量子ビームでさぐるソフトマターの物性

中性子非弾性散乱と準弾性散乱

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Inelastic Neutron Scattering

2.3　非弾性散乱

　散乱体となっている結晶は運動の自由度を持っているので、エネルギー保存則は中性子＋散乱体の全系で成り立っている。

$$E_f - E_i = \frac{\hbar^2}{2m}(k_f^2 - k_i^2) = \hbar\omega \qquad (2.11)$$

ここでE_i, E_fはそれぞれ結晶の始状態と終状態のエネルギー。$\hbar\omega$は中性子の散乱によるエネルギー損失である。エネルギーのやり取りがある場合の散乱断面積は運動量-エネルギー空間でのスペクトルとして表される。

$$\frac{d^2\sigma}{d\Omega d\omega} = \frac{m^2}{(2\pi\hbar^2)^2}\left|\left\langle \mathbf{k}_f, f\middle|V\middle|\mathbf{k}_i, i\right\rangle\right|^2 \delta(\hbar\omega - E_f + E_i) \qquad (2.12)$$

ここで$|\mathbf{k}_i, i\rangle$と$|\mathbf{k}_f, f\rangle$はそれぞれ全系の始状態と終状態を意味する。ここで

$$\delta(t) = \frac{1}{2\pi}\int_{-\infty}^{\infty} e^{i\omega t}\, d\omega \qquad (2.13)$$

等を用いると、

$$\frac{d^2\sigma}{d\Omega d\omega} = \int \sum_{ij} \overline{b_i b_j \left\langle i\middle|e^{-K\cdot r_i}\middle|f\right\rangle\left\langle f\middle|e^{K\cdot r_j}\middle|i\right\rangle} e^{i(\frac{E_f}{\hbar}-\frac{E_i}{\hbar})t} e^{i\omega t} dt \qquad (2.14)$$

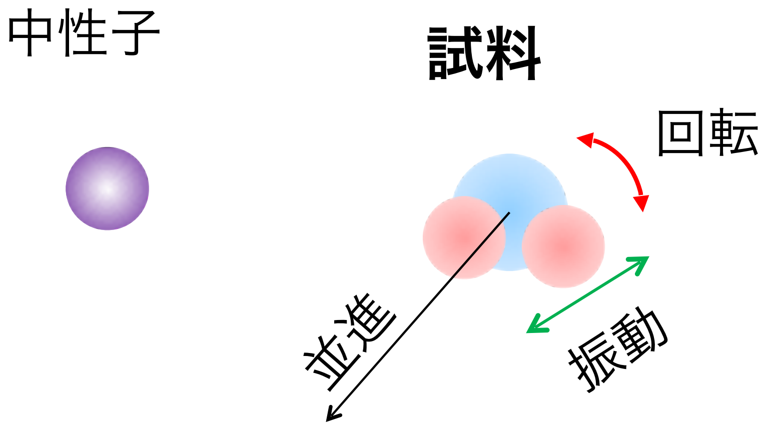
（バーは結晶の始状態に対する熱平均）となる。ここで中性子が感じる粒子密度関数

$$\rho_N(\mathbf{r},t) = \sum_i b_i \delta(\mathbf{r} - \mathbf{r}_i(t)) \qquad (2.15)$$

を定義すると、散乱断面積は

$$\frac{d^2\sigma}{d\Omega d\omega} = \int \langle \rho_N(\mathbf{r},0)\rho_N(\mathbf{r}',t) \rangle e^{i\mathbf{k}\cdot(\mathbf{r}-\mathbf{r}')-i\omega t} d\mathbf{r}d\mathbf{r}'dt \qquad (2.16)$$

すなわち中性子の散乱断面積は、散乱体の粒子密度分布の場所と時間に関する二体相関関数のFourier変換と考えることができる。



弾性散乱 ($E_i = E_f$):

中性子のエネルギー変化を見ない場合

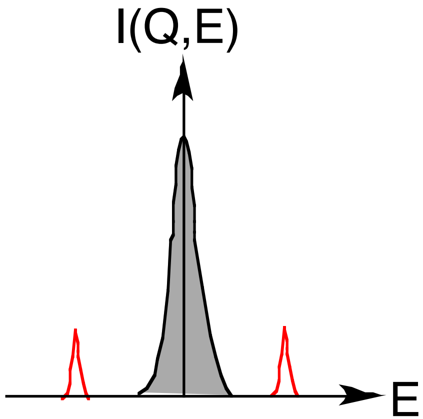
非弾性散乱 ($E_i \neq E_f$):

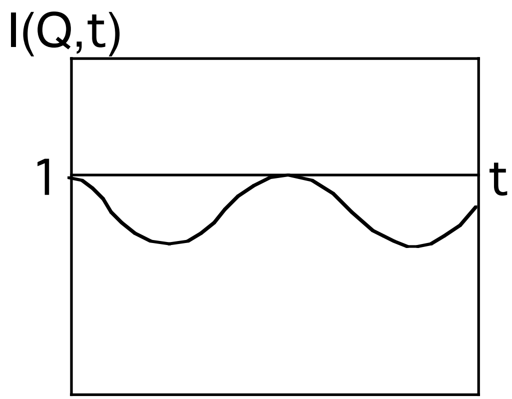
中性子のエネルギー変化を見る場合

非弾性散乱と準弾性散乱

非弾性散乱

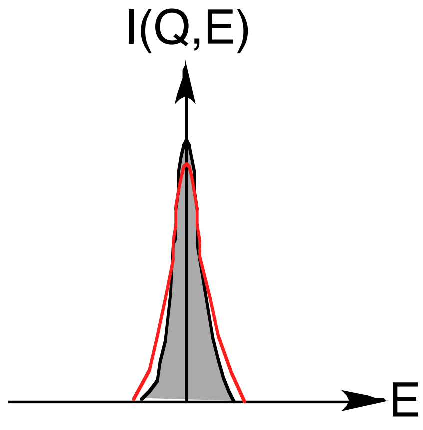
励起

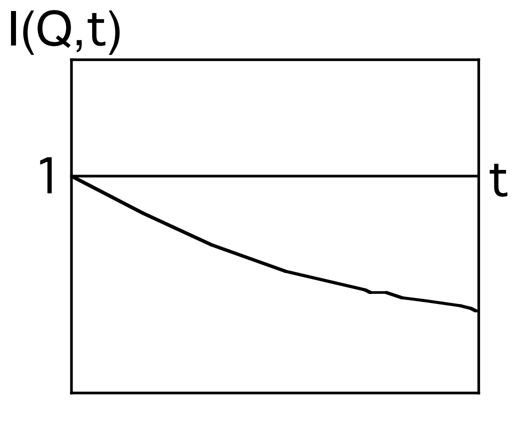




準弾性散乱

緩和





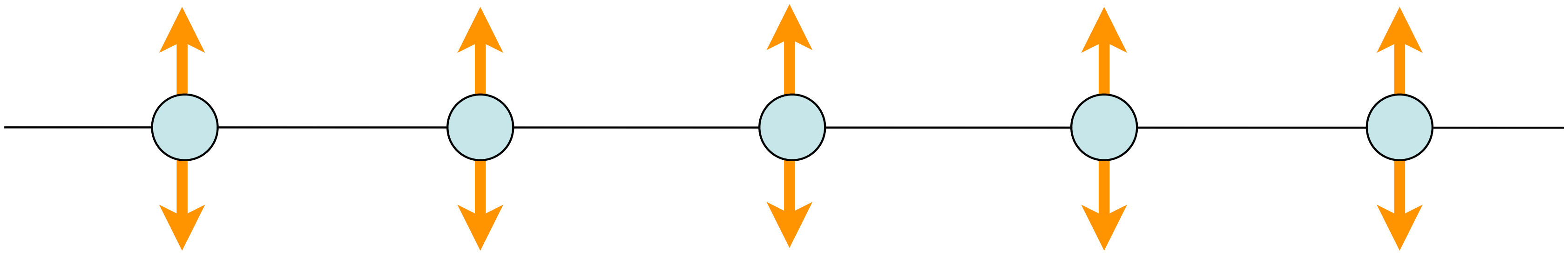
中性子非弾性散乱→素励起

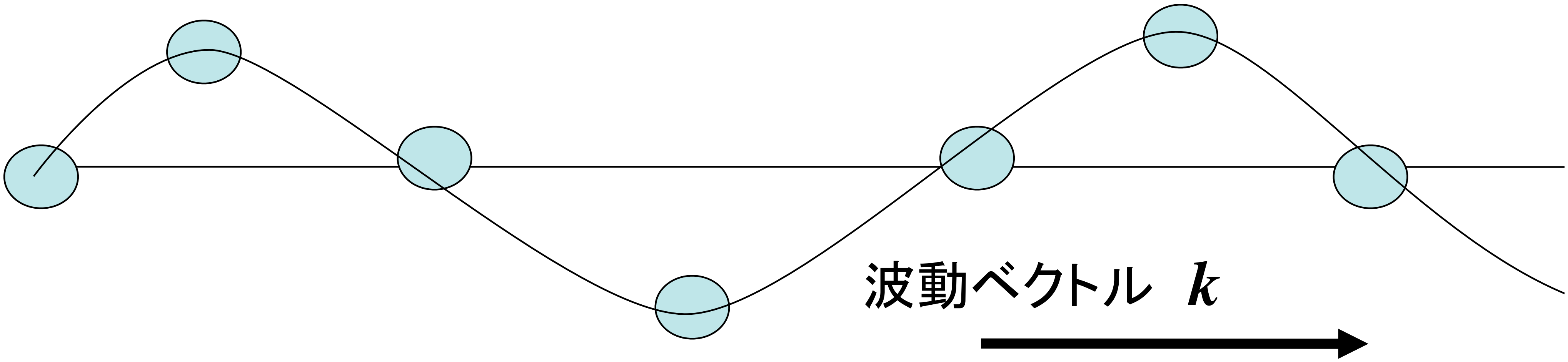
– 熱中性子の波長とエネルギーは、物質中の原子間距離や、格子振動やスピン波等の素励起の振動数とほぼ一致する。
– 物質中の素励起は、波長と振動数に特徴的な関係（分散関係）が存在する。よって中性子の非弾性散乱実験で散乱ベクトルとエネルギー遷移を素励起の波数ベクトルと振動数に等しくなるように選べば、強い散乱が得られる。

フォノン：結晶を構成する原子の弾性振動が、原子間の相互作用を通して波として固体中を伝播する集団励起。

フォノン

連成振動　　　　　　　　　　　　質量M　間隔a　力定数c

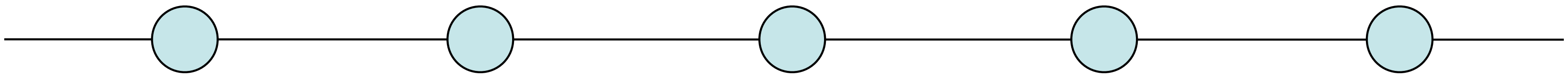




フォノン

連成振動

質量M　間隔a 力定数c



原子の変位に対してフックの法則が成り立つとすると、

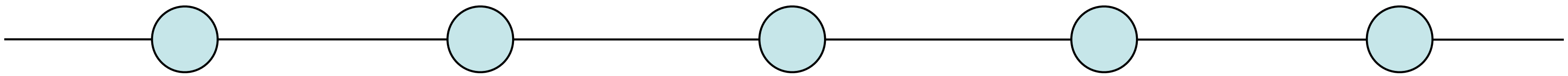
連成振動の振動数ωと波動ベクトルkの間の関係を導くことができる。

$$w = 2\sqrt{\frac{c}{M}}\left|sin(\frac{ka}{2})\right|$$

フォノン

連成振動

質量M　間隔a 力定数c



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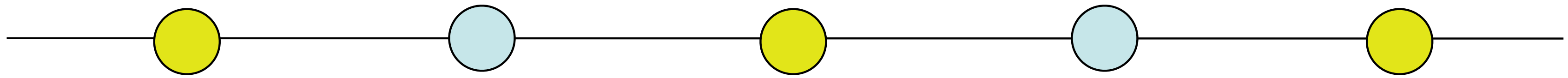
$$w = 2\sqrt{\frac{c}{M}}\left|\sin\left(\frac{ka}{2}\right)\right|$$

kがゼロの近傍（長波長の波）では

$$\omega = a(c/M)^{1/2}k = v_g k$$

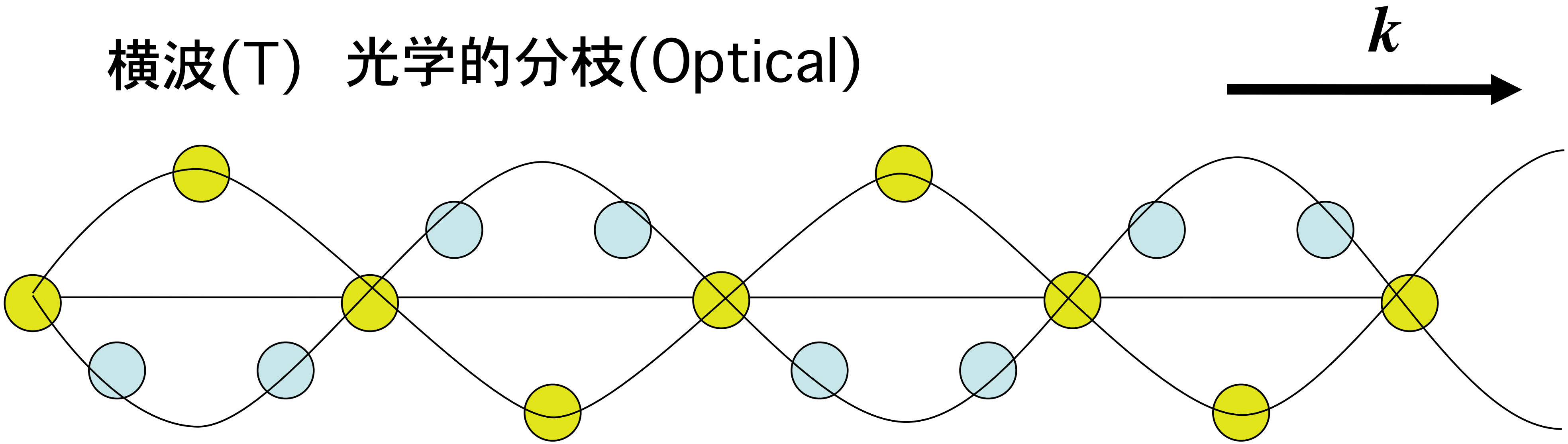
v_g: 音速（群速度）

質量が違う2つの原子が交互に並んだ場合

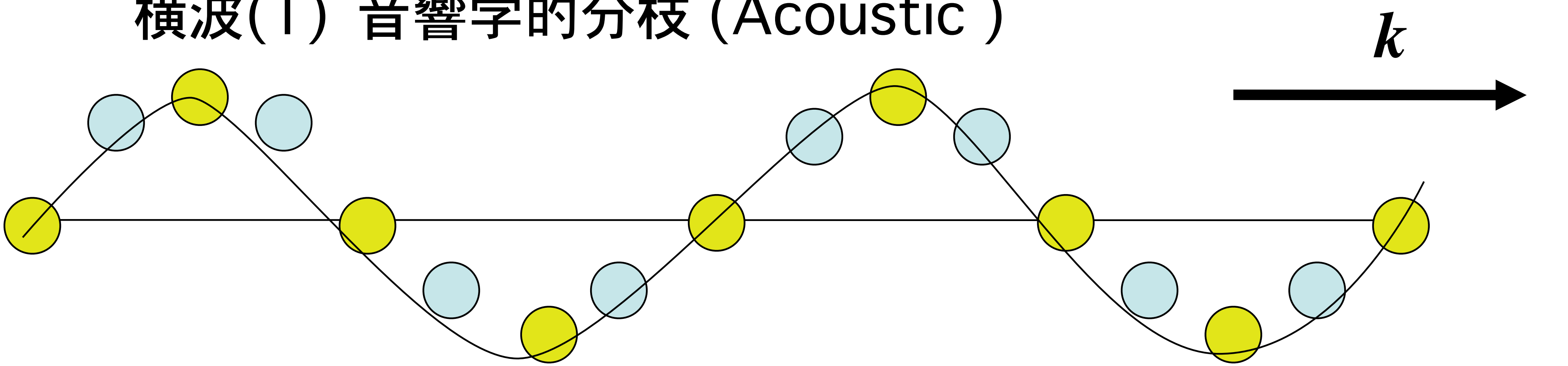


質量M1、M2　間隔a 力定数c

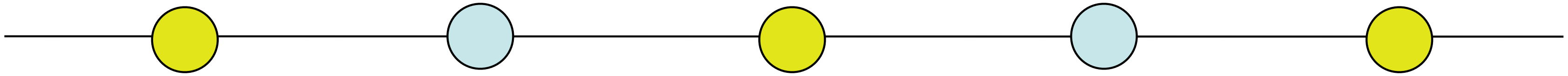
横波(T) 光学的分枝(Optical)



横波(T) 音響学的分枝 (Acoustic)



質量が違う2つの原子が交互に並んだ場合



質量M1、M2　間隔a 力定数c

kが小さい長波長の波に対して

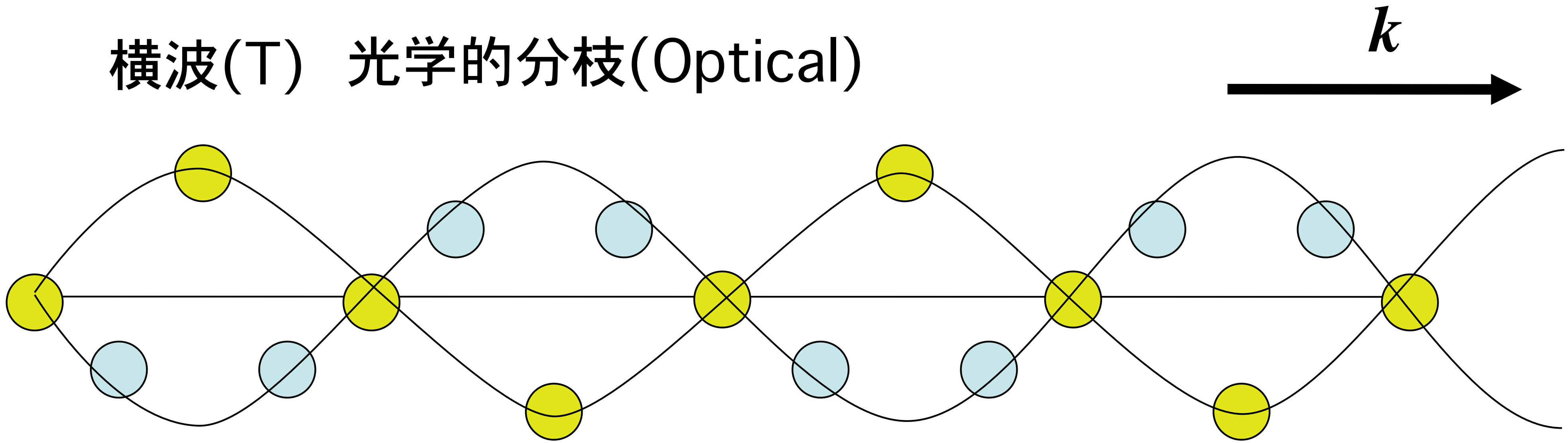
$$w^2 = \frac{2c}{M_1 + M_2} k^2 a^2$$

音響学的分枝
Acoustic branch

$$w^2 = 2c\left(\frac{1}{M_1} + \frac{1}{M_2}\right)$$

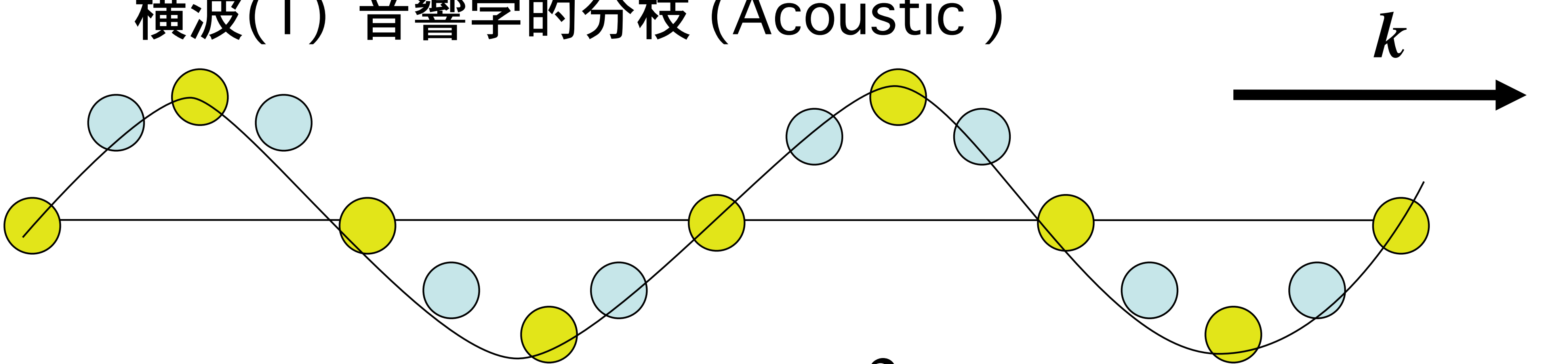
光学的分枝
Optical branch

横波(T) 光学的分枝(Optical)



$$w^2 = 2c\left(\frac{1}{M_1} + \frac{1}{M_2}\right)$$

横波(T) 音響学的分枝 (Acoustic)



$$w^2 = \frac{2c}{M_1 + M_2} k^2 a^2$$

フォノンの観測

結晶中のk番目の原子にl番目の原子の変位が引き起こす力が、変位の差u_l-u_kに比例するとしてk番目の原子に及ぼす全体の力を考えると、質量M_kのk番目の原子の運動方程式は次式で与えられる。

$$M_k \frac{d^2 u_k}{dt^2} = \sum_l C_{lk}(u_l - u_k) \qquad (1)$$

これは力が変位に比例する、すなわちフックの法則を表す。ここでC_{lk}はk番目とl番目の原子間のバネ定数である。簡単のため同一原子(M_k=M)からなる1次元結晶を考え、最近接の原子間にのみ相互作用があるとしてC_{lk}=Cとするとこの式は次のように書ける。

$$M_k \frac{d^2 u_k}{dt^2} = C(u_{k+1} - 2u_k + u_{k-1}) \qquad (2)$$

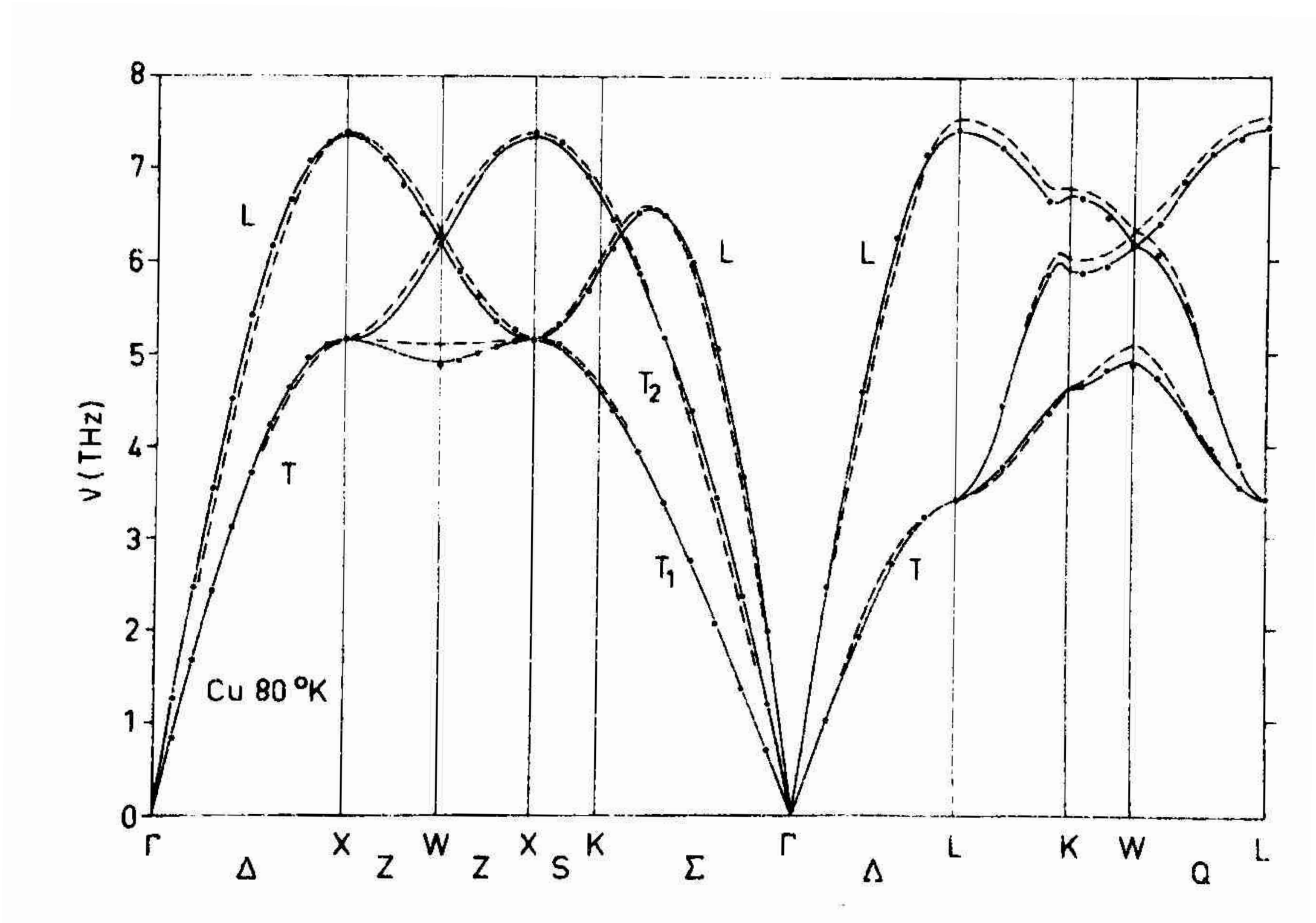
格子定数をaとすると、進行波解は次のように書ける。

$$u_k = u \exp[i(kaq - \omega t)] \quad (3)$$

これを(2)式に代入すると以下の分散関係（振動数ωと波数qの関係）が得られる。

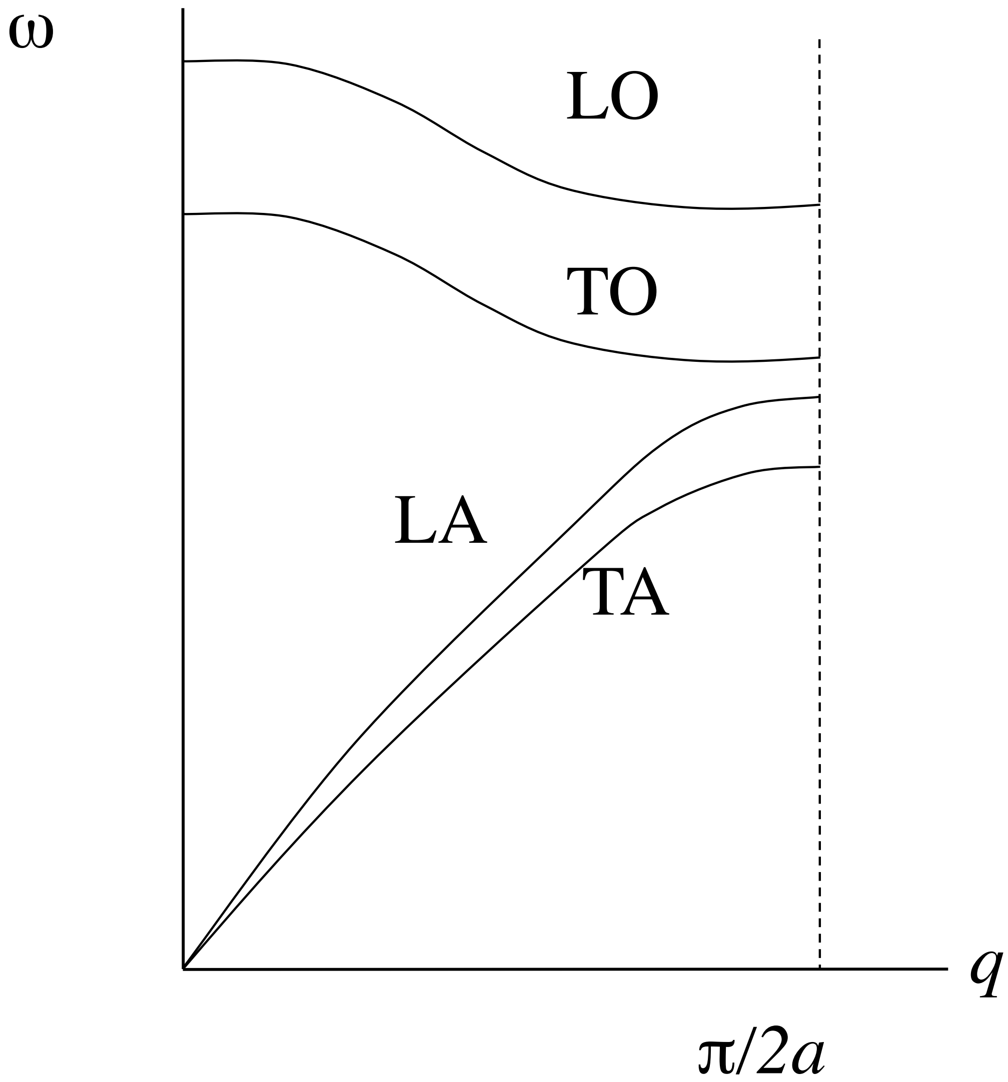
$$\omega = \sqrt{\frac{2C}{M}} \left| \sin \frac{aq}{2} \right| \quad (4)$$

実際の結晶では原子は3次元的に配列しているので、格子振動は各方向に伝播する。単位胞に1つの原子がある場合には、ある方向に伝播する格子振動には縦波1(L)、横波2(T)の3つのモードがある。



銅の80KにおけるX格子振動の分散関係。Γ点からX点までは(4)の依存性を示す。ただし測定点と(4)式はわずかにずれているので、第8近接までの相互作用を取り入れて計算している。

3次元結晶 ⇨ 縦波(L)と横波(T)がある



音響学的分枝 (Acoustic)

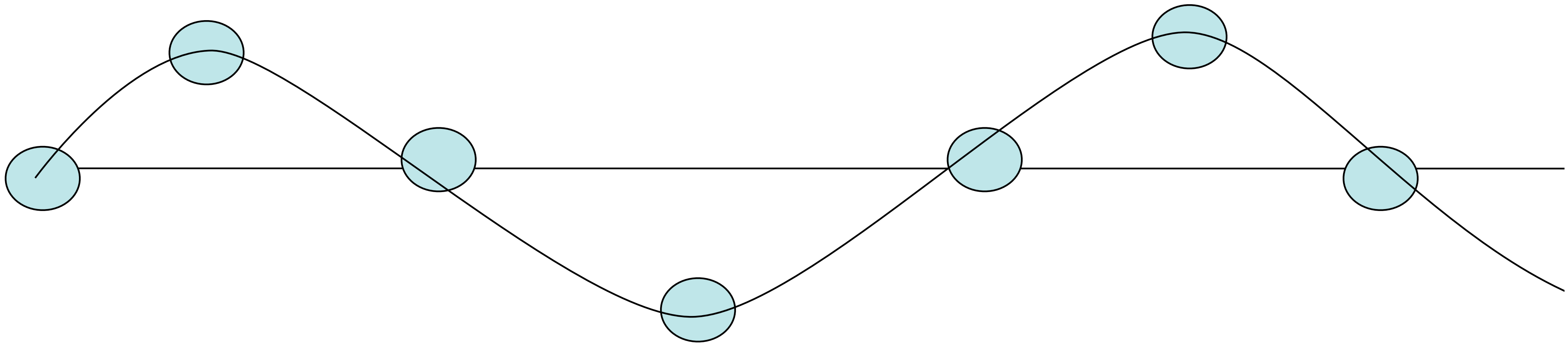
$$w^2 = \frac{2c}{M_1 + M_2} k^2 a^2$$

光学的分枝(Optical)

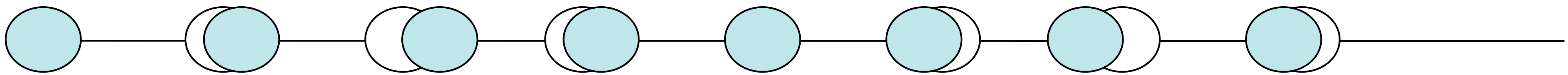
$$w^2 = 2c\left(\frac{1}{M_1} + \frac{1}{M_2}\right)$$

フォノンの分散関係の概念図

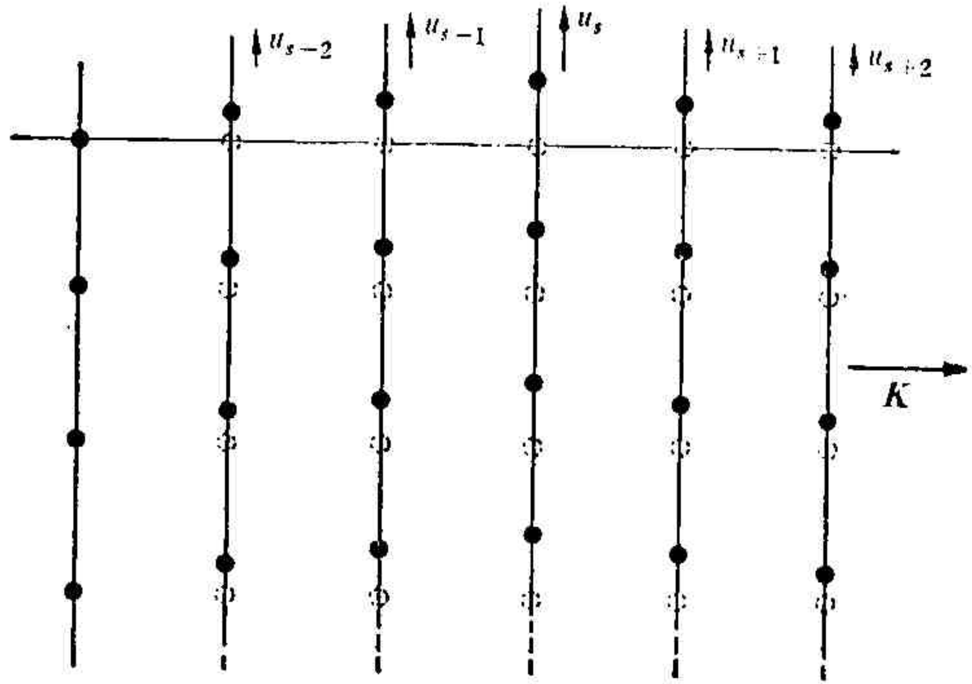
横波(T)



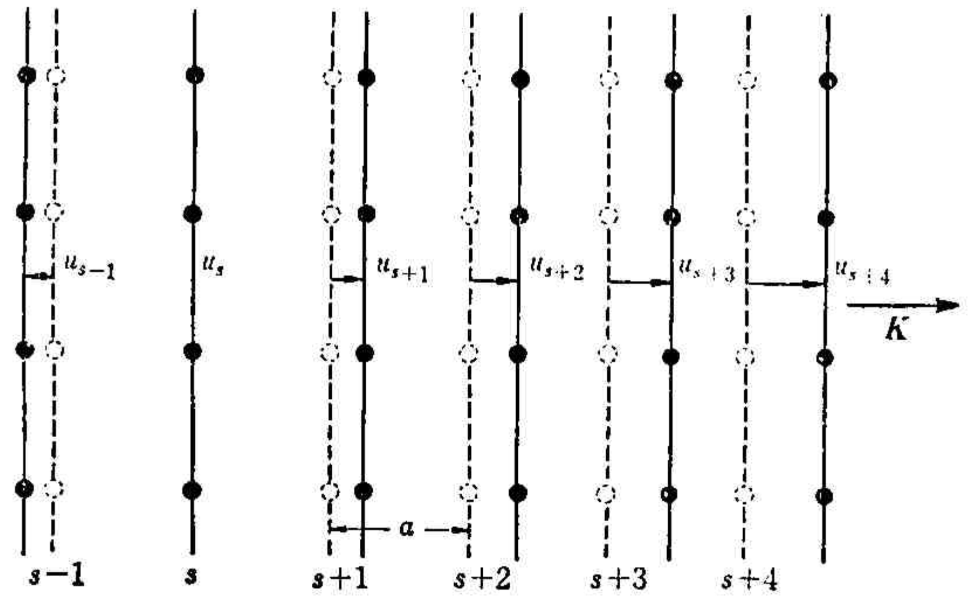
縦波(L)



横波(T)



縦波(L)



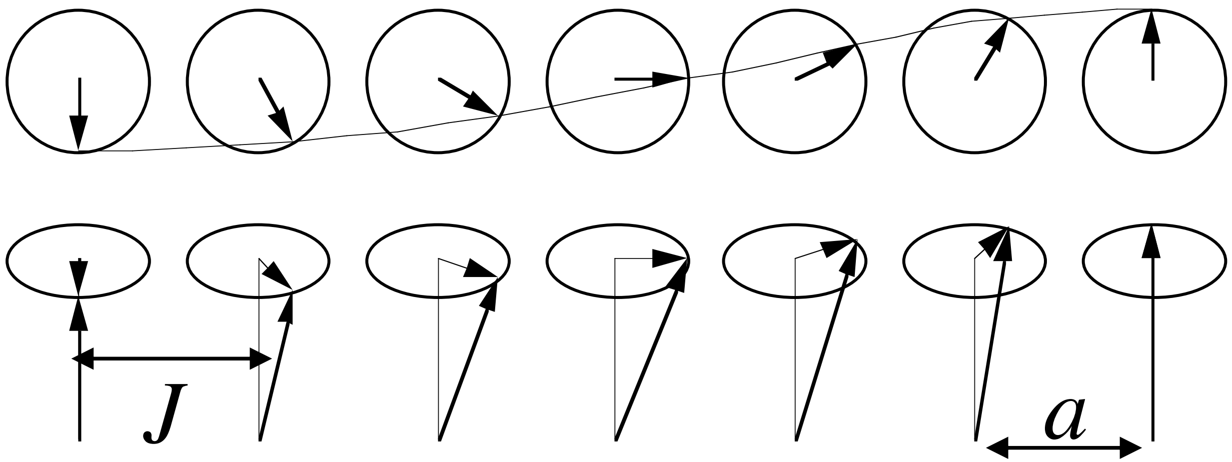
スピン波の観測

磁性を記述するための一つの方法は、ハイゼンベルクのハミルトニアンである。結晶格子のi番目の磁性原子のスピンを$\boldsymbol{S}_i$、j番目の磁性原子のスピンを$\boldsymbol{S}_j$とするとき、$\boldsymbol{S}_i$と$\boldsymbol{S}_j$との間に$-2J_{ij}\boldsymbol{S}_i\boldsymbol{S}_j$の「交換相互作用」を仮定すると、結晶全体のハミルトニアンは

$$H = -\sum_{<i,j>} 2J_{ij}\mathbf{S_i}\mathbf{S_j} \qquad (5)$$

和$<i,j>$は結晶内の異なる全てのi,jの組に対して取る。$J_{ij}>0$ならば隣接スピンは平行の時に安定なので、系全体は強磁性に秩序化する。逆に$J_{ij}<0$ならば反強磁性状態が安定である。

秩序化した状態ではスピンの揺らぎは交換相互作用を通して波として結晶中を伝播する。これをスピン波（マグノン）と呼ぶ。



簡単のため、同一の磁性原子（スピン量子数S）からなる一次元結晶を考え、最近接の原子間にのみ強磁性の交換相互作用J>0があるとすると、ハミルトニアンは

$$H = -2J\sum_{k} \mathbf{S_k}\mathbf{S_{k+1}} \quad (6)$$

磁気モーメント$\boldsymbol{\mu}$と磁場$\boldsymbol{H}$の相互作用は$-\boldsymbol{\mu}\boldsymbol{H}$なので、式(6)はスピン$\boldsymbol{S}_k$の作る磁気モーメント$\boldsymbol{\mu}_k=g\mu_\mathrm{B}\boldsymbol{S}_k$に最近接スピンの作る磁場$\boldsymbol{H}_k=(2J/g\mu_\mathrm{B})(\boldsymbol{S}_{k-1}$—$\boldsymbol{S}_{k+1})$が作用している、と解釈できる。

磁気モーメントが磁場から受けるトルクは$\boldsymbol{\mu}\times\boldsymbol{H}$で、トルクは角運動量の時間微分に等しい。また$\boldsymbol{S}_k$に対するスピン角運動量は$\hbar\boldsymbol{S}_k$なので運動方程式は次のように書ける。

$$\hbar\frac{d\mathbf{S_k}}{dt} = g\mu_B\mathbf{S_k}\times\frac{2J}{g\mu_B}(\mathbf{S_{k-1}}+\mathbf{S_{k+1}}) \tag{7}$$

励起の振幅が小さければ、$S_k^z=S$とおいて、

$$\begin{aligned}\frac{dS_k^x}{dt} &= \frac{2SJ}{\hbar}(2S_k^y - S_{k-1}^y - S_{k+1}^y)\\ \frac{dS_k^y}{dt} &= \frac{2SJ}{\hbar}(2S_k^x - S_{k-1}^x - S_{k+1}^x)\end{aligned} \tag{8}$$

と近似できる。また、$dS_k^z/dt=0$である。

格子定数をaとして、波数q、振動数の進行波の形を持つ解を

$$\begin{aligned} S_k^x &= u \exp[i(kaq - \omega t)] \\ S_k^y &= v \exp[i(kaq - \omega t)] \end{aligned} \tag{9}$$

とおいて式(8)に代入し、uとvがともに0でない解を持つことから次の分散関係が得られる。

$$\hbar\omega = 4JS(1 - \cos aq) \tag{10}$$

反強磁性(J<0)の場合には2k番目のスピンは上向きの部分格子、2k+1番目のスピン波下向きの部分格子を作っていると考えて同様に計算すると、次の分散関係が得られる。

$$\hbar\omega = 4S|J||\sin aq| \tag{11}$$

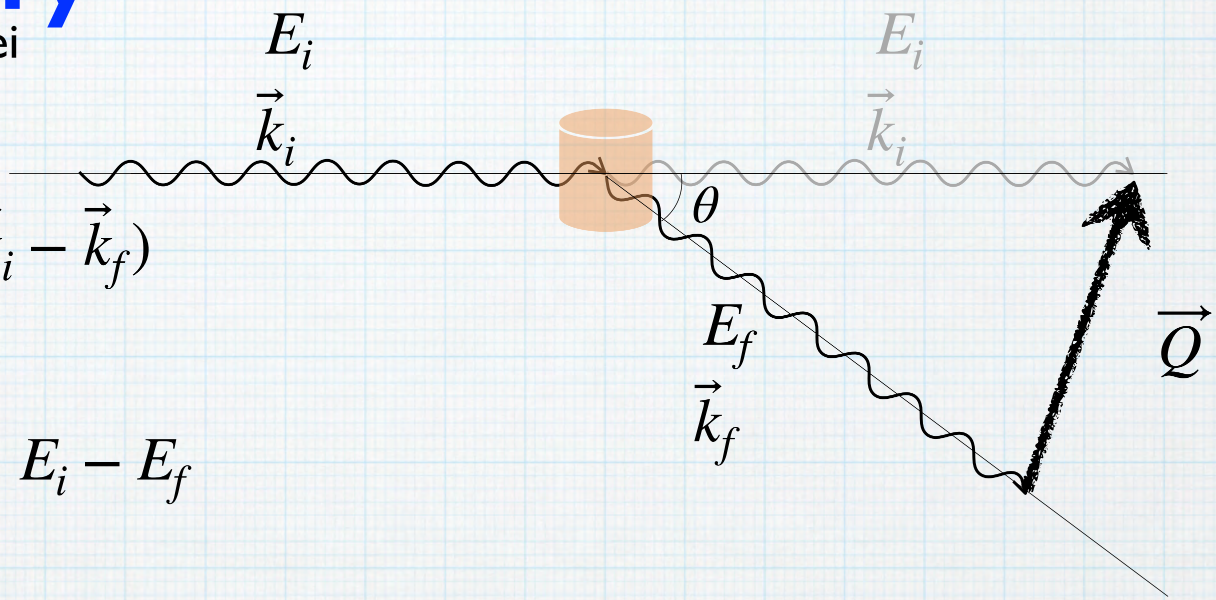
すなわち強磁性では$\hbar\omega \propto q^2$なのに対して反強磁性では$\hbar\omega \propto q$となる。

Quasi-Elastic Neutron Scattering

Scattering geometry

✓ Interaction of neutron with nuclei

- Exchange momentum
  - $\hbar\overrightarrow{Q} = \hbar(\vec{k}_i - \vec{k}_f)$
- Exchange energy
  - $\hbar\omega = E = E_i - E_f$

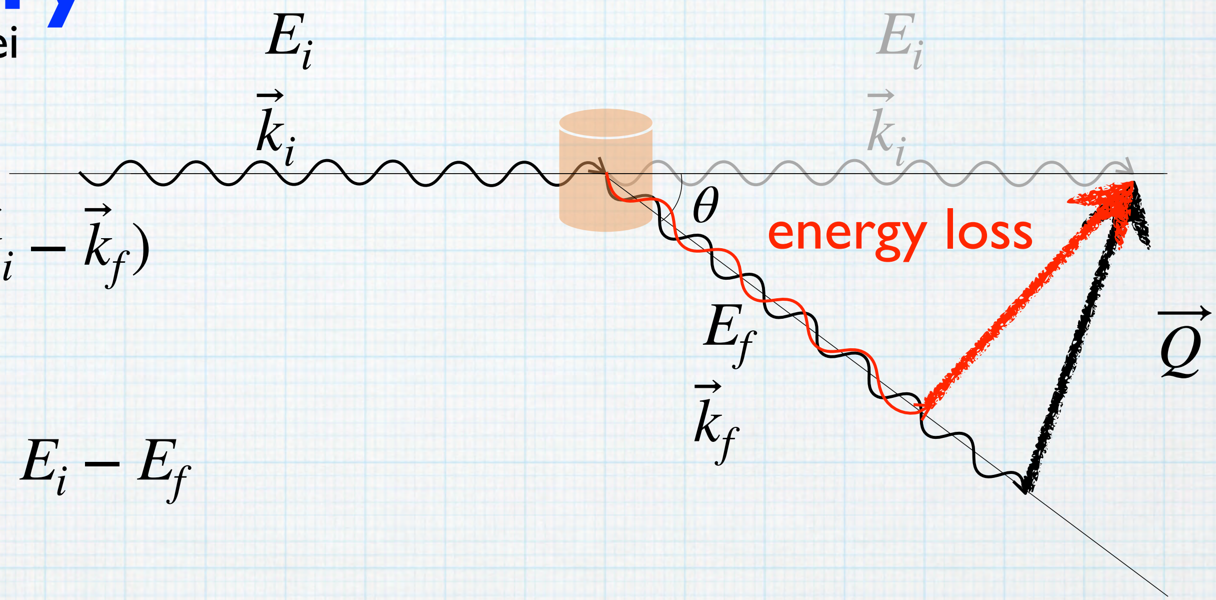


✓ Elastic scattering

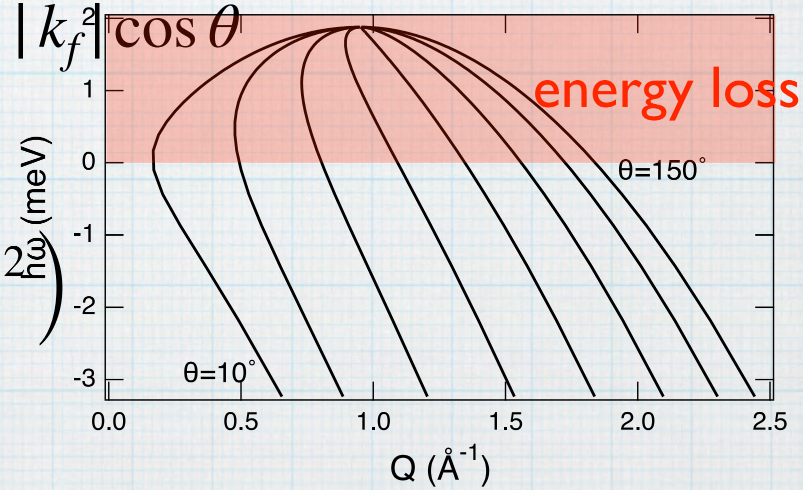
- Exchange momentum
  - $|\vec{k}_i| = |\vec{k}_f| = \dfrac{2\pi}{\lambda}, Q = \dfrac{4\pi}{\lambda}\sin\left(\dfrac{\theta}{2}\right)$
- No exchange energy
  - $\hbar\omega = E = E_i - E_f = 0$

Scattering geometry

- ✓ Interaction of neutron with nuclei
  - Exchange momentum
    - $\hbar\vec{Q} = \hbar(\vec{k}_i - \vec{k}_f)$
  - Exchange energy
    - $\hbar\omega = E = E_i - E_f$
- ✓ Inelastic scattering
  - Exchange momentum
    - $|\vec{Q}|^2 = |\vec{k}_i|^2 + |\vec{k}_f|^2 - 2|\vec{k}_i||\vec{k}_f|\cos\theta$
  - Exchange energy
    - $\hbar\omega = E = \frac{\hbar^2}{2m_n}\left(|\vec{k}_i|^2 - |\vec{k}_f|^2\right)$



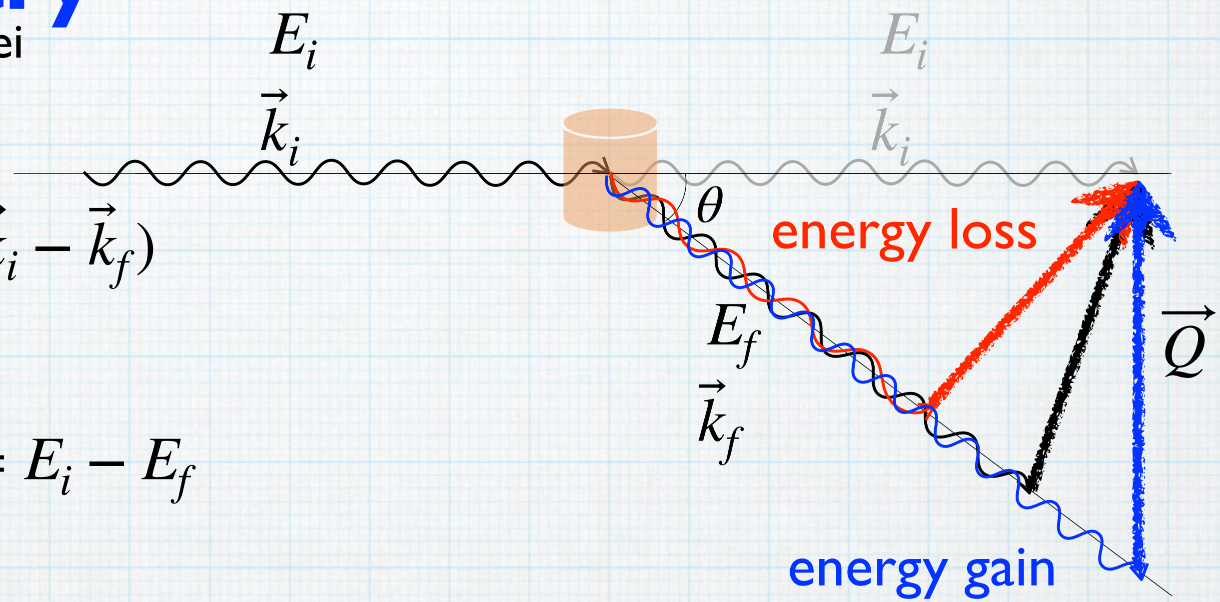
Kinematically allowed region



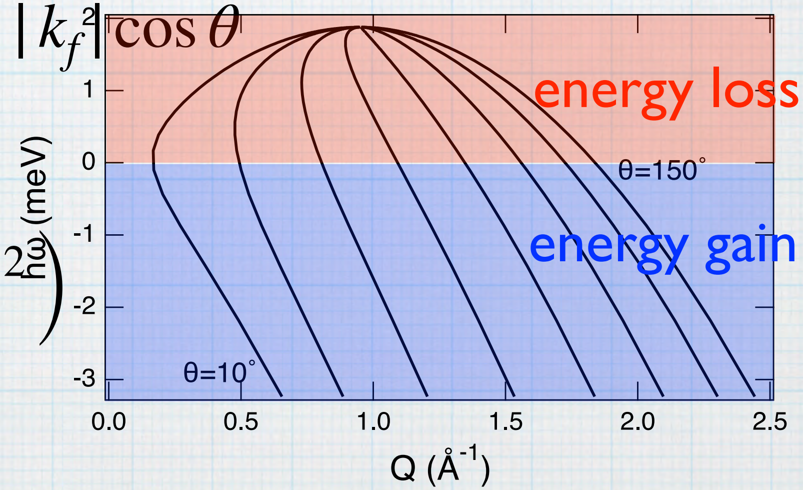
direct geometry case

Scattering geometry

- ✓ Interaction of neutron with nuclei
  - Exchange momentum
    - $\hbar\overrightarrow{Q} = \hbar(\vec{k}_i - \vec{k}_f)$
  - Exchange energy
    - $\hbar\omega = E = E_i - E_f$
- ✓ Inelastic scattering
  - Exchange momentum
    - $|\overrightarrow{Q}|^2 = |\vec{k}_i|^2 + |\vec{k}_f|^2 - 2|\vec{k}_i||\vec{k}_f|\cos\theta$
  - Exchange energy
    - $\hbar\omega = E = \dfrac{\hbar^2}{2m_n}\left(|\vec{k}_i|^2 - |\vec{k}_f|^2\right)$



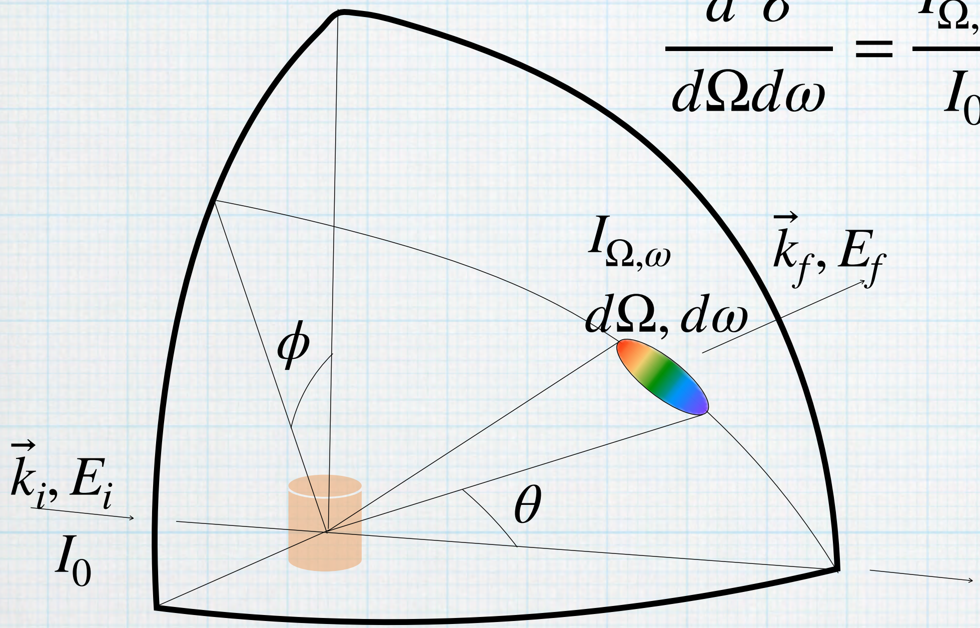
Kinematically allowed region



direct geometry case

Scattering cross section

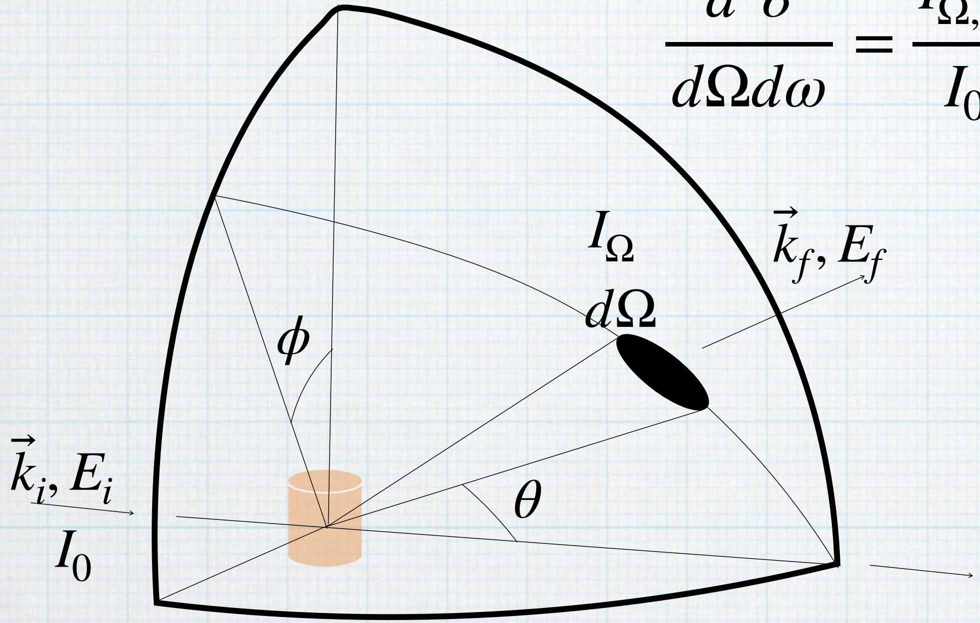
$$\frac{d^2\sigma}{d\Omega d\omega} = \frac{I_{\Omega,\omega}}{I_0}$$



- ✓ double differential scattering cross section, $\dfrac{d^2\sigma}{d\Omega d\omega}$ Dynamic scattering
- ✓ Neutron scattering probability in the solid angle between $\Omega(\theta, \phi)$ and $\Omega + d\Omega$, having exchanged energy between $\hbar\omega$ and $\hbar\omega + \hbar d\omega$

Scattering cross section

$$\frac{d^2\sigma}{d\Omega d\omega} = \frac{I_{\Omega,\omega}}{I_0}$$



✓ double differential scattering cross section, $\dfrac{d^2\sigma}{d\Omega d\omega}$

Dynamic scattering

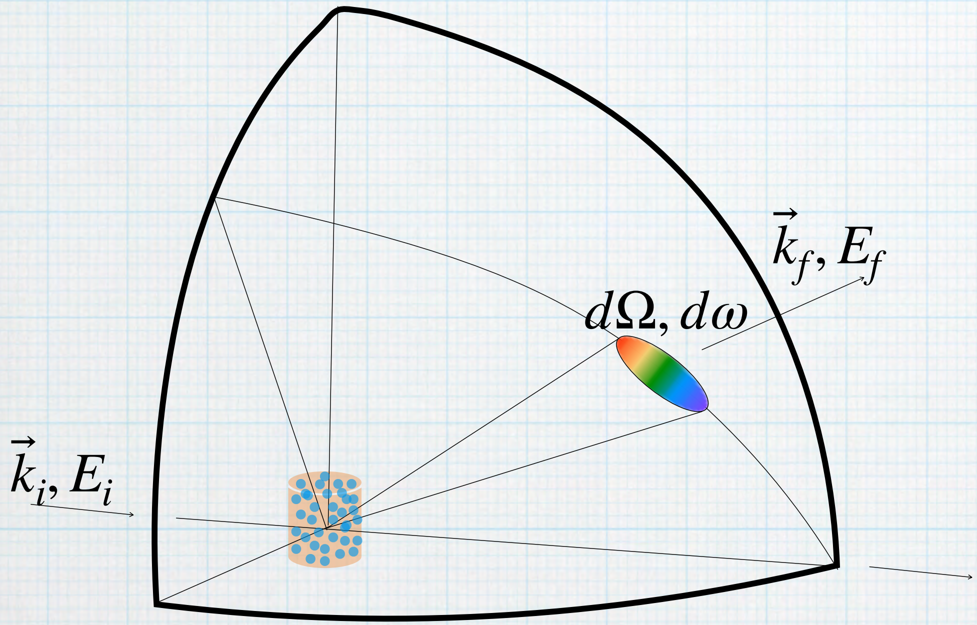
✓ Neutron scattering probability in the solid angle between $\Omega(\theta, \phi)$ and $\Omega + d\Omega$, having exchanged energy between $\hbar\omega$ and $\hbar\omega + \hbar d\omega$

✓ differential scattering cross section, $\dfrac{d\sigma}{d\Omega}$

Static scattering

$$\frac{d\sigma}{d\Omega} = \int_{-\infty}^{\infty} \frac{d^2\sigma}{d\Omega d\omega} d\omega = \frac{I_\Omega}{I_0}$$

Scattering intensity and structure and dynamics of the sample



- ✓ Neutrons interact with the nuclei in the sample. The interaction potential is Fermi's pseudo potential (for nuclear scattering).

$$V(\vec{r}) = \frac{2\pi\hbar^2}{m_n} b_j \delta(\vec{r} - \vec{r}_j)$$

b_j: scattering length

- ✓ Scattered neutrons are the results of the interaction with the nuclei. A little quantum mechanical trick (Fermi Golden Rule) provides

$$\frac{d^2\sigma}{d\Omega d\omega} = \frac{k_f}{k_i}\frac{1}{2\pi\hbar}\sum_{j,k} b_j b_k \int_{-\infty}^{\infty} \left\langle \exp\left[-i\vec{Q}\cdot\left\{\vec{r}_k(0) - \vec{r}_j(t)\right\}\right] \exp[-i\omega t]dt \right\rangle$$

Key points on dynamic neutron scattering

$$\frac{d^2\sigma}{d\Omega d\omega} = \frac{k_f}{k_i}\frac{1}{2\pi\hbar}\sum_{j,k} b_j b_k \int_{-\infty}^{\infty} \left\langle \exp\left[-i\vec{Q}\cdot\boxed{\left\{\vec{r}_k(0)-\vec{r}_j(t)\right\}}\right] \exp[-i\omega t]dt \right\rangle$$

✓ Information on the spatial and time correlation between a couple of atoms

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✓ Information on the spatial and time correlation between a couple of atoms

✓ Geometrical information on the motion is embedded in the data

- The dynamics is probed over a length scale determined by $\overrightarrow{Q}$

Key points on dynamic neutron scattering

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- ✓ Information on the spatial and time correlation between a couple of atoms
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    - The dynamics is probed over a length scale determined by $\vec{Q}$
- ✓ Strength of the scattering is determined by the nature of the nuclei

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✓ Information on the spatial and time correlation between a couple of atoms

✓ Geometrical information on the motion is embedded in the data

- The dynamics is probed over a length scale determined by $\vec{Q}$

✓ Strength of the scattering is determined by the nature of the nuclei

✓ A Fourier transformation relates the correlation to the energy spectra

Key points on dynamic neutron scattering

$$\frac{d^2\sigma}{d\Omega d\omega} = \frac{k_f}{k_i}\frac{1}{2\pi\hbar}\sum_{j,k} b_j b_k \int_{-\infty}^{\infty}\left\langle \exp\left[-i\vec{Q}\cdot\left\{\vec{r}_k(0)-\vec{r}_j(t)\right\}\right]\exp[-i\omega t]dt\right\rangle$$

$$= \boxed{\frac{k_f}{k_i}\frac{N}{2\pi\hbar}}\frac{1}{N}\sum_{j,k} b_j b_k \int_{-\infty}^{\infty}\left\langle \exp\left[-i\vec{Q}\cdot\left\{\vec{r}_k(0)-\vec{r}_j(t)\right\}\right]\exp[-i\omega t]dt\right\rangle$$

Pre-factor relating the experiment conditions

Key points on dynamic neutron scattering

$$\frac{d^2\sigma}{d\Omega d\omega} = \frac{k_f}{k_i}\frac{1}{2\pi\hbar}\sum_{j,k} b_j b_k \int_{-\infty}^{\infty} \left\langle \exp\left[-i\vec{Q}\cdot\left\{\vec{r}_k(0)-\vec{r}_j(t)\right\}\right] \exp[-i\omega t]dt \right\rangle$$

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Pre-factor relating the experiment conditions

Dynamic structure factor, $S(\vec{Q},\omega)$

$$\boxed{S(\vec{Q},\omega) = \frac{1}{N}\sum_{j,k} b_j b_k \int_{-\infty}^{\infty} \left\langle \exp\left[-i\vec{Q}\cdot\left\{\vec{r}_k(0)-\vec{r}_j(t)\right\}\right] \exp[-i\omega t]dt \right\rangle}$$

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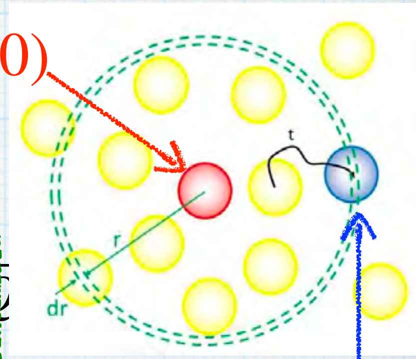
FT in time

$S(Q,\omega)$ and $S(Q,t)$ provide the same information on the spatial and time correlation between a couple of atoms

$$\boxed{S(\vec{Q},t) = \frac{1}{N}\sum_{j,k} b_j b_k \left\langle \exp\left[-i\vec{Q}\cdot\left\{\vec{r}_k(0)-\vec{r}_j(t)\right\}\right] \right\rangle}$$

Intermediate scattering function, $S(\vec{Q},t)$

Correlation functions



✓ FT of $S(\vec{Q},t)$ in space → van Hove space-time correlation function

$$G(\vec{r},t) = \frac{1}{N}\sum_{j,k} b_j b_k \left\langle \delta(\vec{r} - \vec{r}_k(0) + \vec{r}_j(t)) \right\rangle = \int_{-\infty}^{\infty} S(\vec{Q},t)\exp\left[-i\vec{Q}\cdot\vec{r}\right] d\vec{Q}$$

Probability of finding a particle at $\vec{r}_j$ at time t given the same or another particle was at $\vec{r}_k$ at time 0

FT in space

$$S(\vec{Q},t) = \frac{1}{N}\sum_{j,k} b_j b_k \left\langle \exp\left[-i\vec{Q}\cdot\left\{\vec{r}_k(0) - \vec{r}_j(t)\right\}\right]\right\rangle$$

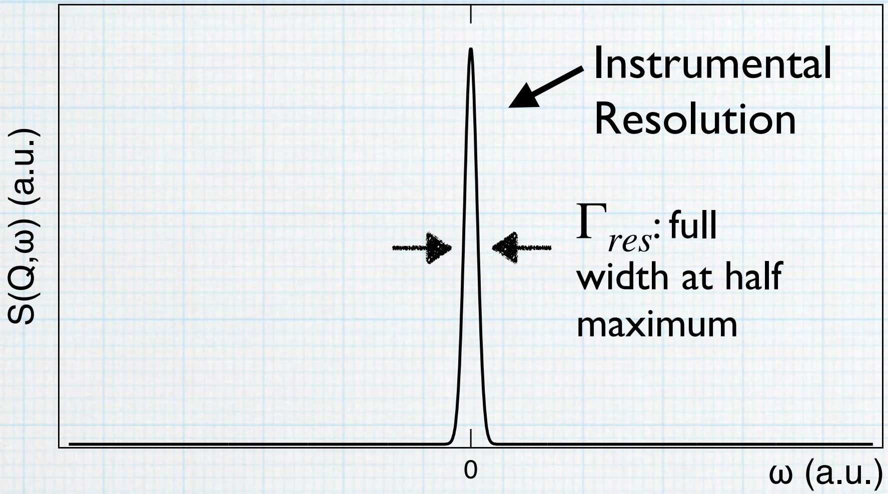
FT in space & time

→including all physics of the system

FT in time

$$S(\vec{Q},\omega) = \frac{1}{N}\sum_{j,k} b_j b_k \int_{-\infty}^{\infty} \left\langle \exp\left[-i\vec{Q}\cdot\left\{\vec{r}_k(0) - \vec{r}_j(t)\right\}\right] \exp[-i\omega t]dt \right\rangle$$

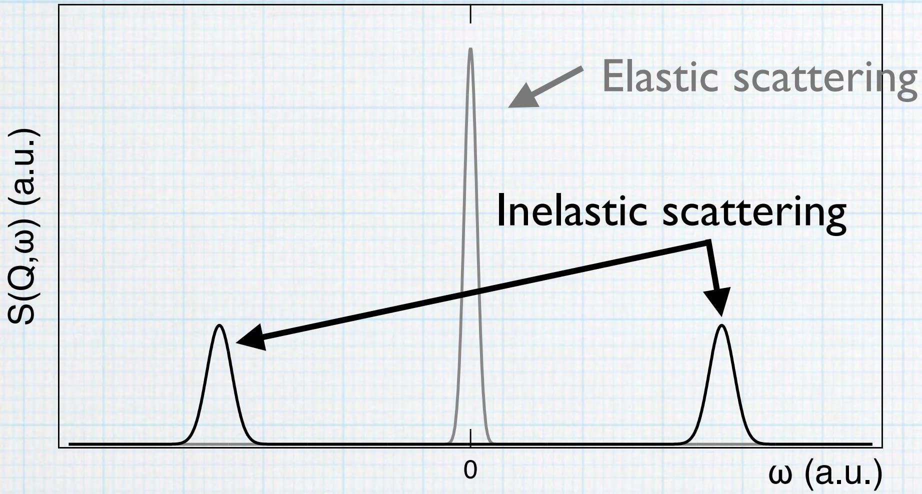
Dynamic scattering



✓ Instrument Resolution

- Minimum energy transfer appreciated by the instrument
- Immobile component within the time scale accessed
- Equals to elastic scattering component

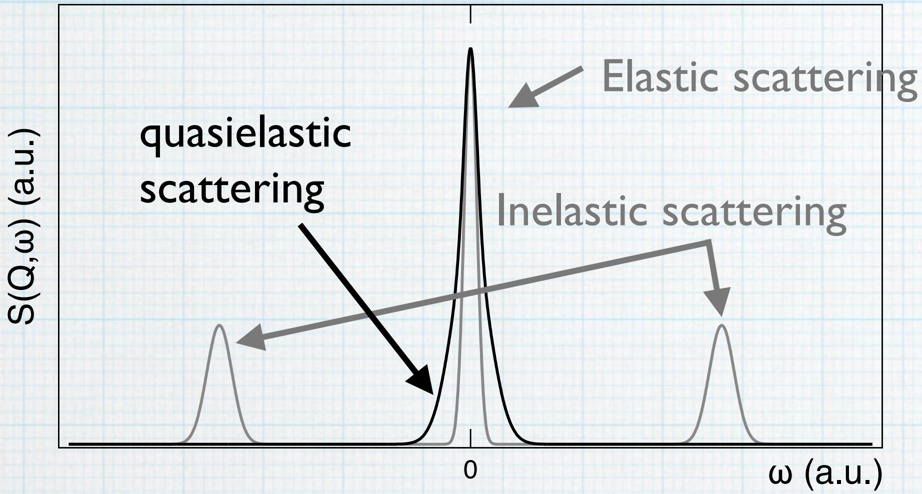
Dynamic scattering



✓ Inelastic scattering

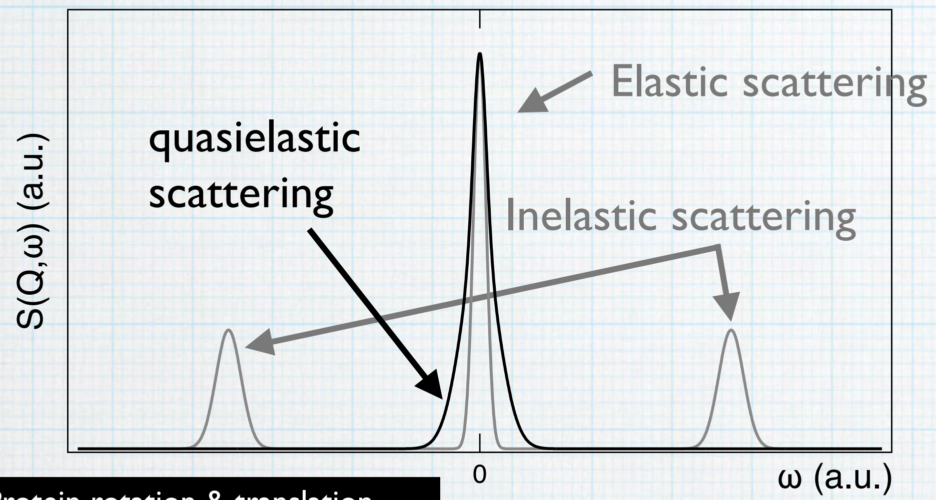
- Excitation: neutrons exchange energy with an oscillatory motion which has a finite energy transfer. E.g.: phonon, …

Dynamic scattering



- ✓ Inelastic scattering
  - Excitation: neutrons exchange energy with an oscillatory motion which has a finite energy transfer. E.g.: phonon, …
- ✓ Quasielastic scattering
  - Relaxation: neutrons exchange energy with random motion which makes another new equilibrium state (no typical finite energy transfer exists). E.g.: rotation, diffusion, …

Dynamic scattering



- ✓ Inelastic scattering
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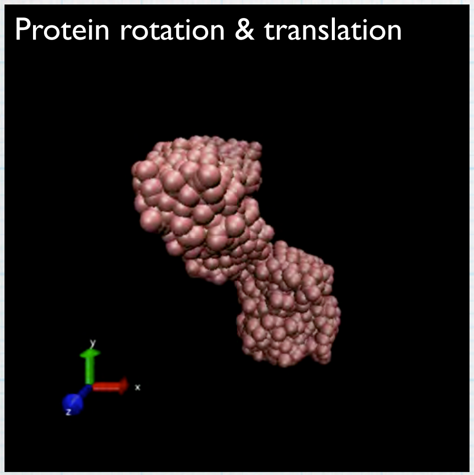
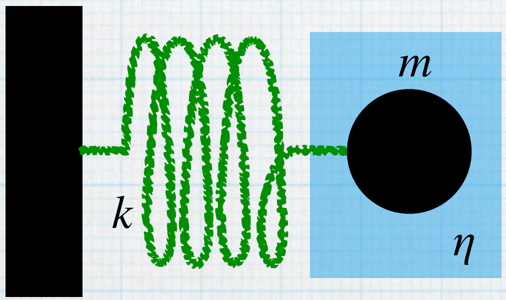
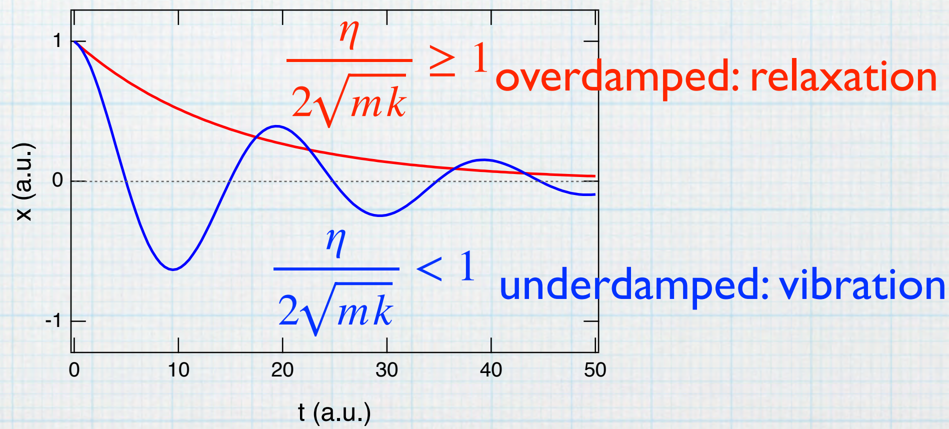


Courtesy of Yanqin Zhai

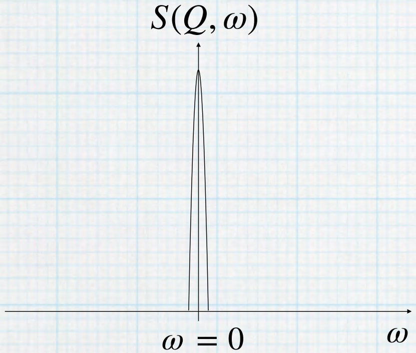
Thermally activated motions take place in the system

Damped oscillator

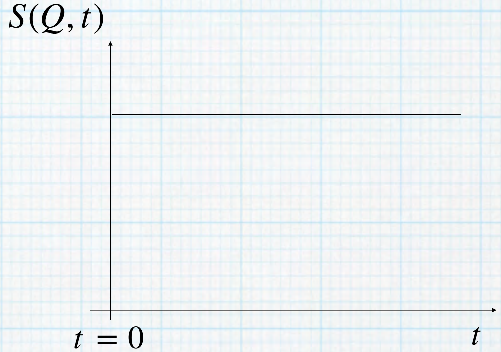




Energy domain vs time domain

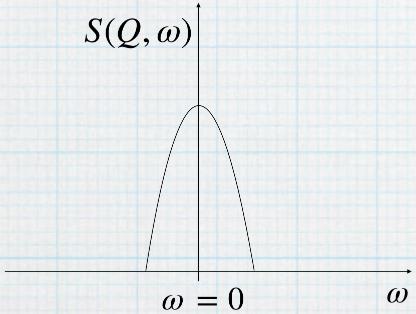


FT

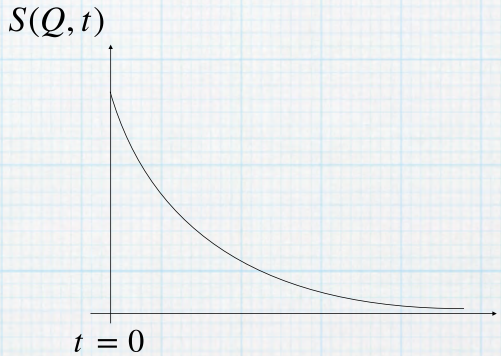


$S(Q,\omega = 0)$

static structure



FT



$S(Q,t = 0)$

Snapshot

$$S_{exp}(Q,\omega) = S_{true}(Q,\omega) \circledast R(Q,\omega)$$

Deconvolution

FT

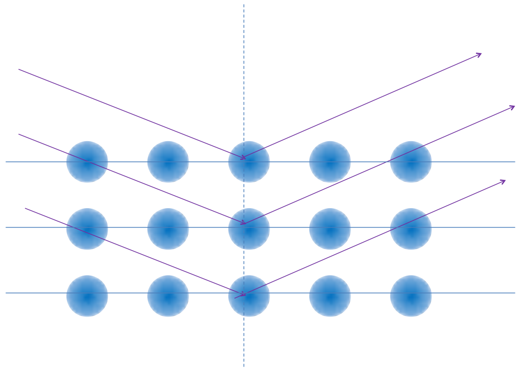
$$S_{exp}(Q,t) = S_{true}(Q,t)R(Q,t)$$

Resolution treatment

Division

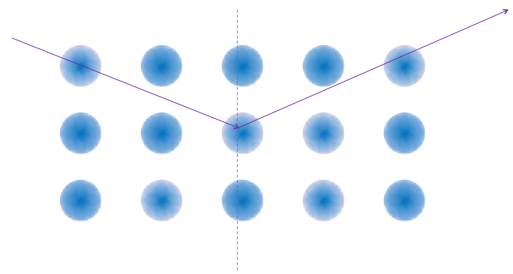
Coherent / Incoherent scattering

Coherent scattering : $2d\sin\theta = n\lambda$



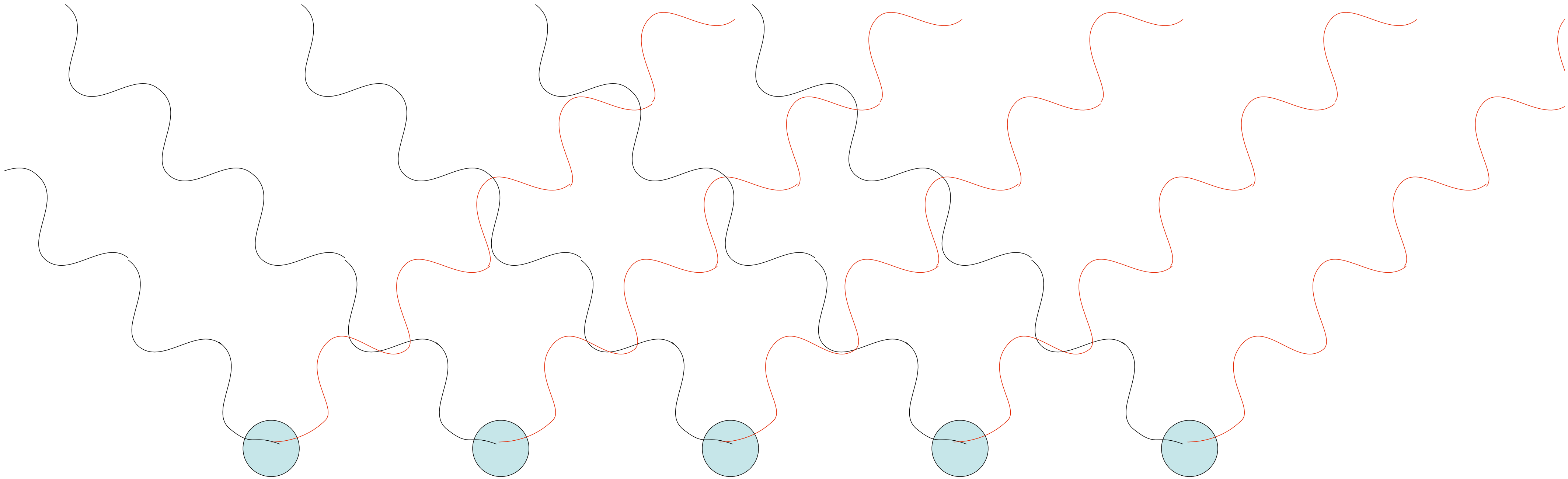
Mutual correlation among particles
    structural properties
    (static/dynamic)

Incoherent scattering: no interference

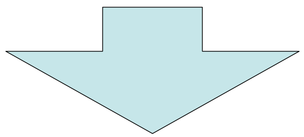


Scattering from independent particles
    self-correlation
    no information of structure
    dynamical property of each particle

Coherent scattering

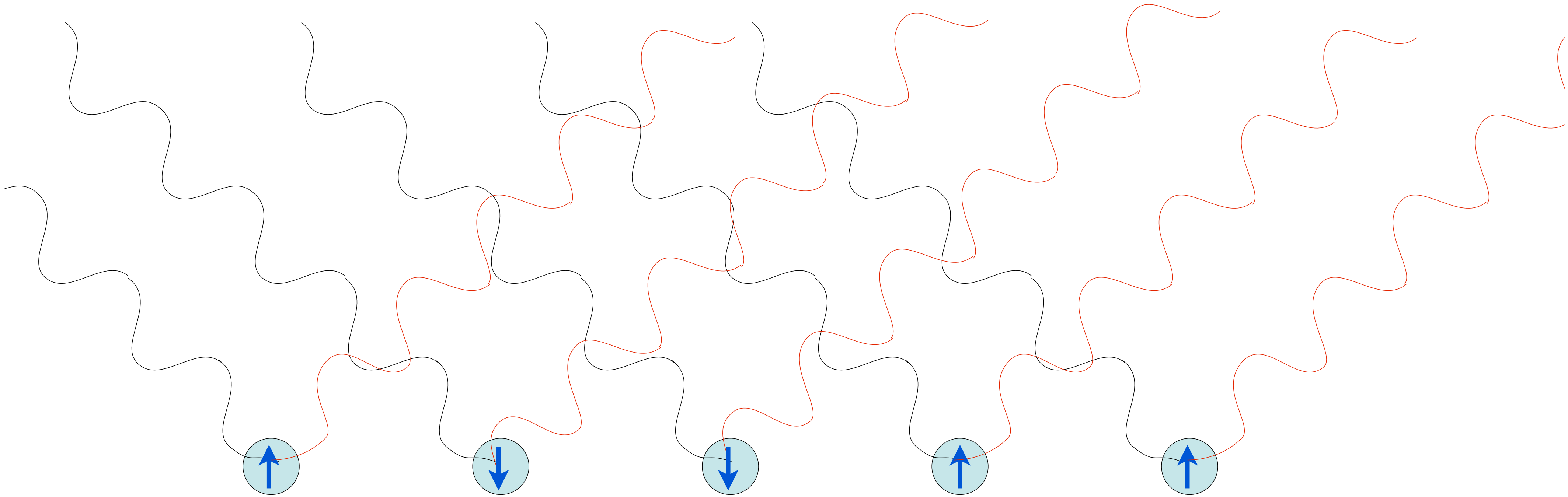


all nucleus scatter neutrons at the same manner

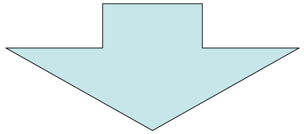


phases of scattered neutrons do not change and an interference occurs

Incoherent scattering

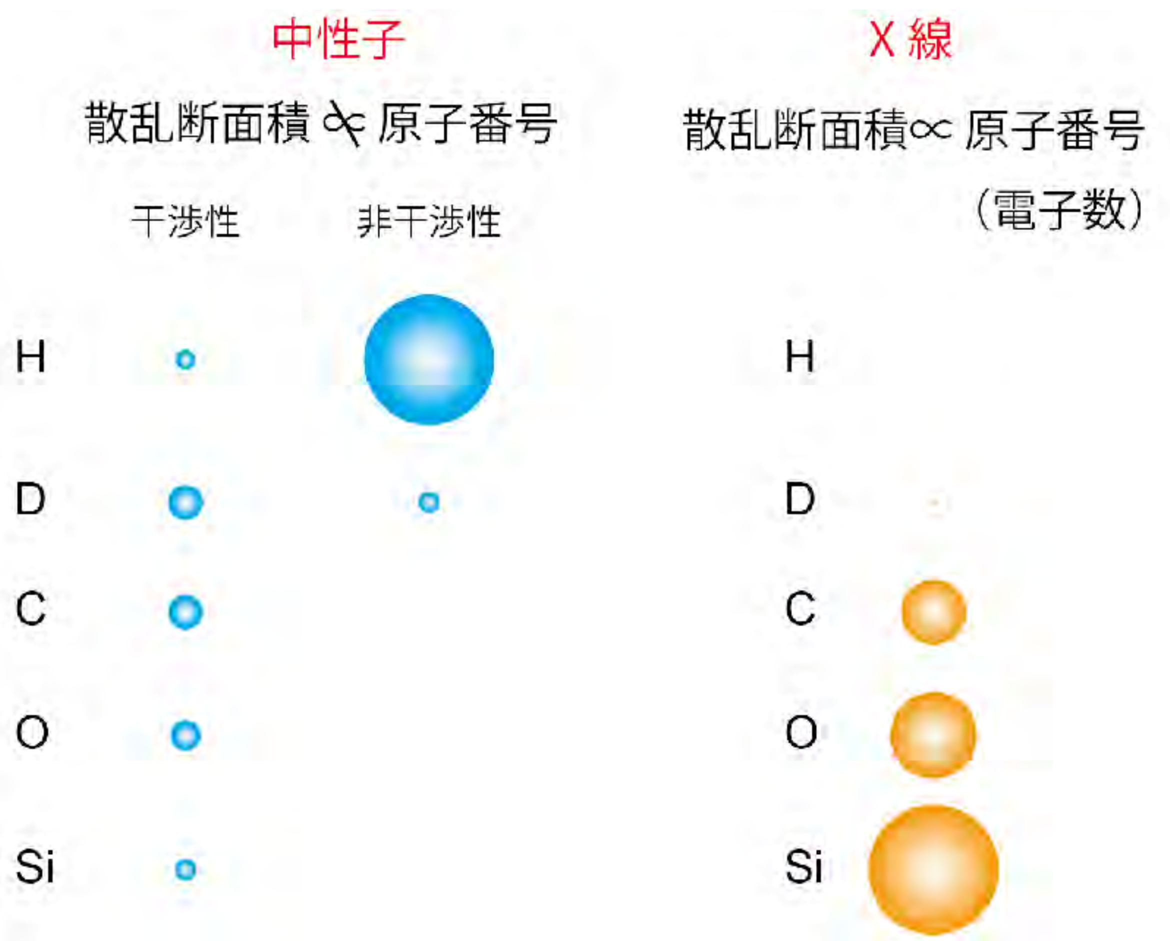


nucleus spin distribute randomly



phases of scattered neutrons change randomly and no interference

Scattering cross section of atoms



Incoherent scattering cross section of H is much larger than the others: dynamics of molecules containing H could be well investigated by QENS

Highlight targeted molecules by selective deuteration

Coherent and incoherent scattering

$$S(\vec{Q},\omega) = \frac{1}{N}\sum_{j,k} \boxed{b_j b_k} \int_{-\infty}^{\infty} \left\langle \exp\left[-i\vec{Q}\cdot\left\{\vec{r}_k(0)-\vec{r}_j(t)\right\}\right] \exp[-i\omega t]dt \right\rangle$$

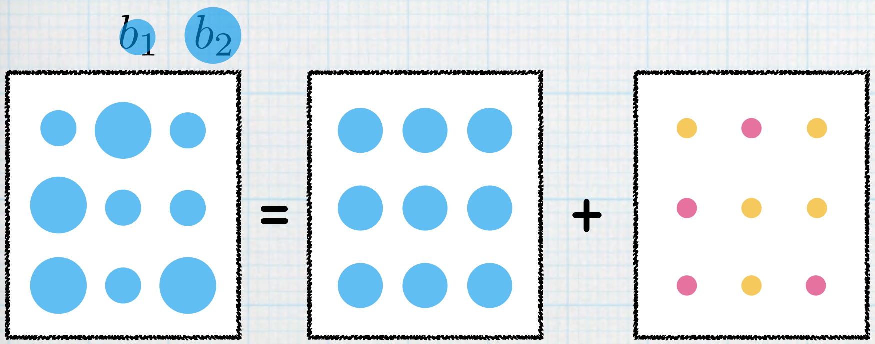
- ✓ Even for the same type of atom, the scattering length b_j might vary due to the presence of different
    - Isotopes
    - Nuclear spin states

$\bar{b}_j$: the mean of the scattering length of the same type of atom

$$\sum_{j,k} b_j b_k = \sum_{j,k} (\bar{b}_j\bar{b}_k + b_j b_k - \bar{b}_j\bar{b}_k) = \sum_{j,k} \bar{b}_j\bar{b}_k + \sum_{j,k} (b_j b_k - \bar{b}_j\bar{b}_k)$$

Average

Difference from the average

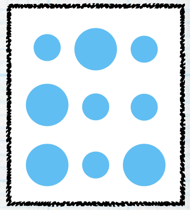


$$\langle b_j b_k - \bar{b}_j\bar{b}_k\rangle = \langle b_j\rangle\langle b_k\rangle - \bar{b}_j\bar{b}_k = 0 \text{ when } j \neq k$$

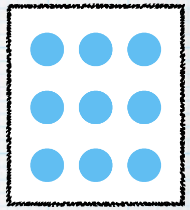
$$\langle b_j b_j - \bar{b}_j\bar{b}_j\rangle = \langle b_j b_j\rangle - \bar{b}_j\bar{b}_j = \langle b_j^2\rangle - \bar{b}_j^{\,2} \text{ when } j = k$$

Random orientation $\rightarrow$ no correlation between different atoms

Coherent and incoherent scattering



$$S(\overrightarrow{Q},\omega) = \frac{1}{N}\sum_{j,k} b_j b_k \int_{-\infty}^{\infty} \left\langle \exp\left[-i\overrightarrow{Q}\cdot\left\{\vec{r}_k(0)-\vec{r}_j(t)\right\}\right]\exp[-i\omega t]dt\right\rangle$$



Average

$$= \boxed{\frac{1}{N}\sum_{j,k} \bar{b}_j \bar{b}_k \int_{-\infty}^{\infty} \left\langle \exp\left[-i\overrightarrow{Q}\cdot\left\{\vec{r}_k(0)-\vec{r}_j(t)\right\}\right]\exp[-i\omega t]dt\right\rangle}$$

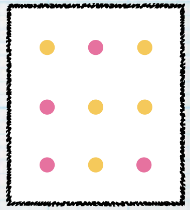
Coherent dynamic structure factor,

$S_{coh}(\overrightarrow{Q},\omega)$

Information on relative positions and motions

coherent scattering cross section

$$\sigma_{coh} = 4\pi\bar{b}^2$$



Difference from the average

$$+\boxed{\frac{1}{N}\sum_{j} \left(\langle b_j^2\rangle - \bar{b}_j^{\,2}\right) \int_{-\infty}^{\infty} \left\langle \exp\left[-i\overrightarrow{Q}\cdot\left\{\vec{r}_j(0)-\vec{r}_j(t)\right\}\right]\exp[-i\omega t]dt\right\rangle}$$

Incoherent dynamic structure factor,

$S_{inc}(\overrightarrow{Q},\omega)$

Information on the single particle dynamics

incoherent scattering cross section

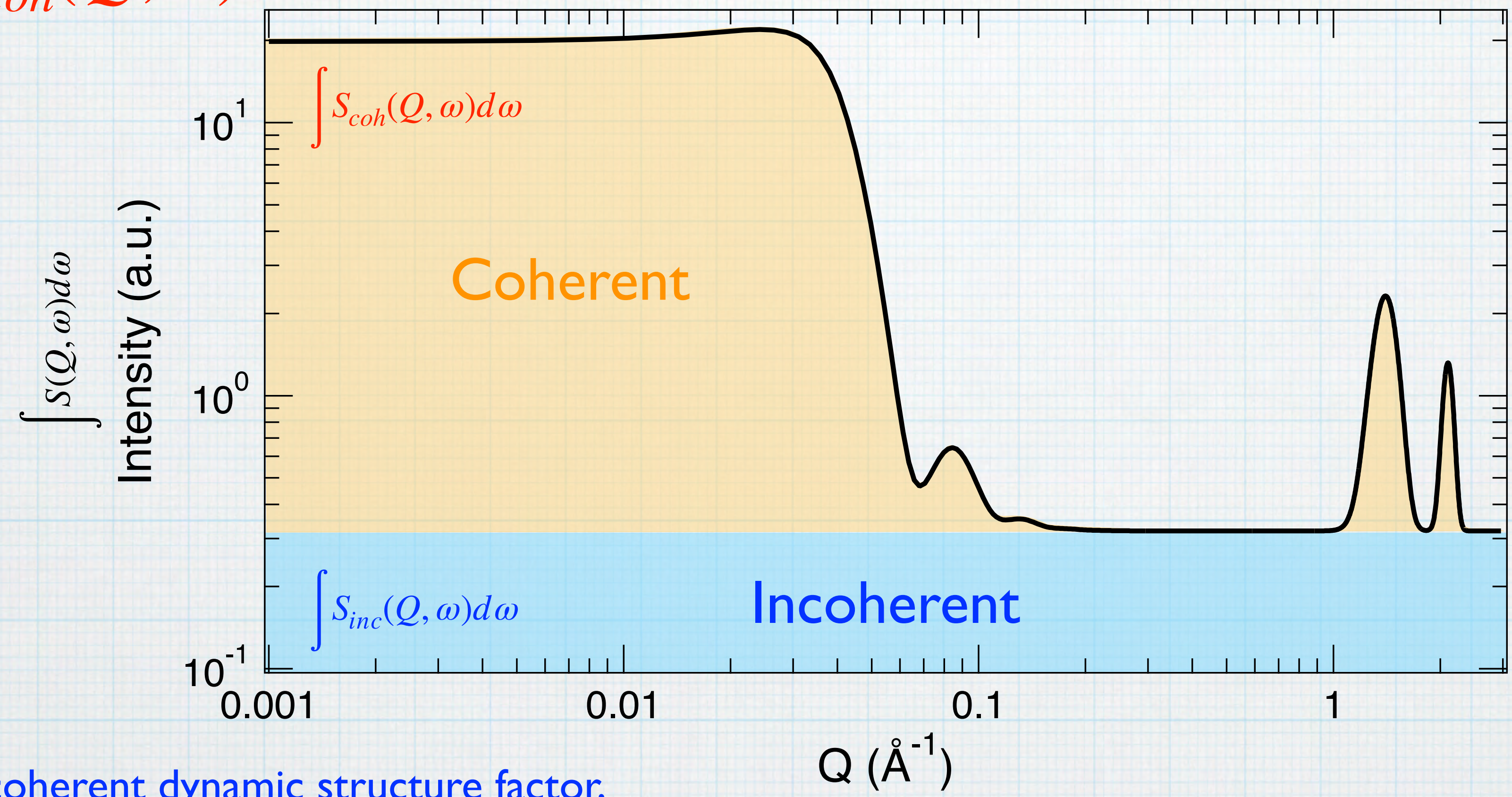
$$\sigma_{inc} = 4\pi\left(\langle b^2\rangle - \bar{b}^2\right)$$

Coherent and incoherent scattering

Coherent dynamic structure factor,

$S_{coh}(\overrightarrow{Q}, \omega)$

Information on relative positions and motions



Incoherent dynamic structure factor,

$S_{inc}(\overrightarrow{Q}, \omega)$

Information on the single particle dynamics

Coherent/incoherent scattering cross sections of some elements

	Nuclear	σ_{coh} (barn)	σ_{inc} (barn)	σ_{abs} (barn)
Hydrogen (^{1}H)	1/2	1.76	80.27	0.33
Deuterium	1	5.59	2.05	0
Carbon (^{12}C)	0	5.56	0	0
Nitrogen (^{14}N)	1	11.03	0.50	1.90
Oxygen (^{16}O)	0	4.23	0	0
Aluminium (^{27}Al)	5/2	1.49	0.01	0.23
Silicon (^{28}Si)	0	2.12	0	0.17

incoherent scattering cross section of hydrogen dominates other elements

H containing materials: incoherent dynamics is dominated by single particle motions of H

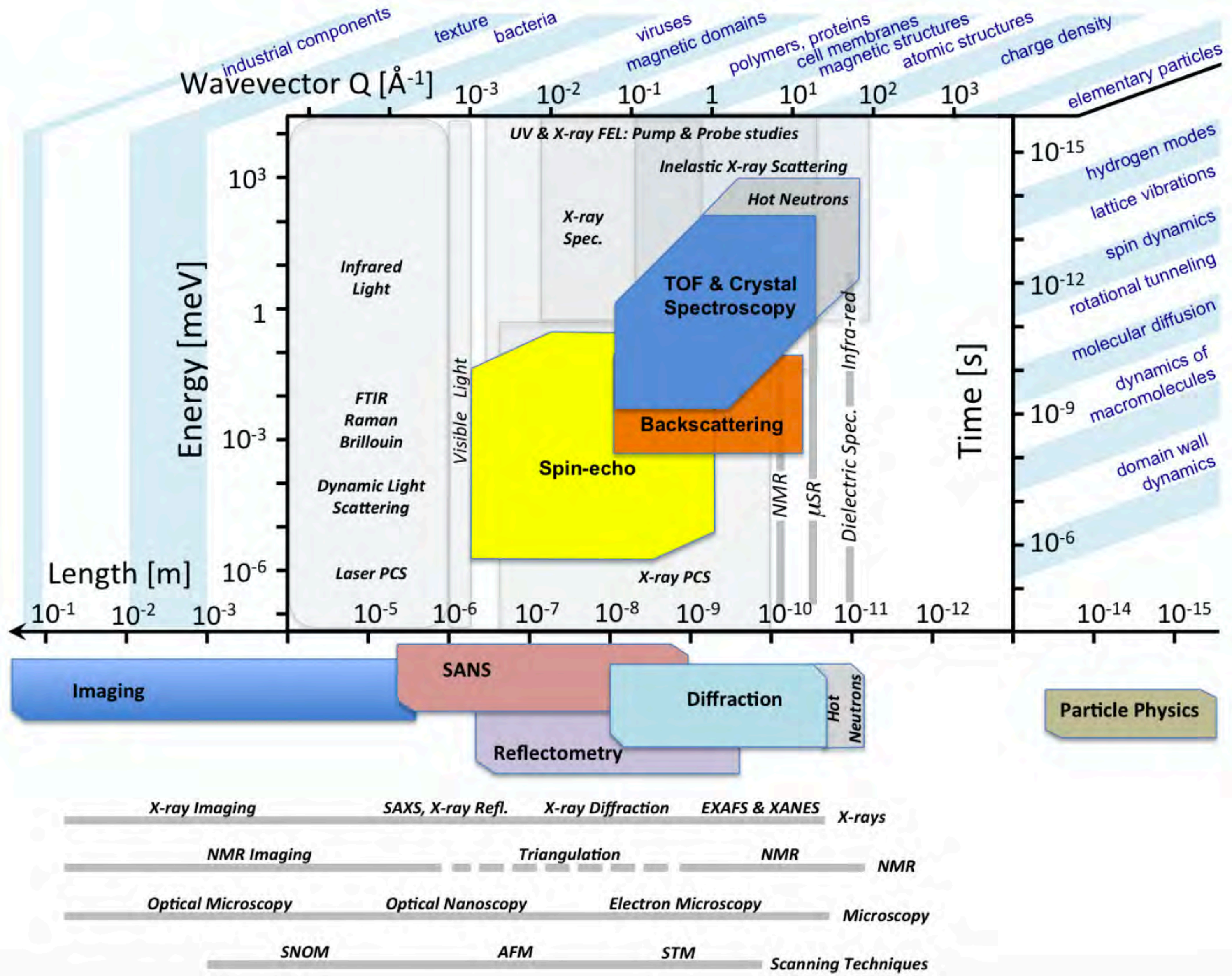
Science cases for QENS

- ✓ Materials science
  Å to nm & < ns
  - Hydrogen storage, fuel cells, surface science, glass ionomer cements, …
- ✓ Chemistry
  Å to nm & < ns, could be longer in time
  - Molecular liquids, porous media, …
- ✓ Physics
  Å to nm & < ns, could be longer in time
  - Relaxor, spin-glass relaxation, glass forming liquids, …
- ✓ Soft Materials
  Å to 10s to 100s of nm & < 100 ns, could be longer in length & time
  - Polymer (melt, gel, solution), surfactant, …
- ✓ Biology
  Å to 100s of nm & < 100 ns, could be longer in length & time
  - Protein, hydration water, lipid-protein interaction, lipid membranes, …

Dynamic range

Complemental techniques

- NMR
- Dielectric spectroscopy
- IR
- PCS
- Computer simulation
- …



https://europeanspallationsource.se/science-using-neutrons

Dynamic ran

Complemental techniques

- NMR
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https://
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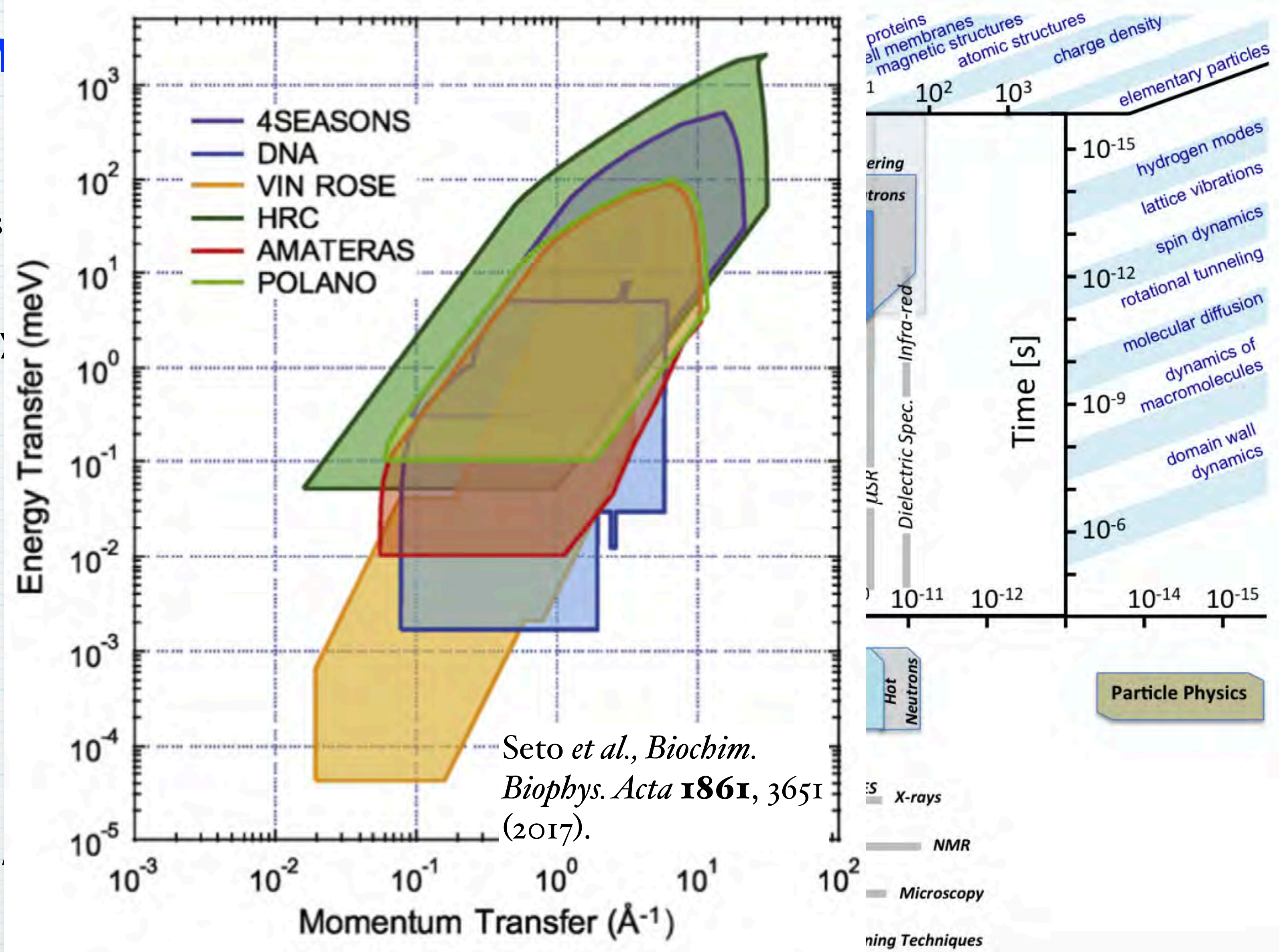

Seto *et al.*, *Biochim. Biophys. Acta* **1861**, 3651 (2017).

Dynamic ran

Complemental techniques

- NMR
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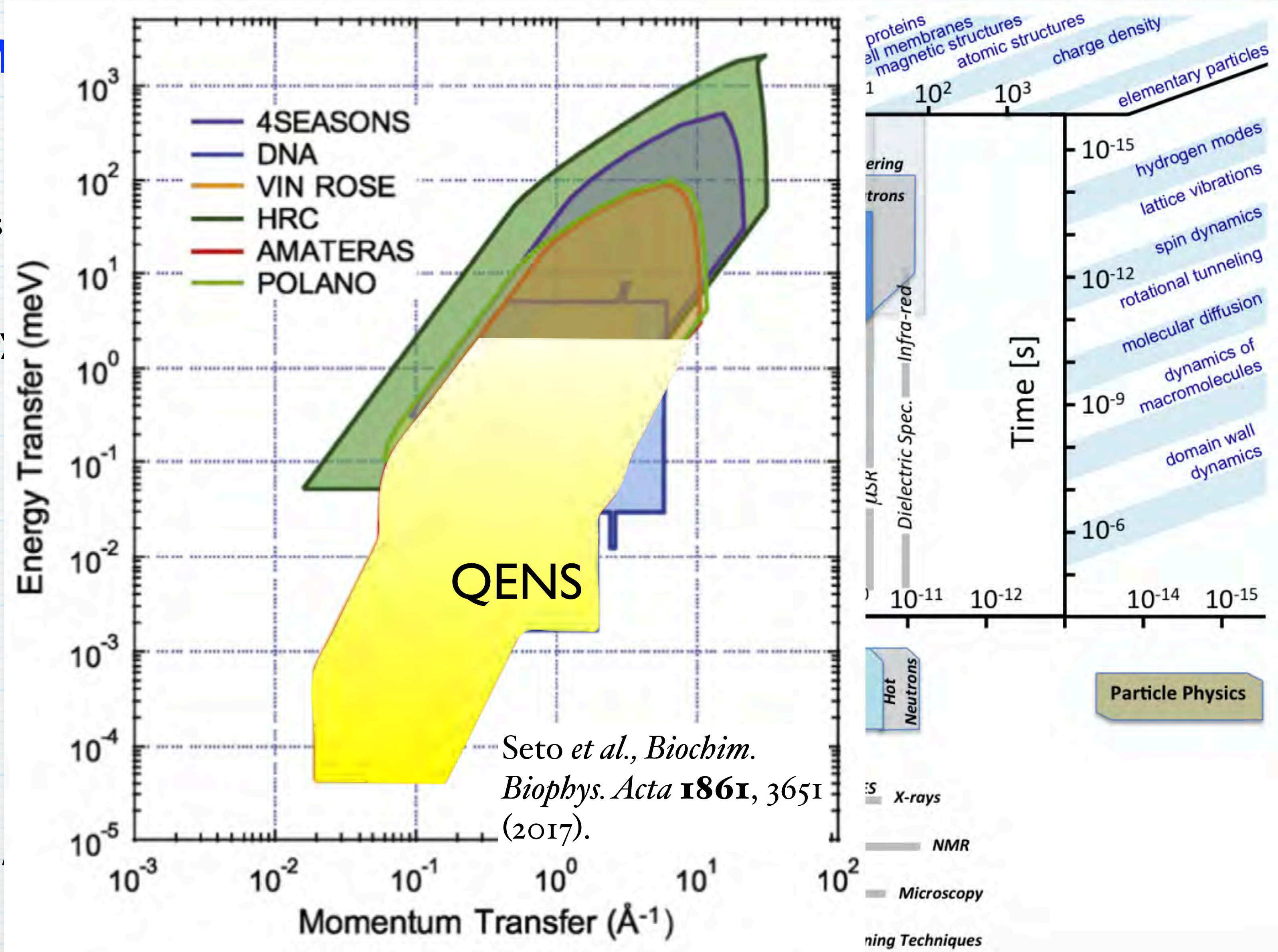

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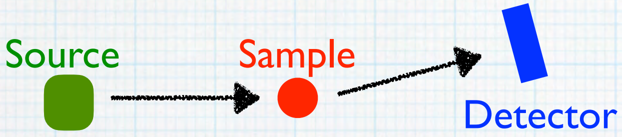
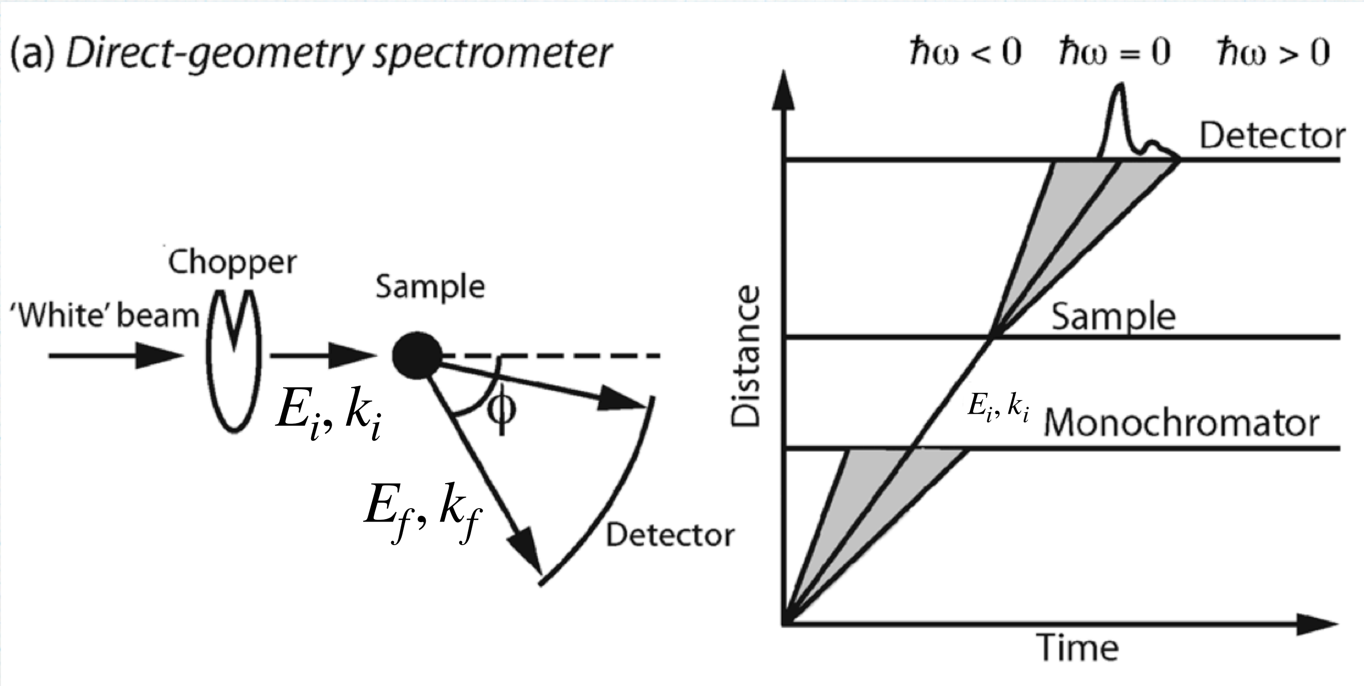
https://
europeanspallationsource.se/
science-using-neutrons

Instrumentations - direct geometry

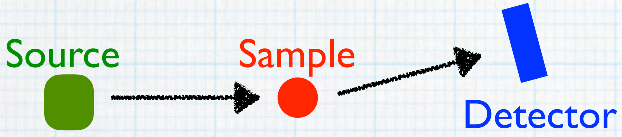


- ✓ Fixed E_i and analyze variation of E_f
- ✓ Neutron Time-of-Flight



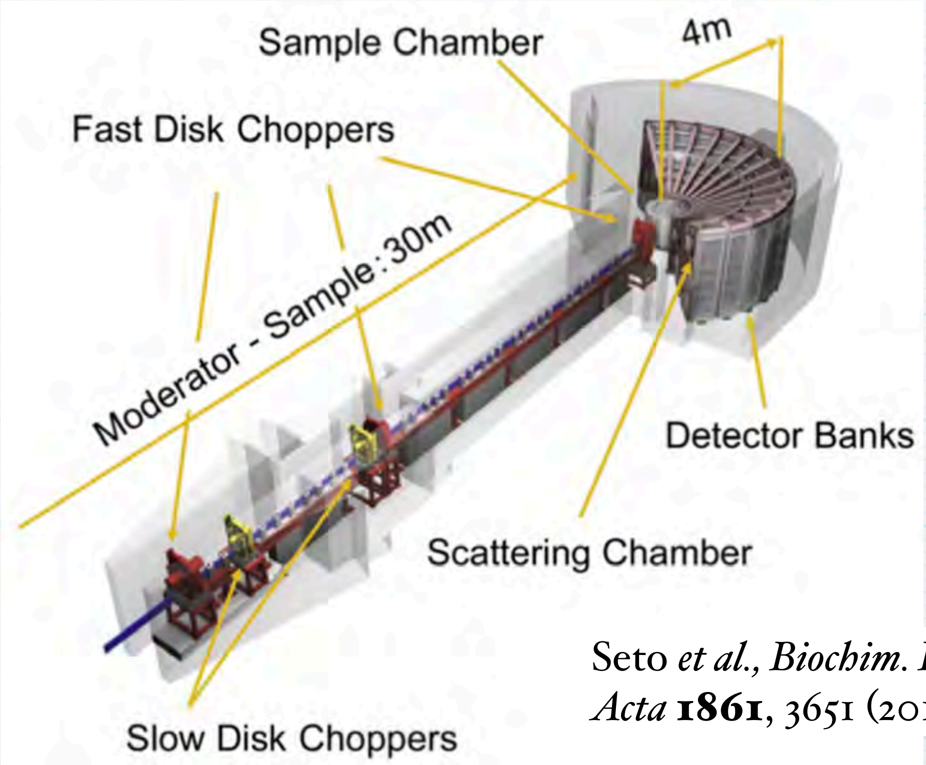
Karlsson, *Phys. Chem. Chem. Phys.* **17**, 26 (2015). "Proton dynamics in oxides: insight into the mechanics of proton conduction from quasielastic neutron ..."

Instrumentations - direct geometry



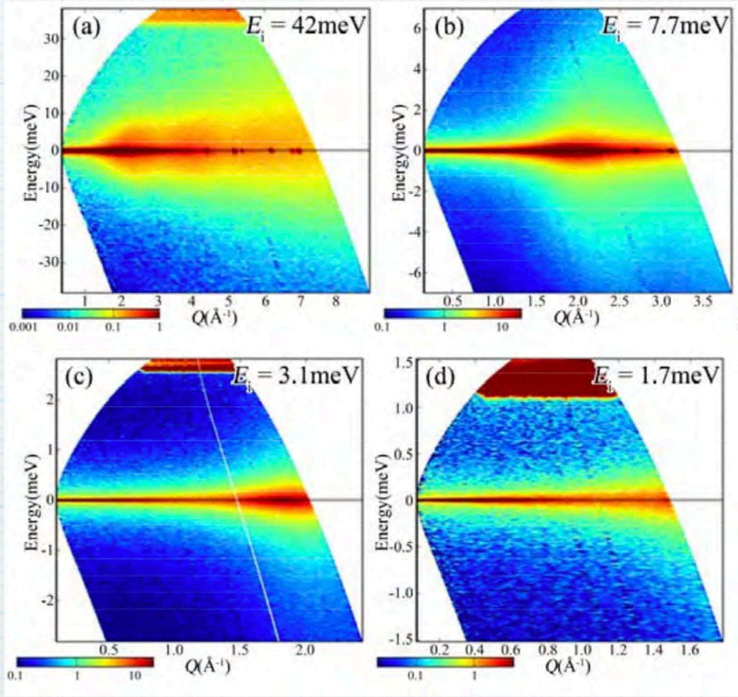
- ✓ Fixed E_i and analyze variation of E_f
- ✓ Neutron Time-of-Flight

✓ AMATERAS @ J-PARC



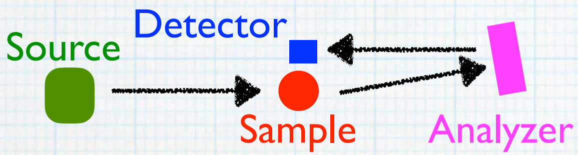
Seto *et al.*, *Biochim. Biophys. Acta* **1861**, 3651 (2017).

Quasielastic Scattering from liq. D_2O

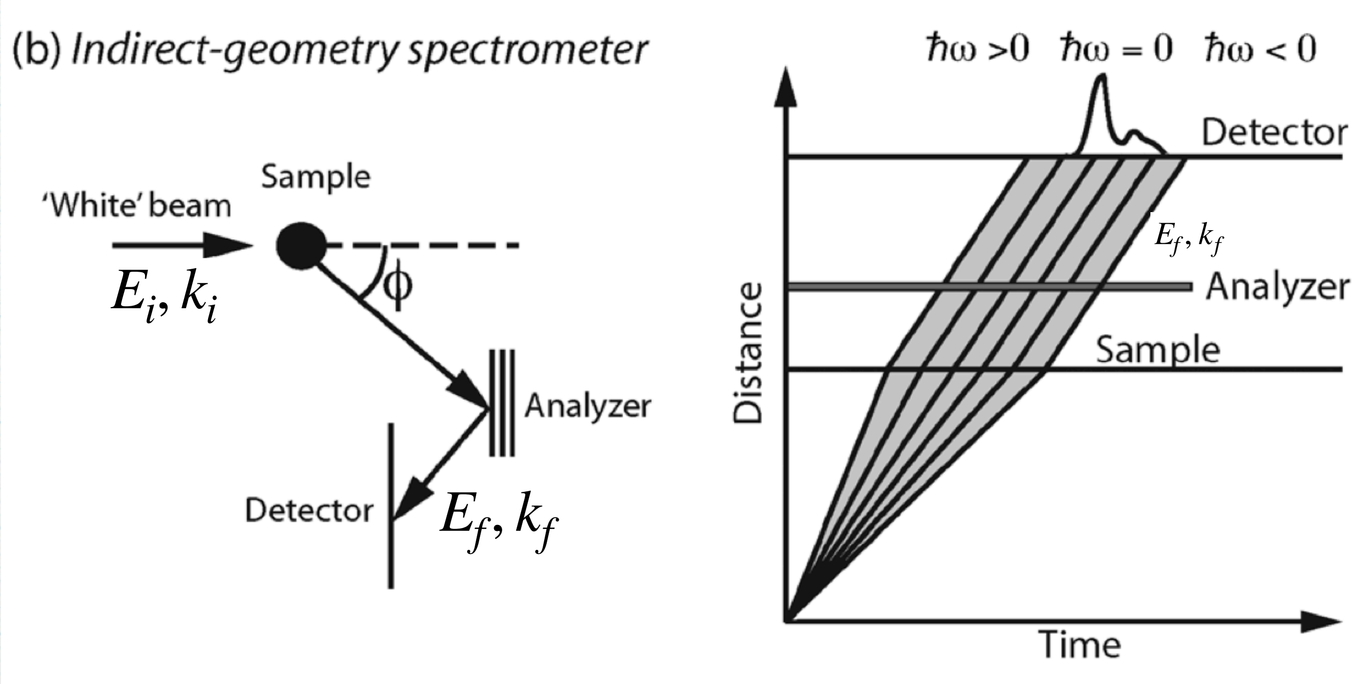


Nakajima *et al.*, *J. Phys. Soc. Jpn.* **80**, SB028 (2011).

Instrumentations - indirect geometry

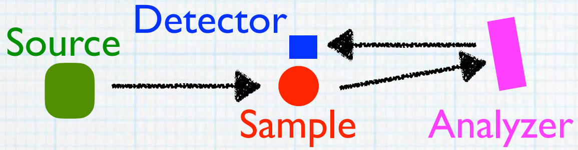


- ✓ Fixed E_f while providing a known band of E_i
- ✓ Higher energy resolution than a direct geometry



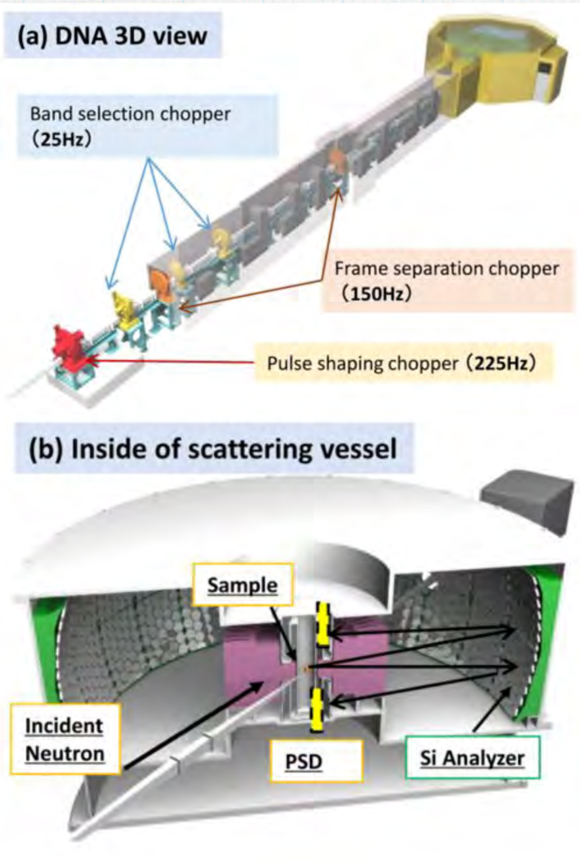
Karlsson, *Phys. Chem. Chem. Phys.* **17**, 26 (2015). "Proton dynamics in oxides: insight into the mechanics of proton conduction from quasielastic neutron ..."

Instrumentations - indirect geometry

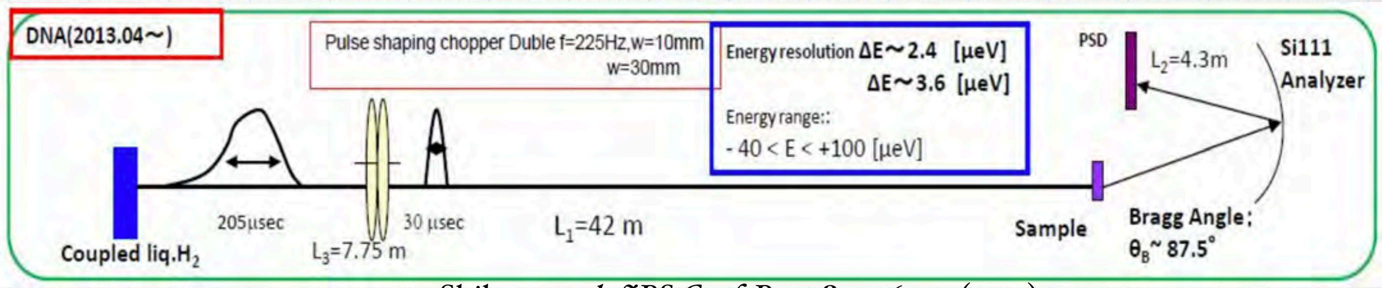


- ✓ Fixed E_f while providing a known band of E_i
- ✓ Higher energy resolution than a direct geometry
  - ✓ Employing (near) backscattering geometry

✓ DNA @ J-PARC

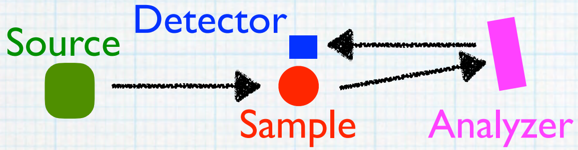


Nakajima *et al.*, *Quantum Beam Sci.* **1**, 9 (2017).



Shibata *et al.*, *JPS Conf. Proc.* **8**, 036022 (2015).

Instrumentations - indirect geometry



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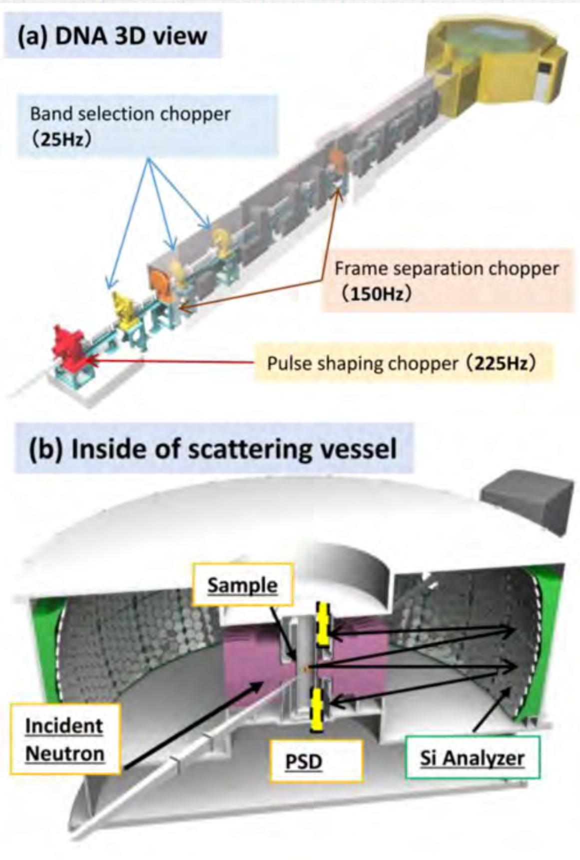
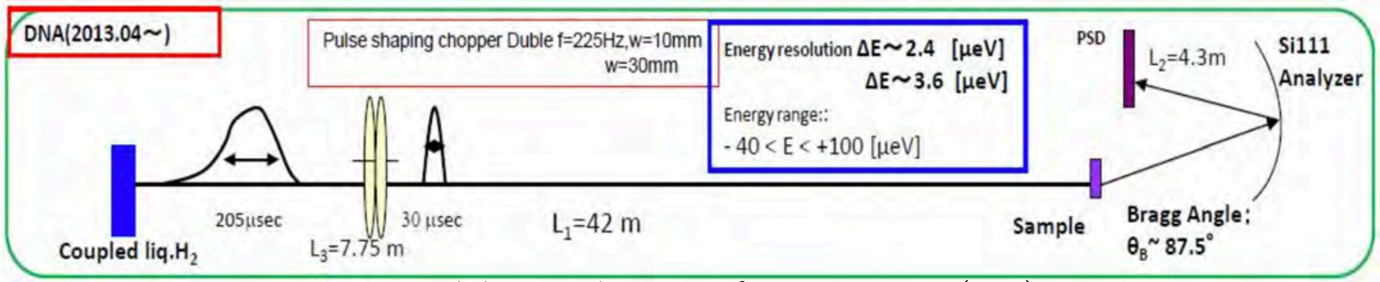
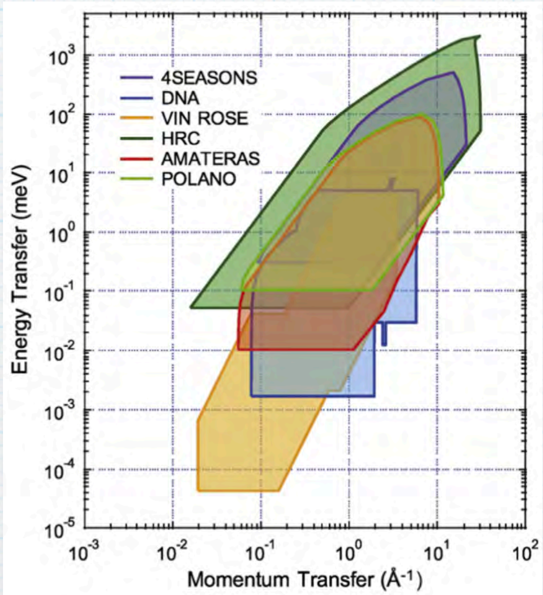


Nakajima *et al.*, *Quantum Beam Sci.* **1**, 9 (2017).



Shibata *et al.*, *JPS Conf. Proc.* **8**, 036022 (2015).



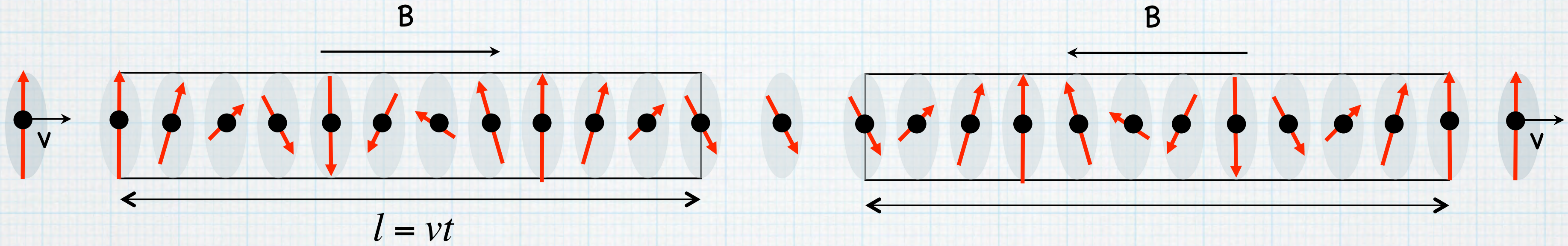
- ✓ Reactor based backscattering machine provides better energy resolution but limited energy window
  - ~1 μeV for HFBS@NIST

Seto *et al.*, *Biochim. Biophys. Acta* **1861**, 3651 (2017).

Instrumentations - neutron spin echo

✓ Neutron spin direction rotates in a magnetic field

✓ Rotation angle depends on the magnetic field strength and time spent in the field



✓ Net precession angle in the two magnetic fields is set to 0

✓ Neutron velocity change at the center of the two fields breaks the symmetry

- → net precession angle in the two magnetic fields is not equal to 0

✓ Energy resolution of the instrument and energy of incoming or outgoing neutron are decoupled

✓ Provide highest energy resolution spectroscopy

✓ Working in the time domain (measuring intermediate scattering function)

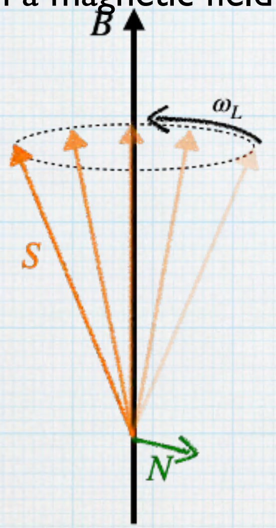
Instrumentations - neutron spin echo

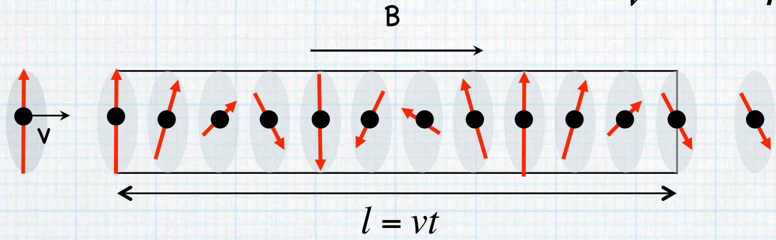
$$J \equiv \int B dl$$

Magnetic field integral along neutron trajectory

Neutron spin precession angle, ϕ, in a magnetic field B

$$\phi = \omega_L t = \gamma B t = \frac{\gamma J}{v} = \frac{\gamma m_n}{h} J \lambda$$





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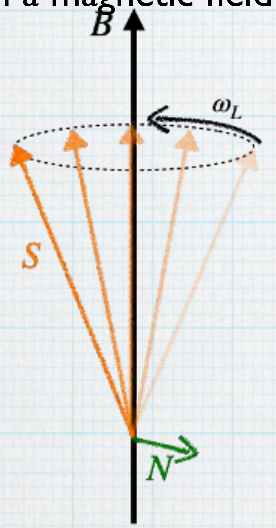

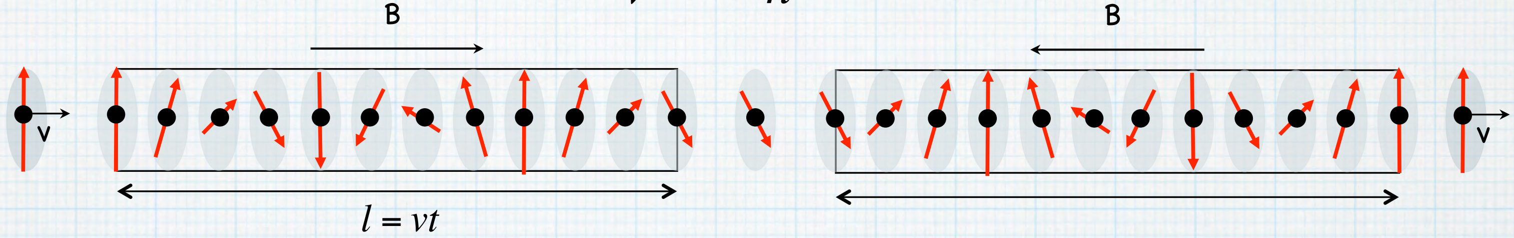

Initial spin polarization P_0

Final spin polarization

$P = P_0$ No energy change (elastic scattering)

$P \neq P_0$ Energy exchanged (inelastic scattering)

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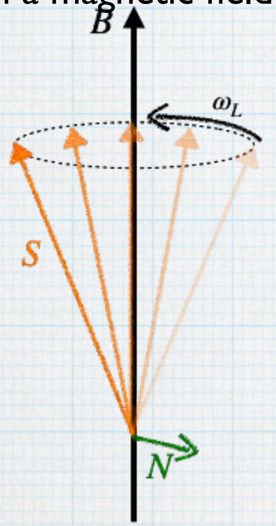

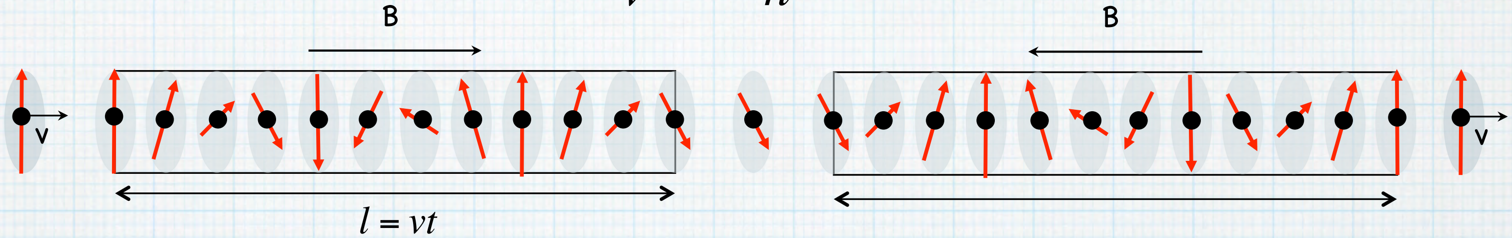

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Neutron energy change $\hbar\omega = \frac{h^2}{2m_n}\left[\frac{1}{\lambda^2} - \frac{1}{(\lambda + \delta\lambda)^2}\right] \approx \frac{h^2}{m_n}\frac{\delta\lambda}{\lambda^3}$

$$\Delta\phi = \boxed{\frac{\gamma m_n^2}{2\pi h^2} J\lambda^3}\,\omega = \omega t$$

Fourier time (spin echo time)

Instrumentations - neutron spin echo

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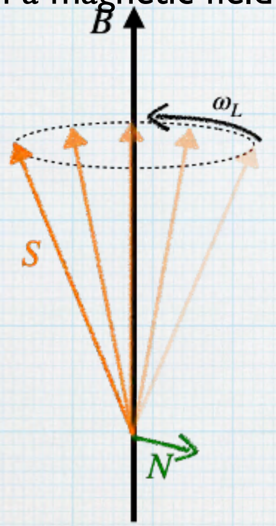

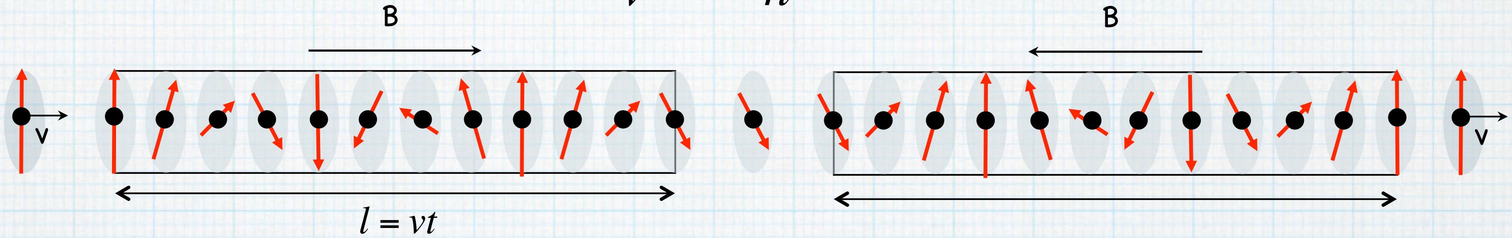

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Fourier time (spin echo time)

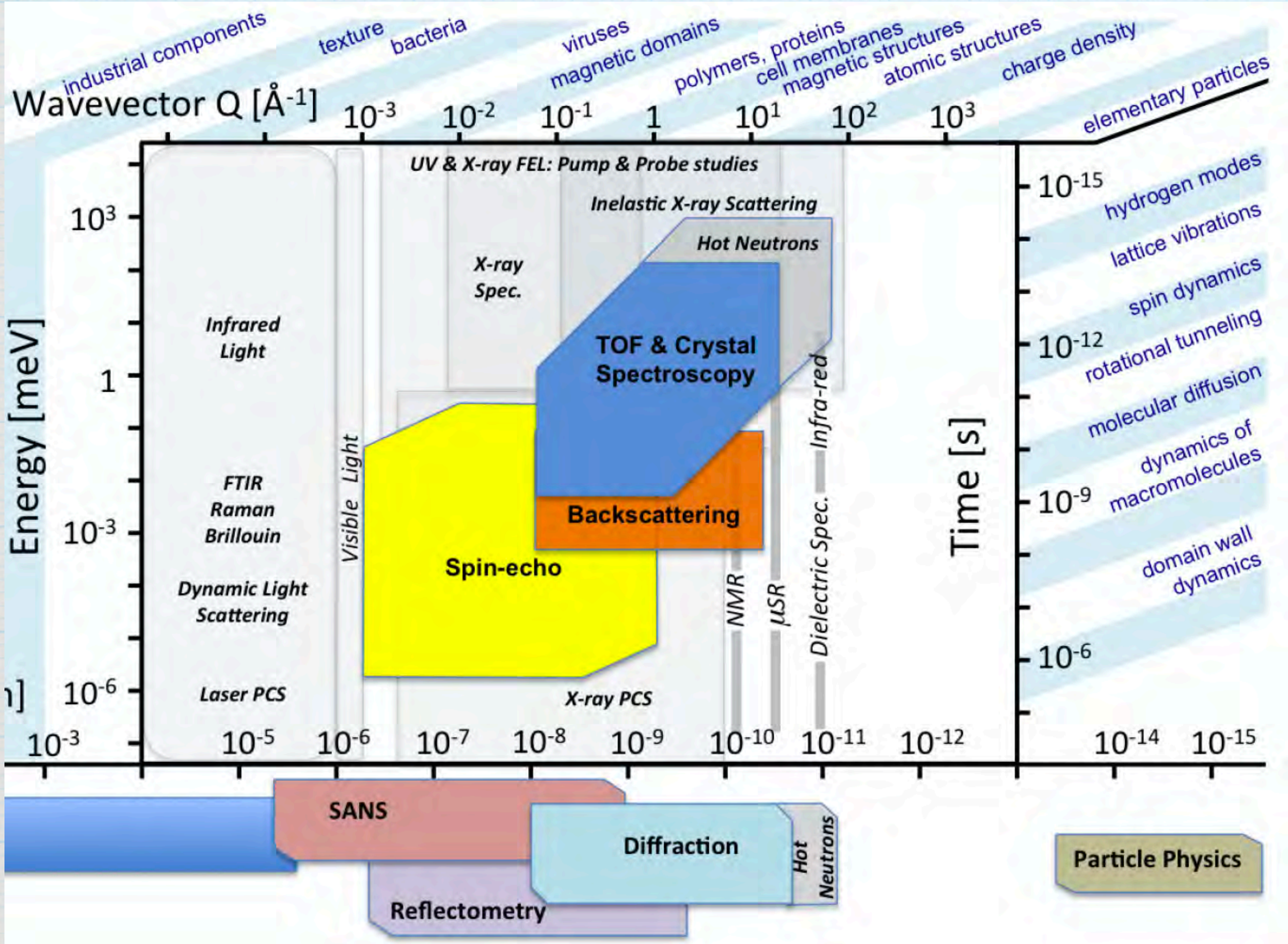
Neutron polarization is analyzed using spin analyzer which transmit neutrons as $I_{analyzer} = \frac{1 + \cos\Delta\phi}{2}$

$$\int S(Q,\omega)\frac{1+\cos\Delta\phi}{2}d\omega = \frac{1}{2}\left[\int S(Q,\omega)d\omega + \boxed{\int S(Q,\omega)\cos(\omega t)d\omega}\right]$$

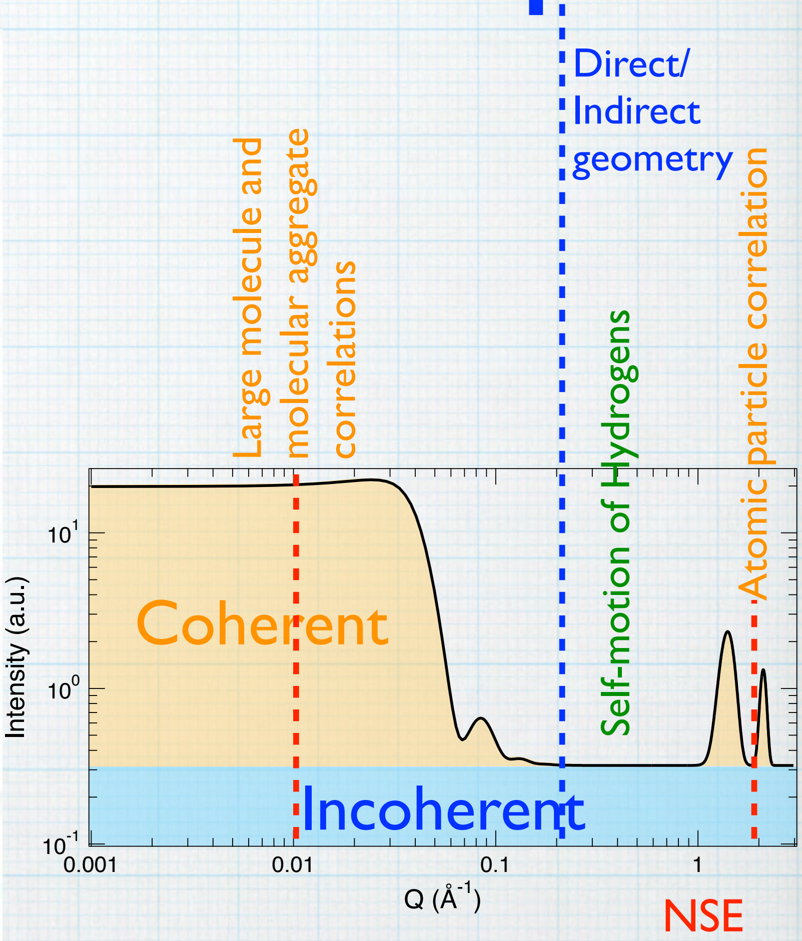
Cosine Fourier transform of $S(Q,\omega) \rightarrow S(Q,t)$

Highest energy resolution neutron spectroscopy

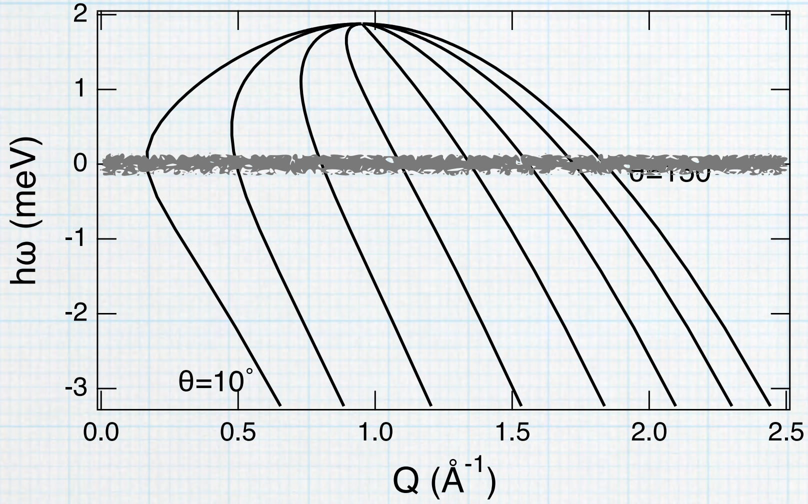
Dynamic range and type of dynamics to be captured



https://europeanspallationsource.se/science-using-neutrons



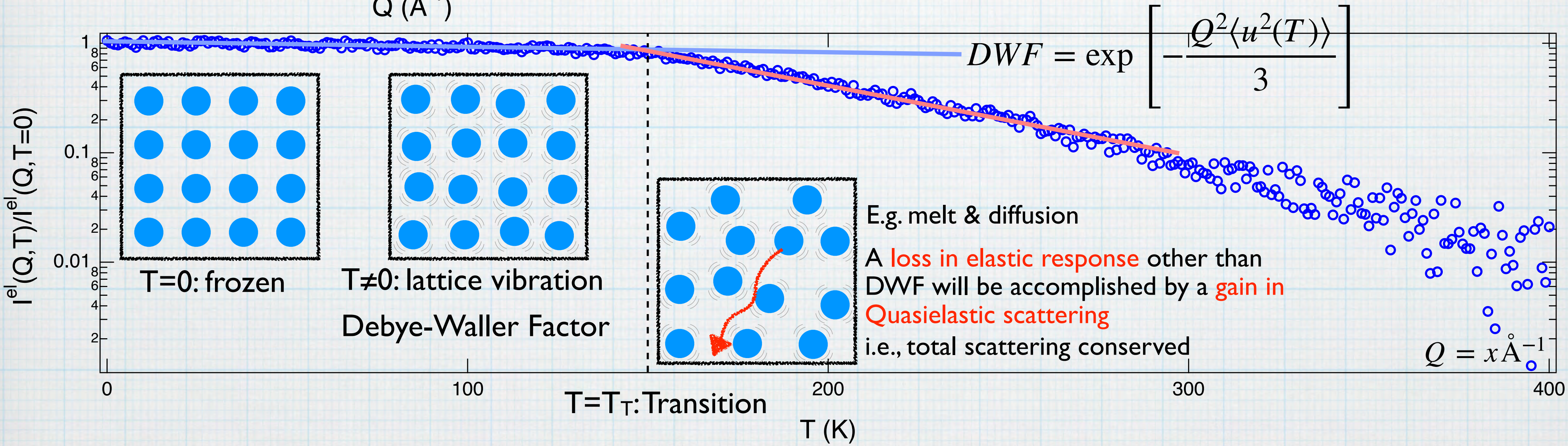
Elastic Fixed Window Scan



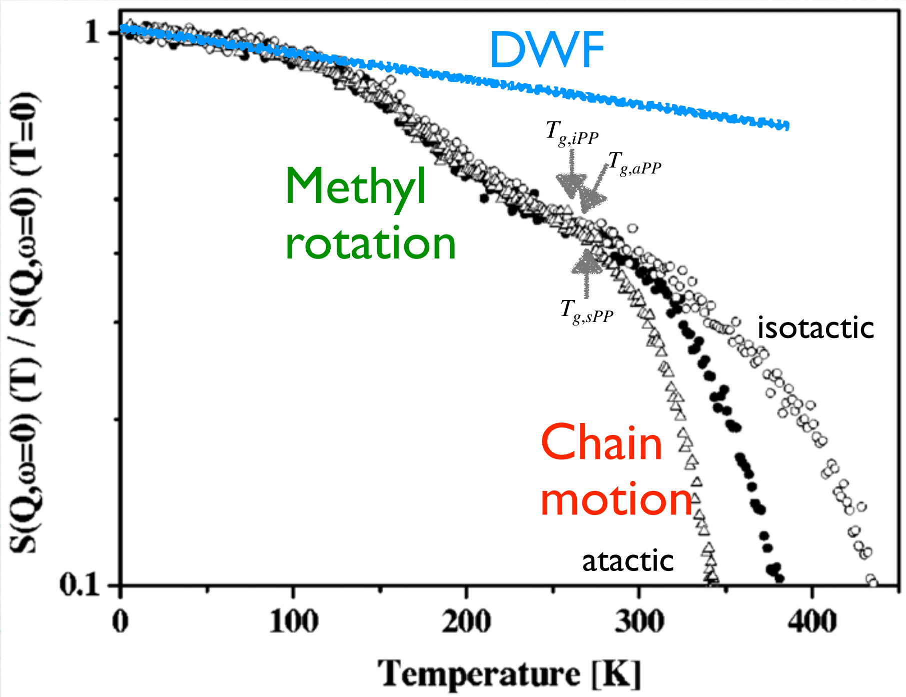
$$I^{el}(\vec{Q},T) = S(\vec{Q},\omega \approx 0,T)$$

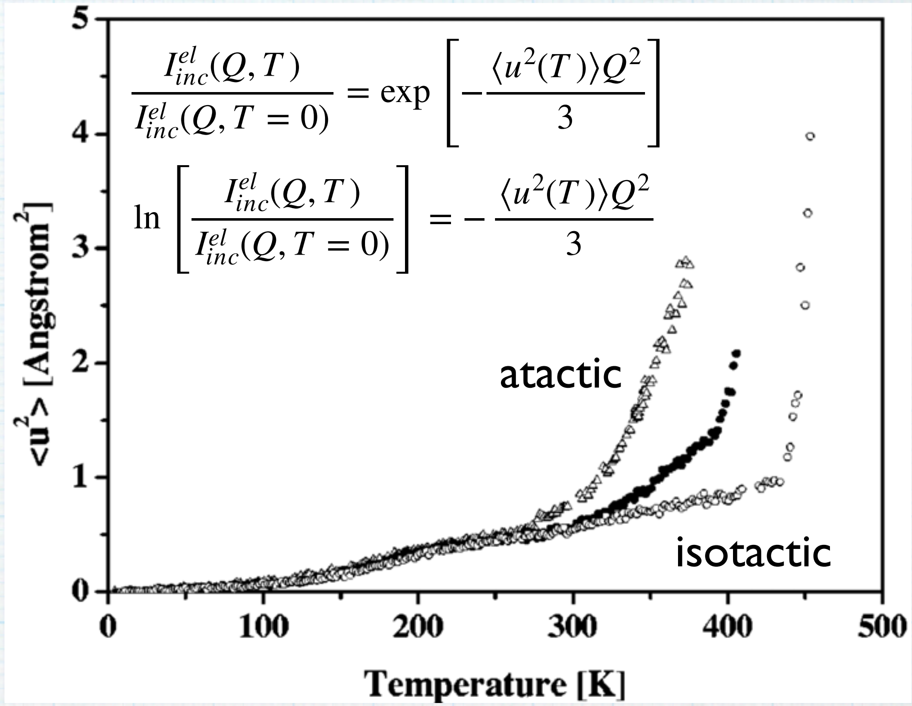
$$= \int_{-\Gamma_{res}/2}^{\Gamma_{res}/2} S(\vec{Q},\omega,T)d\omega \quad \text{Typical}$$

✓ Elastic intensity decreases with temperature

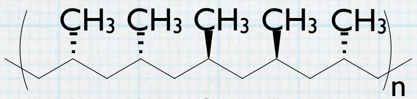


Example: How tacticity of polymer affects dynamics

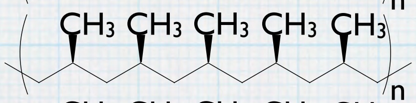




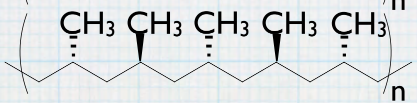
- ✓ Atactic polypropylene (aPP)



- ✓ Isotactic PP (iPP)



- ✓ Syndiotactic PP (sPP)



- ✓ Effective mean squared displacement $\langle u^2(T)\rangle$: average harmonic displacement amplitude of all atomic motions in the sample
- ✓ Gaussian approximation: $Q^2\langle u^2(T)\rangle \ll 1$

Arrighi *et al., J. Chem. Phys.* **119**, 1271 (2003). "Effect of tacticity on the local dynamics of polypropylene melts"

QENS data is sensitive to a motion as well as the geometry

$$S(Q,\omega) = \underbrace{\exp\left(-\frac{Q^2\langle u^2\rangle}{3}\right)}_{\text{Debye-Waller factor}} \Big[\underbrace{A_0(Q)\delta(\omega)}_{\text{Elastic component}} + \underbrace{(1 - A_0(Q))S_{inc}(Q,\omega)}_{\text{QENS component}}\Big]$$

- ✓ A_0: elastic incoherent scattering factor (EISF)

Telling, *A Practical Guide to Quasi-elastic Neutron Scattering*, Royal Society of Chemistry (2020).

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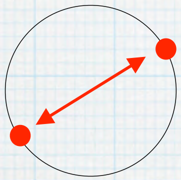
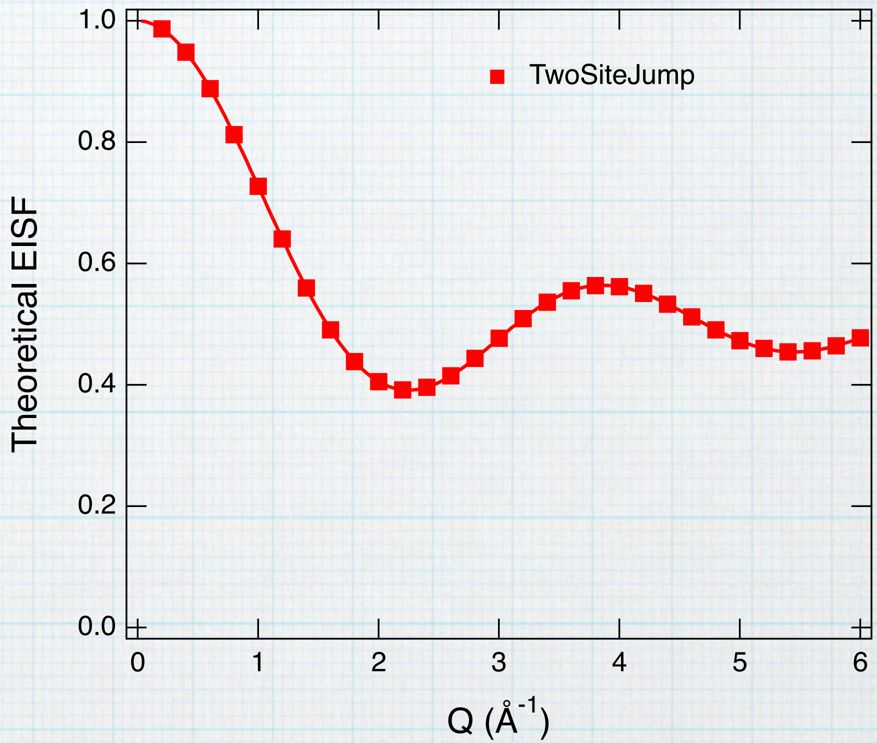
2-site jump



$$A_{0,jump}(Q) = \frac{1}{2}\left[1 + j_0\left(2Qr\right)\right]$$



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Debye-Waller factor — Elastic component — QENS component

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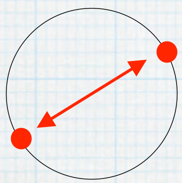

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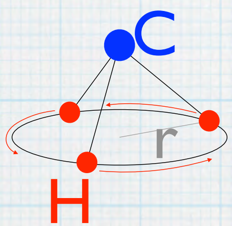
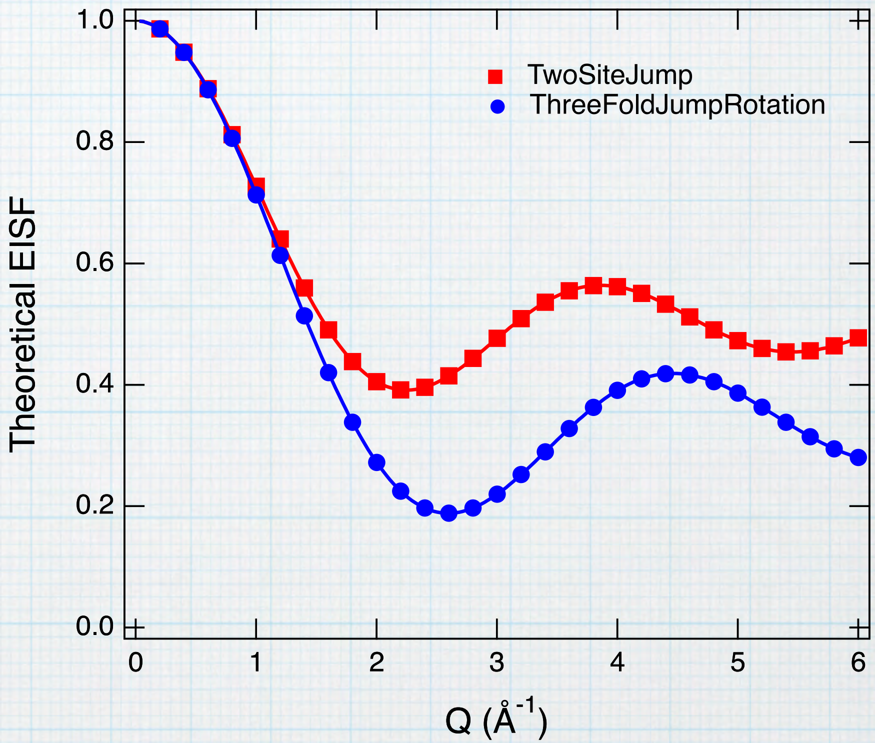
3-fold jump rotation with radius r



$$A_{0,CH_3}(Q) = \frac{1}{3}\left[1 + 2j_0\left(\sqrt{3}Qr\right)\right]$$



Telling, *A Practical Guide to Quasi-elastic Neutron Scattering*, Royal Society of Chemistry (2020).

QENS data is sensitive to a motion as well as the geometry

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Debye-Waller factor | Elastic component | QENS component

✓ A_0: elastic incoherent scattering factor (EISF)

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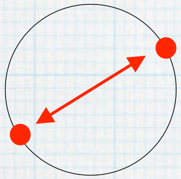

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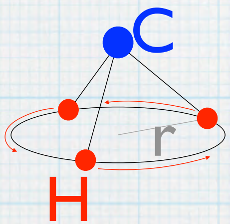

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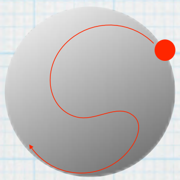
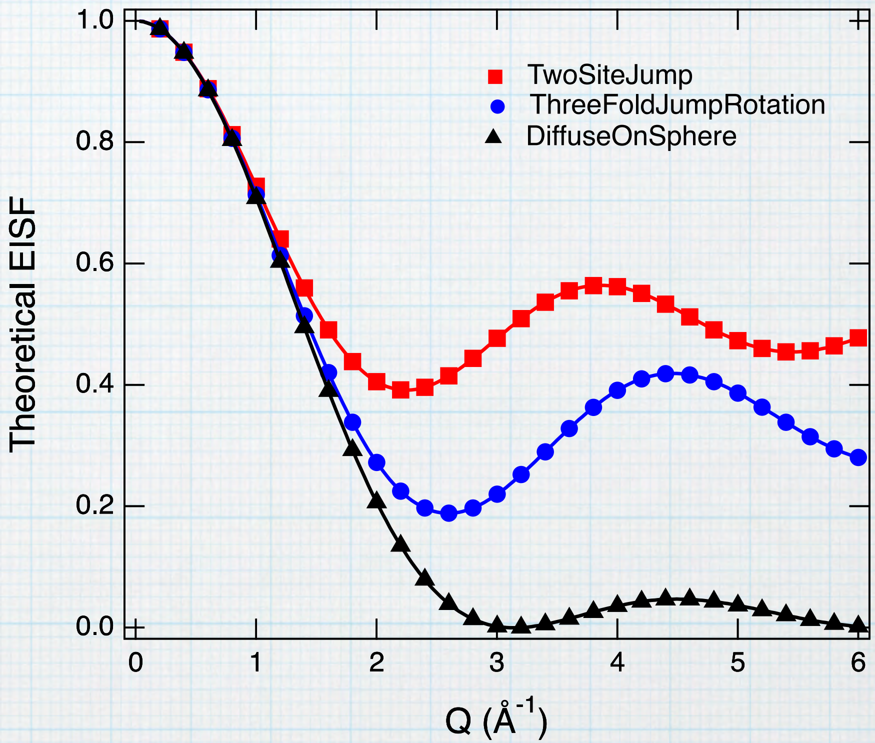
Diffusion on sphere

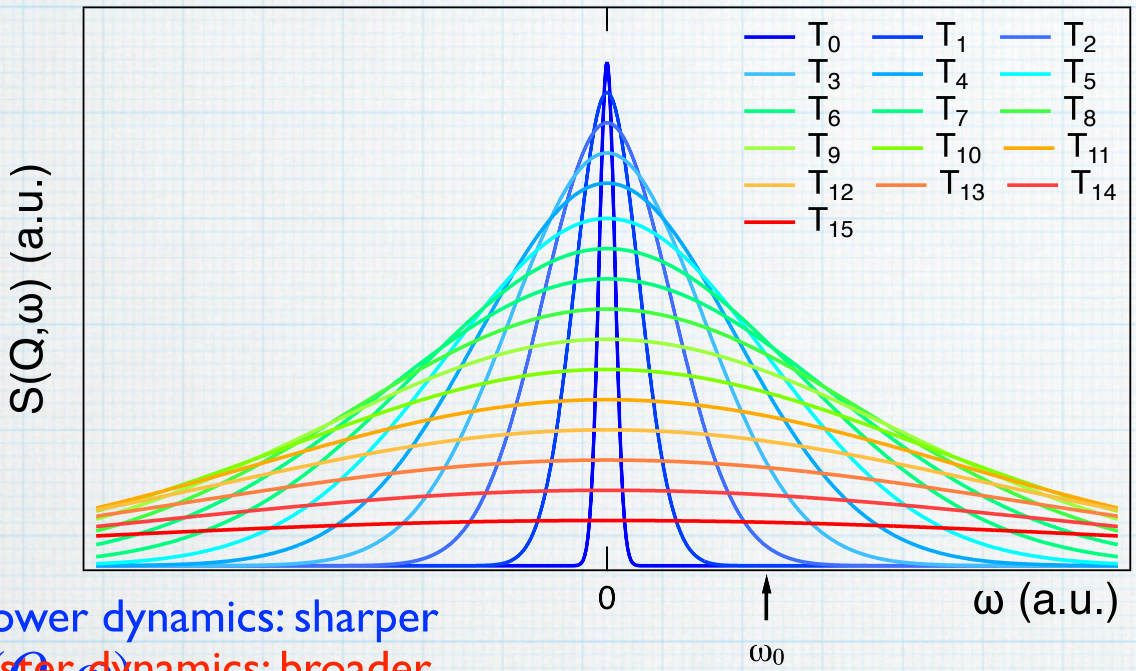


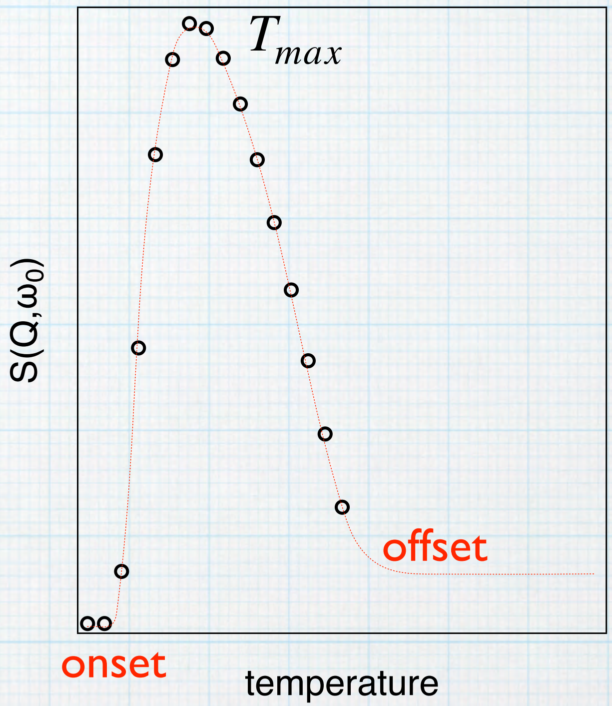
$$A_{0,spherical}(Q) = \left[j_0\left(Qr\right)\right]^2$$



Telling, *A Practical Guide to Quasi-elastic Neutron Scattering*, Royal Society of Chemistry (2020).

Inelasic Fixed Window Scan tells the range of inst. sensitivity

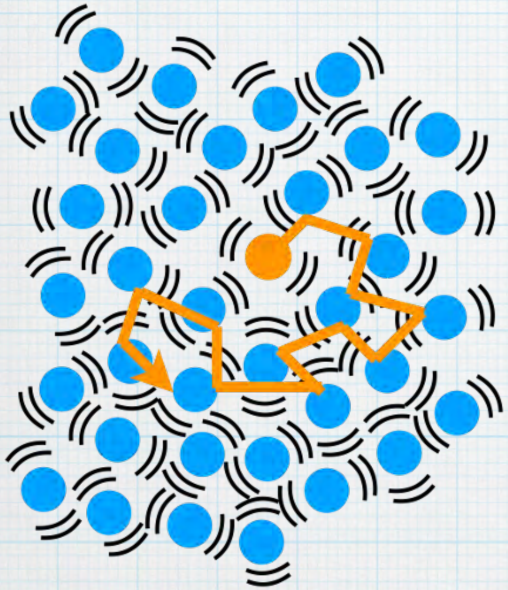




Slower dynamics: sharper $S(Q,\omega)$
Faster dynamics: broader $S(Q,\omega)$

- ✓ IFWS≈0 at lowest T: immobile
- ✓ IFWS=const at high T: dynamics too fast to capture with the instrument
- ✓ IFWS=max in-between: the time scale of the motion matches well with the instrumental resolution

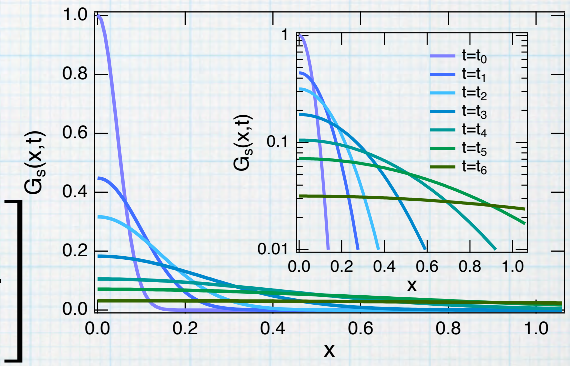
Translational diffusion



✓ MSD $\langle r^2 \rangle$ is calculated as the second moment of van Hove correlation function

$$\langle r^2 \rangle = \int_{\infty}^{\infty} r^2 G_s(r,t)dr = 6Dt$$

$$G_s(r,t) = \frac{1}{(2\pi)^{3/2}\sigma^3(t)} \exp\left[-\frac{r^2}{2\sigma^2(t)}\right]$$



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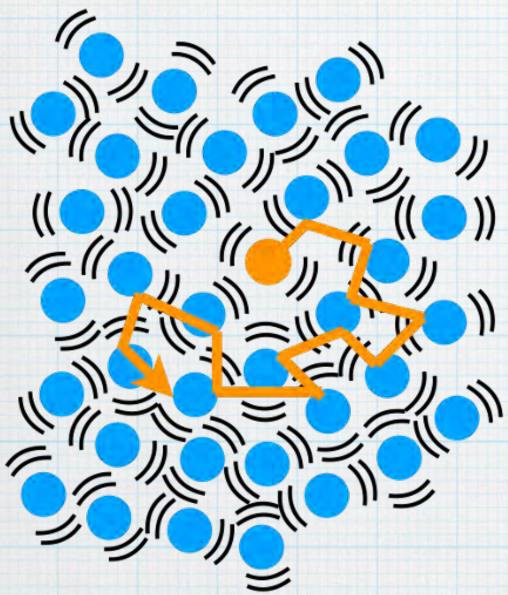

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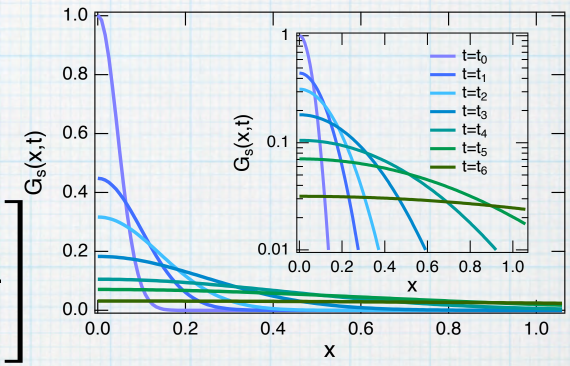

✓ A property of Gaussian functions connects MSD and $S(Q,t)$

$$\left\langle \exp\left[iQ\left\{r_i(t) - r_i(0)\right\}\right]\right\rangle = \exp\left[-\frac{Q^2}{6}\left\langle |r_i(t) - r_i(0)|^2 \right\rangle\right]$$

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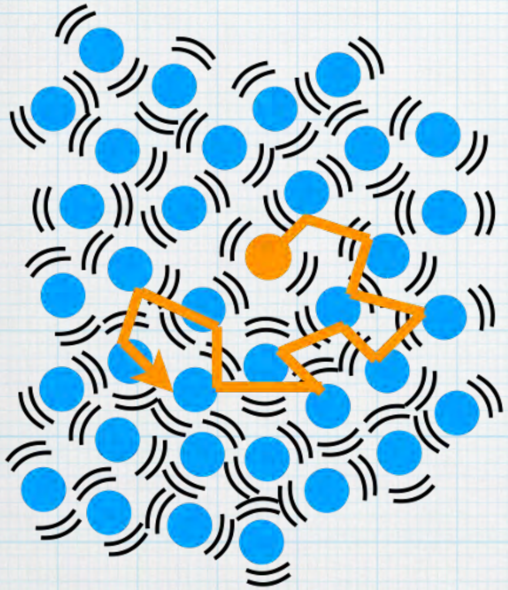

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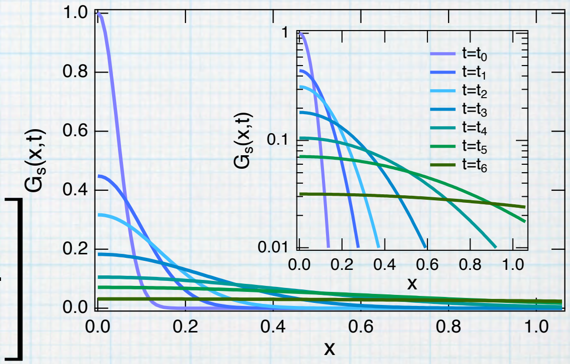

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$$S(Q,t) = \exp\left[-DQ^2t\right] \quad \longleftrightarrow \quad S_{inc}(Q,\omega) = \frac{A}{\pi}\frac{DQ^2}{\omega^2 + (DQ^2)^2}$$

FT in time

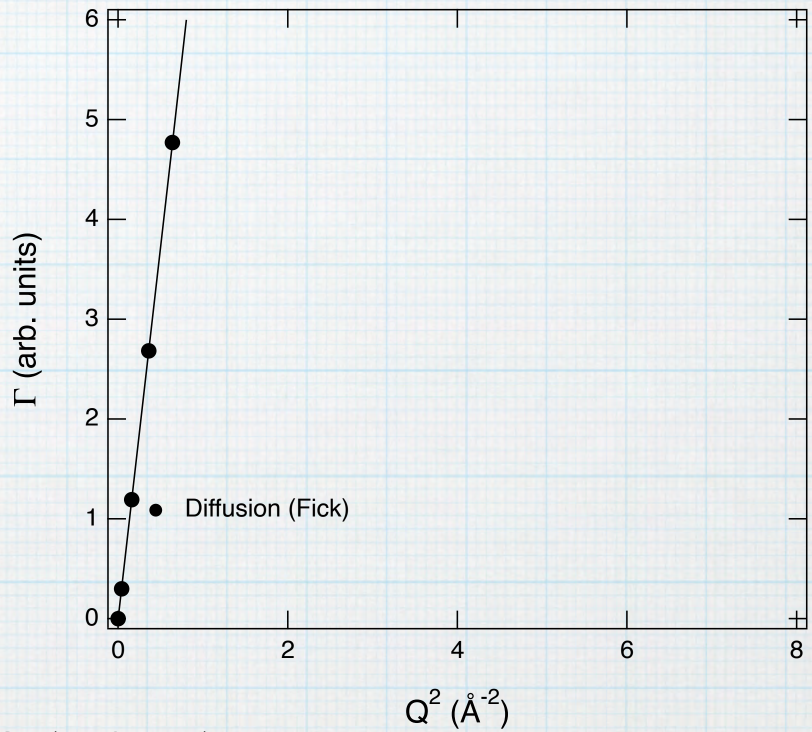
Nature of diffusion affects the QENS broadening

✓ When diffusing entity is geometrically constrained

$$S(Q,\omega) = \exp\left(-\frac{Q^2\langle u^2\rangle}{3}\right)\left[A_0(Q)\delta(\omega) + \frac{(1-A_0(Q))}{\pi}\frac{\Gamma}{\omega^2+\Gamma^2}\right]$$

Fick's law: D: diffusion constant,
$\langle l^2 \rangle$: mean squared displacement

$$\Gamma = DQ^2 = \frac{\langle l^2\rangle}{6}Q^2$$



Telling, *A Practical Guide to Quasi-elastic Neutron Scattering*, Royal Society of Chemistry (2020).

Nature of diffusion affects the QENS broadening

✓ When diffusing entity is geometrically constrained

$$S(Q,\omega) = \exp\left(-\frac{Q^2\langle u^2\rangle}{3}\right)\left[A_0(Q)\delta(\omega) + \frac{(1-A_0(Q))}{\pi}\frac{\Gamma}{\omega^2+\Gamma^2}\right]$$

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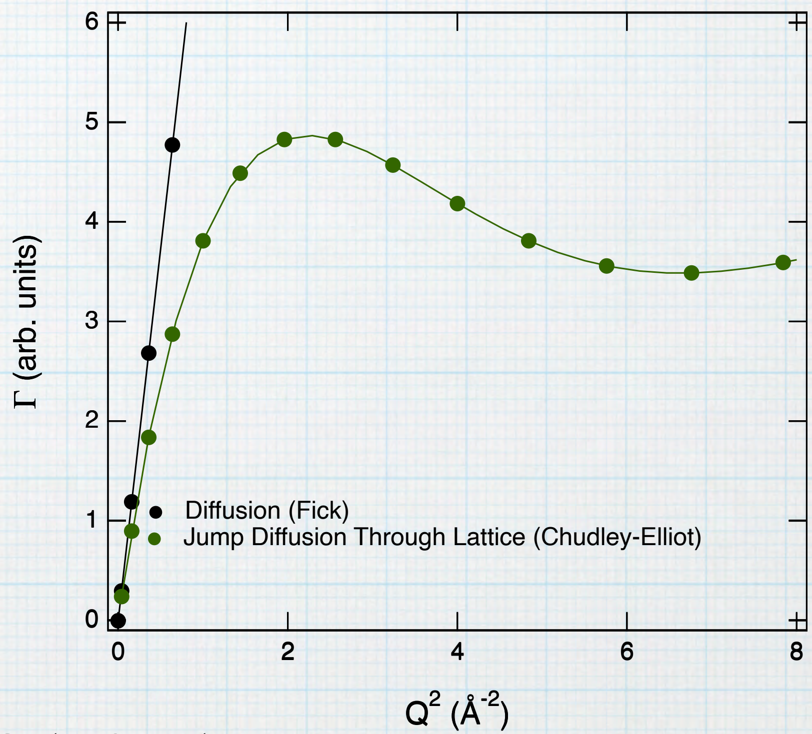
$$\Gamma = \frac{1}{\tau_0}\left[1 - \frac{\sin(Ql)}{Ql}\right]$$



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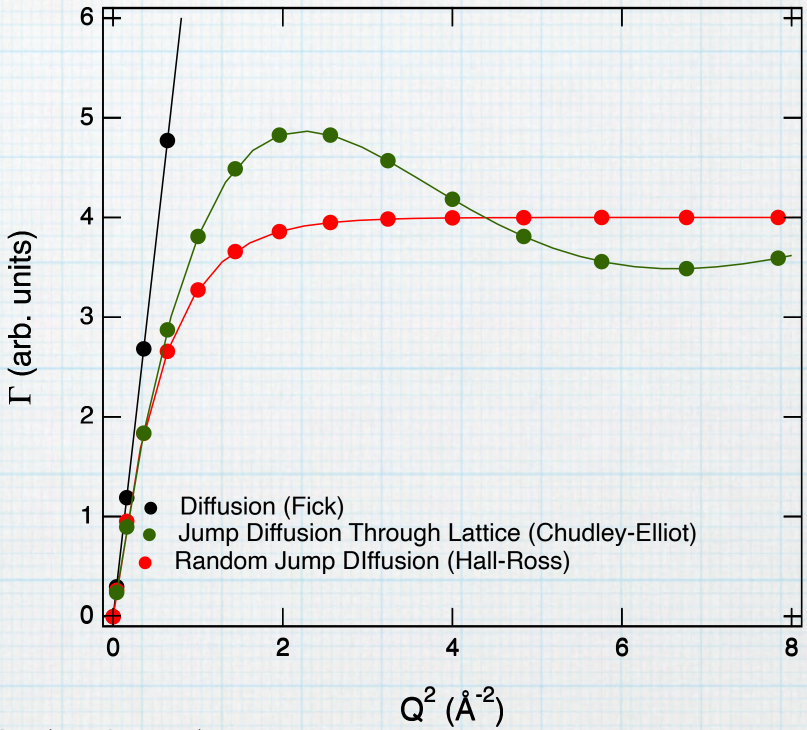

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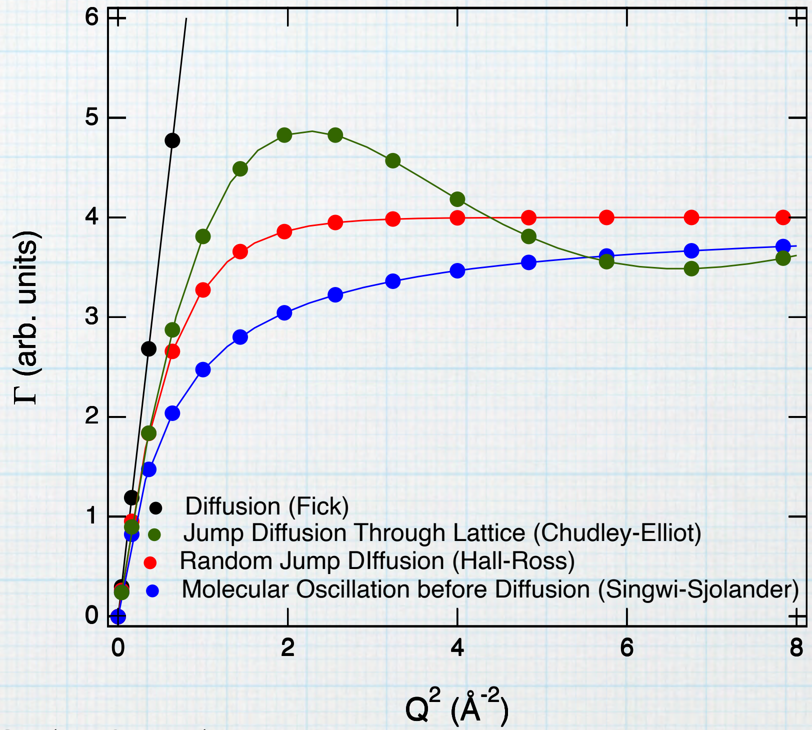
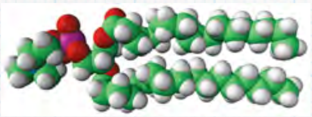
Singwi-Sjölander: molecule oscillates for a mean time τ_0 before continuous linear diffusive motion. $\langle R^2 \rangle$: mean square radius of the thermal cloud due to the oscillation, $\langle l^2 \rangle$: mean jump length

$$\Gamma = \frac{1}{\tau_0}\left[1 - \frac{\exp\left(-2DQ^2\tau_0\frac{\langle R^2\rangle}{\langle l^2\rangle}\right)}{1+DQ^2\tau_0}\right]$$



Telling, *A Practical Guide to Quasi-elastic Neutron Scattering*, Royal Society of Chemistry (2020).

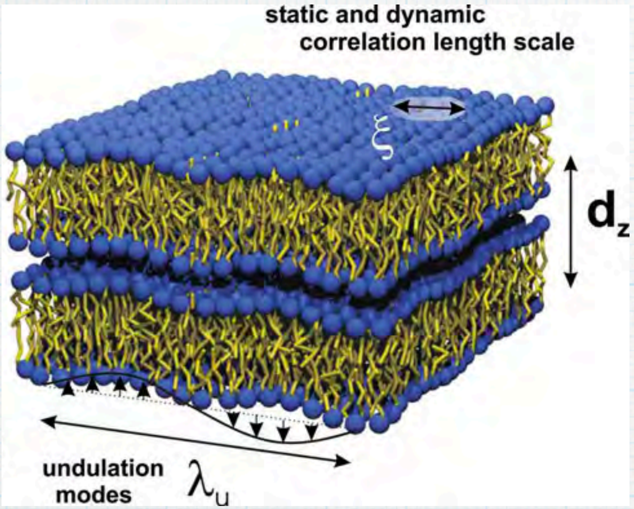
Lipid molecular movements

Lipid molecule 

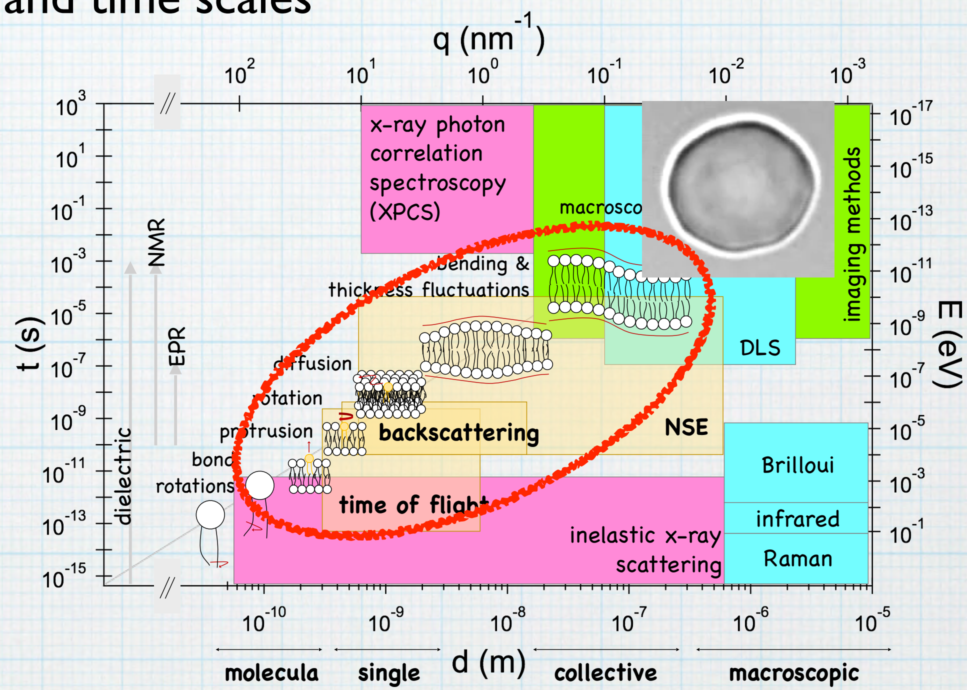
Hydrophilic Hydrophobic

✓ Lipid molecules are basic building block for cell membranes

✓ Lipid bilayers are dynamic entity in various length and time scales

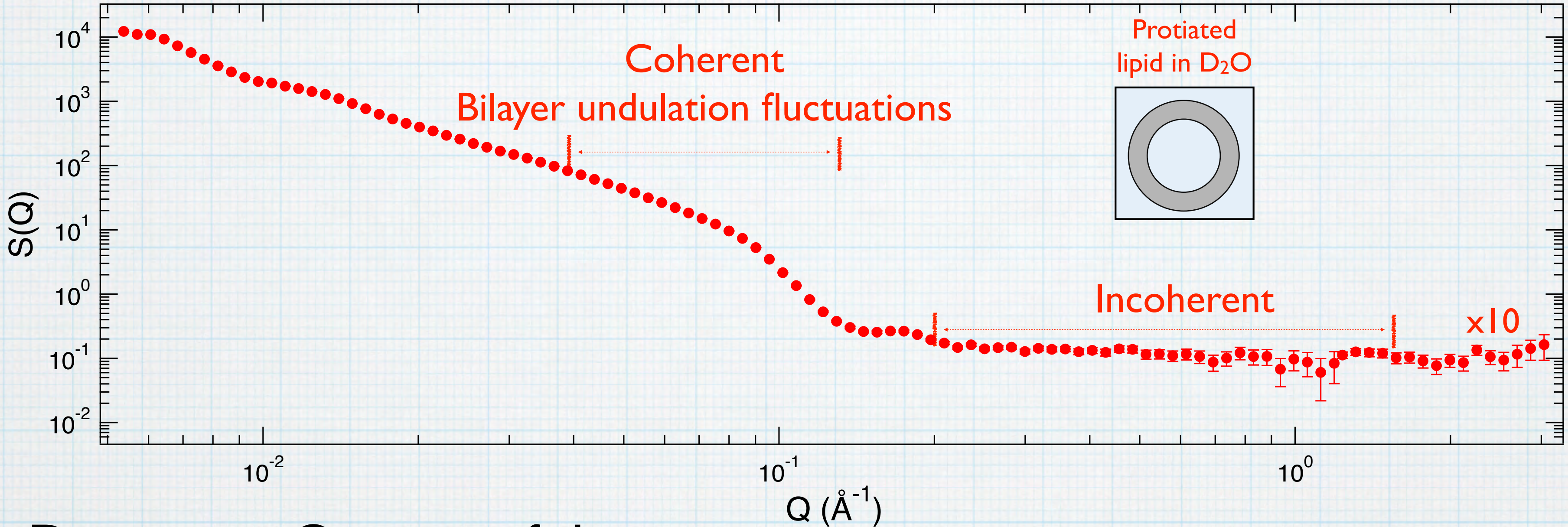


Rheinstädter, *Biointerphases* **3**, FB83 (2008).



Kelley, Butler, Nagao, *Characterization of Biological Membranes* **Chapter 4** (2019).

Static structure factor by TAIKAN



✓ Determine Q range of the interest

- Incoherent: molecular motion: self-dynamics of H
- Coherent: membrane motion at low-Q: undulation

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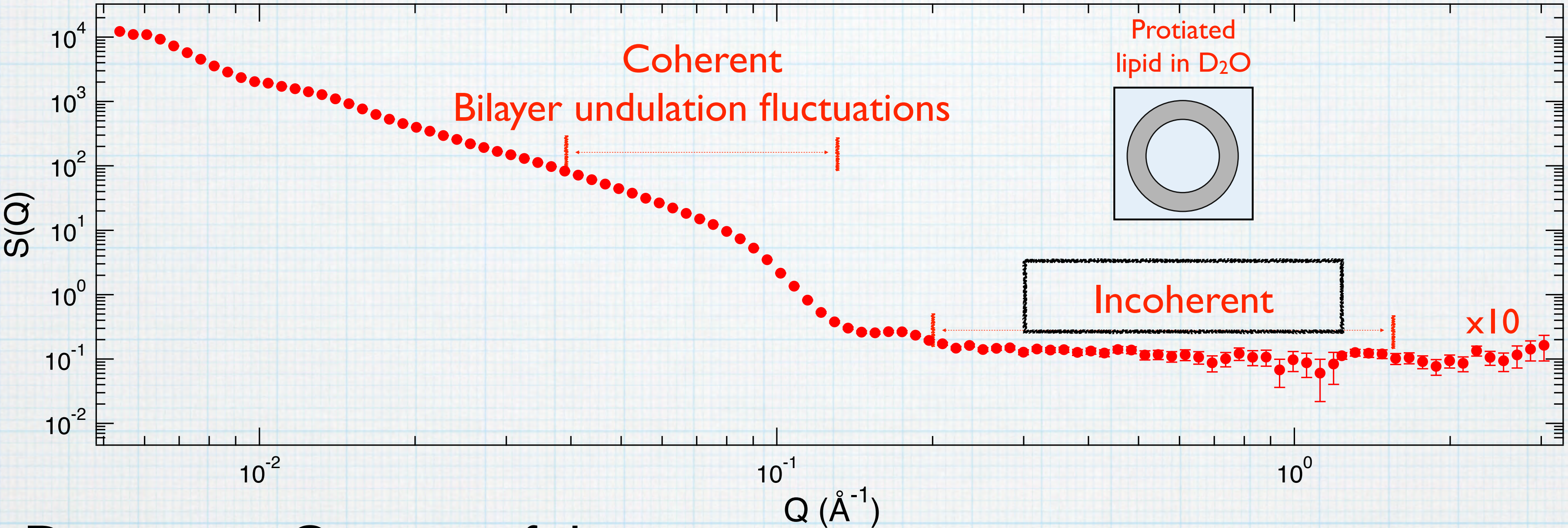

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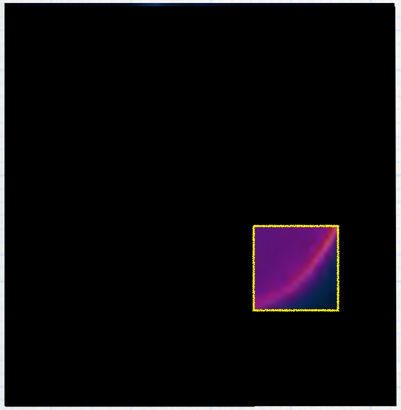
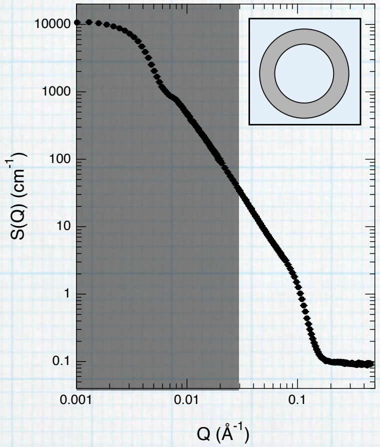
Collective membrane dynamics - undulation fluctuations

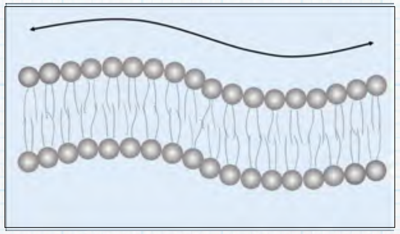
Flickering vesicle



https://www.youtube.com/watch?v=p1hXn-jurkE&feature=emb_title



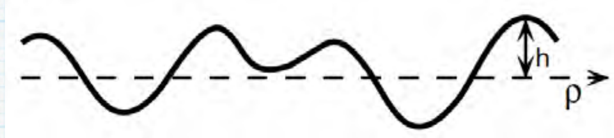
Protiated lipids in D_2O



Bending fluctuations

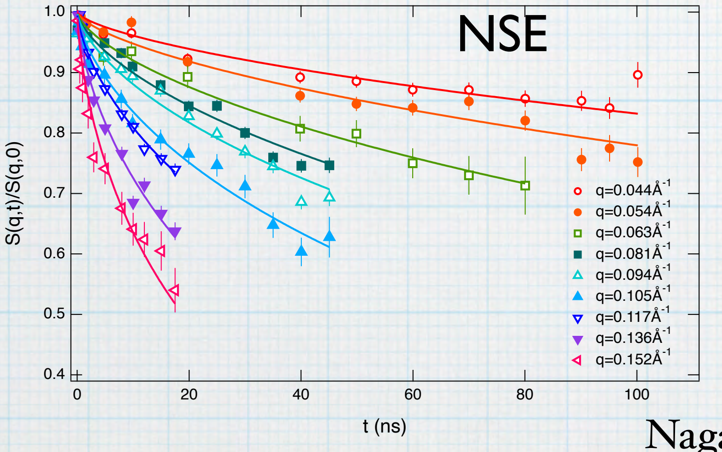
Bending modulus: κ

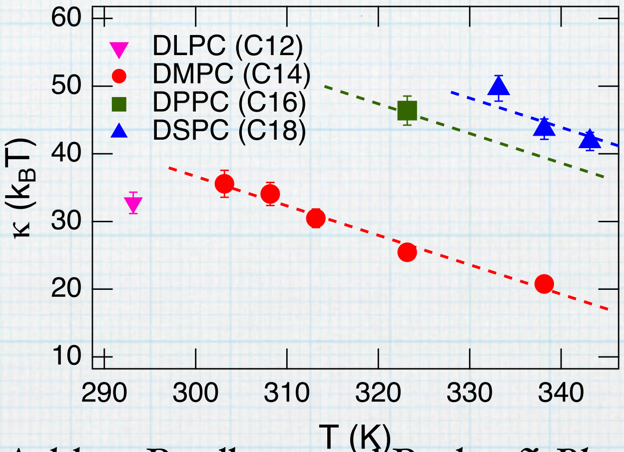
Zilman and Granek, *Phys. Rev. Lett.* **77**, 4788 (1996).; Watson and Brown, *Biophys. J.* **98**, L09 (2010).



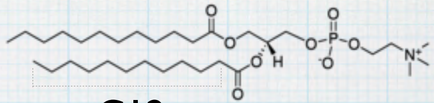
$$\frac{S(Q,t)}{S(Q,0)} = \exp\left[-(\Gamma t)^{2/3}\right]$$

$$\Gamma = 0.025\gamma\sqrt{\frac{k_BT}{\kappa_{eff}}}\frac{k_BT}{\eta}Q^3$$





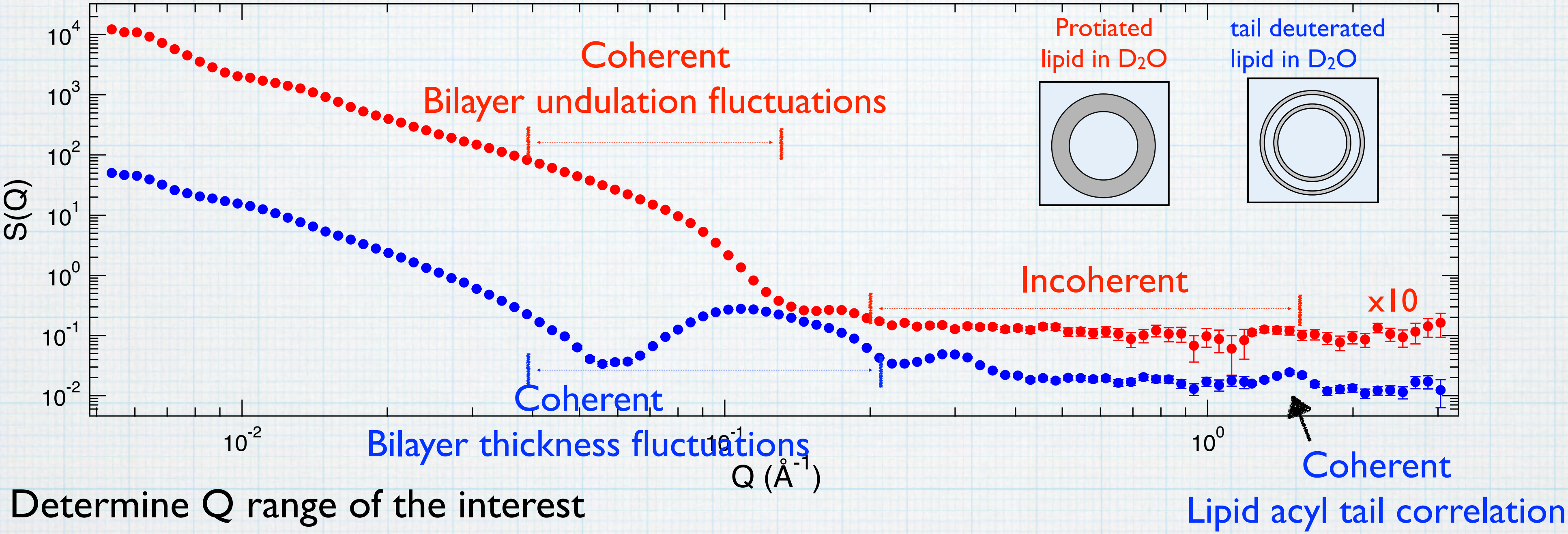
DLPC



C12

Nagao, Kelley, Ashkar, Bradbury and Butler, *J. Phys. Chem. Lett.* **8**, 4679 (2017).

Static structure factor by TAIKAN



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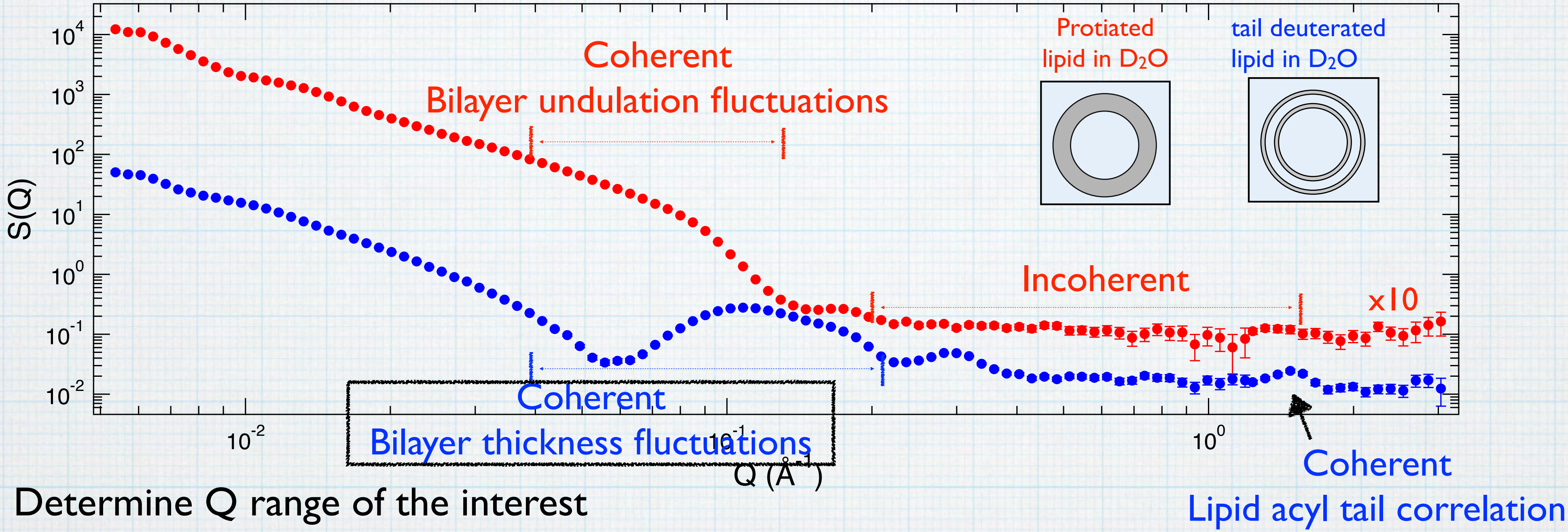

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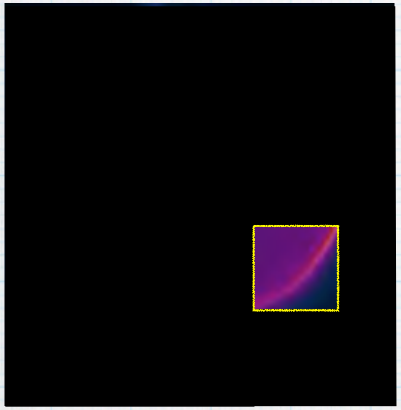

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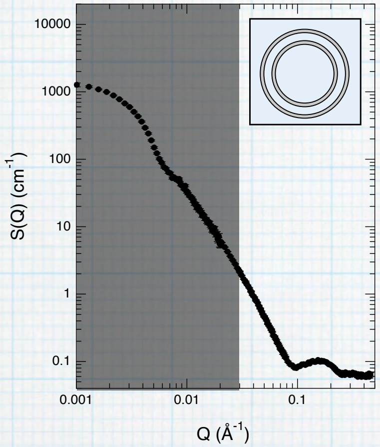
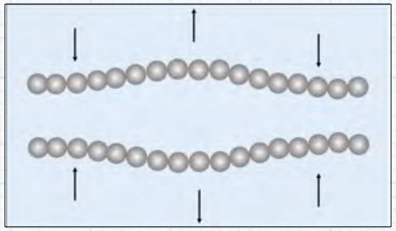


Tail-deuterated lipids in D_2O



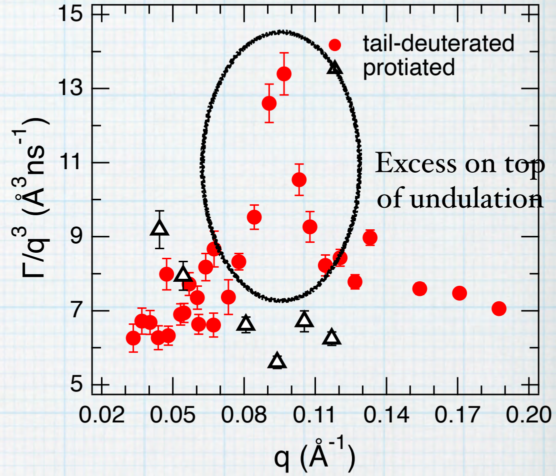
Thickness fluctuations

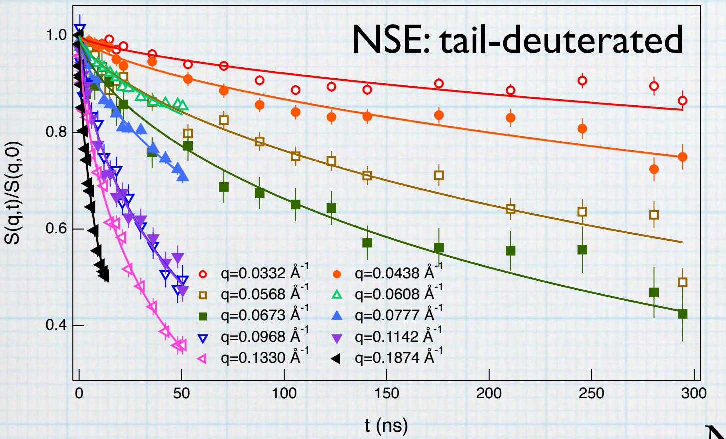
Compressibility modulus: K_A

Membrane viscosity: η_m

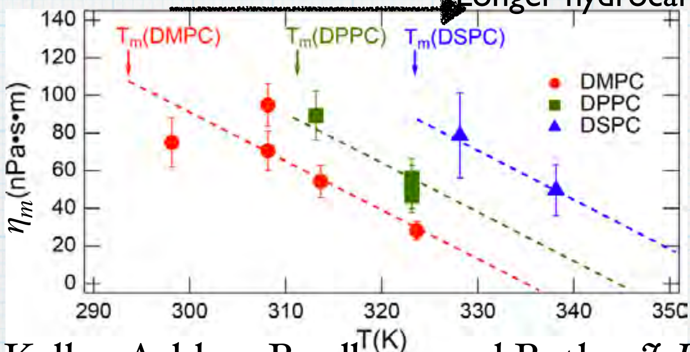
Relaxation time: $\tau_{TF} = \dfrac{\eta_m}{K_A}$

Bingham, Smye and Olmsted, *Europhys. Lett.* **111**, 18004 (2015).





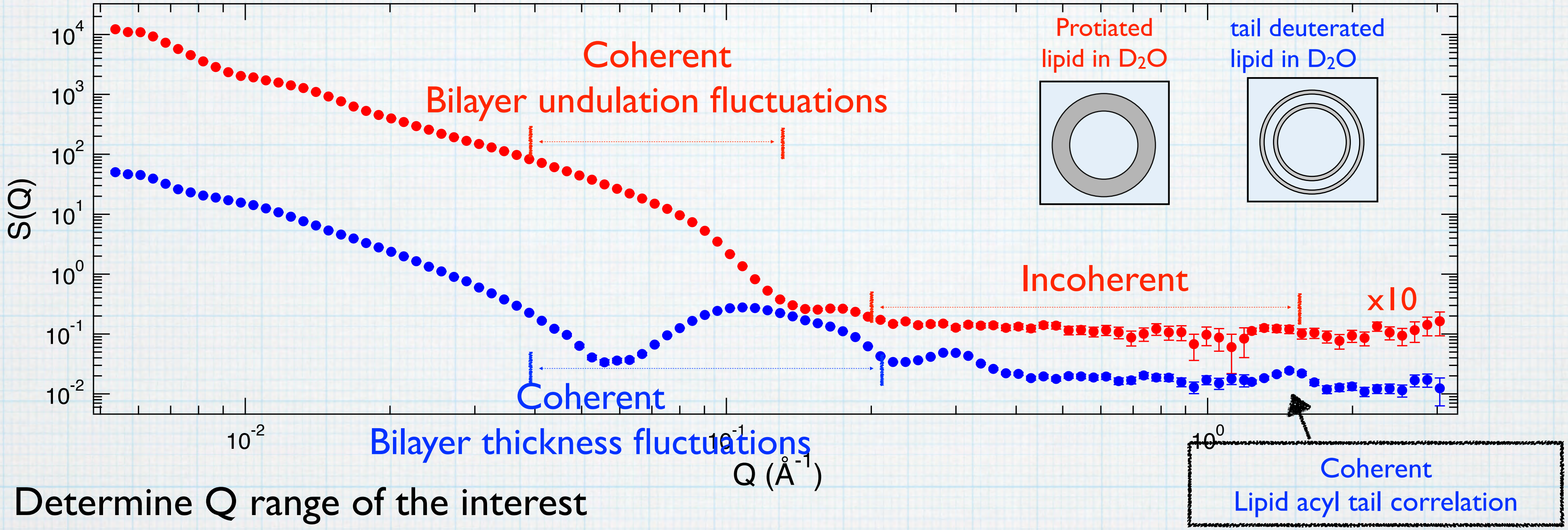
Longer hydrocarbon chains



QENS accesses elastic and viscous properties of amphiphilic membranes

Nagao, Kelley, Ashkar, Bradbury and Butler, *J. Phys. Chem. Lett.* **8**, 4679 (2017).

Static structure factor by TAIKAN



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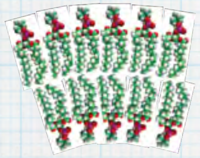
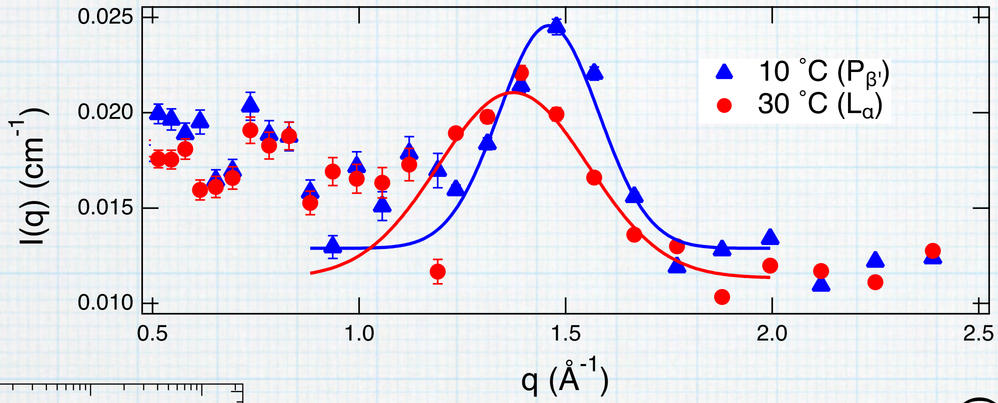
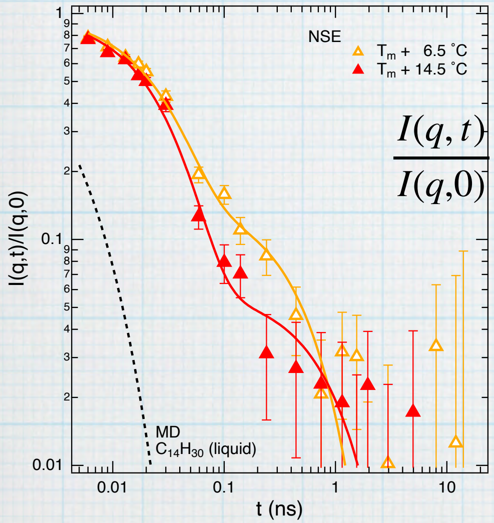
Structural relaxation at structure factor peak in lipid bilayer

Tail-deuterated DMPC

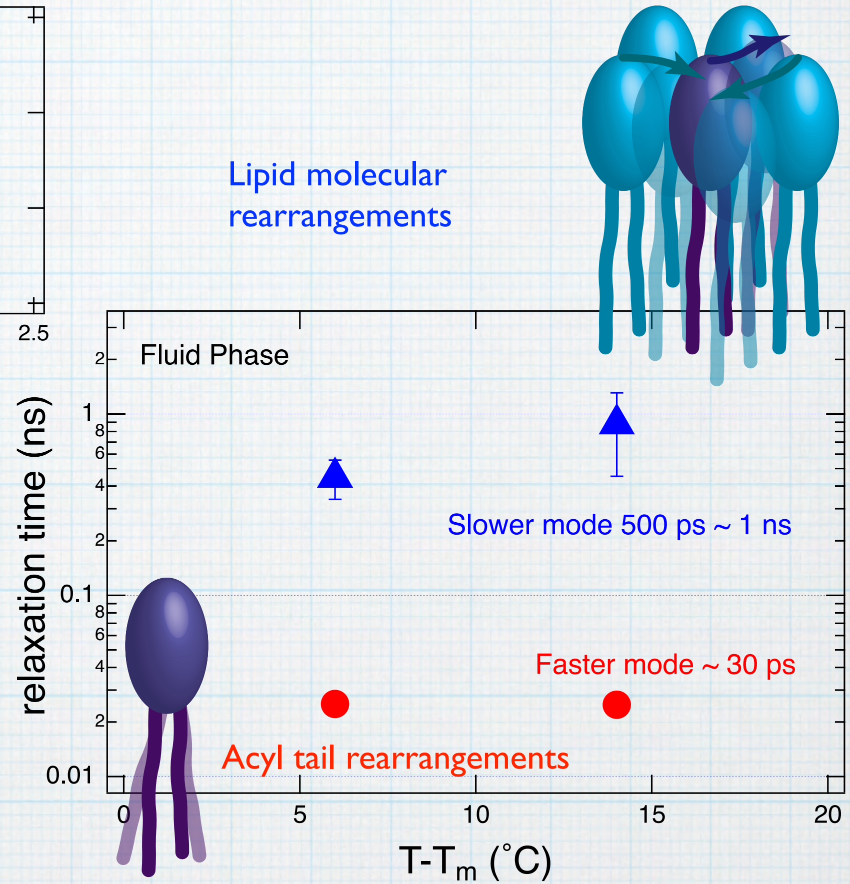


Acyl tail correlation peak





$$\frac{I(q,t)}{I(q,0)} = A\exp\left(-\frac{t}{\tau_f}\right) + (1-A)\exp\left(-\frac{t}{\tau_s}\right)$$



Nagao *et al.*, *Phys. Rev. Lett.* **127**, 078102 (2021). "Relationship between Viscosity and Acyl Tail Dynamics in Lipid Bilayers"

Summary

- ✓ Neutron scattering measures FT of van Hove space-time correlation function; thus provides space-time correlation of a couple of atoms
- ✓ QENS is a technique to measure (mainly) relaxation of atoms and molecules
- ✓ QENS measures time scale of relaxation as well as the geometrical constraints
- ✓ Incoherent scattering provides information of single particle dynamics
- ✓ Coherent scattering provides information of relative positions and motions of particles
- ✓ Depending on the target processes (length and time scales) a proper QENS machine (direct/indirect geometry and NSE) needs to be selected
- ✓ QENS techniques can serve to access paradigm of structure-dynamics-function relationship

Further readings

- ✓ T. Springer, "Quasi-elastic neutron scattering for the diffusive motions in solids and liquids", Springer Tracts in Modern Physics 64, 197, Springer Verlag (1972).
- ✓ M. Bée, "Quasielastic Neutron Scattering - Principles and Applications in Solid State Chemistry, Biology and Materials Science", Adam Hilger, Bristol and Philadelphia (1988).
- ✓ R. Hempelmann, "Quasi-elastic neutron scattering and solid state diffusion", Oxford Series on Neutron Scattering in Condensed Matter 13, Clarendon Press, Oxford (2000).
- ✓ M. T. F. Telling, "A Practical Guide to Quasi-elastic Neutron Scattering", Royal Society of Chemistry (2020).