Neutrons scattering on the nonequilibrium statistical medium and generalized Van Hove's formula

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A. L. KUZEMSKY

ABSTRACT

In this report we will present a direct statistical-mechanical method for calculating the differential cross section of the slow neutron scattering on nonequilibrium statistical medium.

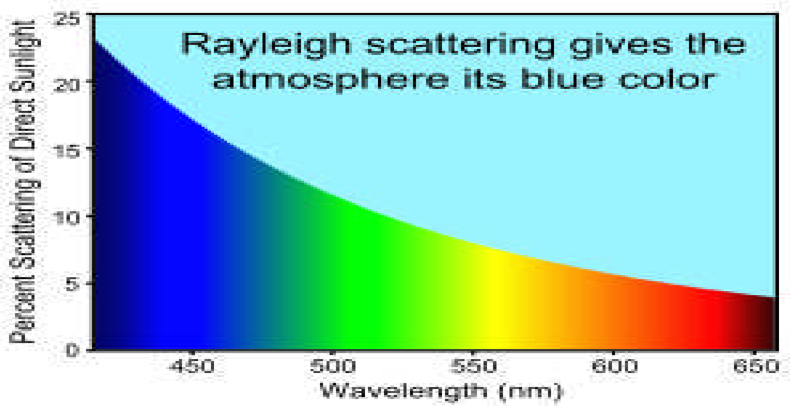
Our aim was to deduce the time-dependent generalization of the familiar Van Hove formula, to indicate its utility from the standpoint of nonequilibrium statistical mechanics, and to establish its role in scattering processes for the nonequilibrium systems. A combination of the scattering theory and the Zubarev's method of the nonequilibrium statistical operator leads to a compact and workable formalism which gives a generalization of the Van Hove approach.

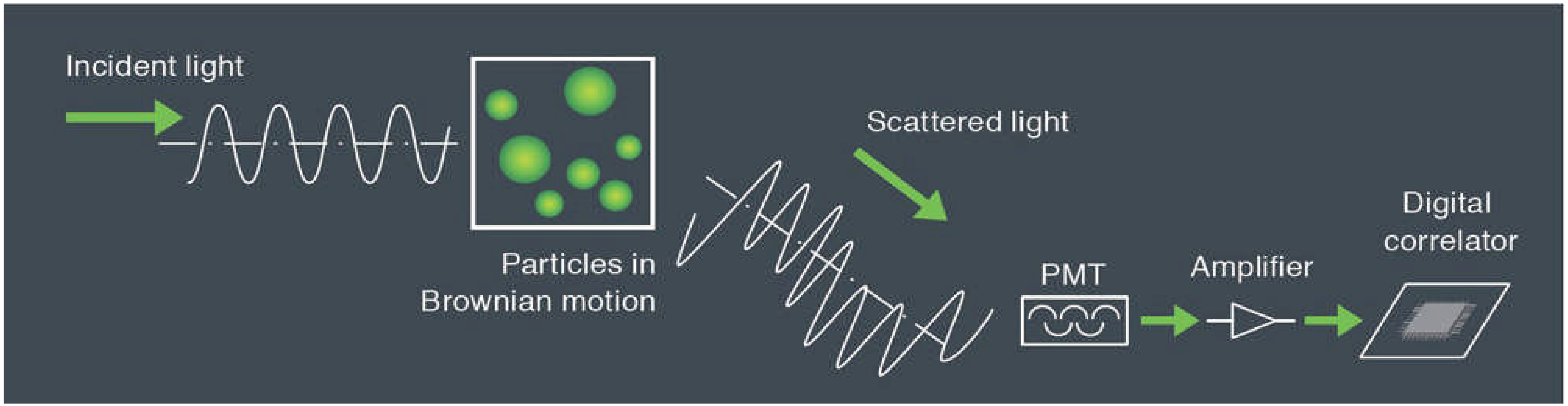
The generalized scattering function contains an essential additional factor connected to the entropy production.

This new derivation clarifies conceptually the physics of irreversibility and entropy generation in transport phenomena.

We believe that this approach will be of use as a practical tool when makiing analysis for various concrete complex nonequilibrium systems

Microscopic descriptions of condensed matter dynamical behavior use the notion of correlations over space and time
Correlations over space and time in the density fluctuations of a fluid are responsible for the scattering of light when light passes through the fluid.
Light scattering from gases in equilibrium was originally studied by Rayleigh and later by Einstein, who derived a formula for the intensity of the light scattering.





The relation between the cross-sections for scattering of slow neutrons by an assembly of nuclei and space-time correlation functions for the motion of the scattering system has been given by Van Hove. The concept of time-dependent correlations has been used widely in connection with particle scattering by solids and fluids.
A fundamental formula for the differential scattering cross section of a slow neutron in the Born approximation was deduced by Van Hove. He derived a compact formula, and related the differential scattering cross section to a space-time pair correlation function.
As was shown by Van Hove in his seminal paper, the Born approximation scattering cross section can be expressed in terms of the four-dimensional Fourier transform of a pair distribution function depending on a space vector and a time variable. The formula obtained by Van Hove provided a convenient method of analyzing the properties of slow neutron scattering by systems of particles, of light scattering by media, etc.
The advantage of using the Van Hove formula for analysis of scattering data is its compact form and intuitively clear physical meaning (see: W. Marshall and S. W. Lovesey, Theory of Thermal Neutron Scattering. (Oxford University Press, Oxford, 1971).

Leon Van Hove (1924 - 1990)

From 1949 to 1954 LEON VAN HOVE worked at the Princeton Institute for Advanced Study by virtue of his meeting with Robert Oppenheimer.
At Princeton LEON VAN HOVE met G. Placzek, who was working on the theory of neutron scattering.
working on the theory of neutron scattering. He started to work in this field and published a few important papers on the subject. Three of them are:
G. Placzek and L. Van Hove, Crystal Dynamics and Inelastic Scattering of Neutrons,Phys. Rev. 93 (1954) 1207;
L. Van Hove, Correlations in Space and Time and Born Approximation Scattering in Systems of Interacting Particles,Phys. Rev. 95 (1954) 249;
This paper was cited more than 2000 times.
L. Van Hove, Time-Dependent Correlations between Spins and Neutron Scattering in Ferromagnetic Crystals,Phys. Rev. 95 (1954) 1374;
It has ever since served as the foundation of the entire field.

VAN HOVE'S PAPER PRESENTED A CENTRAL QUANTITY IN THE STUDY OF FLUCTUATIONS, THE DENSITY-DENSITY SPACETIME CORRELATION THAT HAS COME TO BE KNOWN AS THE VAN HOVE FUNCTION.

Here Van Hove offers:

"a natural time-dependent generalization for the well-known pair distribution function g(r) of systems of interacting particles. The pair distribution in space and time thus defined, denoted by G(r,t), gives rise to a very simple and entirely general expression for the angular and energy distribution of [the] Born approximation scattering by the system" (Van Hove). Van Hove's paper was considered seminal. Another way of stating this is to say that the Van Hove formula provides the relation between the cross-sections "for scattering of slow neutrons by an assembly of nuclei and space-time correlation functions for the motion of the scattering system. His papers shows that the Born approximation scattering cross section can be expressed in terms of the four-dimensional Fourier transform of a pair distribution function depending on a space vector and a time variable. The formula by Van Hove provided a convenient method of analyzing the properties of slow neutron scattering by systems of particles, of light scattering by media, etc. The advantage of using it for analysis of scattering data is its compact form and intuitively clear physical meaning".

The nonequilibrium statistical medium

Although there have have been many light and neutron scattering investigations of complex statistical systems during last decades, it is true to say that until recently the properties and implications of the particle scattering by the nonequilibrium statistical medium were not yet understood fully.

There was not a fully satisfactory theoretical formalism of the interpretation of the light or thermal neutron scattering experiments for a system in the nonequilibrium state.

Fermi Golden Rule

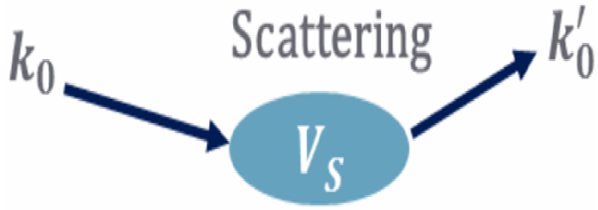
- **Treat beta decay as transition that depends upon strength of coupling between the initial and final states**
- **Decay constant given by Fermi's Golden Rule**

$$\lambda_\beta = \frac{2\pi}{\hbar}|M|^2 \rho(E_o); M = \int \psi_f V \psi_i dv$$

  - **matrix element couples initial and final states**
  - **phase space factor which describes volume of phase space available for the outgoing leptons**
    - → **Electron is charged lepton**
      - * **electron, muon, and tau**
    - → **Neutral lepton is neutrino**
  - **Small system perturbation**
    - → **Contained within M**
- **E is Q value**
- **Rate proportional to strength of coupling between initial and final states factored by the density of final states available to system**

FERMI Golden Rule

$$w_{fi} = \frac{2\pi}{\hbar} |\langle \Psi_f^N | H_{int} | \Psi_i^N \rangle|^2 \delta(E_f^N - E_i^N - h\nu)$$



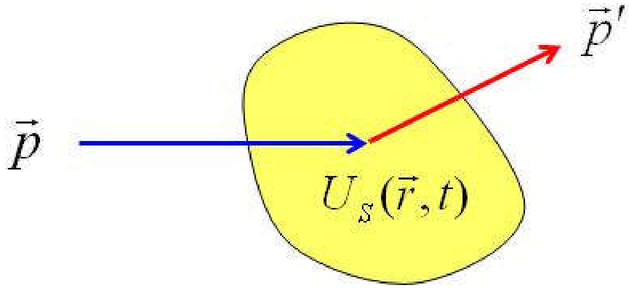
Wavefunction for final state

Wavefunction for initial state

$$M_{if} = \int \Psi_f^* V \Psi_i \, dv$$

Operator for the physical interaction which couples the initial and final states of the system.

Fermi's Golden Rule



$$S(\vec{p},\vec{p}\,') = \frac{2\pi}{\hbar}\left|H_{p'p}\right|^2 \delta(E' - E - \Delta E)$$

$$H_{\vec{p}',\vec{p}} = \int_{-\infty}^{+\infty} \psi_f^* U_S(\vec{r})\psi_i d\vec{r}$$

$$E' = E_0 + \Delta E$$

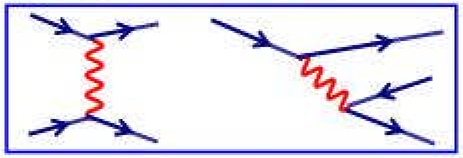
$\Delta E = 0$ for a static U_S

$\Delta E = \pm\,\hbar\omega$ for an oscillating U_S

$$\frac{1}{\tau(\vec{p})} = \sum_{\vec{p}'\uparrow} S(\vec{p},\vec{p}\,') \propto D_f(E)$$

For an electron with energy, *E*, its scattering rate is (often) proportional to the density of final states at energy, *E* (1D, 2D, 3D). Electrostatic interactions (II, POP), however, prefer small angle scattering.

Cross Sections and Decay Rates



- In particle physics we are mainly concerned with particle interactions and decays, i.e. transitions between states
  - these are the experimental observables of particle physics
- Calculate transition rates from Fermi's Golden Rule

$$\Gamma_{fi} = 2\pi |T_{fi}|^2 \rho(E_f)$$

Γ_{fi} is number of transitions per unit time from initial state $|i\rangle$ to final state $\langle f|$ – not Lorentz Invariant !

T_{fi} is Transition Matrix Element

$$T_{fi} = \langle f|\hat{H}|i\rangle + \sum_{j\neq i} \frac{\langle f|\hat{H}|j\rangle\langle j|\hat{H}|i\rangle}{E_i - E_j} + \ldots$$

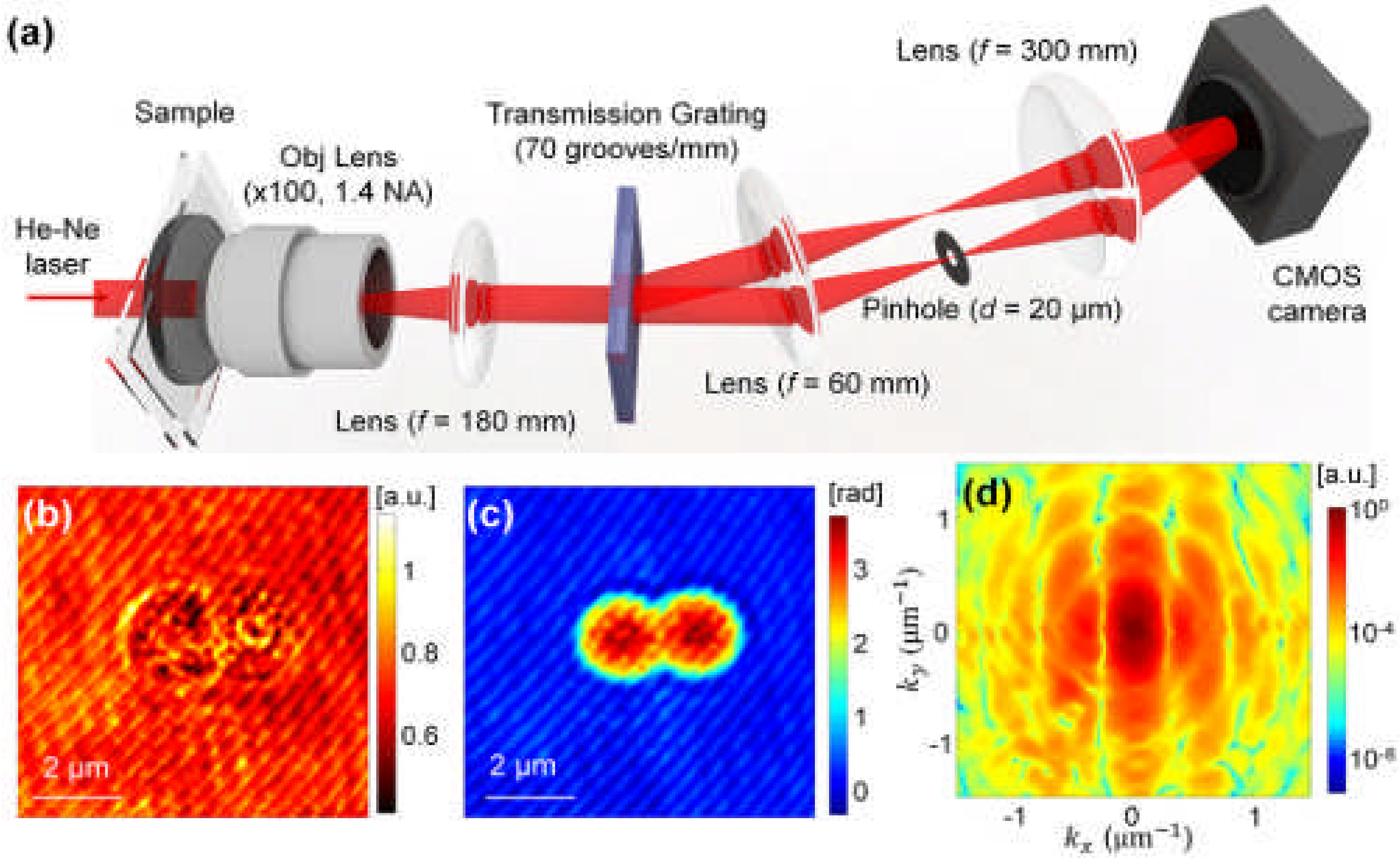
$\hat{H}$ is the perturbing Hamiltonian

$\rho(E_f)$ is density of final states

★ Rates depend on MATRIX ELEMENT and DENSITY OF STATES

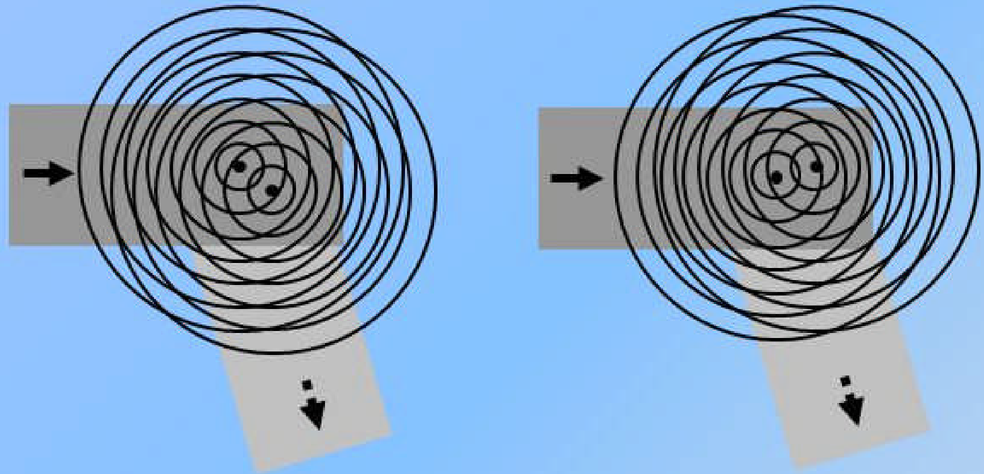
the ME contains the fundamental particle physics

just kinematics


(a)
Sample
Obj Lens
(x100, 1.4 NA)
He-Ne
laser
Transmission Grating
(70 grooves/mm)
Lens (f = 300 mm)
CMOS
camera
Pinhole (d = 20 μm)
Lens (f = 60 mm)
Lens (f = 180 mm)
(b)
[a.u.]
1
0.8
0.6
2 μm
(c)
[rad]
3
2
1
0
2 μm
(d)
[a.u.]
10^0
10^{-4}
10^{-8}
k_y (μm^{-1})
k_x (μm^{-1})
1
0
-1

1.3. Dynamic Light Scattering

Brownian motion of the solute particles leads to fluctuations of the scattered intensity



change of particle position with time is expressed by van Hove selfcorrelation function, DLS-signal is the corresponding Fourier transform (dynamic structure factor)

$$G_s(\vec{r},\tau) = < n(\vec{0},t) n(\vec{r},t+\tau) >_{V,T} \quad \Leftrightarrow \quad F_s(\vec{q},\tau) = \int G_s(\vec{r},\tau) \exp(i\vec{q}\vec{r}) d\vec{r}$$

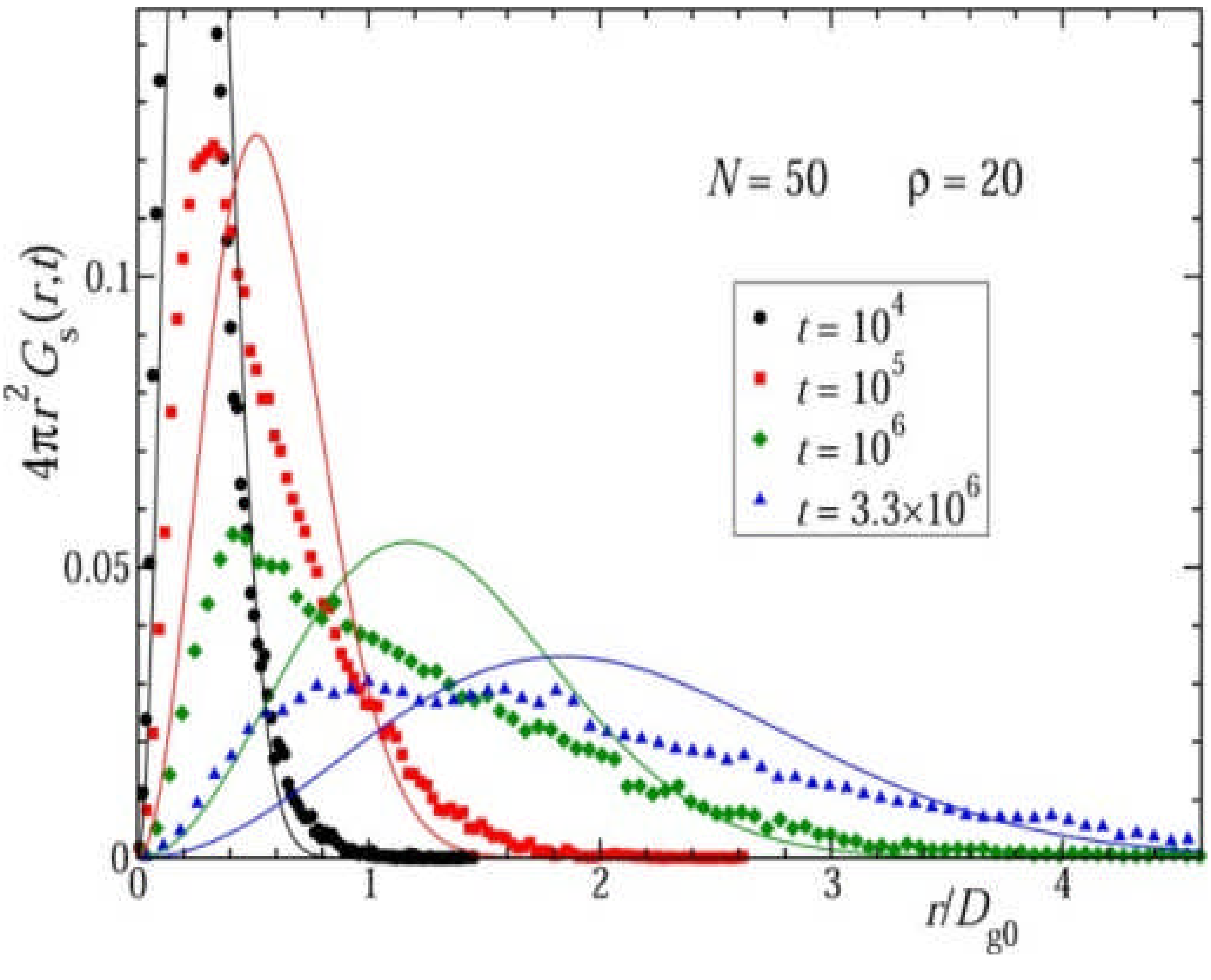
isotropic diffusive particle motion $G_s(r,\tau) = [2\pi/3 < \Delta R(\tau)^2 >]^{3/2} \exp(-\frac{3r(\tau)^2}{2 < \Delta R(\tau)^2 >})$

mean-squared displacement of the scattering particle:

$$\left\langle \Delta R(\tau)^2 \right\rangle = 6 D_s \tau$$

$$D_s = \frac{kT}{f} = \frac{kT}{6\pi\eta R_H}$$

Stokes-Einstein,
Fluctuation - Dissipation



$4\pi r^2 G_s(r,t)$
0.1
0.05
0
0
1
2
3
4
r/D_{g0}
$N = 50$ $\rho = 20$
$t = 10^4$
$t = 10^5$
$t = 10^6$
$t = 3.3\times10^6$

The dynamical properties of a system

- **The dynamical properties of a system of interacting particles are all contained in the response of the system to external perturbations. The basic quantities are then the dynamical susceptibilities, which in the general case describe the response of the system to external perturbations that vary in both space and time.**

- **For simple liquids the two basic susceptibilities describe the motion of single particles and their relative motions. The fluctuating properties are conveniently described in terms of time-dependent correlation functions formed from the basic dynamical variables, e.g. the particle number density. The fluctuation-dissipation theorem, shows that the susceptibilities can be expressed in terms of the fluctuating properties of the system in equilibrium.**

Correlation functions in the frequency domain

- Many experimental techniques do not give information in the time domain but only in the frequency domain (spectroscopy)

$\Rightarrow$ what one measures is $\phi'(\omega)$ and $\phi''(\omega)$, the real and imaginary part of the time-Fourier transform of a time correlation function $\phi(t)$

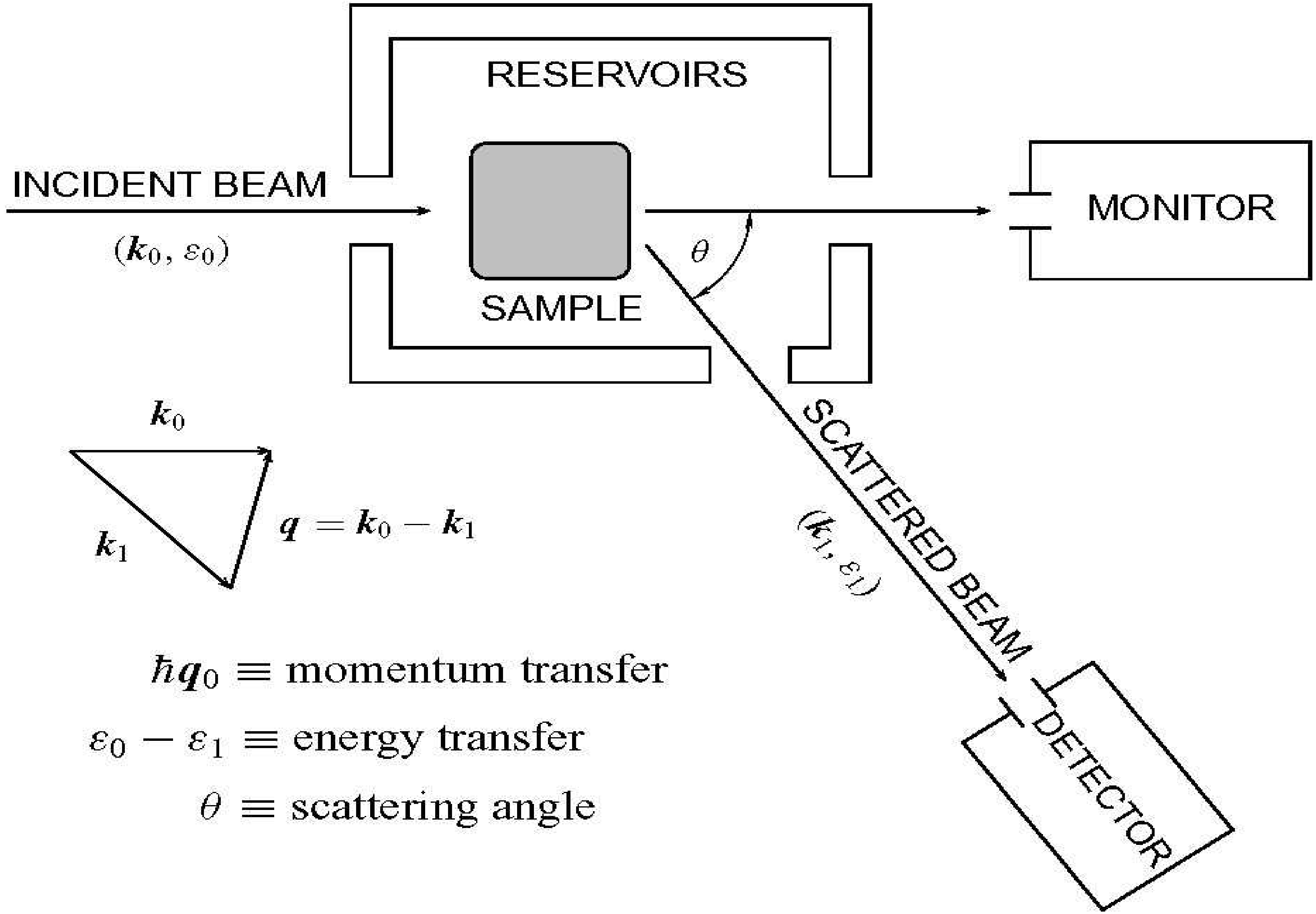
or

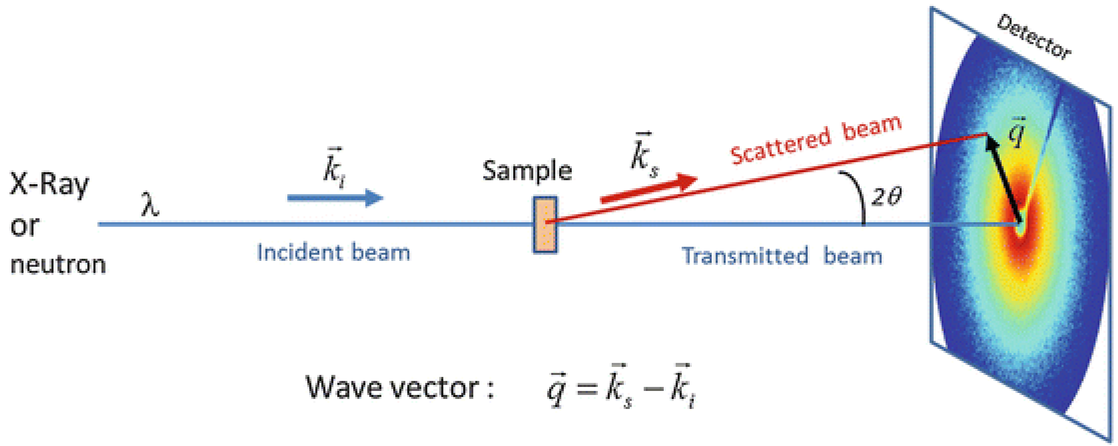
$\chi'(\omega)$ and $\chi''(\omega)$, the real and imaginary part of the dynamic susceptibility

- Fluctuation – Dissipation-Theorem: Important connection between $\phi''(\omega)$ and $\chi''(\omega)$:

$$\chi''(\omega) = \omega\, \phi''(\omega) / (k_B T)$$

NB: The FDT is valid only in thermal equilibrium! In out of equilibrium situations (e.g. in a glass) one can measure $\chi''(\omega)$ and $\phi''(\omega)$ in order to define an “effective temperature” of the system (see talks by Kurchan and Franz)

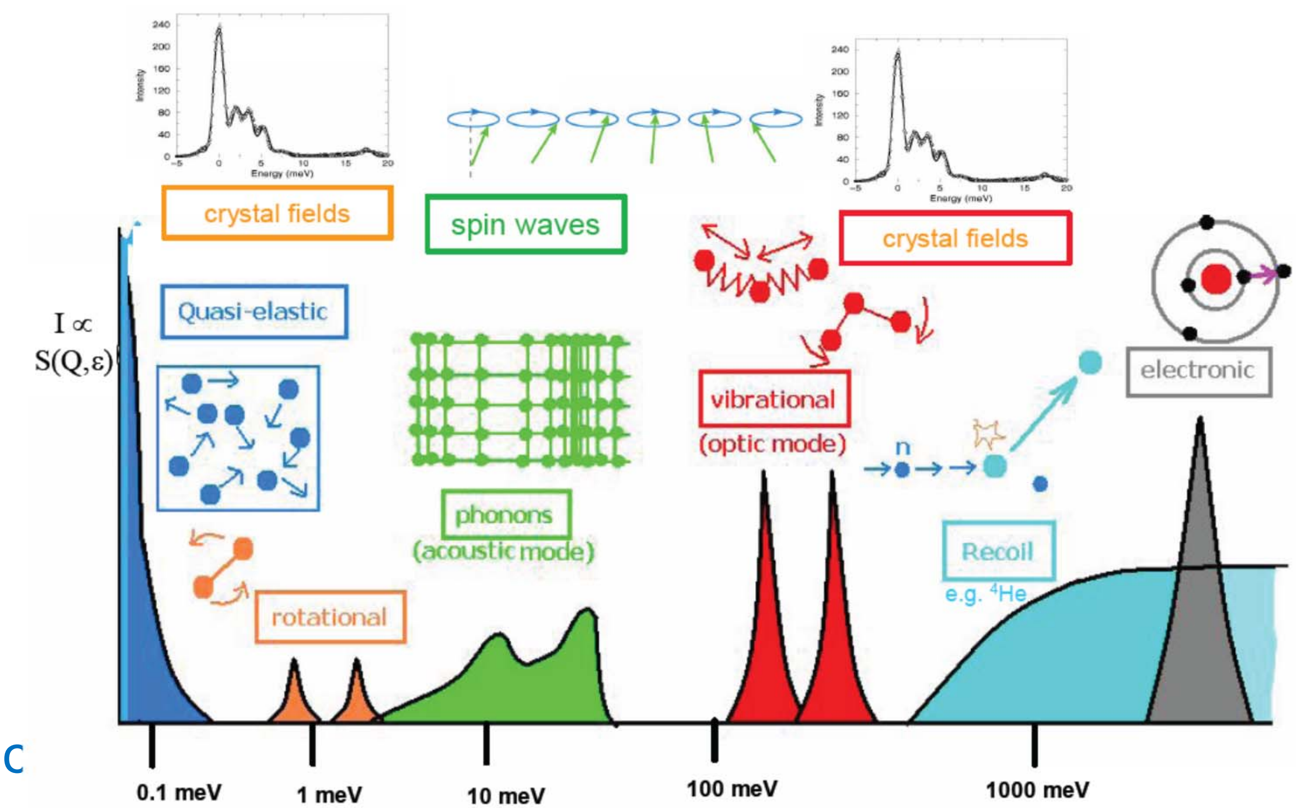

RESERVOIRS
INCIDENT BEAM
$(\boldsymbol{k}_0, \varepsilon_0)$
MONITOR
θ
SAMPLE
SCATTERED BEAM
$(\boldsymbol{k}_1, \varepsilon_1)$
DETECTOR
$\boldsymbol{k}_0$
$\boldsymbol{k}_1$
$\boldsymbol{q} = \boldsymbol{k}_0 - \boldsymbol{k}_1$
$\hbar \boldsymbol{q}_0 \equiv$ momentum transfer
$\varepsilon_0 - \varepsilon_1 \equiv$ energy transfer
$\theta \equiv$ scattering angle


X-Ray
or
neutron
λ
$\vec{k}_i$
Incident beam
Sample
$\vec{k}_s$
Scattered beam
2θ
Transmitted beam
$\vec{q}$
Detector
Wave vector : $\vec{q} = \vec{k}_s - \vec{k}_i$

Excitations in Condensed Matter

Neutron Diffraction is dominated by scattering processes where the neutron energy does not change and the state of the sample is constant.

Inelastic neutron scattering is where the neutron gives (or takes) energy to (or from) the sample and the state of the sample is changed, we say it is excited.



The two mc

es

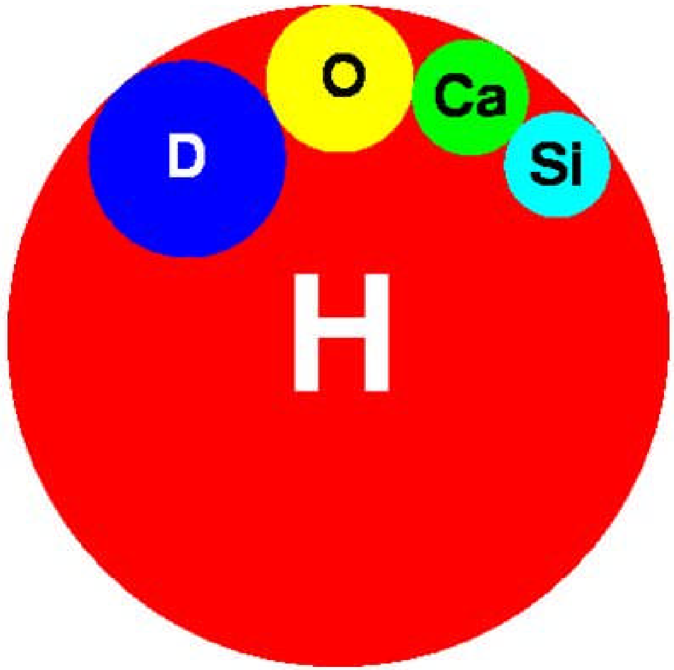
Nuclear Interaction

scattering power varies "randomly" from isotope to isotope

Cross section (σ) - Area related to the probability that a neutron will interact with a nucleus in a particular way (*e.g.* scattering or absorption)

For systems containing a reasonable proportion of H atoms, scattering from H tends to dominate

For a single nucleus $\sigma \sim 10^{-24}$ cm^2



Relative total scattering cross sections for a few isotopes

The Scattering Cross Section

Scattering Cross Sections

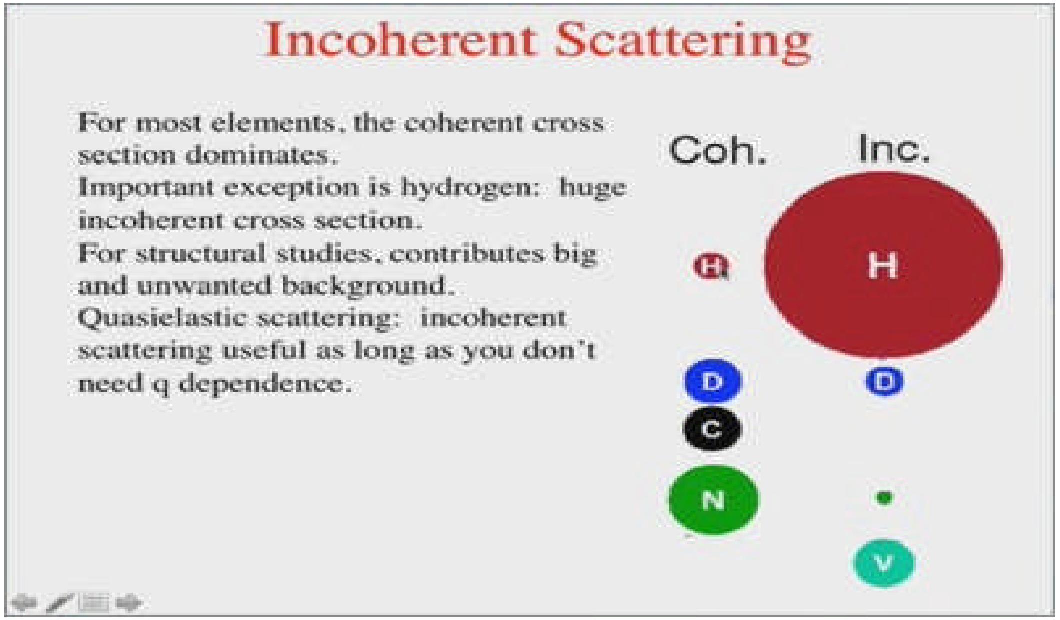
Total $\sigma_{tot} = \frac{\text{Number of scattered neutrons per sec}}{\text{Incident neutron flux}} = \left[\frac{time^{-1}}{time^{-1} area^{-1}} = area \right]$

Differential $\frac{d\sigma}{d\Omega} = \frac{\text{Number of scattered neutrons per sec into angle element d}\Omega}{\text{Incident neutron flux . d}\Omega}$

Double Differential $\frac{d\sigma}{d\Omega dE'} = \frac{\text{Number of ... and with energies between E' and E'+dE'}}{\text{Incident neutron flux . dE' d}\Omega}$

Scattering Law $\frac{d\sigma}{d\Omega dE'} = \frac{k'}{k} S(\mathbf{Q}, \omega)$ S .... Scattering function

Units: 1 barn=10^{-28} m^2 (ca. Nuclear radius^2)



9:1. COHERENT AND INCOHERENT CROSS SECTIONS

Microscopic cross section (in barns): $\frac{d\sigma(Q)}{d\Omega} = \{b\}^2 \sum_{i,j}^{N} < \exp(i\bar{Q}.\bar{r}_{ij}) > + \{\delta b^2\}$

Standard deviation: $\{\delta b^2\} = \{b^2\} - \{b\}^2$

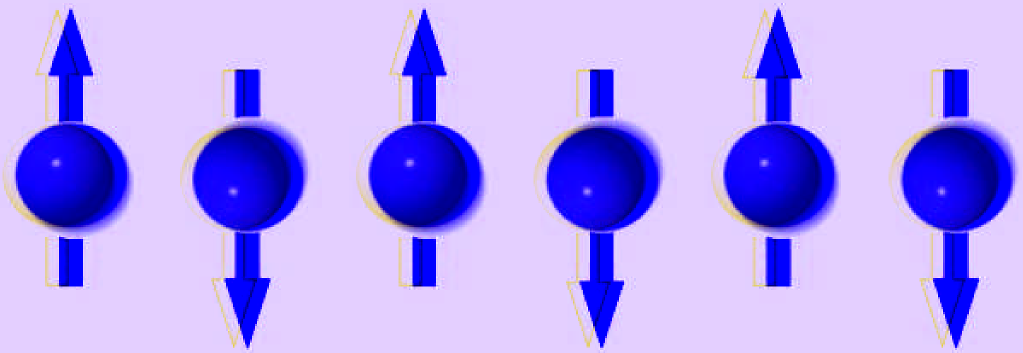
Macroscopic cross section (in cm^{-1}): $\frac{d\Sigma(Q)}{d\Omega} = \left(\frac{N}{V}\right)\frac{d\sigma(Q)}{d\Omega}$

$$\frac{d\Sigma(Q)}{d\Omega} = \left[\frac{d\Sigma(Q)}{d\Omega}\right]_{coh} + \left[\frac{d\Sigma}{d\Omega}\right]_{inc}$$

coherent part	incoherent part
Q-dependent	Q-independent

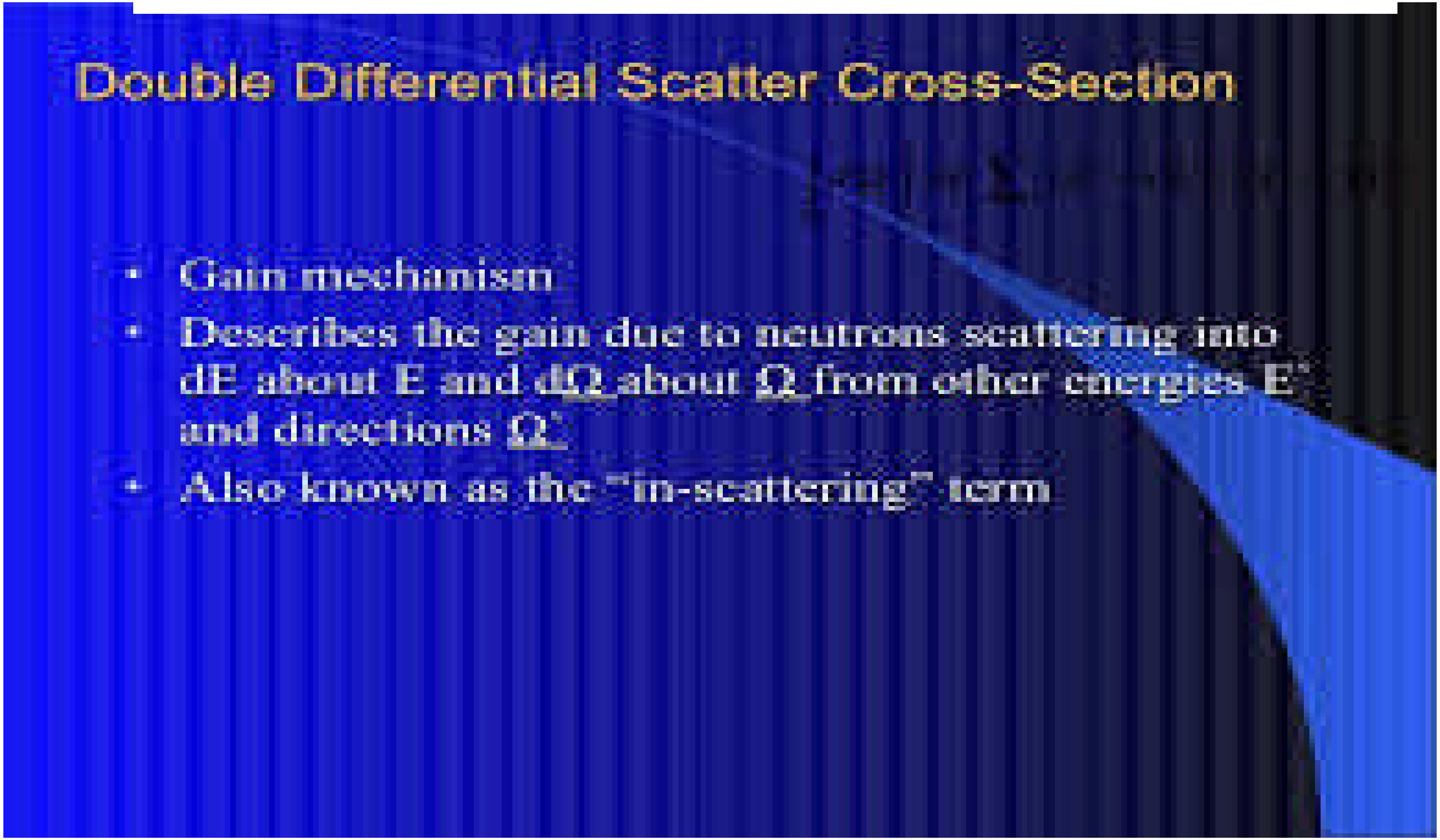
Neutron Scattering

Neutron scattering is more complicated than x-rays because neutrons are defined both by their wavevector, **k**, and spin, σ. They can be polarised - ±S



Scattering cross section will depend on **both** the neutron-nuclear (structure) and the nuclear spin interaction with any magnetic moments

$$\frac{\mathrm{d}^2\sigma}{\mathrm{d}\Omega\mathrm{d}E} = \frac{k_1}{k_0}\frac{1}{4\pi\hbar}\left[\sigma_{\mathrm{coh}}S_{\mathrm{coh}}(Q,\omega)+\sigma_{\mathrm{inc}}S_{\mathrm{inc}}(Q,\omega)\right].$$



<u>**Neutron Scattering Cross Section:**</u>

$d^2\sigma/d\Omega\ dE' = (\gamma\, r_0)^2/(2\pi\hbar)\ \ k'/k\ \ N\{1/2\ g\ F_d(\kappa)\}^2$

magnetic form factor

$\times\ \Sigma_{\alpha\,\beta}\ (\delta_{\alpha\,\beta} - \kappa_\alpha\ \kappa_\beta)\ \Sigma_l\ \exp(i\kappa\cdot\mathbf{l})$

only measure S ⊥ κ

$\times\ \int \langle \exp(-i\kappa\cdot\mathbf{u}_0))\exp(i\kappa\cdot\mathbf{u}_l(t))\rangle$

$\times\ \langle S_0^\alpha(0)\ S_l^\beta(t)\rangle \exp(-i\omega\ t)\ dt$

scattering ~ S²

so s=1/2 is the hardest case

Why do Neutron Scattering?

- To determine the positions and motions of atoms in condensed matter
  - 1994 Nobel Prize to Shull and Brockhouse cited these areas
    (see http://www.nobel.se/physics/educational/poster/1994/neutrons.html)

- Neutron advantages:
  - Wavelength comparable with interatomic spacings
  - Kinetic energy comparable with that of atoms in a solid
  - Penetrating => bulk properties are measured & sample can be contained
  - Weak interaction with matter aids interpretation of scattering data
  - Isotopic sensitivity allows contrast variation
  - Neutron magnetic moment couples to ***B*** **=>** neutron "sees" unpaired electron spins

- Neutron Disadvantages
  - Neutron sources are weak => low signals, need for large samples etc
  - Some elements (e.g. Cd, B, Gd) absorb strongly
  - Kinematic restrictions (can't access all energy & momentum transfers)

Scattering cross section & $\Sigma(\kappa\omega)$

$$\mathrm{H}' = \mathrm{H} + \frac{\hat{p}^2}{2m} + \hat{V}$$

$$\frac{d^2\sigma}{d\Omega dE'} = \frac{k'}{k}\left(\frac{m}{2\pi\hbar^2}\right)^2 \sum_{\lambda\lambda'} p_\lambda \left|\langle k'\lambda' | V | k\lambda\rangle\right|^2 \delta\left(E_\lambda - E_{\lambda'} + \hbar\omega\right)$$

$$Q_{-\boldsymbol{\kappa}} = \frac{1}{\sqrt{N}}\frac{1}{b}\frac{m}{2\pi\hbar^2}\int d^3\mathbf{r}\, V(\mathbf{r}) e^{i\boldsymbol{\kappa}\cdot\mathbf{r}}$$

$$\frac{d^2\sigma}{d\Omega dE'} = \frac{k'}{k} N b^2 \Sigma(\kappa\omega)$$

$$\Sigma(\kappa\omega) = \sum_{\lambda\lambda'} p_\lambda \left|\langle \lambda' | Q_{-\boldsymbol{\kappa}} | \lambda\rangle\right|^2 \delta\left(E_\lambda - E_{\lambda'} + \hbar\omega\right)$$

The Neutron has Both Particle-Like and Wave-Like Properties

- Mass: $m_n = 1.675 \times 10^{-27}$ kg
- Charge = 0; Spin = ½
- Magnetic dipole moment: $\mu_n = - 1.913\ \mu_N$
- Nuclear magneton: $\mu_N = eh/4\pi m_p = 5.051 \times 10^{-27}$ J T^{-1}
- Velocity (v), kinetic energy (E), wavevector (k), wavelength (λ), temperature (T).
- $E = m_n v^2/2 = k_B T = (hk/2\pi)^2/2m_n$; $k = 2\ \pi/\lambda = m_n v/(h/2\pi)$

	Energy (meV)	**Temp (K)**	**Wavelength (nm)**
Cold	**0.1 – 10**	**1 – 120**	**0.4 – 3**
Thermal	**5 – 100**	**60 – 1000**	**0.1 – 0.4**
Hot	**100 – 500**	**1000 – 6000**	**0.04 – 0.1**

l (nm) = 395.6 / v (m/s)

E (meV) = 0.02072 k^2 (k in nm^{-1})

Cross Sections

F = number of incident neutrons per cm^2 per second

s = total number of neutrons scattered per second / F

$$\frac{ds}{dW} = \frac{\text{number of neutrons scattered per second into } dW}{F \; dW}$$

$$\frac{d^2 s}{dW dE} = \frac{\text{number of neutrons scattered per second into } dW \;\&\; dE}{F \; dW \; dE}$$

s measured in barns:
1 barn = 10^{-24} cm^2

Attenuation = exp(-Ns t)
N = # of atoms/unit volume
t = thickness

Inelastic neutron scattering measures atomic motions

The concept of a pair correlation function can be generalized:

G(r,t) = probability of finding a nucleus at (r,t) given that there is one at r=0 at t=0

$G_s(r,t)$ = probability of finding a nucleus at (r,t) if the *same* nucleus was at r=0 at t=0

Then one finds:

$$\left(\frac{d^2\sigma}{d\Omega.dE}\right)_{coh} = b_{coh}^2 \frac{k'}{k} N S(\vec{Q},\omega)$$

$$\left(\frac{d^2\sigma}{d\Omega.dE}\right)_{inc} = b_{inc}^2 \frac{k'}{k} N S_i(\vec{Q},\omega)$$

(h/2π)**Q** & (h/2π)ω are the momentum & energy transferred to the neutron during the scattering process

where

$$S(\vec{Q},\omega) = \frac{1}{2\pi\hbar}\iint G(\vec{r},t)e^{i(\vec{Q}.\vec{r}-\omega t)}d\vec{r}dt \text{ and } S_i(\vec{Q},\omega) = \frac{1}{2\pi\hbar}\iint G_s(\vec{r},t)e^{i(\vec{Q}.\vec{r}-\omega t)}d\vec{r}dt$$

Inelastic coherent scattering measures *correlated* motions of atoms

Inelastic incoherent scattering measures *self-correlations* e.g. diffusion

The Neutron Scattering Factor

Total Differential Cross-Section

$$\left(\frac{d^2\sigma}{d\Omega dE}\right)_{k_0\rightarrow k_1} = \frac{1}{N}\frac{k_f}{k_i}\left(\frac{m}{2\pi\hbar^2}\right)^2 \sum p_i p_f \sum |<\mathbf{k}_f|V|\mathbf{k}_i>|^2 \delta(E+E_i-E_f)$$

$$\left(\frac{d^2\sigma}{d\Omega dE}\right)_{k_0\rightarrow k_1} = N\frac{k_f}{k_i} b^2 S(\mathbf{Q},\omega)$$

Neutron Structure Factor

$$S(\mathbf{Q},\omega) = \frac{1}{2\pi\hbar}\int G(\mathbf{r},t)e^{i(\mathbf{Q}\cdot r-\omega t)}d\mathbf{r}dt$$

Pair Correlation Function

Fourier Transform

$$G(\mathbf{r},t) = (\frac{1}{2\pi})^3\frac{1}{N}\int\sum_{jj'} e^{i\mathbf{Q}\cdot\mathbf{r}} < e^{-i\mathbf{Q}\cdot\mathbf{r}_{j'}(0)}e^{i\mathbf{Q}\cdot\mathbf{r}_j(t)} > d\mathbf{Q}$$

Squires, Introduction to the theory of thermal neutron scattering (1996)

Time-Space Correlation Function

In an isotropic medium, time-space pair correlation function: $G(r,t) = \langle n(0,0)n(r,t) \rangle$

where $n(r,t) = \sum_{j}^{N} \delta(r - r_j(t))$ presents coordinate of all atoms at time t.

G(r,t) has self and distinct part, $G(r,t)=G_S(r,t)+G_d(r,t)$. If at time $t_1=0$ a particle was at position $r_1=0$, $G_S(r,t)$ gives a probability to find the same particle around position r at time t, and $G_d(r,t)$ gives a probability to find another particle around position r at time t.

Intermediate scattering function is a space-Fourier transform of G(r,t): $I(q,t) = \int_V G(r,t)\exp(iqr)d^3r$

Definition from quantum mechanics: $I(q,t) = \sum_i \sum_j \langle \exp[-iqr_i(0)]\exp[+iqr_j(t)] \rangle = \sum_i \sum_j \langle \exp[-iq(r_i(0) - r_j(t))] \rangle$

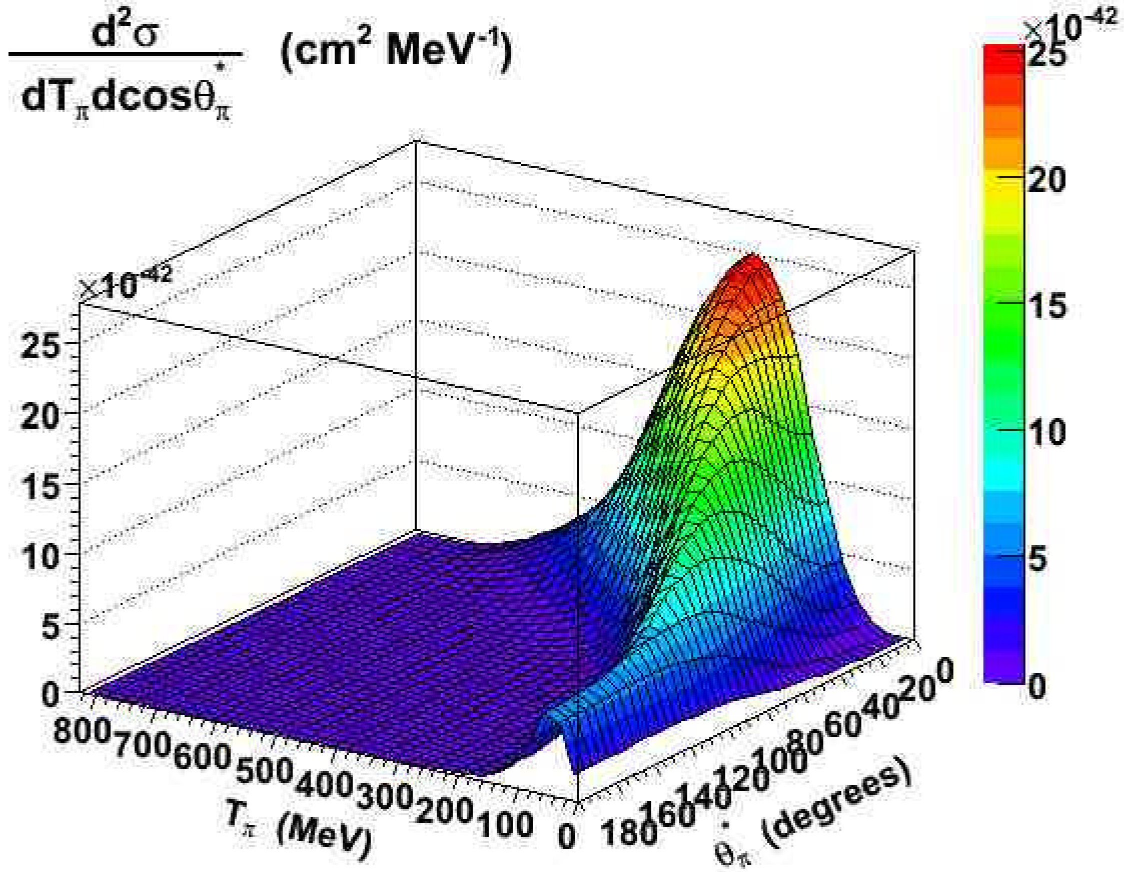
Time-Fourier transform of I(q,t) gives dynamic structure factor: $S(q,\omega) = \frac{1}{2\pi}\int_{-\infty}^{\infty} \exp(-i\omega t) I(q,t)dt$

There are coherent and incoherent $S(q,\omega)$:

$$S_{inc}(q,\omega) = \frac{1}{2\pi}\int_{-\infty}^{\infty} dt \int_V G_S(r,t)\exp[i(qr - \omega t)]d^3r$$

$$S_{coh}(q,\omega) = \frac{1}{2\pi}\int_{-\infty}^{\infty} dt \int_V G_d(r,t)\exp[i(qr - \omega t)]d^3r$$

These equations were first introduced by van Hove [van Hove, **Phys.Rev. 95**, 249 (1954)].



$\frac{d^2\sigma}{dT_\pi d\cos\theta^*_\pi}$ (cm^2 MeV^{-1})
$\times 10^{-42}$
25
20
15
10
5
0
$\times 10^{-42}$
25
20
15
10
5
0
800 700 600 500 400 300 200 100 0
T_π (MeV)
180 160 140 120 100 80 60 40 20 0
θ^*_π (degrees)

van Hove Correlation Function

Differential probability that given particle at origin at t=0, any particle will be at position r at time t.

different particle

same particle

$$G(\mathbf{r},t) = G_d(\mathbf{r},t) + G_s(\mathbf{r},t)$$

$$G(\mathbf{r},t) = (2\pi)^{-3}\int I(\mathbf{Q},t)e^{-i\mathbf{Q}\mathbf{r}}d\mathbf{Q}$$

$$S(\mathbf{Q},\omega) = (2\pi\hbar)^{-3}\iint e^{i(\mathbf{Q}\mathbf{r}-\omega t)}G(\mathbf{r},t)d\mathbf{r}\,dt$$

$$S_i(\mathbf{Q},\omega) = (2\pi\hbar)^{-3}\iint e^{i(\mathbf{Q}\mathbf{r}-\omega t)}G_s(\mathbf{r},t)d\mathbf{r}\,dt$$

van Hove self-correlation function

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Correlation Function Uses

- Complete description of bulk dynamical properties
- Space-time Fourier Transform of van Hove function
- Elastic properties of materials
- Energy dissipation
- Sound propagation

Obtained directly from neutron scattering

where horizontal bar denotes for the appropriate relevant averages over and above those included in the weight p_α. Usually for an equilibrium statistical medium the canonical Gibbsian ensemble averaging is used [5].
In other words, because the initial state of the system remains unknown the transition amplitude must finally be averaged thermally to represent the effect of the real processes. Let us consider again the expression (3.15) and perform the relevant averaging explicitly. As a result we obtain

$$dw(\mathbf{k} \to \mathbf{k}') = \sum_{\alpha\ '} Q^{-1} \exp(-E_\alpha/k_B T) \frac{2\pi}{\hbar} |\langle \alpha'\, \mathbf{k}'|V|\alpha\, \mathbf{k}\rangle|^2 \delta\left(\hbar\omega_{\alpha'\alpha} - \hbar\omega\right) dk'_x dk'_y dk'_z. \quad (3.19)$$

Let us take into account the equality $\langle \alpha'\, \mathbf{k}'|V|\alpha\, \mathbf{k}\rangle^\dagger = \langle \alpha\, \mathbf{k}|V|\alpha'\, \mathbf{k}'\rangle$ and the integral representation of the delta-function. Then the last expression for the transition amplitude take the form

$$dw(\mathbf{k} \to \mathbf{k}') = \sum_{\alpha\ '} Q^{-1} \exp(-E_\alpha/k_B T) \frac{1}{\hbar^2} \langle \alpha'\, \mathbf{k}'|V|\alpha\, \mathbf{k}\rangle \langle \alpha\, \mathbf{k}|V|\alpha'\, \mathbf{k}'\rangle \quad (3.20)$$
$$\int_\infty^\infty \exp\Big(\frac{i}{\hbar}\left(\frac{k'^2}{2m} - \frac{k^2}{2m} + E_{\alpha'} - E_\alpha\right) t\Big) dt dk'_x dk'_y dk'_z.$$

By a contraction of this expression we get

$$dw(\mathbf{k} \to \mathbf{k}') = \frac{1}{\hbar^2} \int_\infty^\infty \langle V_{\mathbf{k}\mathbf{k}'} V_{\mathbf{k}'\mathbf{k}}(t)\rangle e^{-i\omega t}\, dt dk'_x dk'_y dk'_z, \quad (3.21)$$

where

$$\langle \ldots \rangle = \sum_\alpha (Q^{-1} \exp(-E_\alpha/k_B T) \ldots), \quad Q = \sum_\alpha \exp(-E_\alpha/k_B T),$$

and

$$\langle \alpha'\, \mathbf{k}'|V(t)|\alpha\, \mathbf{k}\rangle = \langle \alpha'\, \mathbf{k}'|V|\alpha\, \mathbf{k}\rangle \exp\left(\frac{i}{\hbar}(E_{\alpha'} - E_\alpha)\right) t.$$

3.3 Scattering Function and Cross-section

It is instructive to rewrite the expression for the cross section in another form to obtain a better picture of scattering process. We will consider a target as a crystal with lattice period a. As was shown above, the transition amplitude is first order in the perturbation and the probability is consequently second order. A perturbative approximation for the transition probability from an initial state to a final state under the action of a weak potential V is written as

$$W_{\boldsymbol{k}\ '} = \frac{2\pi}{\hbar} \left| \int d^3 r \psi^*_{k'} V \psi_k \right|^2 D_{k'}(E'), \quad (3.22)$$

where $D_{k'}(E')$ is the density of final scattered states. The definition of the scattering cross-section is

$$d\sigma = \frac{W_{\boldsymbol{k}\ '}}{\text{Incident flux}}. \quad (3.23)$$

The incident flux is equal to $\hbar k'/m$ and the density of final scattered states is

$$D_{k'}(E') = \frac{1}{(2\pi)^3} \frac{d^3 k'}{dE'} = \frac{m^2}{(2\pi)^3 \hbar^3} d\Omega(\frac{\hbar k'}{m}). \quad (3.24)$$

where the explicit expressions for $K_{k'q}, K_{kk',q'q}$ are given in papers [53, 54, 55].

Returning to Eq.(4.42), it is easy to see that if one confines himself to the diagonal averages $\langle P_{kk} \rangle$ only, this equation may be transformed to give

$$\frac{d\langle P_{kk}\rangle}{dt} = \sum_q K_{kk,qq}\langle P_{qq}\rangle - \left(K_{kk} + K^{\dagger}_{kk}\right)\langle P_{kk}\rangle, \tag{4.43}$$

$$K_{kk,qq} = \frac{1}{\hbar^2} J_{kq,qk}(\frac{E_k - E_q}{\hbar}) = W_{q\to k}, \tag{4.44}$$

$$K_{kk} + K^{\dagger}_{kk} = \frac{1}{\hbar^2}\sum_q J_{qk,kq}(\frac{E_q - E_k}{\hbar}) = W_{k\to q}. \tag{4.45}$$

Here $W_{q\to k}$ and $W_{k\to q}$ are the transition probabilities expressed in the spectral intensity terms. Using the properties of the spectral intensities, it is possible to verify that the transition probabilities satisfy the relation of the detailed balance

$$\frac{W_{q\to k}}{W_{k\to q}} = \frac{\exp(-\beta E_k)}{\exp(-\beta E_q)}. \tag{4.46}$$

Finally, we have

$$\frac{d\langle P_{kk}\rangle}{dt} = \sum_q W_{q\to k}\langle P_{qq}\rangle - \sum_q W_{k\to q}\langle P_{kk}\rangle. \tag{4.47}$$

This equation has the usual form of the Pauli master equation [54, 55].

4.4 Scattering of Beam of Particles by the Nonequilibrium Medium

We consider again a statistical medium (target) with Hamiltonian H_m, a probe (beam) with Hamiltonian H_b and an interaction V between the two.

$$H = H_0 + V = H_m + H_b + V. \tag{4.48}$$

Contrary to the previous cases, this time we will consider statistical medium in a nonequilibrium state. Let us consider the expression for the transition amplitude which describes the change of the state of the probe per unit time

$$dw(\mathbf{k}\to\mathbf{k}') = \frac{1}{\hbar^2}\int_{\infty}^{\infty} dt \mathrm{Tr}_m\left(\rho_m(t)V_{\mathbf{k}'\mathbf{k}}(0)V_{\mathbf{k}'\mathbf{k}}(t)\right)\exp(-i\omega t), \tag{4.49}$$

where $\rho_m(t)$ is the nonequilibrium statistical operator of target.
Thus the partial differential cross-section is written in the form

$$\frac{d^2\sigma}{d\Omega dE'} = A\int_{\infty}^{\infty}\langle V(\mathbf{r})V(\mathbf{r}',t)\rangle_m e^{[-i/\hbar(\mathbf{k}-\mathbf{k}')(\mathbf{r}-\mathbf{r}')-i\omega t]}dt d\mathbf{r} d\mathbf{r}', \tag{4.50}$$

where

$$A = \frac{m^2}{(2\pi)^3\hbar^5}\frac{k'}{k}, \quad E' = \frac{k'^2}{2m}. \tag{4.51}$$

and $\langle \ldots \rangle_m = \mathrm{Tr}_m(\rho^m(t)\ldots)$. Again, we took into account that

$$\langle \alpha' \, \mathbf{k}' | V | \alpha \, \mathbf{k} \rangle = \langle \mathbf{k}' | V(\mathbf{r}) | \mathbf{k} \rangle \sum_{i=1}^{N} \langle \alpha' | e^{-\frac{i}{\hbar}(\mathbf{k}'\mathbf{R}_i)} e^{\frac{i}{\hbar}(\mathbf{k}\mathbf{R}_i)} | \alpha \rangle. \tag{4.52}$$

Thus we obtain

$$\frac{d^2\sigma}{d\Omega dE'} = \tag{4.53}$$

$$\frac{-1}{(i\hbar)^2} \tilde{A} \sum_{i,j=1}^{N} \int_0^t d\tau \sum_{\alpha} \langle \alpha | \{ \exp[\frac{i}{\hbar}\vec{\kappa}\mathbf{R}_i(\tau - t)] \exp[\frac{i}{\hbar}\vec{\kappa}\mathbf{R}_j(0)] \exp(i\omega(\tau - t))$$
$$+ \exp[\frac{i}{\hbar}\vec{\kappa}\mathbf{R}_i(0)] \exp[\frac{i}{\hbar}\vec{\kappa}\mathbf{R}_j(\tau - t)] \exp(-i\omega(\tau - t)) \} \rho^m(t) | \alpha \rangle.$$

It can be rewritten in another form

$$\frac{d^2\sigma}{d\Omega dE'} = \tag{4.54}$$

$$\frac{-1}{(i\hbar)^2} \tilde{A} \sum_{i,j=1}^{N} \int_0^t d\tau \{ \left\langle \exp[\frac{i}{\hbar}\vec{\kappa}\mathbf{R}_i(\tau - t)] \exp[\frac{i}{\hbar}\vec{\kappa}\mathbf{R}_j(0)] \right\rangle_m \exp(i\omega(\tau - t))$$
$$+ \left\langle \exp[\frac{i}{\hbar}\vec{\kappa}\mathbf{R}_i(0)] \exp[\frac{i}{\hbar}\vec{\kappa}\mathbf{R}_j(\tau - t)] \right\rangle_m \exp(-i\omega(\tau - t)) \}.$$

This will give the expression

$$\frac{d^2\sigma}{d\Omega dE'} = \tag{4.55}$$

$$\frac{-1}{(i\hbar)^2} \tilde{A} \sum_{i,j=1}^{N} \int_0^t d\tau \{ 2\mathrm{Re} \left\langle \exp[\frac{i}{\hbar}\vec{\kappa}\mathbf{R}_i(\tau - t)] \exp[\frac{i}{\hbar}\vec{\kappa}\mathbf{R}_j(0)] \right\rangle_m \exp(i\omega(\tau - t)).$$

In terms of the density operators $n_{\vec{\kappa}} = \sum_i^N \exp\left(i\vec{\kappa}\mathbf{R}_i/\hbar\right)$ the differential cross section take the form

$$\frac{d^2\sigma}{d\Omega dE'} = \tilde{A} 2\mathrm{Re}\mathcal{S}(\vec{\kappa}, \omega, t), \tag{4.56}$$

where

$$\mathcal{S}(\vec{\kappa}, \omega, t) = \frac{-1}{(i\hbar)^2} \int_0^t d\tau \exp[i\omega(\tau - t)] \langle n_{\vec{\kappa}}(\tau - t) n_{-\vec{\kappa}} \rangle_m, \tag{4.57}$$

Our approach is to construct the nonequilibrium statistical operator of the medium. To do so, we should follow the basic formalism of the nonequilibrium statistical operator method [54, 55, 56]. According to this approach we should take into account that

$$\rho^m = \overline{\rho_q(t,0)} = \varepsilon \int_{-\infty}^{0} d\tau e^{\varepsilon\tau} \rho_q(t + \tau, \tau) = \tag{4.58}$$
$$\varepsilon \int_{-\infty}^{0} d\tau e^{\varepsilon\tau} \exp\left(-\frac{H_m \tau}{i\hbar}\right) \rho_q(t + \tau, 0) \exp\left(\frac{H_m \tau}{i\hbar}\right)$$
$$= \varepsilon \int_{-\infty}^{0} d\tau e^{\varepsilon\tau} \exp\left(-S(t + \tau, \tau)\right).$$

Thus the nonequilibrium statistical operator of the medium will take the form

$$\rho^m(t,0) = \exp\left(-S(t,0)\right) + \tag{4.59}$$

$$\int_{-\infty}^{0} d\tau e^{\varepsilon\tau} \int_{1}^{1} d\tau' \exp\left(-\tau' S(t+\tau,\tau)\right) \dot{S}(t+\tau,\tau) \exp\left(-(\tau'-1)S(t+\tau,\tau)\right),$$

where

$$\dot{S}(t,\tau) = \exp\left(-\frac{H_m\tau}{i\hbar}\right) \dot{S}(t,0) \exp\left(\frac{H_m\tau}{i\hbar}\right) \tag{4.60}$$

and

$$\dot{S}(t,0) = \frac{\partial S(t,0)}{\partial t} + \frac{1}{i\hbar}[S(t,0),H] = \tag{4.61}$$

$$\sum_m \left(\dot{P}_m F_m(t)(P_m - \langle \dot{P}_m\rangle_q^t)\dot{F}_m(t)\right).$$

Finally, the general expression for the scattering function of beam of neutrons by the nonequilibrium medium in the approach of the nonequilibrium statistical operator method is given by

$$\mathcal{S}(\vec{\kappa},\omega,t) = \frac{-1}{(i\hbar)^2} \int_0^t d\tau \langle n_{\vec{\kappa}}(\tau-t) n_{-\vec{\kappa}}(0)\rangle_q^t \exp[i\omega(\tau-t)] + \tag{4.62}$$

$$\frac{-1}{(i\hbar)^2} \int_0^t d\tau \int_{-\infty}^{0} d\tau' e^{\varepsilon\tau'} \left(n_{\vec{\kappa}}(\tau-t) n_{-\vec{\kappa}}(0), \dot{S}(t+\tau')\right)^{t+\tau'} \exp[i\omega(\tau-t)].$$

Here the standard notation [56] for $(A,B)^t$ were introduced

$$(A,B)^t = \int_0^1 d\tau \mathrm{Tr}\left[A\exp(-\tau S(t,0))(B - \langle B\rangle_q^t)\exp((\tau-1)S(t,0))\right], \tag{4.63}$$

$$\rho_q(t,0) = \exp(-S(t,0)); \quad \langle B\rangle_q^t = \mathrm{Tr}(B\rho_q(t,0)). \tag{4.64}$$

Now we show that the problem of finding of the nonequilibrium statistical operator for the beam of neutrons has many common features with the description of the small subsystem interacting with thermal reservoir.
Let us consider again the Hamiltonian (4.48). The state of the overall system at time t is given by the statistical operator

$$\rho(t) = \exp\left(\frac{-iH_0t}{\hbar}\right)\rho(0)\exp\left(\frac{iH_0t}{\hbar}\right), \tag{4.65}$$

where the initial state

$$\rho(0) = \rho^m(0)\otimes\rho^b(0) \tag{4.66}$$

assumes a factorized form ($\rho^m(0)$ and $\rho^b(0)$ correspond to the density operators that represent the initial states of the system and the probe, respectively). The state of the system and the probe at time t can be described by the reduced density operators

$$\rho^b(t) = \mathrm{Tr}_m[\rho(t)] = \mathrm{Tr}_m\left(\exp(\frac{-iH_0t}{\hbar})\rho^m(0)\otimes\rho^b(0)\exp(\frac{iH_0t}{\hbar})\right), \tag{4.67}$$

$$\rho^m(t) = \mathrm{Tr}_b[\rho(t)] = \mathrm{Tr}_b\left(\exp(\frac{-iH_0t}{\hbar})\rho^m(0)\otimes\rho^b(0)\exp(\frac{iH_0t}{\hbar})\right), \tag{4.68}$$

Concluding Remarks

We have presented a direct statistical mechanical method for calculating the differential cross section of the slow neutron scattering on the nonequilibrium medium.

A combination of the scattering theory and the method of the nonequilibrium statistical operator leads to a compact and workable formalism which gives a generalization of the Van Hove approach.

The generalized scattering function G(q,E) contains an essential factor connected to the entropy production d/dt S

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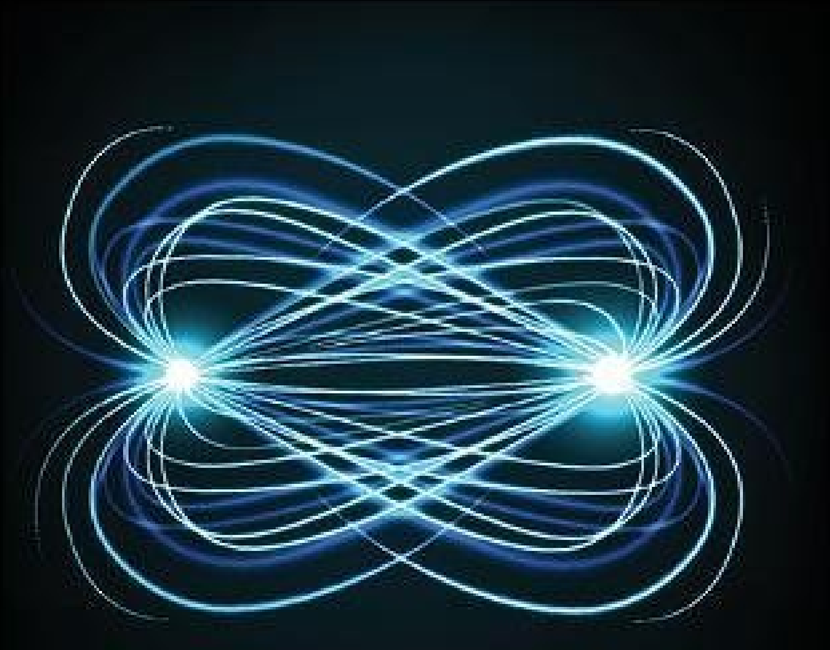
Statistical Mechanics and the Physics of Many-Particle Model Systems

Alexander Leonidovich Kuzemsky



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