no matter how small the measure of the set of points, the set will be spread out uniformly on the energy surface as the system develops in time. This means that any two points in this set will typically head to very different regions of phase space no matter how close the two points may have been initially. The trajectories of the points must then be very sensitive functions of the initial coordinates and momenta of the particles of the system. This sensitive dependence of trajectories on initial conditions is the characteristic feature of chaotic systems.

A simple example of this separation of nearby trajectories is illustrated in Fig. 7.2. Here we illustrate the classical Lorentz gas. A collection of fixed scatterers is placed at random in space - here we use hard disks on a plane - and a point particle moves with constant velocity along straight line paths until it collides with a scatterer whereupon it makes a specular, energy conserving collision. This is a well known model for studying the diffusion of electrons in amorphous materials. We show two trajectories that start at the same point in space, but with slightly different directions of the velocity vector. Note that the two trajectories separate at each collision with a scatterer in exactly the same way that a beam of light is dispersed by a convex mirror. After a number of collisions the two trajectories are sufficiently far apart that one trajectory includes a collision with a scatterer that is just missed by the other one. After that, the two trajectories are completely different, each exploring a different region of space. Something like this takes place in the much higher dimensional phase space for systems where all of the particles are moving, and this picture is at the heart of the ergodic theory of billiard systems developed by Sinai and others.

Moreover, one can argue that most of the constants of the motion for a mixing system must be very singular functions of the initial coordinates and momenta, as well. One knows from elementary mechanical considerations that a system of N particles in three dimensions has $6N$ constants of the motion. One of these constants is the total energy of the system, another constant fixes the initial point on the trajectory. Except for perhaps a few

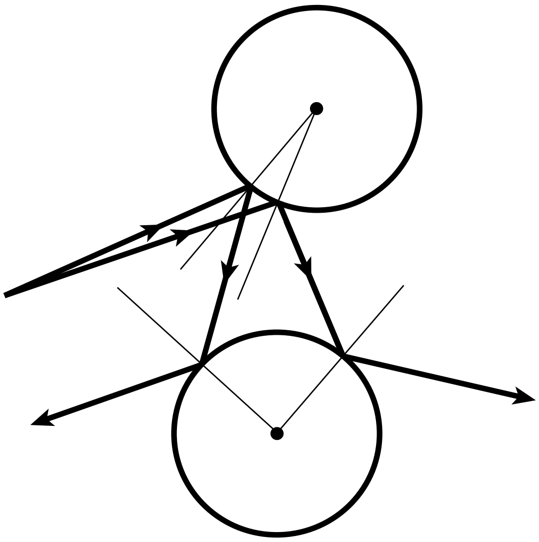

Figure 7.2: Separation of Trajectories in a Lorentz Gas.

other constants of the motion, such as the total momentum, we cannot fix the other constants of the motion when we prepare a system in the laboratory. Now if the system is ergodic its trajectory must pass arbitrarily close to almost every point on the constant energy surface. All of these other points may have very different values for these "uncontrolled" constants of the motion, so the values of these other constants of the motion must be such singular functions of the phase points that in any close neighborhood of almost every point the "uncontrolled" constants take on all possible values! In the theory of functions of complex variables one defines an "essential singularity" of a function as a point where the function takes on all values (for example, the point $z = 0$ for the function $f(z) = \exp(-1/z)$). We might say that the "uncontrolled" constants of the motion have essential singularities at almost every point on the constant energy surface.

Consequently, we are able to justify the methods of non-equilibrium statistical mechanics for systems that show sensitive dependence on initial conditions, and very complex behavior of the phase space trajectories, such that we can prove them to be mixing systems.

As the first example of the application of the idea that phase space trajectories may depend very sensitively upon the parameters used to specify the state of the system, we turn to one of the most interesting controversies in non-equilibrium statistical mechanics: van Kampen's objections to linear response theory.

Chapter 8

The Green-Kubo Formulae

8.1 Linear Response Theory

[Reference: N.G. van Kampen, "The Case Against Linear Response Theory", Physica Norvegica, **5**, 279, (1971).]

Linear Response Theory describes the changes that a small applied external field induces in the macroscopic quantities of a system in equilibrium. The external field is supposed to be turned on at some initial time, when the system is in equilibrium, and then treated as a perturbation. As an example of linear response theory we show how to use it to obtain the time correlation function expression - often called the Green-Kubo expression - for the electrical conductivity of a system that contains charged particles. If the applied electric field is small enough that heating effects can be ignored, then Ohm's law can be expressed as $\vec{J}_e = \sigma\vec{E}$, where $\vec{J}_e$ is the electrical current density, $\vec{E}$ is the applied electric field, and σ is the electrical conductivity that we wish to compute. The time correlation formula is an example of a set of formulae which relate transport coefficients in a fluid to time integrals of time correlation functions. In the last section of this chapter we will give an example of the derivation of such formulae for the case of tagged particle diffusion. First we wish to examine one particular derivation of the formula for the electrical conductivity which has provoked a great deal of very instructive discussion, which, in turn, is closely connected to the general theme of these lectures.

Suppose that a small electric field is applied to a system of charged particles at $t = 0$. Liouville's equation, Eq. 4.3, can be written in the form :

$$\frac{\partial \rho}{\partial t} + \{\rho, H\} = 0, \tag{8.1}$$

where $\{,\}$ are the Poisson-brackets :

$$\{A, B\} = \sum_i \left[\frac{\partial A}{\partial \vec{r}_i} \frac{\partial B}{\partial \vec{p}_i} - \frac{\partial A}{\partial \vec{p}_i} \frac{\partial B}{\partial \vec{r}_i} \right]$$

The Hamiltonian, H, depends on the time and it consists of two parts $H = H_0 + H_1$; the free field Hamiltonian with the kinetic and potential energy of the particles,

$$H_0 = \sum_i \frac{{p_i}^2}{2m} + \sum_{i<j} \phi_{ij}$$

and a term for the interaction of the particles with the electrical field,

$$H_1 = -\sum_i q_i (\vec{r}_i \cdot \vec{E}(t))$$

where q_i is the charge of the i th particle. Since the electric field is weak an expansion of the phase space density ρ can be obtained as an expansion in powers of the electric field :

$$\rho = \rho_0 + \rho_1 + \dots$$

Substituting this in Liouville's equation and examining each power of $\vec{E}$, we obtain the zeroth order equation :

$$\frac{\partial \rho_0}{\partial t} + \{\rho_0, H_0\} = 0. \tag{8.2}$$

The first order terms give

$$\frac{\partial \rho_1}{\partial t} + \{\rho_0, H_1\} + \{\rho_1, H_0\} = 0 \tag{8.3}$$

and so on. Now the following assumptions are made :

1) ρ_0 is the equilibrium distribution of the system without the electric field. A canonical ensemble is taken :

$$\rho_0 = \frac{1}{Z} e^{-\beta H_0},$$

where the normalization factor, Z , is the partition function.

Since the zeroth order equation 8.2 can be solved, the inhomogeneous term in the first order equation 8.3 is known and Eq. 8.3 can be written as

$$\frac{\partial \rho_1}{\partial t} + L\rho_1 = -\{\rho_0, H_1\}$$

Here L is a linear operator, called the Liouville operator defined by the Poisson bracket, $L\rho_1 = \{\rho_1, H_0\}$.

2) Equation 8.3 can be integrated :

$$\rho_1(t) = e^{-(t-t_0)L}\rho_1(t_0) - \int_{t_0}^{t} e^{-(t-\tau)L}\{\rho_0, H_1(\tau)\}d\tau$$

3) At $t = t_0$ the electric field is turned on, $t < t_0 : \vec{E}(t) = 0$, $\rho_1(t_0) = 0$

Then to first order in the electric field, the phase space density ρ is given as

$$\begin{aligned} \rho = \rho_0 + \rho_1 &= \rho_0 - \int_{t_0}^{t} e^{-(t-\tau)L}\{\frac{1}{Z}e^{-\beta H_0}, -\sum_i q_i(\vec{r}_i \cdot \vec{E}(\tau))\}d\tau \\ &= \rho_0 - \int_{t_0}^{t} e^{-(t-\tau)L}\sum_i \left[\frac{\partial}{\partial \vec{r}_i}\frac{1}{Z}e^{-\beta H_0}\frac{\partial H_1}{\partial \vec{p}_i} - \frac{\partial H_1}{\partial \vec{r}_i}\frac{\partial}{\partial \vec{p}_i}\frac{1}{Z}e^{-\beta H_0}\right] d\tau \end{aligned} \tag{8.4}$$

The first term in the brackets on the right hand side is zero, because H_1 doesn't depend on p_i, but the second term gives :

$$\rho = \rho_0 - \int_{t_0}^{t} e^{-(t-\tau)L}(-\sum_i -q_i\vec{E}_i(\tau) \cdot (-\frac{\beta \vec{p}_i}{m})\rho_0)d\tau \tag{8.5}$$

The microscopic form of the total electrical current $\vec{j}$ is defined by $\vec{j} = \sum_i q_i\vec{v}_i$, then

$$\rho = \rho_0 + \beta\int_{t_0}^{t} e^{-(t-\tau)L}\rho_0\vec{j} \cdot \vec{E}(\tau)d\tau$$

We need a slight digression in order to understand this result. To do this we consider some function in phase-space that has no explicit time-dependence, $A = A(r_i, p_i)$. Then A will still change with time since it is a function of the coordinates and momenta, and these quantities do change with time along a trajectory in phase space. Therefore the time dependence of A is determined by

$$\frac{dA}{dt} = \sum_i \frac{\vec{p_i}}{m} \cdot \frac{\partial A}{\partial \vec{r_i}} + \sum_i \vec{p_i} \cdot \frac{\partial A}{\partial \vec{p_i}} = LA,$$

so

$$A(\Gamma_t) = e^{tL} A(\Gamma). \tag{8.6}$$

The operator e^{tL} is a time-displacement operator that moves a phase-point forwards in time. This can be used to write Eq. 8.5 as

$$\rho = \rho_0 + \beta \int_{t_0}^{t} d\tau \vec{j}(-(t-\tau)) \cdot \vec{E}(\tau) \rho_0(-(t-\tau))$$

Here we have used a short-hand notation where $A(\Gamma_{-(t-\tau)}) \equiv A(-(t-\tau))$. Because $H_0(\Gamma)$ is constant in time it follows from assumption 1 that $\rho_0(\Gamma)$ is independent of time and can be taken outside the integral so that

$$\rho(\Gamma, t) = \rho_0(\Gamma) \left[1 + \beta \int_{t_0}^{t} d\tau \vec{E}(\tau) \cdot \vec{j}(\Gamma(-(t-\tau)) \right]$$

With this result for the phase space distribution function, we can express the ensemble-average of $\vec{j}$ at time t to first order in the electric field as :

$$\langle \vec{j} \rangle_t = \int d\Gamma \vec{j}(\Gamma) \rho(\Gamma, t) = \int d\Gamma \vec{j}(\Gamma) \rho_0 \left[1 + \beta \int_{t_0}^{t} d\tau e^{-(t-\tau)L} (\vec{E}(\tau) \cdot \vec{j}(\Gamma)) \right] \tag{8.7}$$

The first term is the average electrical current in the absence of an electric field. Written out in full this term looks like

$$\int d\vec{r}_1 d\vec{p}_1 \ldots d\vec{r}_n d\vec{p}_n (\sum_j q_j \vec{v}_j) \frac{1}{Z} e^{-\beta(\sum_i \frac{p_i^2}{2m} + \Phi)} = 0,$$

because each term in the integrand is odd under $\vec{v}_i \to -\vec{v}_i$. In equilibrium there is no current.

In the second term, we change the integration variable to $\tau' = t - \tau$ so that Eq. 8.6 can be used to obtain

$$\begin{aligned} \langle \vec{j} \rangle_t &= \beta \int d\Gamma \rho_0(\Gamma) \vec{j}(\Gamma) \int_0^{t-t_0} d\tau' e^{-\tau' L} (\vec{E}(t-\tau') \cdot \vec{j}(\Gamma)) \\ &= \beta \int_0^{t-t_0} d\tau < \vec{j}(\Gamma) \vec{j}(\Gamma_{-\tau}) > \cdot \vec{E}(t-\tau). \end{aligned}$$

The $<>$ denotes the equilibrium canonical ensemble-average. We take $\vec{E}(t)$ to be an oscillating field, $\vec{E}(t) = \vec{E}_0 e^{i\omega t},\ t > 0$, so that we have

$$\langle \vec{j} \rangle_t = \beta \int_0^{t-t_0} d\tau e^{-i\omega\tau} \langle \vec{j}(\Gamma) \vec{j}(\Gamma_{-\tau}) \rangle \cdot \vec{E}_0 e^{i\omega t}.$$

Let $t_0 = 0$ and $t \to \infty$. Then we obtain Ohm's Law for $\vec{J}_e = \langle \vec{j} \rangle_t / V$:

$$\vec{J}_e = \sigma(\omega) \cdot \vec{E}(t),$$

where $\sigma(\omega)$ is a tensor of rank two

$$\sigma(\omega) = \beta \frac{1}{V} \int_0^{\infty} d\tau e^{-i\omega\tau} < \vec{j}(\Gamma) \vec{j}(\Gamma_{-\tau}) >,$$

which depends on the whole history of the system. This is the famous Green-Kubo formula for the electrical conductivity of a system of charged particles.

The average in the integrand is an equilibrium time-correlation function

$$\langle \vec{j}(\Gamma) \vec{j}(\Gamma_t) \rangle = \frac{1}{Z} \int d\Gamma e^{-\beta H_0} \sum_i \sum_j q_i q_j \vec{v}_i(0) \vec{v}_j(t) \tag{8.8}$$

Equation 8.6, written out

$$A(\Gamma(t)) = e^{t \sum_i (\vec{v}_i \cdot \frac{\partial}{\partial \vec{r}_i} + F_i \cdot \frac{\partial}{\partial \vec{p}_i})} A(\Gamma)$$

shows that the combination of $\vec{v} \to -\vec{v}$ and $t \to -t$ is a symmetry. Since the time-correlation function is symmetrical under $\vec{v} \to -\vec{v}$, we also have

$$< \vec{j}(\Gamma) \vec{j}(\Gamma_t) > = < \vec{j}(\Gamma) \vec{j}(\Gamma_{-t}) >$$

Thus the electrical conductivity can be written as :

$$\sigma(\omega) = \beta \frac{1}{V} \int_0^\infty d\tau e^{-i\omega t} < \vec{j}(\Gamma)\vec{j}(\Gamma_t) >$$

This formula is generally believed to be correct, and it is in agreement with experimental and computer simulation results for small electrical fields. Moreover, it is possible to derive similar expressions for all of the transport coefficients - viscosities, thermal conductivities, etc. by devising external fields that induce shearing in a fluid, or temperature gradients. There are also alternative derivations which do not rely on external fields but instead are based upon Chapman-Enskog solutions of the Liouville equation, similar in spirit, at least, to the Chapman -Enskog solution of the Boltzmann equation presented in Chapter 3.

N.G. van Kampen has argued that linear-response theory derivations of the Green-Kubo formulae as given above for the electrical conductivity are at best questionable.

8.2 van Kampen's Objections

[Responses to van Kampen's objections can be found in G.P. Morriss, D.J. Evans, E.G.D. Cohen, and H. van Beijeren, Phys. Rev. Lett. **62**, 1579, (1989); R. Kubo, M. Toda, and N. Hashitsume, *Statistical Physics II,* 2nd. ed., Springer-Verlag, Berlin, (1991).; and N.I. Chernov, G.L. Eyink, J.L. Lebowitz, and Ya. G. Sinai, Comm. Math. Phys. **154,** 569, (1993)]

While not objecting particularly to the Green-Kubo formulae themselves, van Kampen argues that the linear-response derivation of them is artificial and misses the essential points needed for a precise understanding of the validity of the linear laws.

To understand his concerns let's summarize the steps in the derivation just presented.

1) We solved Liouville's equation by following the phase space trajectory through every point in Γ space backward in time.

2) We assumed that the trajectory in an electric field can be determined by an expansion about the unperturbed trajectory in powers of the electric field $\vec{E}$. That is, the full equations of motion for the system in the presence of $\vec{E}$ were not solved in the derivation of the Green-Kubo formula, instead the dynamics were only kept to first order in E.

The $\vec{E}$-field accelerates the charged particles which leads to "ohmic" heating which was not taken into account. This heating is neglected because it is of order $\vec{E}^2$.

3) We then obtained Ohm's law $\vec{J}_e = \sigma\vec{E}$.

This derivation occasioned two objections from van Kampen:

Objection I : The deviation of the trajectory of a particle from its path can only be approximated by linearization if the electric field is extremely small. If the particle moves freely without colliding, its motion is given by $\vec{x}(t) = \vec{x}_0 + \vec{v}_0 t + \frac{q\vec{E}t^2}{2m}$. Even neglecting the collisions (which are in fact crucial to our understanding of what is going on here) during a time t the linearized equation is only correct if the third term is very small with respect to the average distance between particles. An estimate can be found in van Kampen's paper : $|\vec{E}| < 10^{-18}$Volts/cm.

Objection II : The derivation suggests that the linear dependence of the macroscopic quantity $\langle J \rangle$ on the electric field originates from a linear effect the field has on the trajectory of a particle, but the actual trajectory of a single particle changes very drastically as a result of the field (see Fig. 8.1). 'Macroscopic linearity is different from microscopic linearity'.

It is here that the discussion of chaos in the last chapter becomes very relevant! Remember that two nearby trajectories will eventually move into very different regions of phase space if the system is mixing. Consider as an example the Lorentz model of an electron moving in an array of fixed scatterers placed at random in space. Now suppose that we consider a trajectory starting at some phase point for the electron given by $\vec{r}_0, \vec{v}_0$. Suppose we compare the trajectory of the electron starting from this point obtained without an external electric field with the trajectory from this point but when an external electric

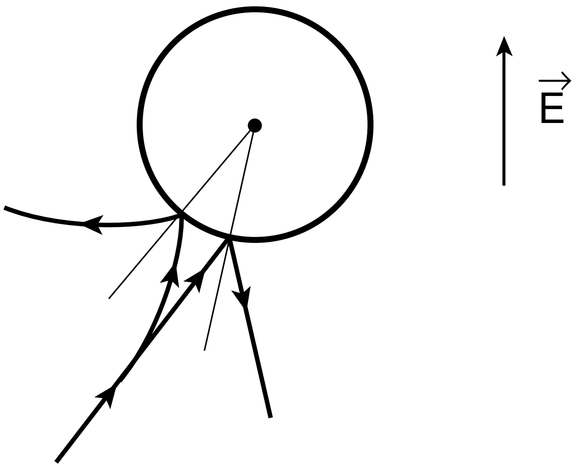

Figure 8.1: Non-linear Divergence of Trajectory in a Field from a Field- Free Trajectory With Identical Initial Conditions.

field is applied to the system. After a few collisions the trajectories will be very different - the field free and the non-zero field trajectories will be in very different parts of configuration and velocity space. The difference between the two trajectories will not in any sense be able to be described as being linear in the applied electric field, no matter how small the field may be. Thus van Kampen's objections to this linear response theory derivation of the Green-Kubo formulae is perfectly consistent with our understanding of the chaotic behavior of physical systems in which normal transport processes are taking place. We conclude that a careful derivation of the Green-Kubo formulae requires a linearization in the applied fields to be carried out only *after* the effects of the external fields on the dynamics has been correctly accounted for. The linear laws of hydrodynamics such as Ohm's law are not only due to the smallness of the applied field but must also be due to some very ergodic behavior of the system in the presence of the field which allows an expansion of the average properties of the system in powers of the field strength when all of the phase space averaging has been carried out properly.

The responses to van Kampen's objections in the papers and book mentioned above are based on the following very plausible line of reasoning: Statistical mechanical calculations really refer to probability distributions for the behavior of a large number of independent electrons rather than to the behavior of an individual electron. The crucial quantity for such probability distribution in any more rigorous theory for the average behavior of the electron is very likely to be the range of times t for which the velocity of the electron, $\vec{v}(t)$, is correlated to its initial velocity, $\vec{v}(0)$. We know both from theoretical studies as well as from computer simulations, that this time interval will be on the order of a mean free time, t_0. One would certainly expect this on the basis of ergodic arguments alone, since after a few scatterings, the particle's velocity becomes randomized. Therefore, the time, t that should be inserted in the formula to determine the range of validity in Kubo's argument, $\frac{q\vec{E}t^2}{2m}$, is the mean free time t_0, rather than the physical time t. For a dilute gas, t_0 is on the order of 10^{-9} sec. This effect alone is sufficient to get the value of E, for which this fraction is small, in the range of physically realistic values. Nevertheless, it is still necessary to refine the mathematical support for the Green-Kubo formulae to the point that these arguments become clearer and more rigorous, rather than just plausible. A really fundamental derivation of these formulae must certainly rely on an ergodic theorem which will allow the linearization of ensemble averages, and will show that Green-Kubo formulae can be applied to systems subjected to realistic external fields.

In the derivation of $\vec{J}_T = -D\vec{\nabla}P$ from the Boltzmann equation we obtained a linear law only after we had used some kind of ensemble-averaging to derive the Boltzmann equation, in contrast to the derivation of the Green-Kubo formula, where the ensemble-averaging took place after linearization. Green's derivation of the Green-Kubo formulae used a Fokker-Planck equation in phase-space, and had many similarities to Boltzmann's derivation of hydrodynamic equation from the Boltzmann-equation. In his derivation the ensemble averages were carried out first and only then were the resulting equations linearized to give the G-K formulae.

8.3 The Green-Kubo Formula: Diffusion

[References: J.R. Dorfman, "Kinetic and Hydrodynamic Theory of Time Correlation Functions", in *Fundamental Problems in Statistical Mechanics, III,* E.G.D. Cohen, ed., North Holland Publ. Co., Amsterdam, (1975); J.-P. Boon and S. Yip, *Molecular Hydrodynamics,* reprinted by Dover Publ. Co., New York (1980)]

Now that we have discussed the linear response derivation of the time correlation function expression for the coefficient of electrical conductivity, and the various problems associated with this derivation, we now turn to the standard derivation of the Green-Kubo formulae. This derivation does not rely on perturbation theory for determining the phase space trajectories of a system. Instead, its roots are in the Chapman-Enskog solution of the Boltzmann transport equation. A non-equilibrium macroscopic state is set up, and we follow the relaxation of this state to an equilibrium state. As a result, any ergodic type theorems that may be required for a rigorous understanding of the method may be formulated in terms of the behavior of certain time correlation functions, as we will see presently.

As we did for the Boltzmann equation, we consider a simple transport process where we study the diffusion of a tagged particle in a fluid of particles that are mechanically identical to the tagged one, and where the "bath" particles are maintained in an state of thermal equilibrium. More complicated transport processes can and have been discussed in the literature, but this case will suffice to illustrate the method.

We begin by observing that if the fluid were in total equilibrium - including the tagged particle- then the probability of finding the tagged particle in a region of volume $d\vec{r}$ about a point $\vec{r}$ in the fluid would be $d\vec{r}/V$ for a finite system of volume V. We thus consider an initial situation where the tagged particle has a spatial probability distribution $W(\vec{r}_1) \neq 1/V$, and we use the subscript 1 to denote the tagged particle. The rest of the fluid is supposed to be in thermal equilibrium at the initial time. The properly normalized

N-particle distribution function which satisfies the above conditions at time $t = 0$, is given by

$$\rho(\Gamma, t = 0) = \frac{V}{Z}[\exp(-\beta H_N)]W(\vec{r}_1), \tag{8.9}$$

where Z is given by

$$Z = \int d\Gamma \exp(-\beta H_N), \tag{8.10}$$

and

$$\int d\vec{r}_1 W(\vec{r}_1) = 1. \tag{8.11}$$

After a time t, the phase space distribution becomes $\rho(\Gamma, t)$ given by

$$\rho(\Gamma, t) = e^{-tL}\rho(\Gamma, t = 0) = \frac{V}{Z}e^{-tL}e^{-\beta H_N}W(\vec{r}_1). \tag{8.12}$$

The probability of finding the tagged particle at a point $\vec{r}$ at time t, averaged over the configurations and velocities of all of the other particles is then

$$\begin{aligned} P(\vec{r}, t) &= \int d\Gamma \delta(\vec{r}_1 - \vec{r})\rho(\Gamma, t) \\ &= \frac{V}{Z}\int d\Gamma \delta(\vec{r}_1 - \vec{r})e^{-tL}e^{-\beta H_N}W(\vec{r}_1). \end{aligned} \tag{8.13}$$

This expression may be transformed using Liouville's theorem to

$$P(\vec{r}, t) = \frac{V}{Z}\int d\Gamma e^{-\beta H_N}W(\vec{r}_1)\delta(\vec{r}_1(t) - \vec{r}) \tag{8.14}$$

where $\delta(\vec{r}_1(t) - \vec{r}) = \exp(tL)\delta(\vec{r}_1 - \vec{r})$. It is now useful to insert the Fourier expansion of the delta function in this expression so as to obtain

$$P(\vec{r}, t) = \frac{1}{V}\sum_{\{\vec{k}\}} \exp(-i\vec{k} \cdot \vec{r})P_{\vec{k}}(t), \tag{8.15}$$

where

$$P_{\vec{k}}(t) = \frac{V}{Z}\int d\Gamma \exp(-\beta H_N)W(\vec{r}_1)\exp(i\vec{k} \cdot \vec{r}_1(t)). \tag{8.16}$$

The point of this manipulation is to get the probability distribution in a form where we can follow the time dependence of the long wavelength component of it. The long wave length component is the part that should show hydrodynamic behavior for long times (since it should change on spatial scales on the order of the range of the density gradients), so we need to look at $P_{\vec{k}}(t)$ for small $|\vec{k}|$. Expression 8.16 can be simplified some more if we remember that both H_N and $\vec{r}_1(t) - \vec{r}_1$ depend only on relative distances $\vec{r}_{ij} = \vec{r}_i - \vec{r}_j$. If we suppose that we place periodic boundary conditions on the system we can write

$$\begin{aligned} P_{\vec{k}}(t) &= \frac{V}{Z}\int d\Gamma \exp(i\vec{k}\cdot\vec{r}_1)W(\vec{r}_1)\exp(-\beta H_N)\cdot(\exp(i\vec{k}\cdot(\vec{r}_1(t)-\vec{r}_1))) \\ &= W_{\vec{k}}F(\vec{k},t), \end{aligned} \tag{8.17}$$

where

$$W_{\vec{k}} = \int d\vec{r}_1 e^{i\vec{k}\cdot\vec{r}} W(\vec{r}_1),$$

and the "intermediate scattering function" $F(\vec{k}, t)$ is given by

$$\begin{aligned} F(\vec{k},t) &= \frac{1}{Z}\int d\Gamma \exp(-\beta H_N)\exp(i\vec{k}\cdot\Delta\vec{r}_1(t)) \\ &= \left\langle \exp(i\vec{k}\cdot\Delta\vec{r}_1(t))\right\rangle. \end{aligned} \tag{8.18}$$

Here $\Delta\vec{r}_1(t) = \vec{r}_1(t) - \vec{r}_1$, and the angular brackets denote an equilibrium average in the canonical ensemble. The function $F(\vec{k}, t)$ occurs in the theory of neutron scattering, hence its name.

The function $F(\vec{k}, t)$ has a particularly convenient form since it is the generating function for the moments of the displacement of the tagged particle. To obtain a useful expression for $F(\vec{k}, t)$ we first expand it as a power series in the wave-vector $\vec{k}$ and then express the result in an exponential, leading to the so-called cumulant expansion. That is

$$F(\vec{k},t) = 1 - \frac{k^2}{2}\left\langle (\hat{k}\cdot\Delta\vec{r}_1(t))^2\right\rangle + \cdots, \tag{8.19}$$

where $\hat{k}$ is a unit vector in the direction of $\vec{k}$, and $|\vec{k}| = k$. All odd powers of $\vec{k}$ vanish in this series due to the spatial isotropy of the equilibrium average. We omit the higher terms since we will not be concerned with them here, but it is certainly possible to develop this series further. Expression 8.19 can be written in exponential form as

$$F(\vec{k},t) = \exp\{-\frac{k^2}{2}\left\langle(\hat{k}\cdot\Delta\vec{r}_1(t))^2\right\rangle + \cdots\}. \tag{8.20}$$

The quantity appearing in the angular brackets in Eq. 8.20 does not depend on the spatial direction of $\hat{k}$ and we may replace this with the value in any particular direction, the x-direction, say, so that

$$F(\vec{k},t) = \exp\{-\frac{k^2}{2}\left\langle(\Delta r_{1x}(t))^2\right\rangle + \cdots\}. \tag{8.21}$$

Equations 8.15-8.21 can be combined to yield an equation for $P(\vec{r},t)$,

$$\begin{aligned}
\frac{\partial P(\vec{r},t)}{\partial t} &= \frac{1}{V}\sum_{\{\vec{k}\}}\exp(-i\vec{k}\cdot\vec{r})W_{\vec{k}}\frac{\partial F(\vec{k},t)}{\partial t} \\
&= -\langle v_{1x}(t)\Delta r_{1x}(t)\rangle\frac{1}{V}\sum_{\{\vec{k}\}}k^2\exp(-i\vec{k}\cdot\vec{r})W_{\vec{k}}F(\vec{k},t) + \cdots \\
&= D(t)\nabla^2 P(\vec{r},t) + \cdots
\end{aligned} \tag{8.22}$$

which looks suspiciously like the diffusion equation that we encountered in Chapter 3. The time dependent diffusion coefficient $D(t)$ in Eq. 8.22 is given by

$$\begin{aligned}
D(t) &= \langle v_{1x}\Delta r_{1x}\rangle = \int_0^t \langle v_{1x}(t)v_{1x}(\tau)\rangle\, d\tau \\
&= \int_0^t \langle v_{1x}(0)v_{1x}(\tau)\rangle\, d\tau.
\end{aligned} \tag{8.23}$$

Here we have used the fact that the equilibrium average of the product of the velocities of the tagged particle at two different times, t and τ, depends only on the interval $t-\tau$. The time dependent diffusion coefficient is clearly zero at $t = 0$. However, we should only expect to obtain a diffusion equation after the tagged particle has had enough time to collide with a number of particles in the fluid such that its trajectory approaches more and more closely that of a particle undergoing a random walk. Thus we expect that $D(t)$ should approach a constant, non zero value for times long compared to the mean free time between collisions, t_0. If this is so, we can identify the macroscopic diffusion coefficient with the microscopic quantity

$$D = \lim_{t>>t_0} \lim_{N\to\infty, V\to\infty, \frac{N}{V}=n} \int_0^t \langle v_{1x}(0) v_{1x}(\tau)\rangle \, d\tau \tag{8.24}$$

where we have also taken the thermodynamic limit so as to remove any dependence of the diffusion coefficient on the system size or on the boundary conditions at the walls of the container. We have therefore obtained an expression for the coefficient of tagged particle diffusion as a time integral of the velocity autocorrelation function for the tagged particle. This is an example of the Green-Kubo formulae for the transport coefficients of a fluid.

We also note an interesting relation between the mean square displacement of the tagged particle and the diffusion coefficient, namely

$$\begin{aligned} \frac{d}{dt}\left\langle (\Delta r_{1x}(t))^2 \right\rangle &= \frac{d}{dt}\int_0^t dt_1 \int_0^t dt_2 \, \langle v_{1x}(t_1) v_{1x}(t_2)\rangle \\ &= 2\int_0^t d\tau \, \langle v_{1x}(0) v_{1x}(\tau)\rangle \\ &= 2D(t) \\ &= 2D \quad \text{for } t >> t_0. \end{aligned} \tag{8.25}$$

We therefore have arrived at the result announced at the end of Chapter 3, that for large times the mean square displacement of the tagged particle satisfies the relation

$$\left\langle (\Delta r_{1x}(t))^2 \right\rangle = 2Dt \tag{8.26}$$

The evaluation of time correlation functions for systems of physical interest is an entire subject in itself, and of considerable interest to researchers in nonequilibrium statistical mechanics. The references listed above will provide the interested reader an introduction to this subject.

One of the interesting subjects for research in this area is to establish the precise behavior of the time correlation functions using methods of dynamical systems theory, and to compare those results with calculations based on the kinetic theory of gases or with the results of computer simulations.