

22.103 Microscopic Theory of Transport (Fall 2003)
Lecture 5 (9/17/03)

The Density Correlation Functions and Neutron Scattering

References --

Boon and Yip, Sec. 2.2

In the last chapter we discussed the interpretation of the Van Hove self correlation function, (4.1), by regarding the Dirac delta function $\delta(\underline{r} - \underline{R}(t))$ as a measure of the probability that the tagged particle is located at the position \underline{r} at time t (cf. (4.3)). A related interpretation one can give to the delta function is that of a time-dependent density. This is easier to see by considering the following sum of delta functions,

$$n(\underline{r}, t) = \frac{1}{\sqrt{N}} \sum_{i=1}^N \delta(\underline{r} - \underline{R}_i(t)) \quad (5.1)$$

where the coefficient $1/\sqrt{N}$, with N being the number of particles in the system, appears for reasons of normalization (as we will see later). The interpretation of (5.1) is

$$n(\underline{r}, t) d^3r = \text{no. of particles in the volume element } d^3r \text{ about } \underline{r} \text{ at time } t$$

Since the delta function is just a bookkeeping device for locating particles and each term in (5.1) is the probability that particle is at \underline{r} at time t , the sum therefore gives the number of particles found at \underline{r} at time t . Put another way, imagine we can set up a volume element d^3r (a pill box) at \underline{r} and count the number of particles inside the element, and we do this by checking every particle in the system. Aside from the normalization factor, this is exactly the number of particles is just what is given by (5.1). Defining the density as (5.1) means that all the particles are identical.

In the case of the Van Hove self correlation function we are interested (or want to follow) only in one of the particles in the system (which we have been calling the tagged particle). So the corresponding 'density' to (5.1) is just one delta function,

$$n_s(\underline{r}, t) = \delta(\underline{r} - \underline{R}(t)) \quad (5.2)$$

where $\underline{R}(t)$ is the position of the tagged particle at time t . With this definition, we can rewrite the self correlation function in terms of the tagged-particle density (5.2). However, instead of $n_s(\underline{r}, t)$ we will take the deviation from the mean,

$$\delta n_s(\underline{r}, t) = n_s(\underline{r}, t) - \langle n_s(\underline{r}, t) \rangle \quad (5.3)$$

with $\langle n_s(\underline{r}, t) \rangle = 1/V$. The reason for taking (5.3) instead of (5.2) to define the self correlation function is that in linear response theory it is conventional to study correlations of variables which fluctuate with zero mean (one reason for this is that Fourier transforms of these variables are well-defined). Thus the Van Hove self correlation function is defined to be

$$\begin{aligned} G_s(\underline{r} - \underline{r}', t) &= V \langle \delta n_s(\underline{r}', 0) \delta n_s(\underline{r}, t) \rangle \\ &= V \langle n_s(\underline{r}', 0) n_s(\underline{r}, t) \rangle - V^{-1} \end{aligned} \quad (5.4)$$

Comparing (5.4) with (4.1) we see that our earlier definition differs by the second term in (5.4). Strictly speaking, (5.4) is the more proper definition, while in practice, the $1/V$ is negligible because we always take the thermodynamic limit where $N, V \rightarrow \infty$ with $N/V = n$, the equilibrium number density.

Correspondingly we will define the time-dependent density correlation function as

$$\begin{aligned} G(\underline{r} - \underline{r}', t) &= V \langle \delta n(\underline{r}', 0) \delta n(\underline{r}, t) \rangle \\ &= \frac{1}{n} \langle n(\underline{r}', 0) n(\underline{r}, t) \rangle - \frac{1}{n} \\ &= \frac{1}{n} \langle \sum_{i,j=1}^N \delta(\underline{r}' - \underline{R}_i(0)) \delta(\underline{r} - \underline{R}_j(t)) \rangle - n \end{aligned} \quad (5.5)$$

with $\langle n(\underline{r}, t) \rangle = \sqrt{N}/V$. From the third line in (5.5) we see that $G(\underline{r}, t) d^3r$ has the interpretation of being the expected number of particles in the element of volume d^3r about \underline{r} , given that a particle was at the origin at time zero. It is obvious from their definitions that the pair of functions G and G_s are space-time density correlation functions. They are particularly important members of a class of space-time correlation functions, known simply as time correlation functions, because the density is such a fundamental variable in the description of any physical system. Other members which we will encounter are momentum and energy density correlation functions. There are a number of basic properties of time correlation functions which we will discuss the next lecture.

We have already emphasized previously the central role of correlation functions in the theoretical understanding of transport phenomena; they are meaningful quantities from the standpoint of theory, experiment, and simulation. In the case of thermal neutron scattering, the density correlation functions are intimately connected to the double differential scattering cross section, a connection which has been thoroughly discussed in the subject 22.54, Neutron Interactions and Applications, and also in 22.51, Interaction of Radiation with Matter. It is worthwhile to remind ourselves of this connection, in the context of the significance of time correlation functions to experiments.

There are two types of thermal neutron scattering, coherent and incoherent. The former is the more common process, whereas the latter requires the scattering nucleus to have nonzero spin, or the scattering sample have a distribution of isotopes. Incoherent scattering is important because hydrogen, which is a nucleus frequently encountered in all areas of nuclear engineering, has an exceptionally large incoherent scattering cross section (and a rather small coherent scattering cross section). The connection between the double differential scattering cross section, the quantity that one measures in an inelastic scattering experiment, and the density correlation function is

$$\frac{d^2\sigma}{d\Omega d\omega} = a^2 \left(\frac{E_f}{E_i} \right)^{1/2} \frac{1}{2\pi} \int_{-\infty}^{\infty} dt e^{-i\omega t} \int d^3r e^{-i\mathbf{k}\cdot\mathbf{r}} G(\underline{r}, t) \quad (5.6)$$

To define the various quantities in this expression, it is useful to refer to a schematic of the inelastic scattering experiment. As indicated in Fig. 5.1 the incident (initial) beam of

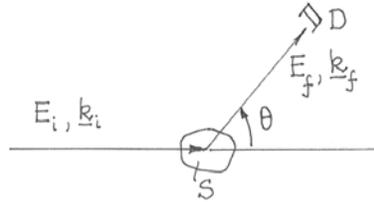


Fig. 5.1. Geometry of inelastic scattering of an incoming beam of thermal neutrons with energy E_i and wave vector \mathbf{k}_i in a sample S at an angle θ . The intensity of the outgoing beam with energy E_f and wave vector \mathbf{k}_f , measured at the detector D , is proportional to the double differential scattering cross section.

thermal neutrons with energy E_i and momentum $\hbar\mathbf{k}_i$ is scattered in the sample at a scattering angle θ , and the outgoing (final) beam has energy E_f and momentum $\hbar\mathbf{k}_f$. The intensity measured at the detector is proportional to the double differential cross section, the left hand side of (5.6). Here $d\Omega = \sin\theta d\theta d\phi$ is the element of solid angle, and $\hbar\omega = E_i - E_f$ is the energy transfer as a result of the scattering. On the right hand side of (5.6), a is the scattering length which is either coherent or incoherent. For coherent scattering the integrand in (5.6) is the density correlation function given by (5.5), whereas for incoherent scattering it is the Van Hove self correlation function (5.4). In either case we see that the measured scattering intensity, aside from the scattering length and the factor $(E_f/E_i)^{1/2}$ which comes from the ratio of outgoing to incoming currents, is just the double Fourier transform of the density correlation function, where $\hbar\mathbf{k} = \hbar\mathbf{k}_i - \hbar\mathbf{k}_f$ is the momentum transfer. For $G(\underline{r}, t)$ the double Fourier transform,

$$S(\underline{k}, \omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dt e^{-i\omega t} \int d^3r e^{i\mathbf{k}\cdot\mathbf{r}} G(\underline{r}, t) \quad (5.7)$$

is known as the dynamic structure factor. For the Van Hove self correlation function there is a corresponding double Fourier transform, $S_s(\underline{k}, \omega)$. Since what one measures in the scattering experiment are the scattering intensity and the energy and momentum transfers, this information is seen to be just the Fourier components (in frequency and wavelength) of the density correlation function.

The connection between the density correlation function, which is fundamental in the theoretical description of structure and dynamics of matter, and the dynamic structure factor, which is the most important quantity measured in inelastic scattering of thermal neutrons, through a double Fourier transform is a particularly significant result. In (5.7) it may appear that the wave vector \underline{k} and frequency ω can take on any value that one wants to specify. While this is true if (5.7) were regarded as a formal definition, it would not be true if we take S to be the experimentally measured quantity in which case the magnitudes of the momentum and energy transfers would be set by the instrumental resolutions of the neutron scattering experiment. That is to say, there are practical limits to what are the practical ranges of momentum and energy transfers that one measure in neutron scattering. This is not a trivial issue in comparing the information that one can obtain from neutron scattering with that given by x-ray or light scattering, for example. For now, we will not be concerned with this aspect, and regard (5.7) as a mathematical relation between two functions, one in space-time and the other in wave vector and frequency.

Before closing we remind the reader that G_s gives dynamical information about tagged-particle motions, where G gives structural and dynamical information about collective motions. For the study of diffusion we will be concerned with G_s . One should also keep in mind that G is the full density correlation function, as such it contains the information that is expressed in G_s . By this we mean that from their definitions one can write G as $G = G_s + G_d$, where G_d is known as the distinct correlation function, that is, it correlates a particle at the origin at time zero with a different particle at r and time t . While this decomposition is exact, it is not always a simple matter to extract G_s when given G . Nonetheless, we can say that G_s describes the tagged particle motion whereas G_d describes the motions between particles (interference effects?), and there is no overlap between the two. In contrast, there is overlap between G and G_s . Since G and G_s are related to coherent and incoherent neutron scattering respectively, the overlap also exists between coherent and incoherent scattering.

In the next lecture we will discuss the basic properties of time correlation functions in general, and those of the density correlation functions in particular. In terms of diffusion, the reader should pay special attention to the connection between the quantities which we have discussed up to now, the diffusion coefficient, the mean square displacement function, the velocity autocorrelation function, and now the Van Hove self correlation function and the density correlation function.