

**22.103 Microscopic Theory of Transport (Fall 2003)**  
**Lecture 6 (9/19/03)**

**Static and Short Time Properties of Time Correlation Functions**

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**References --**

Boon and Yip, Chap 2

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There are a number of properties of time correlation functions which follow from their definitions, sometimes in a straightforward manner and other times not so simply. It is important to make note of them because not only do they have useful physical meanings, but also they are often used to formulate model descriptions of time correlation functions. Actually we have already encountered several examples in our discussion of diffusion, for example, the relation between the long-time behavior of the mean-squared displacement function and the diffusion coefficient.

**Static Correlation Functions**

Since a time correlation function is a function of time, one can always ask about its value at time  $t = 0$ , also known as the initial value. This value is the correlation of two variables (which may be different or the same) at the same time but at different spatial positions. Correlation functions which have spatial variations but do not depend on time are called static. We have seen that the initial value of the Van Hove self correlation function is just the delta function, (4.5). It is an interesting exercise to work out the corresponding initial value for the density correlation function  $G(\underline{r}, t)$ . Setting  $t = 0$  in (5.5) we find

$$G(\underline{r}, 0) = \delta(\underline{r}) + n[g(r) - 1] \quad (6.1)$$

where

$$\begin{aligned} n^2 g(r) &= \sum_{i,j}^N \langle \delta(\underline{r} - \underline{R}_i) \delta(\underline{R}_j) \rangle \\ &= \frac{N(N-1)}{Q_N} \int d^3 R_3 \cdots d^3 R_N e^{-U(0, \underline{R}_3, \dots, \underline{R}_N) / k_B T} \end{aligned} \quad (6.2)$$

The function  $g(r)$  is well-known in liquid-state theory as the equilibrium pair distribution or the radial distribution function (RDF). This is the quantity that one obtains from an x-ray or neutron diffraction measurement. Recall from the previous lecture that  $G$  is the sum of  $G_s$  and  $G_d$ . Eq.(6.1) shows that the first term is the initial value of  $G_s$  as we already know from (4.5). The second term is therefore the initial value of  $G_d$ .

Because  $g(r)$  is the fundamental quantity in the equilibrium theory of liquids [see McQuarrie], we digress somewhat from the present discussion of time-dependent density correlation functions to examine its relation to the canonical distribution function. Suppose we define

$$P_N^{(N)}(\underline{r}_1 \dots \underline{r}_N) d^3 r_1 \dots d^3 r_N = \frac{e^{-\beta U_N}}{Z_N} d^3 r_1 \dots d^3 r_N \quad (6.3)$$

as the probability that atom 1 is in  $d^3 r_1$  about  $\underline{r}_1$ , ..., atom N is in  $d^3 r_N$  about  $\underline{r}_N$ . Integrating this over the positions of atoms n+1 through N gives

$$P_N^{(n)}(\underline{r}_1 \dots \underline{r}_n) = \frac{1}{Z_N} \int \dots \int d^3 r_{n+1} \dots d^3 r_N e^{-\beta U_N} \quad (6.4)$$

gives the probability that atom 1 is in  $d^3 r_1$  about  $\underline{r}_1$ , ..., atom n is in  $d^3 r_n$  about  $\underline{r}_n$  irrespective of the positions of atoms n+1 through N. Now the probability that any atom is in  $d^3 r_n$ , any other atom is in  $d^3 r_2$ , any atom other than the first two is in  $d^3 r_3$ , ..., and any atom other than the previous n-1 atoms is in  $d^3 r_n$  is

$$n^{(n)}(\underline{r}_1 \dots \underline{r}_n) = \frac{N!}{(N-n)!} P_N^{(n)}(\underline{r}_1 \dots \underline{r}_n) \quad (6.5)$$

where  $N!/(N-n)!$  is the number of ways one can pick n objects out of N possible choices. For example, the number of ways of picking two atoms out of an N-particle system is  $N!/(N-2)! = N(N-1)$ . Given (6.5), we have

$$\frac{1}{V} \int d^3 r_1 n^{(1)}(\underline{r}_1) = \frac{N}{V} \equiv \rho \quad (6.6)$$

which is the number density of the system (usually denoted as  $n$  and taken to be a constant). We next define the n-particle correlation function  $g^{(n)}(\underline{r}_1 \dots \underline{r}_n)$  by writing

$$n^{(n)}(\underline{r}_1 \dots \underline{r}_n) = n^n g^{(n)}(\underline{r}_1 \dots \underline{r}_n) \quad (6.7)$$

Notice that if the atoms are not correlated, then  $n^{(n)} = n^n$ , and  $g^{(n)} \equiv 1$ . This is what we mean operationally when we say there is no spatial correlation among the n-particles in the system. Combining (6.4), (6.5), and (6.77) we obtain a definition of the n-particle correlation function in terms of the canonical distribution,

$$g^{(n)}(\underline{r}_1 \dots \underline{r}_n) = \frac{V^n}{N^n} \frac{N!}{(N-n)!} \frac{1}{Z_N} \int \dots \int d^3 r_{n+1} \dots d^3 r_N e^{-\beta U_N} \quad (6.8)$$

which is the desired relation.

To reduce to the pair distribution function  $g(r)$  we note that in a liquid composed of spherical atoms,  $g^{(2)}(\underline{r}_1, \underline{r}_2)$  depends only on the separation distance  $r = |\underline{r}_1 - \underline{r}_2|$ . Thus we can write  $g^{(2)}(\underline{r}_1, \underline{r}_2) \equiv g(r)$ , or

$$n^{(2)}(\underline{r}_1, \underline{r}_2) = n^2 g(r) \quad (6.9)$$

which is a definition of  $g(r)$  in terms of the  $n$ -particle correlation function (158) with  $n=2$ . It then follows from the above probability distributions that

$$ng(r)d^3r = \text{probability (not normalized) of finding an atom in } d^3r \text{ about } \underline{r} \text{ given an atom is at the origin}$$

To find the normalization we take

$$\int d^3r ng(r) = \int_0^\infty ng(r)4\pi r^2 dr = N - 1 \approx N \quad (6.10)$$

Thus,

$$4\pi r^2 ng(r)dr = \text{number of atoms in a shell of radius } r \text{ and thickness } dr \text{ centered about an atom at the origin}$$

A sketch of  $g(r)$ , which is also known as the pair correlation function or the radial distribution function, for a typical liquid shows its most significant features - a prominent peak at the distance of nearest neighbor separation, and a weaker peak at the second-nearest separation, see Fig. 6.1. Below a certain separation distance  $g(r)$  vanishes, signifying a hard core in the interatomic interaction which gives rise to an excluded volume in the spatial distribution of particles. In other words, particles repel each other at very short range, a basic property associated with the existence of a certain density of the system. At the opposite extreme of large separations,  $g$  approaches unity, signifying the loss of spatial correlation (particles are uncorrelated when they are far apart). It is useful to compare the behavior of  $g(r)$  to that of a typical pair potential like the Lennard-Jones. Indeed at low densities a virial expansion of  $g(r)$  gives  $g(r) \approx e^{-\beta V(r)}$ , where  $V(r)$  is the pair potential. This leads to the definition of a 'potential of mean force'  $V_{\text{eff}}(r) \approx -\ln g(r) / \beta$  which one can apply even to hard-sphere fluids. Since the static structure factor  $S(k)$  and  $g(r)$  are related by Fourier transform, an oscillatory behavior in one function means the other function will also show oscillations. The small wiggles in  $g(r)$  at small  $r$  are numerical artifact of the Fourier transformation. The value of  $S(k)$  in

the limit of zero  $k$  is the compressibility factor, which becomes large in the vicinity of the critical point.

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Yarnell et al., Physical Review A7, p.2130 (1973)  
top graph is fig 6 in paper; bottom graph is fig 4.

**Fig. 6.1.** Radial distribution function  $g(r)$  of liquid argon as obtained by Fourier transform of the measured static structure  $S(Q)$ . Data points are neutron diffraction measurements, the curve is the result of molecular dynamics simulation using the Lennard-Jones potential (Yarnell et al., Phys. Rev. A7, 3130 (1973)).

The oscillatory shape of  $g(r)$  has a simple physical meaning. Suppose we sit on any one of the particles and look around to see how the neighboring particles are distributed. We can do this by drawing a sphere of radius  $r$  around us, with some thickness  $dr$ , and ask how many of the neighbors lie inside this spherical shell, doing this repeatedly with increasing  $r$ . Since for a given  $r$  and  $dr$ , the number of neighbors is just  $4\pi r^2 n g(r) dr$ , the fact that  $g(r)$  is an oscillatory suggests that the neighbors are not uniformly distributed, rather they like to arrange themselves in a shell-like structure. Thus the first peak in  $g(r)$ , which is by far the strongest, signifies the position of the nearest-neighbors, the second peak, the second nearest neighbors, and so on. The peaks are seen to damp out fairly quickly, this is a reflection of the fact that there is only local order in a liquid and no long-range order. One expects that for a crystal the corresponding  $g(r)$  would be a set of very sharp lines, each sitting precisely at the position for the particular neighbors.

Returning to the density correlation functions, we note that just as  $g(r)$  can be measured by neutron and x-ray diffraction,  $G$  and  $G_s$  can be directly measured by neutron inelastic scattering and light scattering. Neutron inelastic scattering experiments actually give the double Fourier transforms of the two density correlation functions,

$$S(k, \omega) = \int_{-\infty}^{\infty} dt \int d^3r e^{i(\underline{k}\cdot\underline{r} - \omega t)} G(\underline{r}, t) \quad (6.11)$$

and the same relation exists between  $S_s(k, \omega)$  and  $G_s(\underline{r}, t)$ .  $S(k, \omega)$  is generally known as the dynamic structure factor, which is reasonable since the Fourier transform of  $g(r)$ ,

$$S(\underline{k}) = 1 + n \int d^3r e^{i\underline{k}\cdot\underline{r}} [g(r) - 1] \quad (6.12)$$

is called the static structure factor.

To see the connection between (6.11) and (6.12), we introduce another quantity which is related to  $S(k, \omega)$  (and therefore  $G(\underline{r}, t)$ ) by writing (6.11) as

$$S(k, \omega) = \int_{-\infty}^{\infty} dt e^{-i\omega t} F(k, t) \quad (6.13)$$

so that the intermediate scattering function  $F$  is just the Fourier spatial transform of  $G(r, t)$  (for isotropic systems such as a simple fluid,  $G$  depends only the magnitude of  $\underline{r}$ ),

$$\begin{aligned} F(k, t) &= \int d^3r e^{i\underline{k}\cdot\underline{r}} G(r, t) \\ &= \langle n_k^*(0) n_k(t) \rangle - (2\pi)^3 \delta(\underline{k}) \end{aligned} \quad (6.14)$$

with

$$n_k(t) = \frac{1}{\sqrt{N}} \sum_{i=1}^N e^{i\underline{k}\cdot\underline{R}_i(t)} \quad (6.15)$$

We now ask what is the initial value of  $F(k, t)$ . At  $t = 0$ , (6.14) gives

$$F(k, 0) = \int d^3r e^{i\underline{k}\cdot\underline{r}} G(r, 0) \quad (6.16)$$

where

$$nG(r, 0) = \langle \sum_{\ell, \ell'} \delta(\underline{r}' - \underline{R}_\ell(0)) \delta(\underline{r} - \underline{R}_{\ell'}(0)) \rangle = -n^2 \quad (6.17)$$

Setting  $\underline{r}' = 0$  without any loss of generality, we can write out the double sum explicitly,

$$\begin{aligned}
nG(r, 0) &= N \langle \delta(\underline{R}_1) \delta(\underline{r} - \underline{R}_1) \rangle + N(N-1) \langle \delta(\underline{R}_1) \delta(\underline{r} - \underline{R}_2) \rangle - n^2 \\
&= \frac{N}{Q_N} \int d^3 R_1 \dots d^3 R_N e^{-\beta U} \delta(\underline{R}_1) \delta(\underline{r}) + \frac{N(N-1)}{Q_N} \int d^3 R_1 \dots d^3 R_N e^{-\beta U} \delta(\underline{R}_1) \delta(\underline{r} - \underline{R}_2) - n^2 \\
&= \frac{N}{V} \delta(\underline{r}) + n^2 g(r) - n^2
\end{aligned} \tag{6.18}$$

Inserting this result into (167) we obtain

$$F(k, 0) = 1 + n \int d^3 r e^{i\mathbf{k}\cdot\mathbf{r}} [g(r) - 1] \equiv S(k) \tag{6.19}$$

Since the information needed to calculate the density correlation functions are the time-dependent particle positions, the output of MD simulations, it follows that MD provides a direct means of determining the correlation functions and their Fourier transforms. In this way, MD is able to provide results that can be used to interpret experiments, as well as results that can be used to test various dynamical models of atomic motions in gases and liquids. Examples of both kinds of applications will be discussed in class.

### Short-Time Behavior and Sum Rules

The initial value of a time correlation is the leading term in a Taylor series expansion in time. Because the Fourier transform of a time correlation function is often also of interest, we can make use of the connection between the coefficients of the Taylor expansion and the frequency moments of the corresponding Fourier transform of the time correlation function. Take the example of the density correlation function where we write

$$\begin{aligned}
F(\underline{k}, t) &= \int d^3 r e^{i\mathbf{k}\cdot\mathbf{r}} G(\underline{r}, t) \\
&= \int_{-\infty}^{\infty} dt e^{i\omega t} S(\underline{k}, \omega)
\end{aligned} \tag{6.20}$$

The Taylor series expansion is

$$F(k, t) = F(k, 0) + \left( \frac{dF(k, t)}{dt} \right)_{t=0} t + \frac{1}{2!} \left( \frac{d^2 F(k, t)}{dt^2} \right)_{t=0} t^2 + \dots \tag{6.21}$$

while from (6.20) we have

$$F(k, t) = \int d\omega S(k, \omega) + it \int d\omega \omega S(k, \omega) + \frac{(it)^2}{2!} \int d\omega \omega^2 S(k, \omega) + \dots \quad (6.22)$$

Matching terms with the same power of  $t$  in (6.21) and (6.22) gives relation between the frequency moments of  $S$ , known as sum rules, to the time derivatives of  $F$ , the coefficients in the Taylor series in (6.21). The first few such relations are:

$$\omega^0(k) = \frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega S(k, \omega) = S(k) \quad (6.23)$$

$$\omega_s^0 = \frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega S_s(k, \omega) = 1 \quad (6.24)$$

$$\begin{aligned} \omega^2(k) &= \frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega \omega^2 S(k, \omega) = (kv_o)^2 \\ &= \omega_s^2(k) = \frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega \omega^2 S_s(k, \omega) \end{aligned} \quad (6.25)$$

where  $v_o^2 = k_B T / m$ , with  $v_o$  being the thermal speed of the particle.

The relations between the coefficients of the time expansion and the frequency moments of the Fourier transform of the time correlation function is quite general; it is applicable to any pair of functions which are Fourier transforms of each other. Since we are dealing with classical time correlation functions, they are even functions in time and frequency. So terms that are odd in  $t$  vanish in (6.21) and (6.22). There are a number of properties of classical correlation functions which do not carry over to quantum mechanical definitions of correlation functions. We do not take the time to discuss them here except to refer the reader to Sec. 2,7 Linear Response Theory for some of the details. To finish up this lecture, we note that there are properties such as long time behavior and relation to transport coefficients, the concept of a memory function, linear response theory, and kinetic theory which are treated in Chap 2 of Boon and Yip. We will return to them at various times in future lectures.