Part I

Scattering and liquids

1

Scattering techniques for the liquid state

1.1 Introduction

1.1.1 Radiation scattering used for condensed matter spectroscopy

Spectroscopy measures the structure and dynamics of the ground or low-lying excited states of condensed matter. Radiation is useful as a tool for spectroscopy if it couples weakly (in a sense to be discussed later) to the many-body system. In this case the double differential cross-section (per unit solid angle, per unit energy transfer) for the radiation scattering can be written schematically as

$$\frac{d^2\sigma}{d\Omega d\omega} \approx \left(\frac{d\sigma}{d\Omega}\right)_0 \sum_{i,f} P_i \left| \langle f | \sum_{l=1}^{n} e^{i(\mathbf{k}_1 - \mathbf{k}_2)\cdot \mathbf{r}_1} | i \rangle \right|^2 \delta(\hbar\omega - E_i + E_f). \tag{1.1}$$

In Eq. (1.1) the first factor $\left(\frac{d\sigma}{d\Omega}\right)_0$ refers to the differential scattering cross-section from the basic unit of scattering medium in the system and the second factor, usually called the dynamic structure factor, represents the time-dependent structure of the system as seen by the radiation. This clear separation of the basic scattering problem, as represented in the first factor, from the dynamic structure factor of the many-body system itself, is only possible when the radiation couples weakly to the system, and therefore the use of Born approximation in deriving Eq. (1.1) is valid. Both thermal neutrons and photons with energy up to the X-ray region satisfy this criterion and thus are useful as probes for condensed matter time-dependent structures. The dynamic structure factor contains two parameters related to the energy and momentum of the probe, namely, the momentum transfer (Eq. (1.2a)) and the energy transfer (Eq. (1.2b)) to the system in the scattering process:

$$\hbar\mathbf{Q} = \hbar(\mathbf{k_1} - \mathbf{k_2}), \tag{1.2a}$$

$$\hbar\omega = \hbar(\omega_1 - \omega_2). \tag{1.2b}$$

A schematic diagram of indicating the incident and scattered radiation with respect to the scattering medium is shown in Figure 1.1. In general the double differential cross-section depends on all four parameters: $\vec{k}_1, \omega_1, \vec{k}_2, \omega_2$, namely,

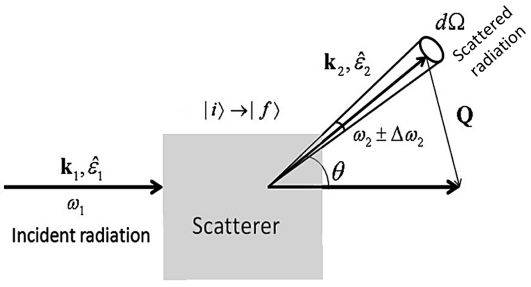

Figure 1.1 Schematic diagram of scattering geometry.

both the incident and the scattered wave vectors and frequencies. But this complexity is reduced greatly when the Born approximation is applicable. In this case the dynamic structure factors depend, apart from the state of the system, on only two external parameters, Q and ω. This has an immediate significant experimental implication. We shall explain in Section 1.1.6 that, qualitatively speaking, when the radiation imparts momentum $\hbar\vec{Q}$ and energy $\hbar\omega$ to the system it effectively probes the structure and dynamics of the system with a spatial resolution of $R = 2\pi Q^{-1}$ and time scale of $\tau = 2\pi\omega^{-1}$. For the purpose of this introductory chapter, we are mostly interested in situations where $nk_1 \simeq nk_2 \simeq k$ and n is the refractive index of the medium. In this case the magnitude of the wave vector transfer Q, which we call the Bragg wave number, can be expressed in terms of the wave number k and scattering angle θ as

$$Q = 2k \sin\frac{\theta}{2}. \tag{1.3}$$

In order to probe the spatial structure of the system at different levels, one would like to change Q accordingly. For instance, to detect a periodic structure of spacing $d \approx 10\,\text{Å}$, one needs to have $Q \simeq 2\pi/d \simeq 0.628\,\text{Å}^{-1}$. One can use cold neutrons of wavelength $\lambda \approx 4\,\text{Å}$ ($k = 2\pi/\lambda = 1.57\,\text{Å}^{-1}$) and work at a scattering angle around $\theta \approx 23°$ so that $2k \sin\frac{\theta}{2} = 2 \times 1.57 \sin\left(\frac{23°}{2}\right) \simeq 0.628\,\text{Å}^{-1}$. Alternatively one can use X-rays of wavelength $\lambda = 0.62\,\text{Å}$ and work at an angle around $\theta \approx 3.6°$. Or one can even use γ-rays of $\lambda = 0.03\,\text{Å}$ (412 keV γ-rays from gold Au^{198}) and work at an angle around $\theta \approx 0.17°$. Similar consideration applies to the frequency or the time scale. Since the relevant variable is the difference between incident and scattered energies, one can tune the dynamic range of the probe by varying the accuracy of the energy difference measurement. A good example is a neutron scattering study of polymer chain dynamics by Higgins *et al.* (1981), using the so-called spin-echo technique. Using 8 Å neutrons ($\hbar\omega_1 = 1279\,\mu\text{eV}$) they were able to measure energy difference of $E = \hbar\omega$ in the scattered neutrons and thus were able to probe the chain dynamics at a time scale τ of $0.4\,\mu\text{s}$ over the

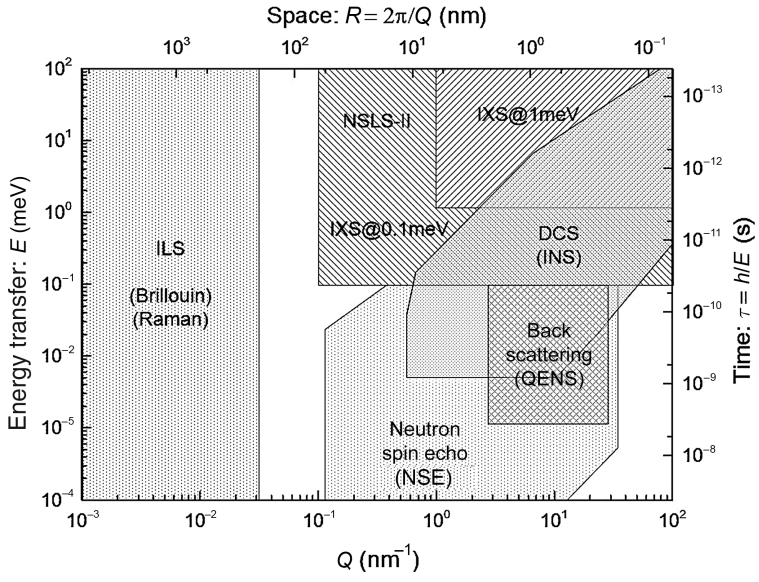

Figure 1.2 The $(Q, E = \hbar\omega)$ ranges covered in the scattering experiment and the corresponding space-time, (R, τ), ranges probed in the material system for each of the three scattering techniques. Due to the recent advances in instrumentation, the overlaps between neutron and X-ray scattering spectroscopy are clearly visible. The disk chopper spectrometer (DCS, used for INS), quasi-elastic backscattering spectrometer (QENS) and neutron spin echo spectrometer (NSE) are presently available in both NIST Center For Neutron Research (NCNR) and Spallation Neutron Source (SNS) in Oak Ridge National Laboratory in USA.

distances scale of up to $2\pi/Q = 200\,\text{Å}$ ($Q = 0.03\,\text{Å}^{-1}$). Figure 1.2 summarises the present status of neutron, X-ray and light-scattering spectroscopy relevant to the discussions here in terms of its (Q, E) and its corresponding (R, τ) space-time coverage. The important point to notice is the regions of overlap of the three scattering methods due to the recent advances in techniques and instrumentations of neutron and X-ray spectroscopies.

The primary purpose of this chapter is to derive the important relation given in Eq. (1.1) and to identify in each of the three cases – thermal neutron, X-ray and light scattering – the corresponding basic scattering unit that contributes to the factor $\left(\frac{d\sigma}{d\Omega}\right)_0$. We shall comment on the meanings of the dynamic structure factor using some examples in Section 1.1.6.

1.1.2 Thermal neutron scattering

Consider a combined system of a material medium, described by a Hamiltonian H_s, and a neutron with a kinetic energy $\frac{p^2}{2m}$ and their mutual interaction V. The time-independent Schrödinger equation for the system is

$$\left(\frac{p^2}{2m} + H_s + V\right)\Phi(\mathbf{r}, \{R\}) = E\Phi(\mathbf{r}, \{R\}). \tag{1.4}$$

We denote by $\mathbf{r}$ position of the neutron and R the collection of coordinates of all particles in the system. The material system has a set of stationary states $\{|n\rangle\}$ defined by

$$H_s|n\rangle = E_n|n\rangle, \tag{1.5a}$$
$$\langle n|n'\rangle = \delta_{nn'}. \tag{1.5b}$$

Using this set of stationary states we expand the total wave function as

$$\Phi(\mathbf{r}, \{R\}) = \sum_n \langle\psi_n(\mathbf{r})|n\rangle. \tag{1.6}$$

Substituting Eq. (1.6) into Eq. (1.4) and taking a scalar product with $\langle n|$ on both sides, we obtain a wave equation for the neutron in the presence of the material system:

$$(\nabla^2 + K_n^2)\psi_n(\mathbf{r}) = \frac{2M}{\hbar^2}\sum_{n'}\langle n|V|n'\rangle\psi_{n'}(\mathbf{r}), \tag{1.7}$$

where $\frac{\hbar^2 K_n^2}{2M} = E - E_n$ is the kinetic energy of the neutron in the system.

The neutron wave (Eq. (1.7)) can be used in two ways. The first application is to consider the propagation of neutrons in the material medium. For this application we take the system to be in the ground state, i.e. $|n\rangle = |n'\rangle = |0\rangle$, and introduce an optical potential $U(r) = \langle 0|V|0\rangle$. Then putting $\psi_0 \equiv \psi$ and $K_0 \equiv K$, Eq. (1.7) reduces to a wave equation:

$$(\nabla^2 + K^2)\psi(\mathbf{r}) = \frac{2M}{\hbar^2}U(\mathbf{r})\psi(\mathbf{r}). \tag{1.8a}$$

One normally takes the optical potential to be a pseudo-potential (Sears, 1978),

$$U(\mathbf{r}) = \frac{2\pi\hbar^2}{M}\sum_{l=1}^{n} b_l\delta(\mathbf{r} - \mathbf{R_l}). \tag{1.8b}$$

A simple example is to take a homo-nuclear system with identical bound atom scattering length $b_j = b$ (Koester *et al.*, 1981),[1] and work out the index of refraction of neutrons in the medium.

[1] Bound scattering length refers to scattering length of a nucleus that is fixed in space. Measurement of scattering length is normally made in a situation where the nucleus is free to recoil. The measurement gives the free scattering length a, which is related to b by $b = \frac{A+1}{A}\alpha$, where A is atomic weight of the nucleus. See Koester *et al.* (1981) for tabulation of values of b.

Write

$$U(\mathbf{r}) = \frac{2\pi\hbar^2 b}{M}\sum_{l=1}^{n}\delta(\mathbf{r}-R_l) = \frac{2\pi\hbar^2 b}{M}n(\mathbf{r}), \tag{1.8c}$$

where $n(r)$ is the local number density of nuclei. Putting Eq. (1.8c) into Eq. (1.8a) we have

$$(\nabla^2 + K^2)\psi(\mathbf{r}) = 4\pi b n(\mathbf{r})\psi(\mathbf{r}). \tag{1.9a}$$

Take a plane wave $\psi(\mathbf{r}) = \exp(i\mathbf{K}'\cdot\mathbf{r})$ propagating in an optically homogeneous medium where we can set $n(r) = n$ (this is valid when no Bragg condition is satisfied). We have from Eq. (1.9a) a relation

$$-K'^2 + K^2 = 4\pi b n. \tag{1.9b}$$

From Eq. (1.9b) the index of refraction follows as

$$n \equiv \frac{K'}{K} = \sqrt{1-\frac{4\pi b n}{K^2}} = 1 - \frac{bn\lambda^2}{2\pi}. \tag{1.10}$$

Take a typical case of nickel for which $n = 9.13\times10^{22}\ \mathrm{cm}^{-3}$ and $b = 1.03\times10^{-12}$ cm. We have for a 4 Å neutron, $\frac{bn\lambda^2}{2\pi} \sim 2.4\times10^{-5}$. The refractive index of a material with $b > 0$ is therefore slightly optically rare with respect to neutron wave. Notice the λ^2 dependence in Eq. (1.10). This means for ultra cold neutrons of $\lambda = 800$ Å (speed ≈ 5 m/sec), the index of refraction is as large as $n = 0.04$ and the total reflection from the surface of Ni film of up to $\theta_c = 87.7°$ is possible. If one takes into account the periodic variation of $n(r)$ in a crystalline solid then one can proceed to work out the dynamic theory of neutron diffraction in a perfect crystal (Rauch and Petrascheck, 1978). The second application is to solve Eq. (1.5) for the scattered wave function of neutrons. Scattering of neutrons in general induces excitation or de-excitation of the medium, so the matrix element $\langle n|V|n'\rangle$ of the interaction potential has to be evaluated between the initial and final states of the scattering medium. To calculate the scattering cross-section, we are interested in the asymptotic wave function at distances large compared to the sample size. First, solve for Green's function:

$$(\nabla^2 + K_n^2)G_n(|\mathbf{r}-\mathbf{r}'|) = -\delta(\mathbf{r}-\mathbf{r}'), \tag{1.11}$$

which gives

$$G_n(|\mathbf{r}-\mathbf{r}'|) = \frac{e^{iK_n|\mathbf{r}-\mathbf{r}'|}}{4\pi|\mathbf{r}-\mathbf{r}'|} \xrightarrow[r>>r']{} \frac{e^{iK_n r}}{4\pi r}e^{iK_n\hat{\mathbf{r}}\cdot\mathbf{r}'}. \tag{1.12}$$

Constructing an inhomogeneous solution from Eq. (1.12) and adding to it the homogeneous solution which represents the incident plane wave, we get

$$\psi_n(\mathbf{r}) = \delta_{nn_0} e^{i\mathbf{K}\cdot\mathbf{r}} - \frac{e^{iK_n r}}{r}\left(\frac{M}{2\pi\hbar^2}\right)\sum_{n'}\int_V d^3r' e^{-i\mathbf{K}_n\cdot\mathbf{r}'} V_{nn'}(\mathbf{r}')\psi_{n'}(\mathbf{r}'), \qquad (1.13)$$

where $\mathbf{K} \equiv \mathbf{k_1}$ denotes the incident wave vector, $\mathbf{K_n} \equiv \mathbf{k_2} = K_n\hat{r}$ denotes the scattered wave vector and the integration is over the volume the system.

To go further from here one makes the Fermi approximation, which essentially consists of two parts: make the Born approximation by taking

$$\psi_{n'}(\mathbf{r}') \simeq \delta_{n'n_0} e^{i\mathbf{K}\cdot\mathbf{r}'}, \qquad (1.14a)$$

and simultaneously use the pseudo-potential

$$V(\mathbf{r}) = \frac{2\pi\hbar^2}{M}\sum_{l=1}^{n} b_l \delta(\mathbf{r} - \mathbf{R_l}), \qquad (1.14b)$$

to get

$$\psi_n(\mathbf{r}) = \delta_{nn_0} e^{i\mathbf{K}\cdot\mathbf{r}} - \frac{e^{iK_n r}}{r}\left(\frac{M}{2\pi\hbar^2}\right)\sum_{n'}\int_V d^3r' e^{i(\mathbf{K}-\mathbf{K}_n)\cdot\mathbf{r}'} V_{nn_0}(\mathbf{r}'). \qquad (1.15)$$

There are a number of discussions in the literature with regard to the Fermi approximation, such as Sachs (1953), so we shall not go into it here. The accuracy of this approximation is estimated to be of the order of 0.1% in the case of a hydrogen atom bound in a molecule. Taking a typical neutron–nuclear potential of depth $-V_0 \approx 36\,\text{MeV}$ and width $r_0 \approx 2 \times 10^{-13}\,\text{cm}$, the validity of the Fermi approximation rests on the following considerations:

(i) $Kr_0 \ll 1$ (in fact $\approx 10^{-4}$) – a consideration for validity of low-energy scattering from a bound nucleus where a scattering length b is sufficient to characterise the cross-section.

(ii) For a square-well potential $b \propto V_0 r_0^3$ and one can redefine fictitious potential parameters $\bar{V}_0$, $\bar{r}_0$ such that not only the scattering length is preserved, i.e. $\bar{V}_0\bar{r}_0^3 = V_0 r_0^3$, but at the same time the condition for validity of the Born approximation is also satisfied, i.e. $\frac{m\bar{V}_0\bar{r}_0^3}{\hbar^2} \ll 1$.

(iii) The fictitious range of nuclear force $\bar{r}_0$ chosen above can still be much smaller than amplitude of the zero point vibration A of the bound nucleus in the molecule.

Physically speaking, even though neutron–nuclear interaction is so strong that the Born approximation is not applicable, a fortunate situation arises because the interaction is over such a short range that one can smear out the interaction range

considerably, so as to decrease its strength in such a way that the Born approximation can be used. In practice, the amplitude of the zero point vibration A is 10^{-9} cm and $\bar{r}_0$ can be taken to be $100\, r_0 = 2 \times 10^{-11}$ cm. We now define the scattering amplitude $f_{nn_0}(\theta)$ by writing Eq. (1.15) in asymptotic form:

$$\psi_n(\mathbf{r}) = \delta_{nn_0} e^{i\mathbf{K}\cdot\mathbf{r}} + f_{nn_0}(\theta)\frac{e^{iK_n r}}{r}, \tag{1.16a}$$

and identify

$$f_{nn_0}(\theta) = -\sum_{l=1}^{N} b_l \langle n| e^{i(\mathbf{k_1}-\mathbf{k_2})\cdot\mathbf{R}_l} |n_0\rangle. \tag{1.16b}$$

The first term in Eq. (1.16a) represents the incident wave ψ_{inc} while the second term represents the scattered wave ψ_{sc} in the region $\theta \neq 0$. The differential cross-section for elastic scattering $d\sigma$ can then be obtained by calculating the ratio of the number of neutrons elastically scattered into $d\Omega$ in the direction of $\mathbf{k_2}$ per second to the incident neutron flux,

$$d\sigma = \frac{k_2|\psi_{sc}|^2}{k_1|\psi_{inc}|^2}\, r^2 d\Omega, \tag{1.17a}$$

or

$$\frac{d\sigma}{d\Omega} = \frac{k_2}{k_1}\sum_{n_0} P_{n_0} |f_{n_0 n_0}(\theta)|^2, \tag{1.17b}$$

where Eq. (1.17b) is obtained from Eq. (1.17a) by averaging over the initial distribution P_{n_0} of the initial states $|n_0\rangle$ of the system.

The inelastic scattering cross-section can likewise be obtained from the scattering amplitude by

$$\frac{d^2\sigma}{d\Omega d\omega_2} = \frac{k_2}{k_1}\sum_{n,n_0} P_{n_0} |f_{n,n_0}(\theta)|^2 \delta\left(\omega_1 - \omega_2 + \frac{E_{n_0} - E_n}{\hbar}\right), \tag{1.18a}$$

where an additional average over the unknown final states $|n\rangle$ is made together with a delta function factor, ensuring the energy conservation

$$\hbar\omega = \hbar\omega_1 - \hbar\omega_2 = E_n - E_{n_0}. \tag{1.18b}$$

Using the expression for the scattering amplitude (Eq. (1.17a)) in Eq. (1.18a) we then get (by writing $|i\rangle \equiv |n_0\rangle$, $|f\rangle \equiv |n\rangle$)

$$\frac{d^2\sigma}{d\Omega d\omega_2} = \frac{k_2}{k_1}\sum_{i,f} P_i |\langle f| \sum_{l=1}^{N} b_l e^{i\mathbf{Q}\cdot\mathbf{R_l}} |i\rangle|^2 \delta\left(\omega + \frac{E_i - E_f}{\hbar}\right). \tag{1.18c}$$

In expression similar to Eq. (1.1) is recovered except for a trivial kinematic factor k_2/k_1. When all nuclei are identical, i.e. $b_j = b$,

$$\frac{d^2\sigma}{d\Omega d\omega_2} = b^2 \frac{k_2}{k_1} \sum_{i,f} P_i |\langle f| \sum_{l=1}^{N} e^{i\mathbf{Q}\cdot\mathbf{R_l}} |i\rangle|^2 \delta\left(\omega + \frac{E_i - E_f}{\hbar}\right). \tag{1.18d}$$

We note that in this case $\left(\frac{d\sigma}{d\Omega}\right)_0 = b^2$ is the differential cross-section for a single bound state nucleus.

Coherence and incoherence

The cross-sections in Eqs. (1.17b) and (1.18c) contain a coherent superposition of phase factors from each nuclei $\exp(i\mathbf{Q}\cdot\mathbf{R_l})$ only when all nuclei look identical to incoming neutrons. In practice there are two sources of incoherence. First, even a chemically homogeneous system contains isotopes of the same element. Second, neutron–nuclear interaction is spin dependent, namely the scattering length is dependent on mutual orientations of neutron spin relative to nuclear spin. Therefore, even for an unpolarised incident neutron beam, Eq. (1.18c) has to be averaged over all possible nuclear isotopic and spin states. We denote this average by a bar. Consider then the factor

$$\overline{\sum_{i,f} P_i |\langle f| \sum_{l=1}^{N} b_l e^{i\mathbf{Q}\cdot\mathbf{R_l}} |i\rangle|^2 \delta\left(\omega + \frac{E_i - E_f}{\hbar}\right)}, \tag{1.19a}$$

which, by using an integral representation of the delta function,

$$\delta\left(\omega + \frac{E_i - E_f}{\hbar}\right) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dt e^{-i\omega t} e^{\frac{i}{\hbar}(E_f - E_i)t}, \tag{1.19b}$$

can easily be transformed into the time-dependent form:

$$\frac{1}{2\pi} \int_{-\infty}^{\infty} dt e^{-i\omega t} \sum_i P_i \overline{|\langle i| \sum_{l,l'}^{N} b_l b_{l'} e^{-i\mathbf{Q}\cdot\mathbf{R_l}(0)} e^{i\mathbf{Q}\cdot\mathbf{R_l}(t)} |i\rangle|}. \tag{1.19c}$$

If one now assumes that the isotopic states and spin states of each nucleus are completely uncorrelated with its position one can rewrite the above expression as

$$\frac{1}{2\pi} \int_{-\infty}^{\infty} dt e^{-i\omega t} \sum_i P_i |\langle i| \sum_{l,l'}^{N} \overline{b_l b_{l'}} e^{-i\mathbf{Q}\cdot\mathbf{R_l}(0)} e^{i\mathbf{Q}\cdot\mathbf{R_l}(t)} |i\rangle|. \tag{1.19d}$$

Consider now the average

$$\overline{b_l\, b_{l'}} = \bar{b}_l^2 = \bar{b}^2, \quad \text{when } l = l',$$
$$\overline{b_l b_{l'}} = (\bar{b})^2, \quad \text{when } l \neq l',$$