Diffusion and the Van Hove Self Correlation Functions

References --
Boon and Yip, Secs 2.2, 2.5
L. van Hove, "Correlations in Space and Time and Born Approximation Scattering in Systems of Interacting Particles", Phys. Rev. **95**, 249-262 (1954).
G. Vineyard, "Scattering of Slow Neutrons by a Liquid", Phys. Rev. **110**, 999-1010 (1958).

The mean squared displacement function and the velocity autocorrelation function are two functions which describe the dynamical behavior of a particle as it interacts with the other particles in the system. Because we are always focused on the same particle, albeit at different times, the behavior is called single-particle motion. The word 'single-particle' does not mean the particle is moving in isolation (like in a vacuum), rather it means that the correlation over time is localized on the same particle. There is another function which, like $<\Delta^2 r(t)>$ and $\psi(t)$, provides a fundamental description of single-particle dynamics. This function is the correlation of particle density. Let us define

$$G_s(\underline{r} - \underline{r}',t) = V < \delta(\underline{r}' - \underline{R}(0))\delta(\underline{r} - \underline{R}(t)) > \tag{4.1}$$

where $\delta(\underline{r})$ is the Dirac delta function. The function $\delta(\underline{r})$ is essentially a bookkeeping device; it is a singular function which is zero everywhere except at the position $\underline{r} = 0$ (the origin of the coordinate system) where it is infinite. Some basic properties are:

$$\int d^3r \delta(\underline{r}) = 1 \qquad \delta(ax) = \frac{1}{a}\delta(x) \qquad \int dx f(x)\delta(x-a) = f(a) \tag{4.2}$$

For the present discussion we can give the following interpretation to the two delta functions in (4.1),

$$\delta(\underline{r} - \underline{R}(t)) \sim \text{probability that the particle whose coordinate} \tag{4.3}$$
$$\text{is } \underline{R}(t) \text{ is at the position } \underline{r} \text{ at time t}$$

Therefore the physical meaning of $G_s(\underline{r} - \underline{r}',t)$ is the conditional probability that given the particle was at $\underline{r}'$ initially (at time t = 0) it is at $\underline{r}$ at time t later. Another way to see that Gs is a probability is from its spatial integral,

$$\int d^3r G_s(\underline{r},t) = 1 \tag{4.4}$$

which is the statement that the probability of finding the particle somewhere in the system is certainty (particle cannot created or lost).

This simple interpretation is depicted in Fig. 4.1. We will call G_s the self correlation function because it involves two positions of the *same* particle, positions separated by an arbitrary time t. It is also named after L. Van Hove for showing that this is the quantity one measures in incoherent thermal neutron scattering. We will see later that G_s is furthermore an important function from the standpoint of atomistic simulation of gases, liquids and solids. Thus G_s is a function that is meaningful for theory, experiment, and simulation.
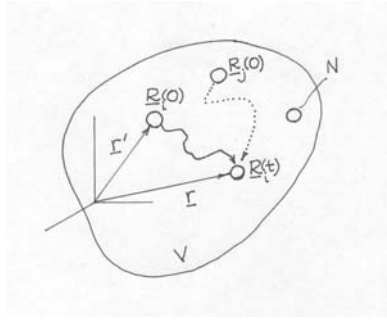
Fig. 4.1. Defining $G_s(\underline{r} - \underline{r}',t)$ as conditioning probability that given the particle is initially at $\underline{r}'$, it will be at $\underline{r}$ at time t. The particle under consideration is particle i. Notice that a different particle, particle j, who was initially somewhere else, can also migrate to position $\underline{r}$ at time t. The contribution from this particle is not included in Gs, but it will be included in another density correlation function $G(\underline{r} - \underline{r}',t)$, to be discussed later.

It is worthwhile to think about what is the dynamical information contained in G_s, especially what connection, if any, it has with molecular diffusion. We first note that the initial value of this function follows directly from its definition, (4.1),

$$G_s(\underline{r},0) = \delta(\underline{r}) \tag{4.5}$$

a result which is physically very intuitive - the probability of finding the particle at time t=0 anywhere other than the origin is zero. Secondly, from Fig. 4.1 we see that by looking at G_s at incremental values of t, we can trace out the path that the particle takes as it moves through the system (the solid wiggly line in Fig. 4.1). Therefore, whatever motion the particle undergoes, including diffusion, it is directly reflected in $G_s(\underline{r},t)$. With $G_s(\underline{r},t)$ being well-defined for any value of t, we expect that only its long-time behavior will show diffusion (if such motions are taking place), while at short times it should show inertial behavior corresponding to the t^2 variation in the mean square displacement function (recall Lecs 2 and 3).

In discussing the mean square displacement function, the velocity autocorrelation function, and now the self correlation function we focus on a single particle as if it has a

label so we can distinguish it from all the other (N-1) particles in the system. This is no problem in computer simulation since every particle does have a label, so we can tell which is particle i at any given time. In theory this is also not a problem because we can give particle i, the particle of interest, an imaginary tag (typically calling it the trace or tagged particle). In experiment, such as neutron scattering, we cannot always any particle that we like. It is sometimes possible to isolate the single particle motions from the collective motions which involve two or more particles. This is the case with incoherent neutron scattering where the scattering nucleus can be tagged if it has a nonzero spin or if there are different isotopes in the sample. This is why we can measure single-particle motions like diffusion with incoherent inelastic scattering, and also collective motions with coherent inelastic scattering. This is essentially the important contribution of Van Hove to the theory of thermal neutron scattering in 1954.

In interpreting (4.1) we have said that the delta function (4.3) can be regarded as the probability of finding the particle at position $\underline{r}$ at time t. It turns out that we can also regard the delta function as a density variable,

$$n_s(\underline{r},t) = \delta(\underline{r} - \underline{R}(t)) \tag{4.6}$$

Normally, we would say the number of particles in an element of volume centered about the position $\underline{r}$ at time t is the time dependent density $n(\underline{r},t)$. With only one tagged particle in the system, the density becomes (4.6) which is also the probability that at time t the particle is at $\underline{r}$. Dimensionally this also works out because the dimension of $\delta(\underline{r})$ is reciprocal volume (see this from the first property in (4.2)). With the interpretation of the delta function as a density, we can rewrite (4.1) as

$$G_s(\underline{r}-\underline{r}',t) = V < n_s(\underline{r}',0)n_s(\underline{r},t) > \tag{4.7}$$

This shows that the Van Hove self correlation function is actually a density correlation function for a tagged particle.

We will have more to say about Gs in the following lectures. For now we will close this lecture by suggesting a connection between the mean squared displacement function $<\Delta^2 r(t)>$ and $G_s(\underline{r},t)$. The connection is that $<\Delta^2 r(t)>$ is the second spatial moment of $G_s(\underline{r},t)$,

$$<\Delta^2 r(t)> = \int d^3 r \, r^2 G_s(\underline{r},t) \tag{4.8}$$

While this may or may not be intuitively reasonable to the reader, it is worth thinking about.