\big(\vec{r} - (\vec{r}_{\alpha} - \vec{r}_0)\big) \right\rangle$$



$\langle n\rangle g(\vec{r})d\vec{r}$ is an average number of particles in the volume $d\vec{r}$ at the separation $\vec{r}$ from a given one (excluding self-correlation).

Pair distribution function

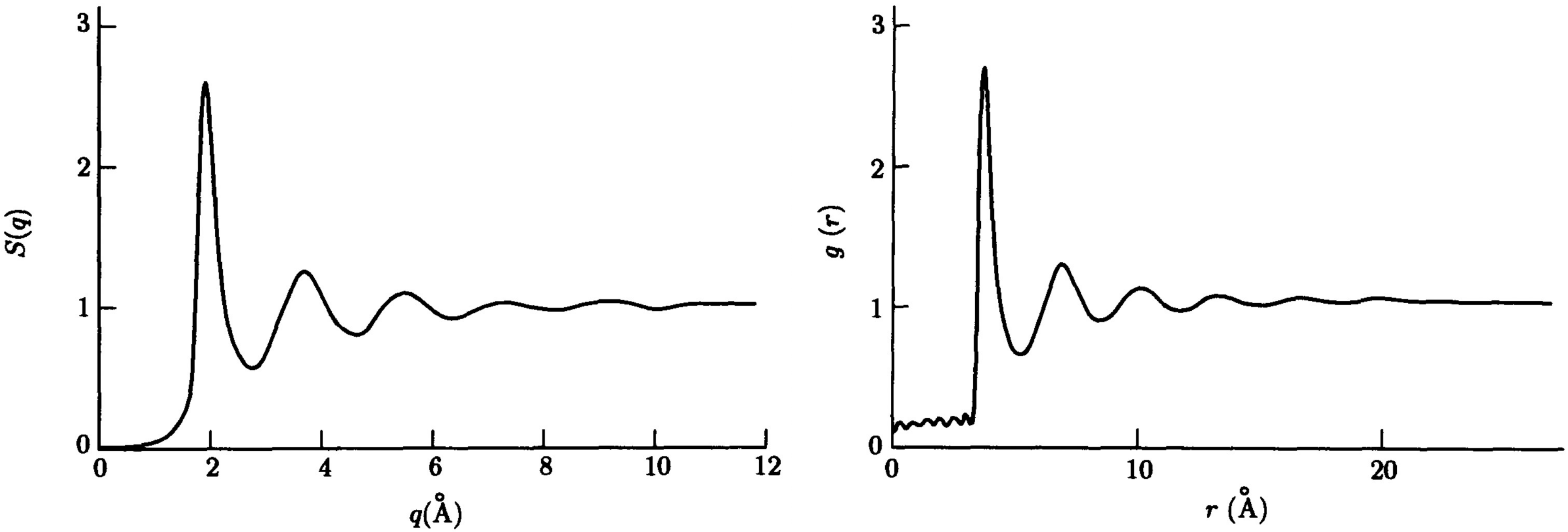


$\langle n\rangle g(r)dr$ – average amount of particles which can be found at the distances from r to $r + dr$ from any given particle

P. Chaikin & T. Lubensky (1995)

Pair distribution function

The structure factor and radial distribution function for liquid argon at T=85 K.

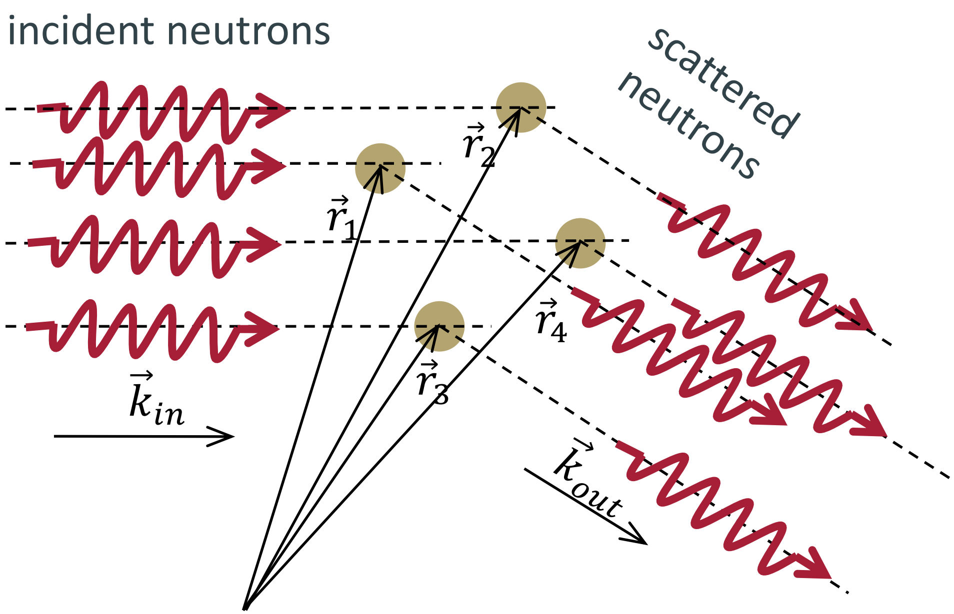


$$g(r) = 1 + \frac{1}{2\pi^2 \langle n \rangle r} \int_0^{+\infty} (S(q) - 1) q \sin(qr)\, dq$$

P. Chaikin & T. Lubensky (1995)

Static system of scatterers

$$I(\vec{q}) \propto \frac{\sigma_{coh}}{4\pi} N \cdot S(\vec{q}) + \frac{\sigma_{inc}}{4\pi} N$$ - scattered intensity



$$\vec{q} = \vec{k}_{out} - \vec{k}_{in}$$

$$S(\vec{q}) = \frac{1}{N} \left\langle \sum_{n,m=1}^{N} e^{-i\vec{q}(\vec{r}_n - \vec{r}_m)} \right\rangle$$

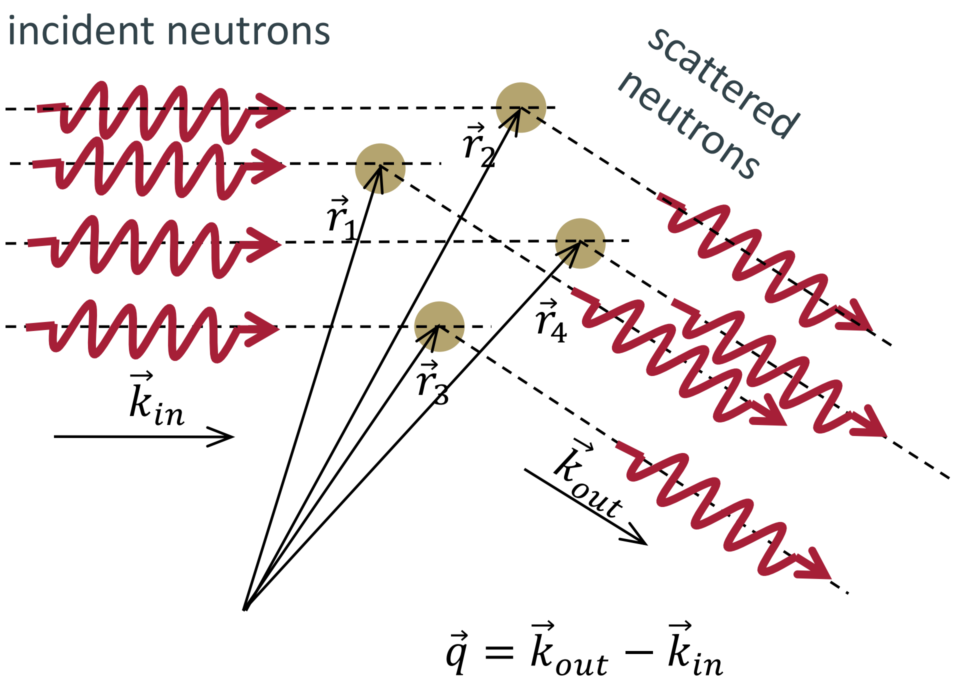
- static structure factor

$$S(\vec{q}) = \int G(\vec{r}) e^{-i\vec{q}\vec{r}} d\vec{r}$$

$$G(\vec{r}) = \frac{1}{N} \left\langle \sum_{n,m=1}^{N} \delta\left(r - ((\vec{r}_n - \vec{r}_m))\right) \right\rangle$$

- correlation function

System of moving scatterers

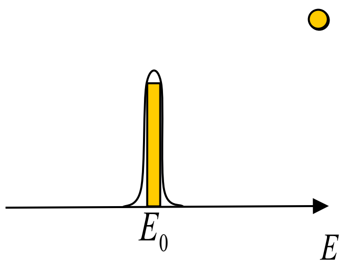


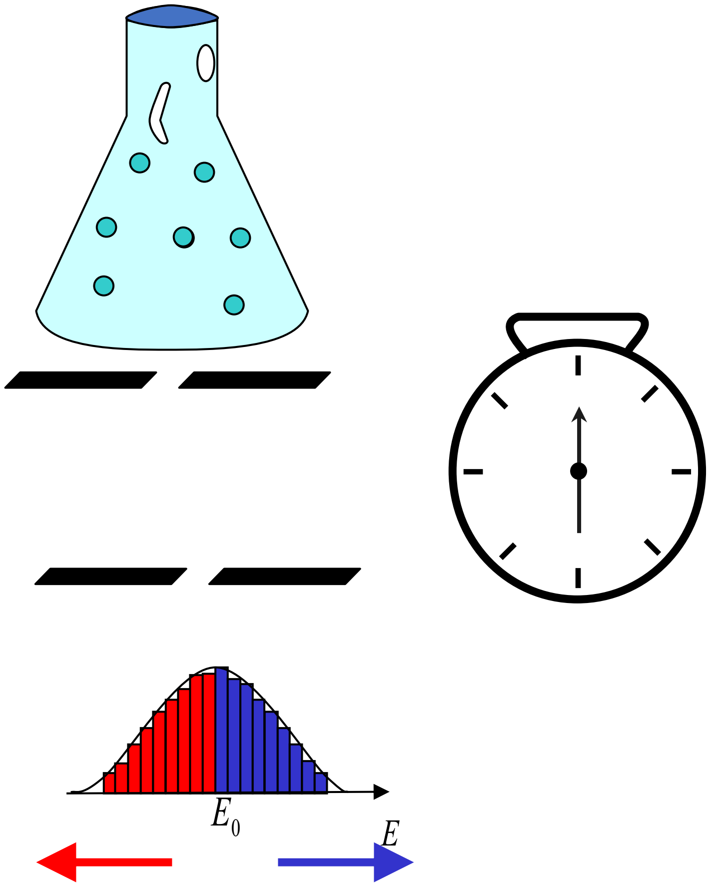
Scatterers are moving, so we have to correlate the positions of the particle “n” at $t = 0$ with the particle “m” at $t \neq 0$

$$G(\vec{r}, t) = \frac{1}{N}\left\langle \sum_{n,m=1}^{N} \delta\left(r - \left((\vec{r}_n(t) - \vec{r}_m(0))\right)\right)\right\rangle$$

- generalized correlation function

Quasielastic neutron scattering (QENS)





The scattered neutrons will have the energy $E = E_0 + \hbar\omega$

Static vs. dynamic

Scatterers have fixed positions:

$$I(\vec{q}) \propto \frac{\sigma_{coh}}{4\pi} N \cdot S(\vec{q}) + \frac{\sigma_{inc}}{4\pi} N$$

$$S(\vec{q}) = \frac{1}{N} \left\langle \sum_{n,m=1}^{N} e^{-i\vec{q}(\vec{r}_n - \vec{r}_m)} \right\rangle$$

$$S(\vec{q}) = \int G(\vec{r}) e^{-i\vec{q}\vec{r}} d\vec{r}$$

$$G(\vec{r}) = \frac{1}{N} \left\langle \sum_{n,m=1}^{N} \delta\left(r - \left((\vec{r}_n - \vec{r}_m)\right)\right) \right\rangle$$

Scatterers can move:

Static vs. dynamic

Scatterers have fixed positions:

$$I(\vec{q}) \propto \frac{\sigma_{coh}}{4\pi} N \cdot S(\vec{q})$$

$$S(\vec{q}) = \frac{1}{N}\left\langle \sum_{n,m=1}^{N} e^{-i\vec{q}(\vec{r}_n - \vec{r}_m)} \right\rangle$$

$$S(\vec{q}) = \int G(\vec{r}) e^{-i\vec{q}\vec{r}} d\vec{r}$$

$$G(\vec{r}) = \frac{1}{N}\left\langle \sum_{n,m=1}^{N} \delta\left(r - ((\vec{r}_n - \vec{r}_m))\right) \right\rangle$$

Scatterers can move:

$$I(\vec{q},\omega) \propto \frac{k_{out}}{k_{in}} \cdot \frac{\sigma_{coh}}{4\pi} N \cdot S_{coh}(\vec{q},\omega)$$

$$J(\vec{q},t) = \frac{1}{N}\left\langle \sum_{n,m=1}^{N} e^{-i\vec{q}(\vec{r}_n(t) - \vec{r}_m(0))} \right\rangle$$

$$S_{coh}(\vec{q},\omega) = \frac{1}{2\pi\hbar} \int G(\vec{r},t) e^{-i\vec{q}\vec{r}} e^{i\omega t} d\vec{r}\, dt$$

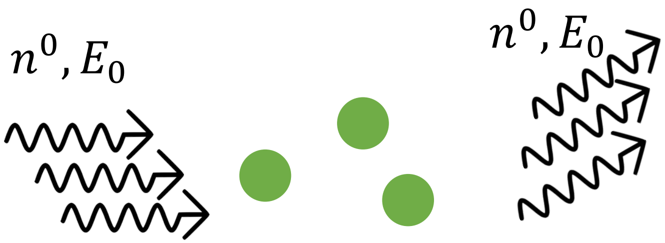
$$G(\vec{r},t) = \frac{1}{N}\left\langle \sum_{n,m=1}^{N} \delta\left(r - ((\vec{r}_n(t) - \vec{r}_m(0)))\right) \right\rangle$$

$$S_{coh}(\vec{q},\omega) = \frac{1}{2\pi\hbar}\int G(\vec{r},t)e^{-i\vec{q}\vec{r}}e^{i\omega t}d\vec{r}\,dt$$

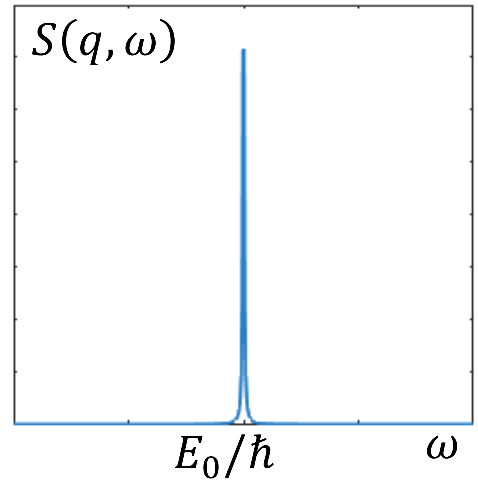
Structure factor	Correlation function
$S(\vec{q},\omega)$	$G(\vec{r},t)$
$\int S(\vec{q},\omega)d\omega$	$G(\vec{r},t=0)$
$\int S(\vec{q},\omega)d\vec{q}$	$G(\vec{r}=0,t)$
$\int S(\vec{q},\omega)d\omega d\vec{q}$	$G(\vec{r}=0,t=0)$
$S(\vec{q},\omega=0)$	$\int G(\vec{r},t)\,dt$
$S(\vec{q}=0,\omega)$	$\int G(\vec{r},t)\,d\vec{r}$

Quasielastic neutron scattering

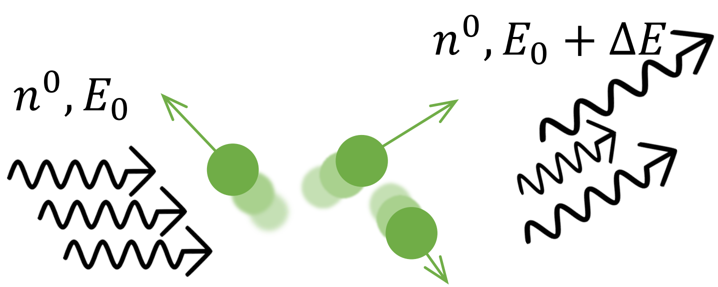
Static sample

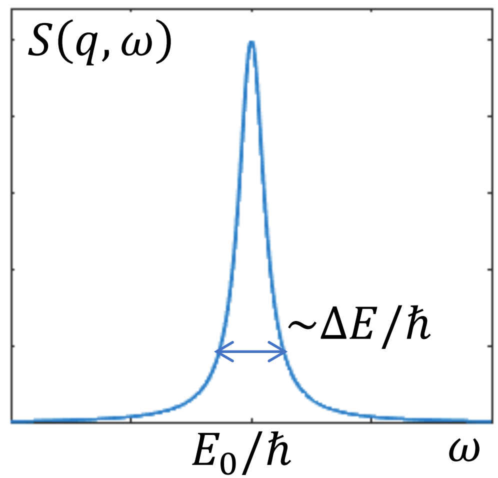


Quasielastic neutron scattering
(spatially incoherent, inelastic)



Dynamic sample





$\tau \propto {}^{1}/_{\Delta E}$

$1ps \Leftrightarrow 4meV$

Van Hove function

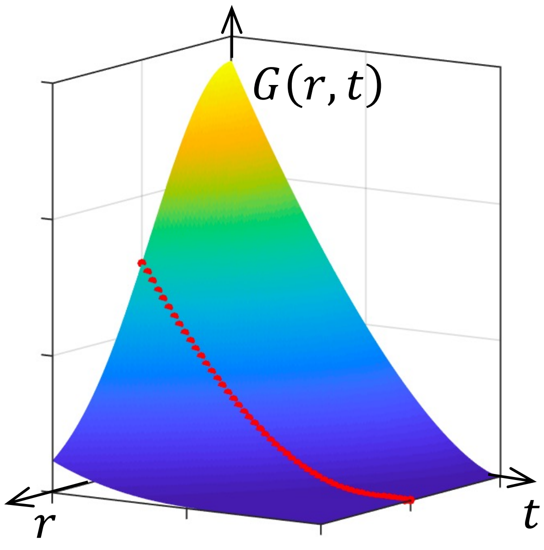
Correlation function in real time and space: $G(\boldsymbol{r},t) = (2\pi)^3\hbar\int d^3\boldsymbol{q}d\omega e^{-i(\boldsymbol{qr}-\omega t)}S(\boldsymbol{q},\omega)$

Scattering function in frequency domain and reciprocal space: $S(\boldsymbol{q},\omega) = \frac{1}{2\pi\hbar}\int d^3\boldsymbol{r}dte^{i(\boldsymbol{qr}-\omega t)}G(\boldsymbol{r},t)$

$$D\nabla^2 n(\boldsymbol{r},t) = \frac{\partial}{\partial t}n(\mathbf{r},t)$$

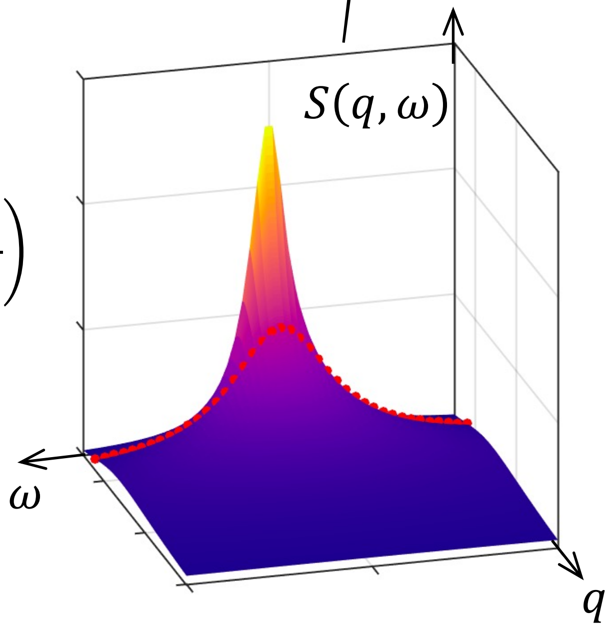
$$G(\boldsymbol{r},t) = \frac{1}{N}\langle n(\boldsymbol{r},t)n(0,0)\rangle = \frac{1}{N}\left\langle\sum_{n=1}^{N}\delta\left(\boldsymbol{r}-\left(\left(\boldsymbol{r}_n(t)-\boldsymbol{r}_n(0)\right)\right)\right)\right\rangle$$

Diffusion:

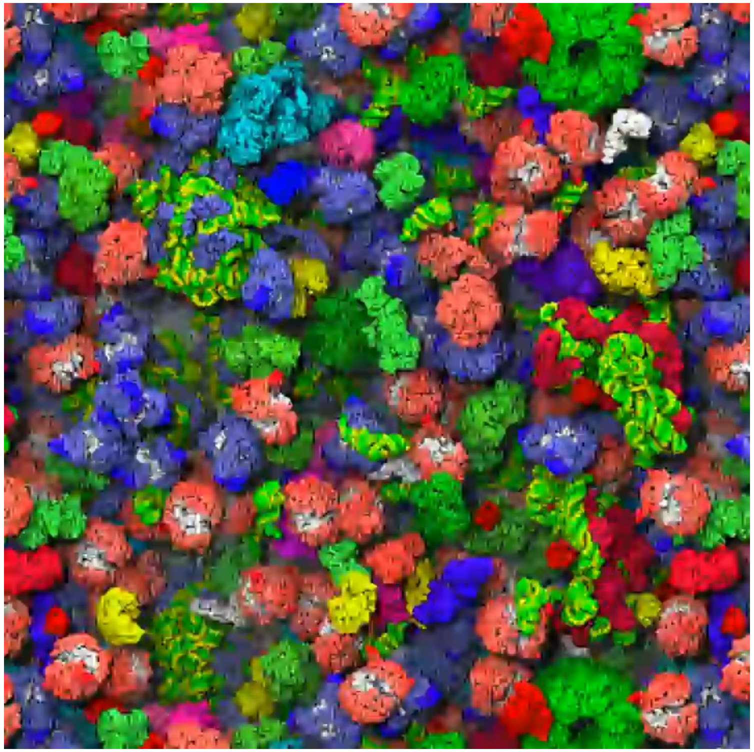


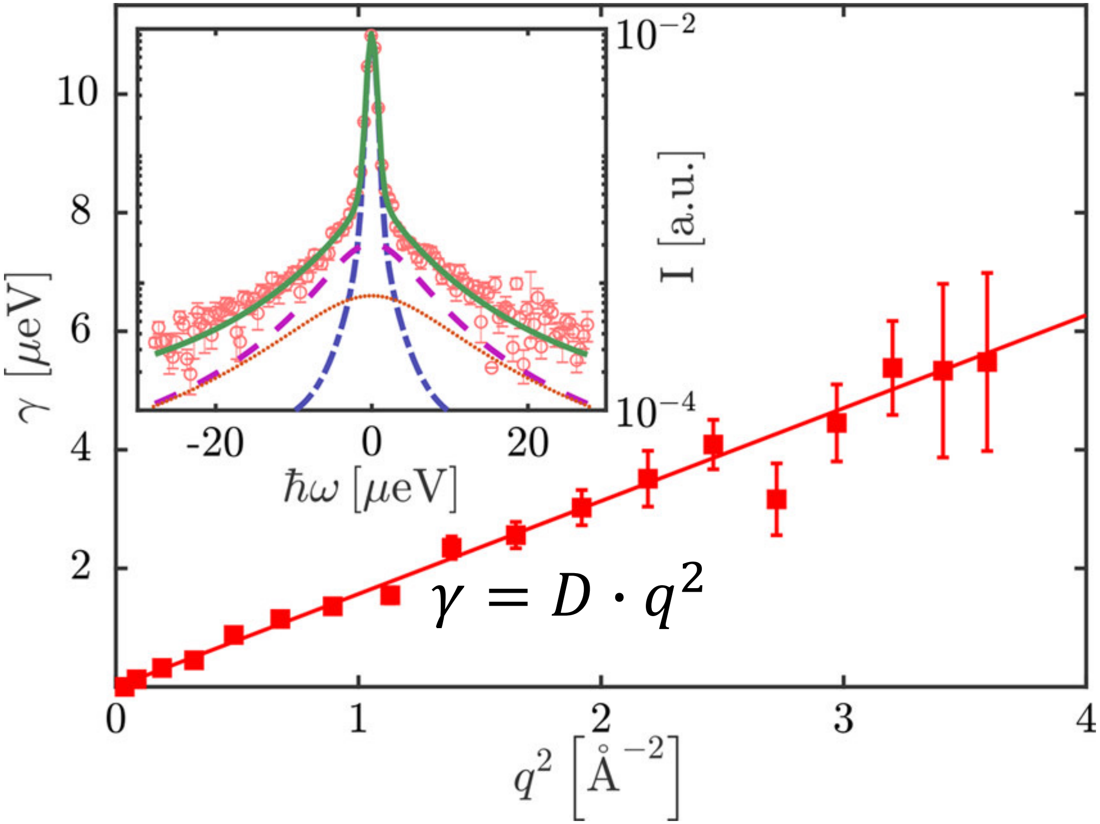
$$G(r,t) = \frac{1}{(4\pi D|t|)^{3/2}}\exp\left(-\frac{r^2}{4D|t|}\right)$$

$$S(q,\omega) = \frac{1}{\pi}\frac{Dq^2}{(Dq^2)^2+\omega^2}$$



Measuring self-diffusion

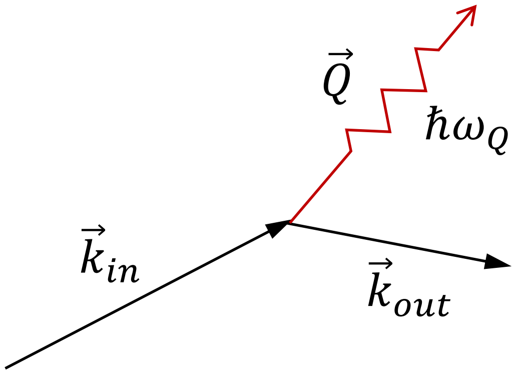


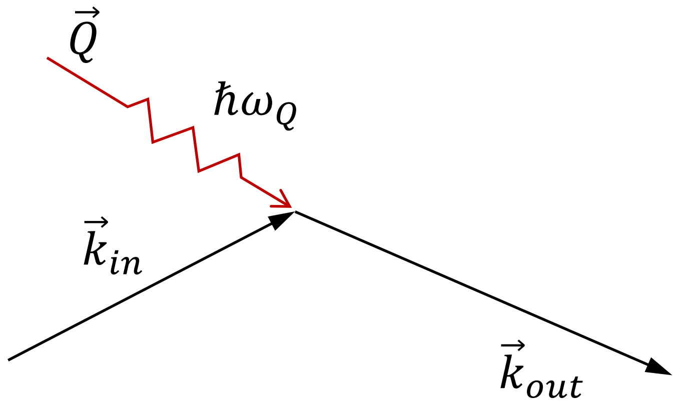


McGuffee & Elcock, PLOS Comp. Biol. 6(3): e1000694 (2010)

M. Grimaldo et al., J. Phys. Chem. Lett. 10 (2019), 1709

Scattering of neutrons by phonons





Stokes scattering

$$\frac{\hbar^2 k_{in}^2}{2m_n} = \frac{\hbar^2 k_{out}^2}{2m_n} + \hbar\omega_Q$$

$$\vec{k}_{in} = \vec{k}_{out} + \vec{Q}$$

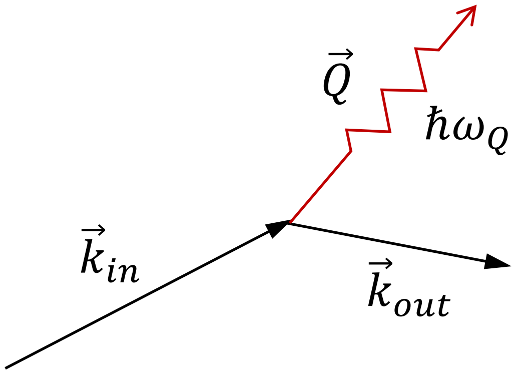
Anti-Stokes scattering

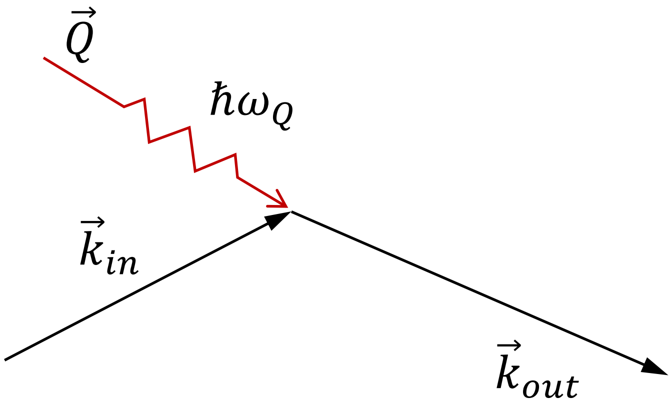
$$\frac{\hbar^2 k_{in}^2}{2m_n} + \hbar\omega_Q = \frac{\hbar^2 k_{out}^2}{2m_n}$$

$$\vec{k}_{in} + \vec{Q} = \vec{k}_{out}$$

N-process (”Normal”, within the first Brillouin zone)

Scattering of neutrons by phonons





Stokes scattering

$$\frac{\hbar^2 k_{in}^2}{2m_n} = \frac{\hbar^2 k_{out}^2}{2m_n} + \hbar\omega_Q$$

$$\vec{k}_{in} = \vec{k}_{out} + \vec{Q} + \vec{G}$$

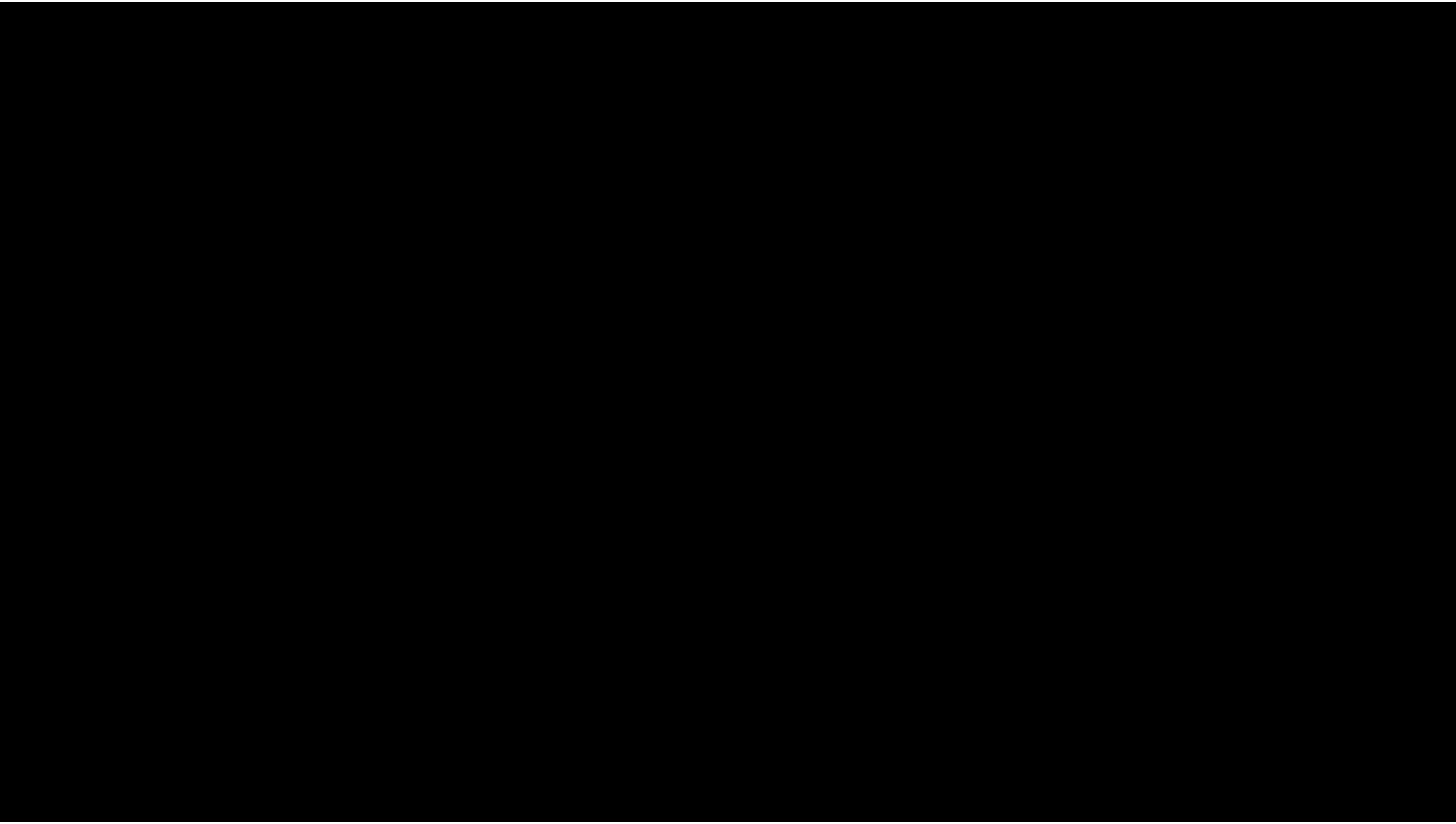
Anti-Stokes scattering

$$\frac{\hbar^2 k_{in}^2}{2m_n} + \hbar\omega_Q = \frac{\hbar^2 k_{out}^2}{2m_n}$$

$$\vec{k}_{in} + \vec{Q} = \vec{k}_{out} + \vec{G}$$

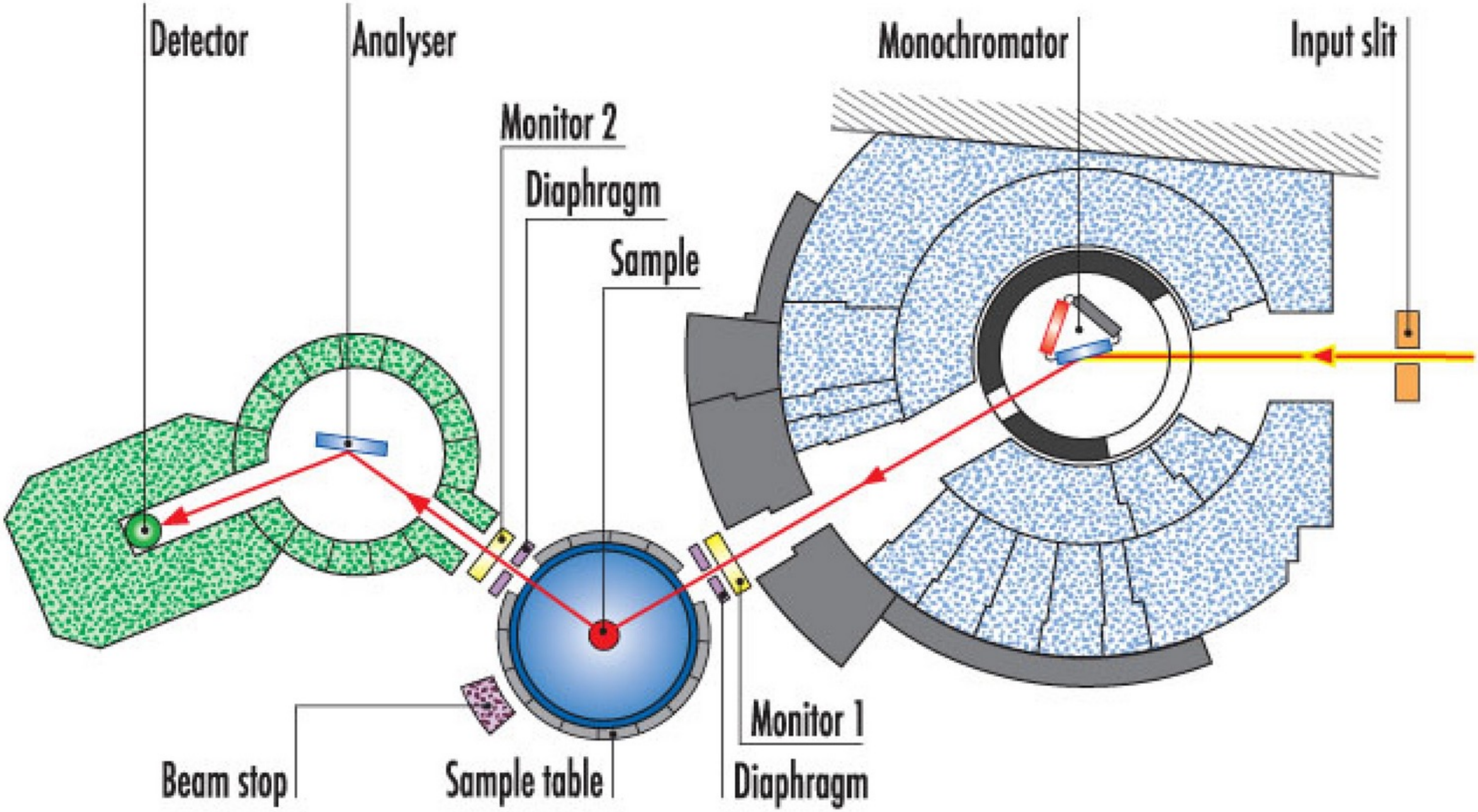
U-process (“Umklapp”, outside of the first Brillouin zone)

Measuring dispersion with neutrons



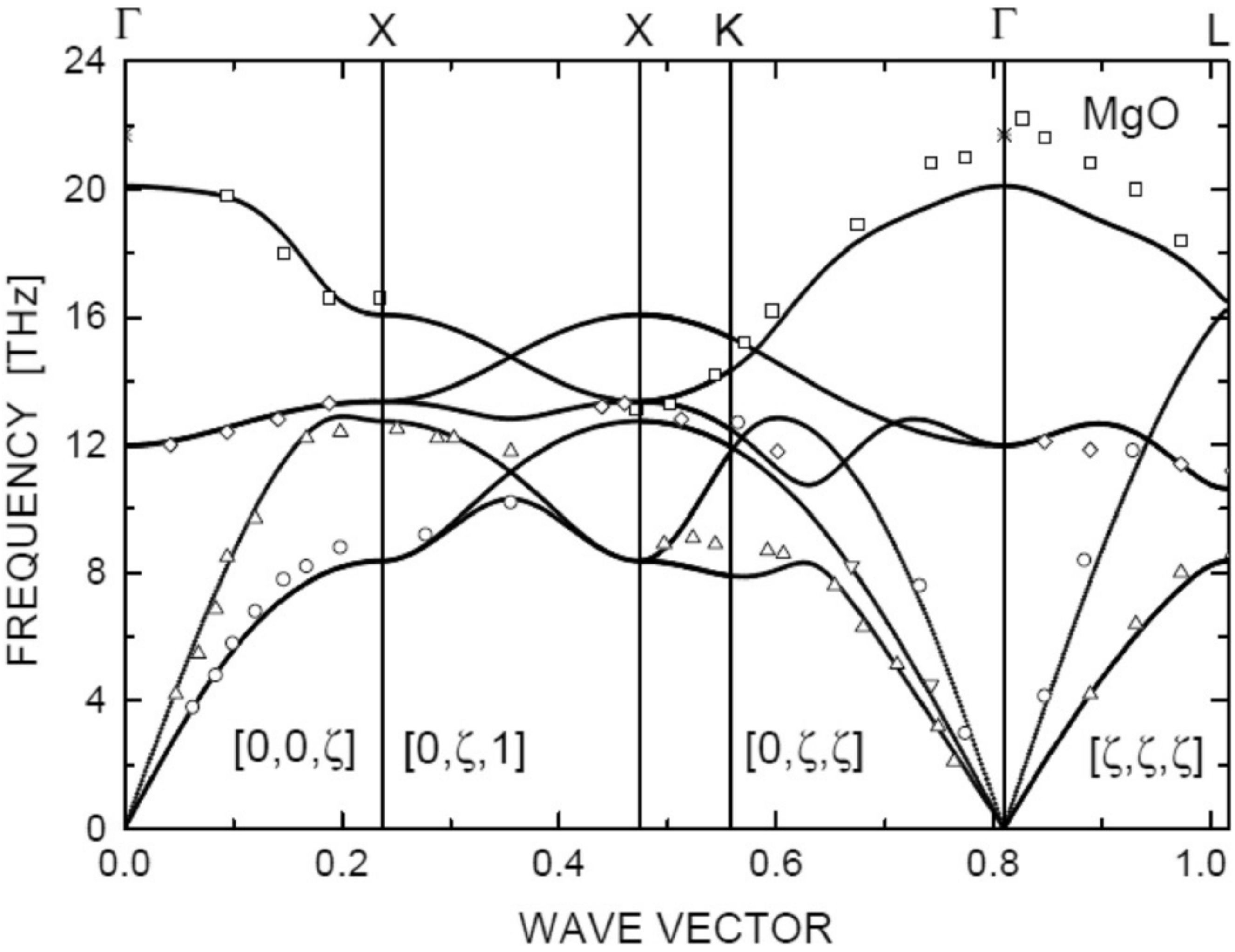
www.quantummadesimple.com

Experimental setup



Triple-axis spectrometer: schematic layout of IN8 at a thermal beam (ILL, Grenoble)

Experimental setup



K. Parlinski et al., J. Phys. Chem. Solids., ***61****, 87–90, (1999)*

Neutrons vs. X-rays

Neutrons:

$$E = \frac{2\pi^2\hbar^2}{m_n\lambda^2} \qquad E[eV] = \frac{0.082}{\lambda^2[\text{Å}^2]} \qquad \frac{\Delta E}{E} = \frac{\hbar\omega}{E} \sim \frac{0.025\ \text{eV}}{0.082\ \text{eV}} \sim 0.3$$

Easy to measure a 30% change in the energy of a neutron

Photons (x-rays):

$$E = \frac{2\pi\hbar c}{\lambda} \qquad E[eV] = \frac{12400}{\lambda[\text{Å}]} \qquad \frac{\Delta E}{E} = \frac{\hbar\omega}{E} \sim \frac{0.025\ \text{eV}}{12400\ \text{eV}} \sim 10^{-6}$$

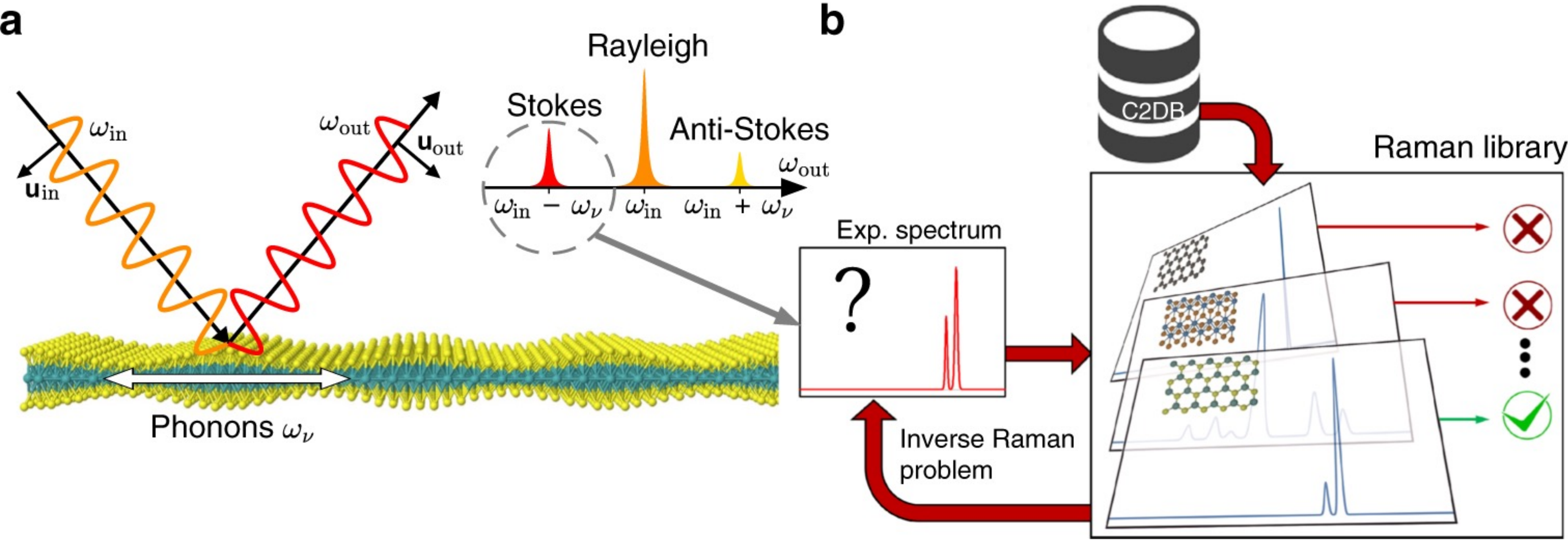
Change of the X-ray photon energy is negligible. Elastic scattering is a good approximation.

Typical phonon in a crystal:

$$\hbar\omega \sim k_B T \sim 0.025\ \text{eV}$$

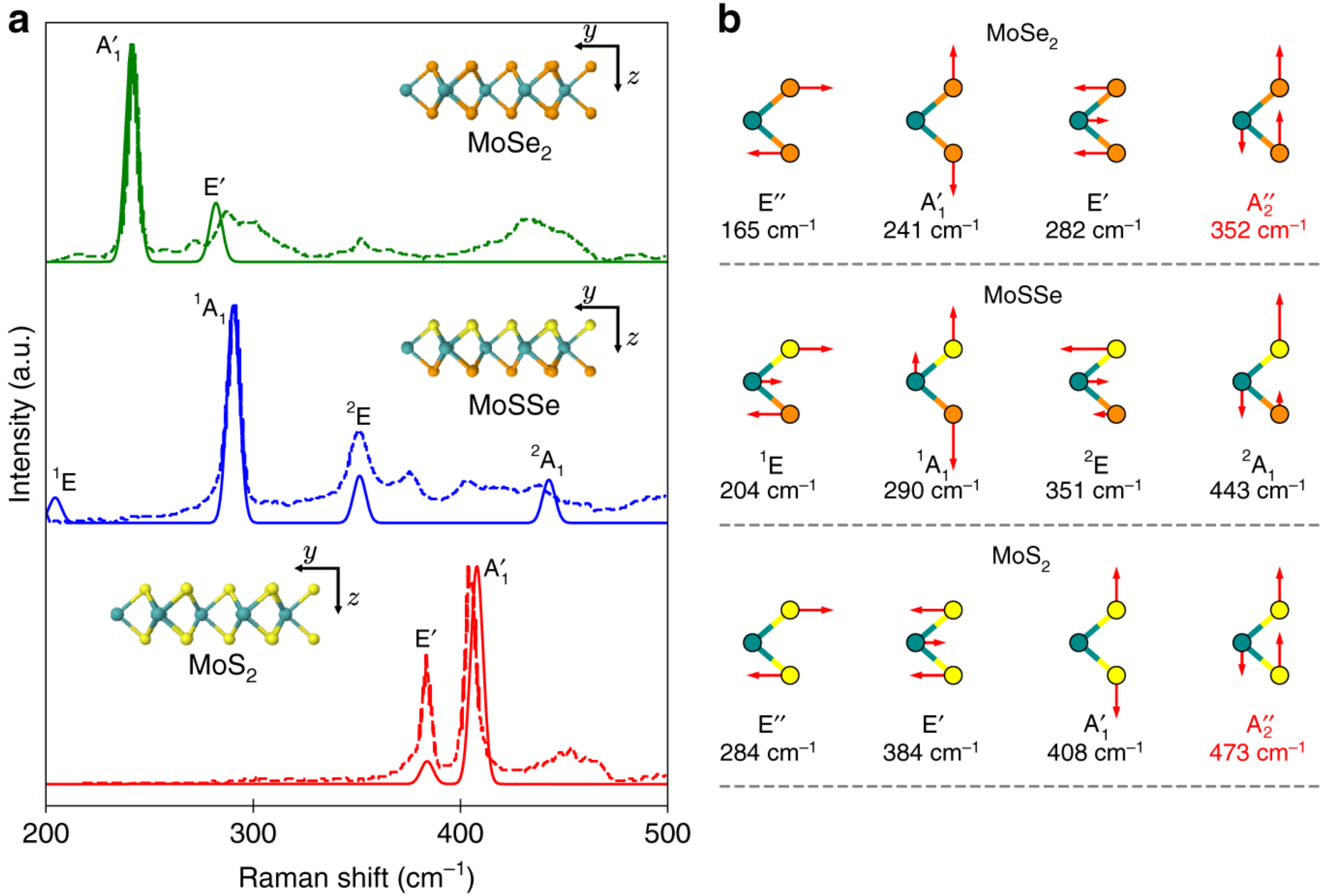
$$q \sim \frac{2\pi}{a} \sim 2\ \text{Å}^{-1}$$

Raman scattering



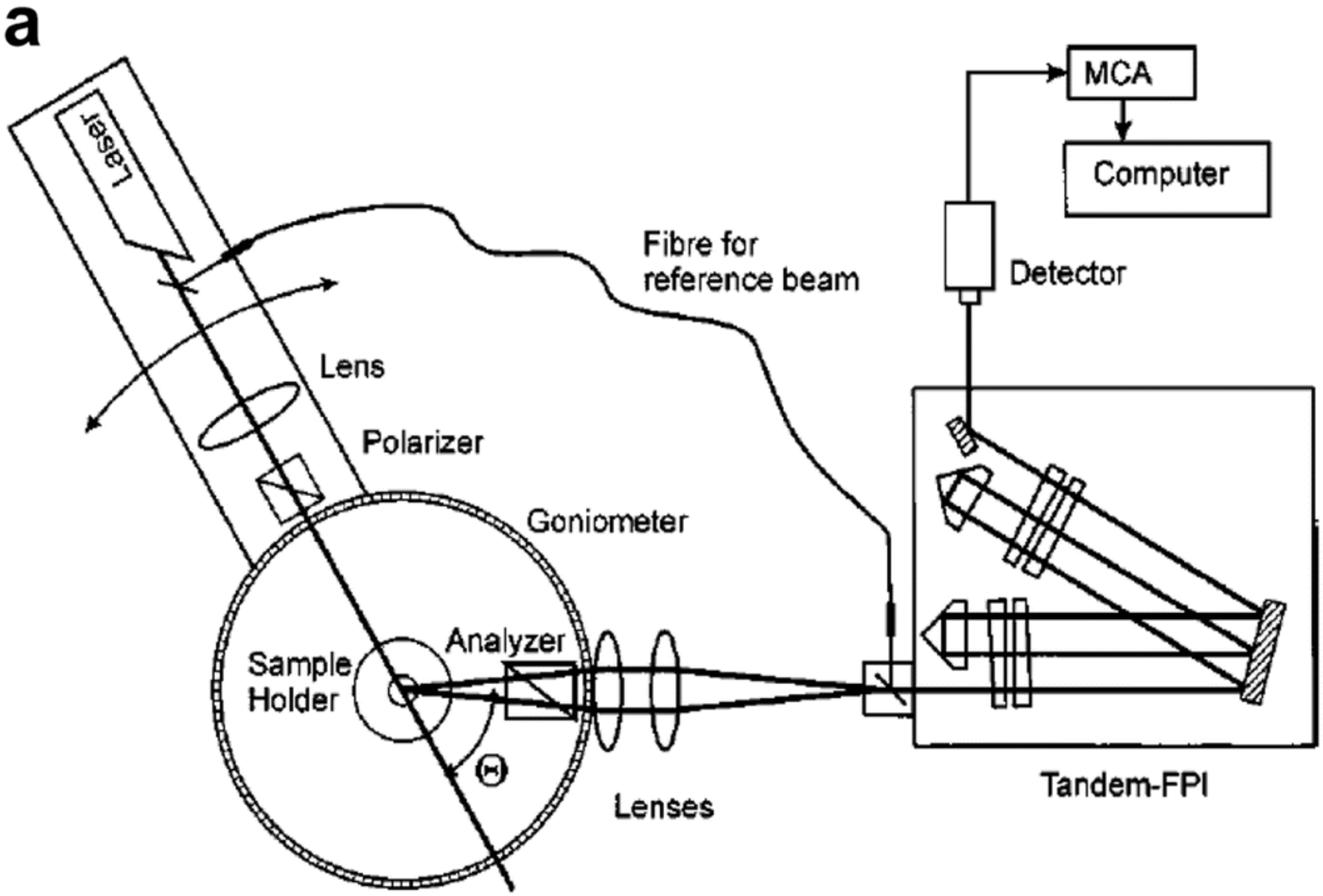
*A. Taghizadeh et al., Nat. Commun., **11**, 3011, (2020)*

Raman scattering



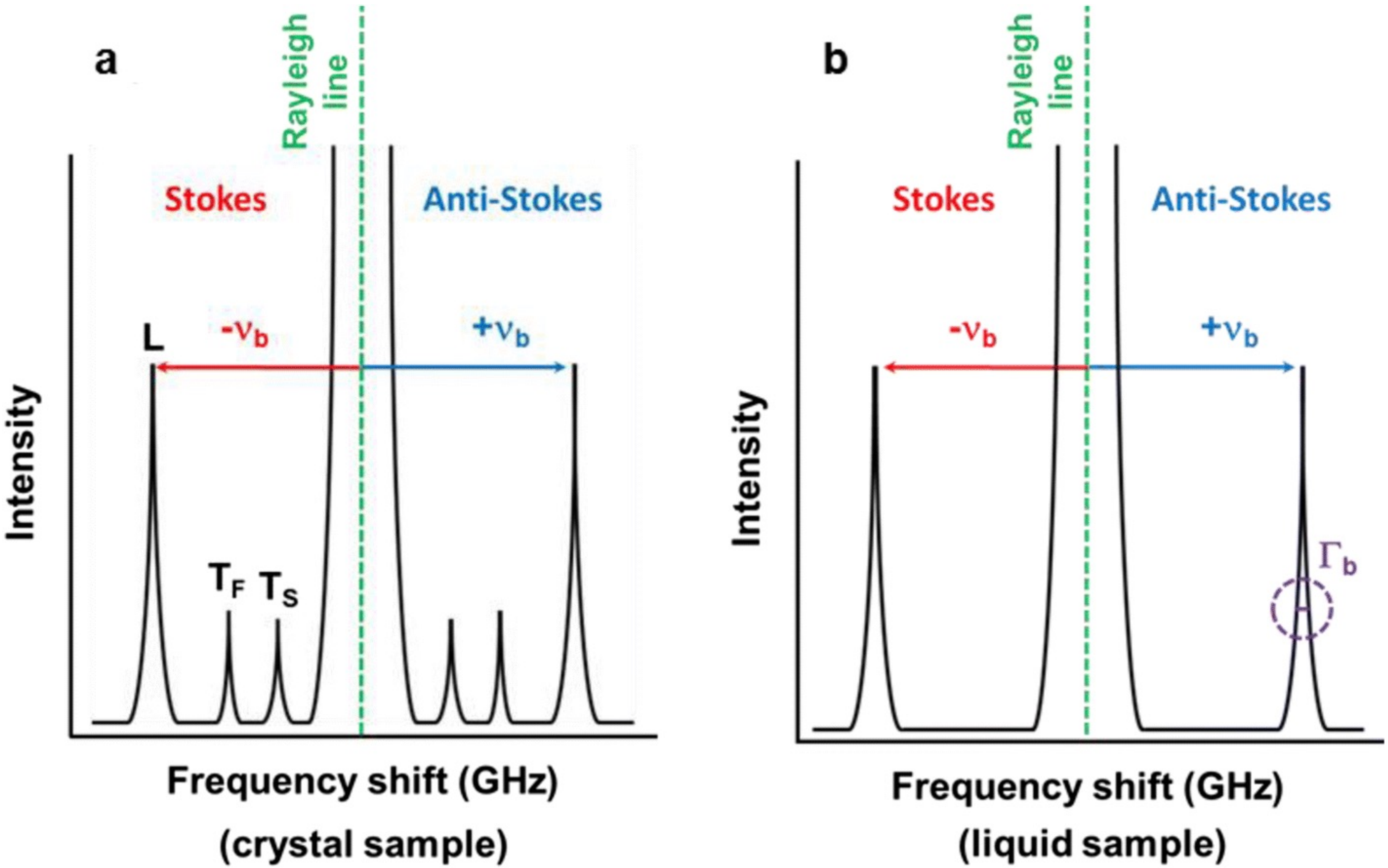
A. Taghizadeh et al., Nat. Commun., ***11****, 3011, (2020)*

Brillouin scattering



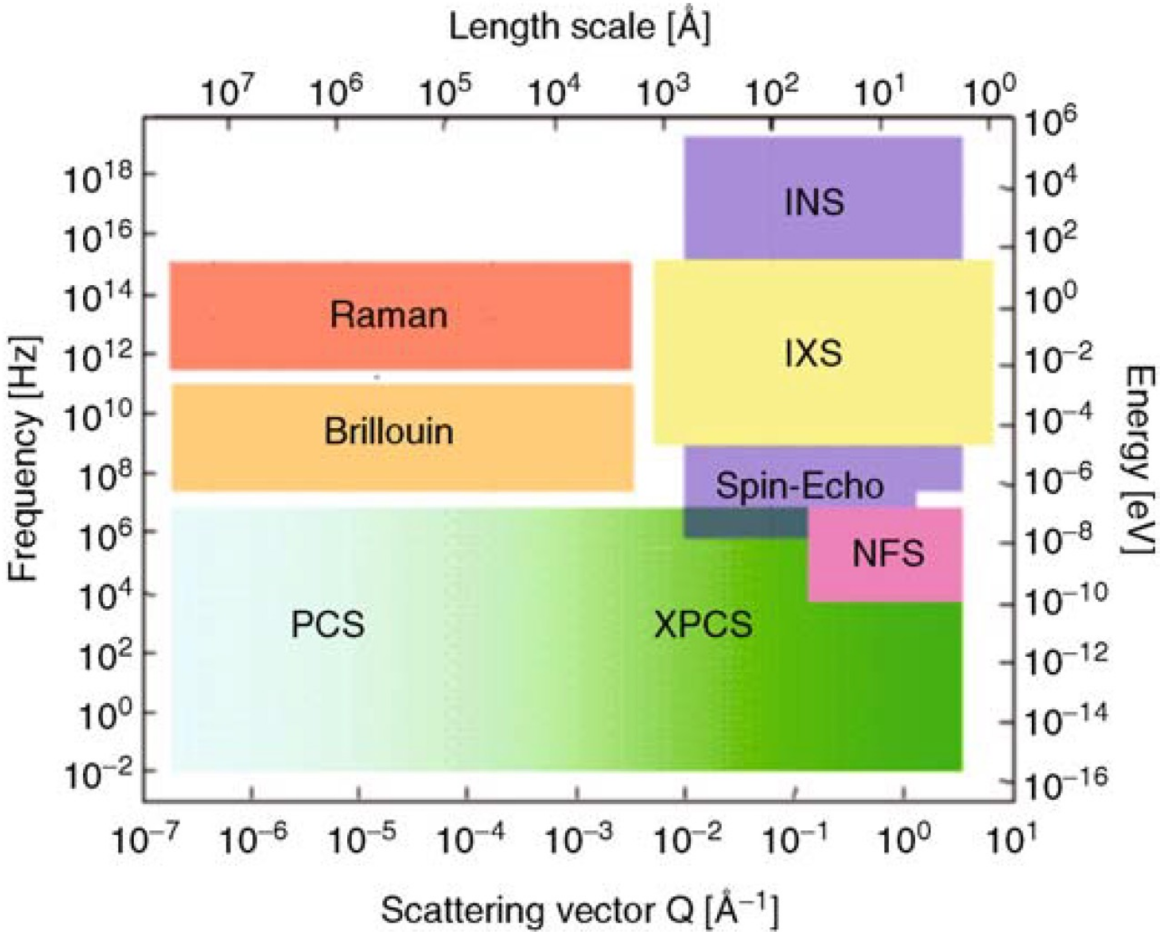
A. Singaraju et al., AAPS PharmSciTech., ***20****, 109, (2019)*

Brillouin scattering



*A. Singaraju et al., AAPS PharmSciTech., **20**, 109, (2019)*

Time-resolved techniques



Raman – inelastic scattering of optical light by molecules
Brillouin – inelastic scattering of optical light by phonons
PCS – photon correlation spectroscopy
XPCS – x-ray photon correlation spectroscopy

NFS – nuclear forward scattering
NSE – neutron spin-echo spectroscopy
IXS – inelastic x-ray scattering
INS – inelastic neutron scattering

What to remember

- Elastic scattering is sensitive to the time-averaged structure

$$G(\vec{r}) = \frac{1}{N}\left\langle \sum_{n,m=1}^{N} \delta\left(r - \left((\vec{r}_n - \vec{r}_m)\right)\right)\right\rangle$$

$$S(\vec{q}) = \int G(\vec{r}) e^{-i\vec{q}\vec{r}} d\vec{r}$$

- Inelastic scattering is sensitive to the dynamics

$$G(\vec{r}, t) = \frac{1}{N}\left\langle \sum_{n,m=1}^{N} \delta\left(r - \left((\vec{r}_n(t) - \vec{r}_m(0))\right)\right)\right\rangle$$

$$S_{coh}(\vec{q}, \omega) = \frac{1}{2\pi\hbar}\int G(\vec{r}, t) e^{-i\vec{q}\vec{r}} e^{i\omega t} d\vec{r}\, dt$$

- Inelastic neutron scattering is the best tool to measure phonon dispersion

- Raman scattering involves optical phonons

- Brillouin scattering involves acoustic phonons