Chapter 4

Calculations of Time Correlation Functions

In the last chapter, we explored the low-frequency, long-wavelength behavior of a system that is disturbed from equilibrium. In the first section of this chapter, we study the opposite limit, and describe how a system behaves at very short times and high frequencies. The study of systems in this limit is referred to as Molecular dynamics.

We are ultimately interested in developing a set of expressions that describe a system at all times and frequencies. In section 2, we will introduce the projection operator and use it to derive the Generalized Langevin Equation. The projection operator allows us to study only the portion of the system we are interested in, and treat the rest as a statistical bath. In section 3, we will use the GLE to derive the viscoelastic model for transverse current. Finally, in section 4, we will introduce mode-coupling theory and discuss its ability to predict long-time tails in velocity correlation functions.

For further information on the subjects covered in this chapter, please consult books by Hansen and McDonald[1], McQuarrie[2], Boon and Yip[3], and Berne [4].

4.1 Short-Time Behavior

4.1.1 Moment Expansion

In chapter 2, we introduced the concept of the time-correlation function. The correlation function for an operator $A(t)$ is given by

$$C(t) = \langle A(t)A(0)\rangle = TrA(t)A(0)\rho_{eq} \tag{4.1}$$

Where the equilibrium density matrix is given by

$$\rho_{eq} = \frac{e^{-\beta\mathcal{H}}}{Q}$$

Here $\mathcal{H}$ and $\mathcal{Q}$ are the Hamiltonian and Partition function for the system. The time evolution of A is given by

$$A(t) = e^{i\mathcal{L}t}A(0)$$

or

$$\dot{A}(t) = i\mathcal{L}A(0)$$

Here, $\mathcal{L}$ is an operator which describes the time evolution of an operator. For quantum mechanical systems, $\mathcal{L}$ is defined as the Liouville operator

$$i\mathcal{L} = \frac{1}{i\hbar}\left[\ldots, \mathcal{H}\right]$$

And for classical systems it is defined as the Poisson operator

$$i\mathcal{L} = \{\ldots, \mathcal{H}\}$$

The evolution operator $\mathcal{L}$ is Hermitian, $\mathcal{L}^+ = \mathcal{L}$. This operator will be discussed in much more detail in section 4.2.

The value of a correlation function in the short time limit $t \to 0$ can be approximated using a moment expansion. As shown in Eq.(4.1), the correlation function of a quantity $A(t)$ is given by

$$C(t) = \langle A(t)A(0)\rangle$$

This quantity $C(t)$ can be written as a Taylor expansion

$$C(t) = \sum_{n=0}^{\infty} \frac{t^n}{n!} C^{(n)}(0)$$

This formula can be simplified by noting that all correlation functions are even in time. As a result, any odd-valued derivative of $C(t)$ will be zero when evaluated at $t = 0$. Therefore, all of the odd terms of this expansion can be dropped

$$C(t) = \sum_{n=0}^{\infty} \frac{t^{2n}}{(2n)!} C^{(2n)}(0)$$

The derivative of a correlation function can be written as

$$C^{(2n)}(t) = (-1)^n \left\langle A^{(2n)}(t)A(0)\right\rangle$$

Using this expression, the Taylor expansion can be written in terms of the function $A(t)$

$$C(t) = \sum_{n=0}^{\infty} (-1)^n \frac{t^{2n}}{(2n)!} \left\langle A^{(2n)}(0)A(0)\right\rangle$$

This expression can be further simplified using the definition $\left\langle A^{(2n)}(0)|A(0)\right\rangle = -\left\langle A^{(n)}(0)|A^{(n)}(0)\right\rangle$, where the notation $\langle A|B\rangle = \langle AB^+\rangle = TrAB^+\rho_{eq}$

$$C(t) = \sum_{n=0}^{\infty} \frac{t^{2n}}{(2n)!} \left\langle A^{(n)}A^{(n)}\right\rangle \tag{4.2}$$

In this expression, we are only concerned with the value of $A(t)$ at time 0, and so the explicit time dependence has been dropped. This expression could also be obtained by performing a Taylor expansion on $A(t)$ and substituting it into Eq.(4.1).

We can use the Fourier transform of $C(t)$ to find a general expression for $C_{(2n)}$. Since

$$C^{(2n)} = \frac{1}{2\pi}\int_{-\infty}^{\infty} \tilde{C}(\omega)e^{-i\omega t}dt$$

the time derivatives can be evaluated easily as

$$C^{(2n)} = (-1)^{(n)}\left(\frac{\partial}{\partial t}\right)^{(2n)} C(t) = \frac{1}{2\pi}\int_{-\infty}^{\infty} \tilde{C}(\omega)\omega^{2n}dt = \left\langle \omega^{2n}\right\rangle \tag{4.3}$$

In the next sections, this method is applied to velocity correlation functions and self-scattering functions.

4.1.2 Velocity Correlation Function and Self-Scattering Functions

1. The Velocity Correlation Function The velocity correlation function for the z-directed motion of a particle is defined as

$$C(t) = \frac{1}{3}\langle \vec{v}(t)\vec{v}(0)\rangle = \langle \dot{z}(t)\dot{z}(0)\rangle$$

This expression can be evaluated using Eq.(4.2). At short times, the value of $C(t)$ can be reasonably approximated by taking the first two moments of the expansion

$$C(t) = \frac{1}{3}\langle \vec{v}|\vec{v}\rangle - \frac{t^2}{2}\frac{1}{3}\left\langle \dot{\vec{v}}|\dot{\vec{v}}\right\rangle + \cdots$$

The first moment is simply the the average thermal velocity in the z-direction

$$\frac{1}{3}\langle \vec{v}|\vec{v}\rangle = \frac{1}{\beta m} = v_o^2$$

where $\beta = (k_B T)^{-1}$. The second moment can be evaluated using Newton's equation, $F = ma$. Since $a = \dot{v}$ and $F = -\nabla U$, where U is the potential energy, $\dot{v} = \frac{F}{m} = -\frac{\nabla U}{m}$. Therefore, the second moment is given by

$$\frac{1}{3}\left\langle \dot{\vec{v}}|\dot{\vec{v}}\right\rangle = \frac{1}{3}\frac{\langle \nabla U|\nabla U\rangle}{m^2}$$

To evaluate this expression, write it in its explicit form

$$\frac{1}{3}\frac{\langle \nabla U|\nabla U\rangle}{m^2} = \frac{1}{3m^2}\int dz\partial_z U\partial_z U e^{-\beta U}$$

Note that $\partial_z U e^{-\beta U} = -\frac{1}{\beta}\partial_z e^{-\beta U}$. This allows us to combine terms in the integral to get the expression:

$$\frac{1}{3m^2}\int dz\partial_z U(\frac{1}{\beta}\partial_z e^{-\beta U})$$

Now, carry out a partial integration to get the expression:

$$\frac{1}{3\beta m^2}\int dz\partial_z^2 U e^{-\beta U} = \frac{1}{3\beta m}\left\langle \frac{\partial_z^2 U}{m}\right\rangle$$

Note that we have proven a general property here. For any operator A

$$\langle \nabla U A \rangle = \frac{1}{Q} \int d\mathbf{r} A \nabla U e^{-\beta U} = k_B T \langle \nabla A \rangle \tag{4.4}$$

We have shown that the second term in the expansion of $C(t)$ is proportional to $\left\langle \frac{\partial_z^2 U}{m} \right\rangle$, the curvature of the potential averaged with the Boltzmann weight. This term is called the Einstein frequency Ω_o^2. It is the average collision frequency of the particles in the system. For the specific case of a harmonic potential this is simply the frequency ω^2. However, it can be defined for many types of systems. Simply find the collision frequency for each pair of particles in the system and sum over all pairs. For the velocity correlation function, this can be expressed as

$$\Omega_o^2 = \frac{1}{3m} \left\langle \nabla^2 U \right\rangle = \frac{\rho}{3m} \int d\mathbf{r} g(\mathbf{r}) \nabla^2 \phi \tag{4.5}$$

where ϕ is the pairwise potential between each set of two particles.

Finally, we can write second moment the expansion of $C(t)$ as

$$C(t) \simeq v_o^2 \left(1 - \frac{t^2}{2} \Omega_0^2 \right)$$

2. Self-Intermediate Scattering Function The moment expansion method of estimating the short time behavior of correlation functions can also be applied to self-scattering functions. In chapter 3, we introduced the self-density of a particle i as

$$n_s(\mathbf{R}, t) = \delta(\mathbf{R} - r(t))$$

Which has the Fourier transform

$$n_s(\vec{k}, t) = e^{-i\vec{k}\vec{r}(t)}$$

The self-intermediate scattering function is defined as

$$F_s(\vec{k}, t) = \left\langle n_s(\vec{k}, t) | n_s(\vec{k}, 0) \right\rangle = \left\langle e^{-i\vec{k}\vec{r}(t)} | e^{-i\vec{k}\vec{r}(0)} \right\rangle = \left\langle e^{-i\vec{k}(\vec{r}(t) - \vec{r}(0))} \right\rangle$$

We can apply Eq.(4.2) to estimate the short time behavior of this function. The zero-th moment term is trivial to evaluate:

$$C_0 = F_s(\vec{k}, 0) = \left\langle e^{-i\vec{k}(\vec{r}(0) - \vec{r}(0))} \right\rangle = 1$$

The second order term is given by

$$C_2 = \left\langle \omega^2 \right\rangle = \langle \dot{n}_s | \dot{n}_s \rangle = \left\langle -i\vec{k}\dot{\vec{r}}(0) e^{-i\vec{k}\vec{r}(0)} | - i\vec{k}\dot{\vec{r}}(0) e^{-i\vec{k}\vec{r}(0)} \right\rangle$$

This can be simplified to

$$C_2 = \left\langle (\vec{k}\vec{v}(0))^2 e^{-i\vec{k}(\vec{r}(0) - \vec{r}(0))} \right\rangle = k^2 v_o^2$$

We can defined $\omega_o = k v_o$, which gives second moment of the correlation function

$$C_2 = \omega_o^2$$

The fourth moment of this correlation function is given by

$$C_4 = \left\langle \omega^4 \right\rangle = \langle \ddot{n}_s | \ddot{n}_s \rangle = \left\langle -i\frac{d}{dt}(\vec{k}\dot{\vec{r}}(0)e^{-i\vec{k}\vec{r}(0)})| - i\frac{d}{dt}(\vec{k}\dot{\vec{r}}(0)e^{-i\vec{k}\vec{r}(0)}) \right\rangle$$

Evaluate these derivatives using the product rule and multiply out the terms. The resulting equation will have four terms, two of which cancel out. The remaining two terms are

$$C_4 = (\vec{k}\vec{v})^4 + \left\langle (\vec{k}\dot{\vec{v}})^2 \right\rangle$$

The first term is simply $3\omega_o^4$. The second term can be evaluated by following a similar method to the one we used to calculate the second moment of the velocity correlation function in the previous section. As we demonstrated in that problem, The derivative of the velocity $\vec{v}$ is equivalent to the derivative of the potential divided by the mass. Therefore, this term can be written as

$$\left\langle (\vec{k}\dot{\vec{v}})^2 \right\rangle = \frac{1}{m^2} k^2 \left\langle \nabla_z V \nabla_z V \right\rangle$$

Using Eq.(4.4), we can rewrite this term as

$$\frac{1}{m^2} k_B T k^2 \left\langle \nabla_z^2 V \right\rangle$$

Finally, by doing some rearranging and using $v_o^2 = \frac{k_B T}{m}$, we find that this term can be written as

$$\frac{k_B T}{m} k^2 \left\langle \frac{\nabla_z^2 V}{m} \right\rangle = k^2 v_o^2 \left\langle \frac{\nabla_z^2 V}{m} \right\rangle = \omega_o^2 \Omega_o^2$$

Where Ω_o^2 is the Einstein frequency, as defined in the previous section. Therefore, the short time expansion of $F_s(\vec{k}, t)$,

$$F_s(\vec{k}, t) = 1 - \left\langle \omega^2 \right\rangle \frac{t^2}{2!} + \left\langle \omega^4 \right\rangle \frac{t^4}{4!} - \cdots$$

can be evaluated to

$$F_s\left(\vec{k}, t\right) = 1 - \omega_o^2 \frac{t^2}{2!} + \left(3\omega_o^4 + \omega_o^2 \Omega_o^2\right) \frac{t^4}{4!} - \cdots \tag{4.6}$$

3. Free-Particle Limit (Ideal Fluid) We can use the short time expansion of the self-intermediate scattering function to find an expression for $F_s(\vec{k}, t)$ in the free-particle limit. In the free-particle limit, we assume that the particles behave as an ideal gas; that is, there is no attraction or repulsion between the particles, and their interaction potential is zero $\phi(\vec{r}) = 0$. Recall that the Einstein frequency can be written as (Eq.(4.5))

$$\Omega_o^2 = \frac{\rho}{3m} \int d\vec{r} g(\vec{r}) \nabla^2 \phi(\vec{r})$$

Therefore, if the interaction potential is zero, the Einstein frequency will also be zero. Our expansion for $F_s(\vec{k}, t)$ becomes

$$F_s(\vec{k}, t) = 1 - \omega_o^2 \frac{t^2}{2!} + \omega_o^4 \frac{t^4}{8} - \cdots$$

This is simply the short time expansion for the function

$$F_s(\vec{k}, t) = e^{-\frac{1}{2}\omega_o^2 t^2}$$

For free particles the self intermediate scattering function takes on a Gaussian form.

Only ideal systems can by truly described with the free-particle model. However, there are many real systems that also show this limiting behaviour. Using these results, we can find the condition for a system that will allow us to ignore the effects of molecular collisions. From Eq.(4.6), we can see that the scattering function will take on a Gaussian form when $\Omega_o^2 = 0$ (the ideal case) or when $\omega_o^2\Omega_o^2$ is sufficiently smaller than $3\omega_o^4$ that it can be ignored. Therefore, the condition for ignoring collisions can be written as

$$\Omega_o^2 \ll 3\omega_o^2$$

Using the definitions of ω_o^2 and v_o^2 and rearranging, we find

$$k \gg \frac{\Omega_o}{\sqrt{\frac{3k_BT}{m}}}$$

Now, define the parameter l as

$$l = \sqrt{\frac{3k_BT}{m}}\Omega_o$$

This term gives the average thermal velocity, $\sqrt{\frac{3k_BT}{m}}$, divided by the average collision frequency Ω_o. Therefore, it can be interpreted as the mean free path of the particles, or the average distance a particle can travel before experiencing a collision. With the definition of l in hand, we can rewrite

$$k \gg \frac{1}{l}$$

or

$$\lambda \ll l \tag{4.7}$$

This indicates that a system can be treated in the free-particle limit when the wavelength, or spatial range, that it used to investigate the system is less than the mean free path travelled by the particles. For further discussion of self-intermediate scattering functions, please see *Dynamics of the Liquid State* by Umberto Balucani [5].

4.1.3 Collective Properties

1. Density Fluctuations We can extend our previous discussion of the self-density function $n_s(\vec{r},t)$ by considering the density function ρ, which is simply a sum of self-density functions

$$\rho(\vec{r},t) = \sum_i \delta(\vec{r} - \vec{r}_i(t))$$

We define the density fluctuation as

$$\delta\rho(\vec{r},t) = \rho(\vec{r},t) - \langle\rho\rangle$$

The Fourier transform of the density fluctuation is given by

$$\rho_k(t) = \sum_i e^{-i\vec{k}\vec{r}_i(t)} - (2\pi)^3\delta(\vec{k})\rho_o$$

where $\rho_o = \langle \rho \rangle$. Then, we define the intermediate scattering function as the correlation function of $\rho_k(t)$

$$F(\vec{k},t) = \frac{1}{N}\left\langle \rho_k(t) | \rho_k(0) \right\rangle = \frac{1}{N}\left\langle \rho(\vec{k},t) | \rho(-\vec{k},0) \right\rangle$$

Once again, we can find an expression for the short time behavior of $F(\vec{k},t)$ using the moment expansion in equation Eq.(4.2). We can find the zeroth moment of $F(\vec{k},t)$ by substituting in the definition of $\rho_k(t)$ and solving at time $t=0$.

$$C_0 = F(\vec{k},0) = \frac{1}{N}\left\langle \sum_j e^{i\vec{k}\vec{r}_j(0)} \sum_i e^{-i\vec{k}\vec{r}_i(0)} \right\rangle$$

Note that when we consider the correlation of a particle with itself (that is, when $i = j$), the terms in the exponentials will cancel, giving a value of 1. Summing over all N particles gives a value of N. Therefore, we can write the zeroth moment as

$$C_0 = 1 + \frac{1}{N}\left\langle \sum_{i \neq j} e^{-i\vec{k}\vec{r}_{ij}} \right\rangle (2\pi)^3 \delta(\vec{k}) \rho_o$$

where $\vec{r}_{ij} = \vec{r}_i(0) - \vec{r}_j(0)$. In Chapter 3, we defined the second term as $\rho_o g(\vec{r})$, where $g(\vec{r})$, is the pair distribution function. The zeroth moment becomes

$$C_0 = 1 + \rho_o g(\vec{r}) - (2\pi)^3 \delta(\vec{k}) \rho_o = 1 + \rho_o \tilde{h} = S(\vec{k})$$

where $S(\vec{k})$ is the static structure factor. From thermodynamics, we know that

$$S(0) = 1 + \rho_o k_B T \chi_T \leqslant 1$$

where χ_T is the isothermal compressibility,

$$\chi_T = \frac{1}{\rho_o}\frac{\partial \rho}{\partial t}$$

The pairwise correlation functions arises from the real space Van Hove Correlation function

$$G(\vec{r},t) = \frac{1}{N}\left\langle \sum_{i,j} \vec{r}(0) - \vec{r}_{ij}(0) \right\rangle - \rho_o = \langle \delta\rho(\vec{r},t)\rho(\vec{r},0) \rangle$$

At time $t = 0$, the Van Hove function becomes

$$G(\vec{r},0) = \delta(\vec{r}) + \rho_o h(\vec{r})$$

where $g = 1 + h$

2. The Short time expansion In the previous section, we demonstrated that the zeroth moment C_0 of the short-time expansion of the intermediate scattering function is given by the static structure factor $S(\vec{k})$. Therefore, we can write

$$F(\vec{k},t) = S(\vec{k}) - \left\langle \omega^2 \right\rangle \frac{t^2}{2!} + \left\langle \omega^4 \right\rangle \frac{t^4}{4!} - \cdots$$

To evaluate the second and fourth moments, we will consider the interactions of each particle with itself (the self-part, $i = j$) separately from the interactions of each particle with other particles (the distinct part, $i \neq j$). To evaluate the self-part, use the results from section 2:

$$\dot{n}_k = \sum_{i=1}^{N} -i(\vec{k}\vec{v}_i)e^{-i\vec{k}\vec{r}_i(t)}$$

$$\ddot{n}_k = \sum_{i=1}^{N} \left[-(\vec{k}\vec{v}_i)^2 - i(\vec{k}\dot{\vec{v}}_i)\right] e^{-i\vec{k}\vec{r}_i(t)}$$

Then we can evaluate the second moment of the self-part as

$$C_2 = \langle \omega^2 \rangle = \frac{1}{N} \langle \dot{n}_k | \dot{n}_k \rangle = \left\langle (\vec{k}\dot{\vec{v}})^2 \right\rangle = \omega_o^2$$

This gives the entire value of the second moment because the $i \neq j$ terms do not contribute. The fourth moment is given by

$$C_4 = \langle \omega^4 \rangle = \frac{1}{N} \sum_{i,j} \left\langle \left[(\vec{k}\vec{v}_i)^2(\vec{k}\vec{v}_j)^2 + i(\vec{k}\dot{\vec{v}}_i)(\vec{k}\vec{v}_j)^2 - i(\vec{k}\dot{\vec{v}}_j)(\vec{k}\vec{v}_k)^2 + (\vec{k}\dot{\vec{v}}_i)(\vec{k}\dot{\vec{v}}_j)\right] e^{-i\vec{k}\vec{r}_{ij}} \right\rangle$$

Both the self-part and the distinct part contribute to the fourth moment.

$$C_4 = \langle \omega^4 \rangle = \frac{1}{N} \left[\sum_{i=j} \langle \cdots\cdots \rangle + \sum_{i \neq j} \langle \cdots\cdots \rangle \right]$$

When $i = j$, the middle two terms of the fourth moment cancel out and the exponential becomes 1. Therefore, the self-part of the fourth moment is given by

$$\frac{1}{N} \left\langle (\vec{k}\vec{v})^4 \right\rangle + \frac{1}{N} \left\langle (\vec{k}\dot{\vec{v}})^2 \right\rangle = 3\omega_o^4 + \omega_o^2\Omega_o^2$$

We can evaluate each of the terms of the distinct part of the fourth moment separately. The first term is given by

$$= \frac{1}{N} \sum_{i \neq j} \left\langle (\vec{k}\vec{v}_i)^2(\vec{k}\vec{v}_j)^2 e^{-i\vec{k}\vec{r}_{ij}} \right\rangle = (k^2 v_o^2)^2 \frac{1}{N} \sum_{i \neq j} \left\langle e^{-i\vec{k}\vec{r}_{ij}} \right\rangle = \omega_o^4 \tilde{g}\rho_o$$

The second and third term can be combined to give

$$\frac{1}{N} \sum_{i \neq j} \left\langle \left[i(\vec{k}\dot{\vec{v}}_i)(\vec{k}\vec{v}_j)^2 - i(\vec{k}\dot{\vec{v}}_j)(\vec{k}\vec{v}_k)^2 \right] e^{-i\vec{k}\vec{r}_{ij}} \right\rangle$$

$$= \frac{1}{N} \sum_{i \neq j} \left\langle (kv_o)^2 \left[\vec{k}\dot{\vec{v}}_i - \vec{k}\dot{\vec{v}}_j \right] e^{-i\vec{k}\vec{r}_{ij}} \right\rangle$$

$$= -2\omega_o^4 \frac{1}{N} \sum_{i \neq j} \left\langle e^{-i\vec{k}\vec{r}_{ij}} \right\rangle = -2\omega_o^4 \tilde{g}\rho_o$$

And the fourth term gives

$$\frac{1}{N} \sum_{i \neq j} \left\langle (\vec{k}\dot{\vec{v}}_i)(\vec{k}\dot{\vec{v}}_j) e^{-i\vec{k}\vec{r}_{ij}} \right\rangle$$

$$= \frac{k^2}{m^2}\frac{1}{N}\sum_{i\neq j}\left\langle \nabla_{zi}U\nabla_{zj}Ue^{-i\vec{k}\vec{r}_{ij}}\right\rangle$$

Using Eq.(4.4), we can write this as

$$\frac{k^2}{m^2}\frac{1}{N}\sum_{i\neq j}\left\langle\left(-\frac{1}{\beta}\frac{\partial}{\partial z_i}\frac{\partial}{\partial z_j}U+\frac{k^2}{\beta^2}\right)e^{-i\vec{k}\vec{r}_{ij}}\right\rangle$$

$$= -\omega_o^2\Omega_L^2+\omega_o^4\tilde{g}\rho_o$$

Then the distinct part of the fourth moment is given by

$$\omega_o^4\tilde{g}\rho_o-2\omega_o^4\tilde{g}\rho_o+\omega_o^4\tilde{g}\rho_o-\omega_o^2\Omega_L^2=-\omega_o^2\Omega_L^2$$

where

$$\Omega_L^2=\frac{1}{m}\left\langle\partial_z^2\phi e^{-i\vec{k}\vec{z}_{ij}}\right\rangle=\frac{\rho_o}{m}\int d\vec{r}e^{-i\vec{k}\vec{z}}\partial_z^2\phi g(\vec{r})$$

Therefore, the fourth moment of the intermediate scattering function is given by

$$C_4=\left\langle\omega^4\right\rangle=3\omega_o^4+\omega_o^2\Omega_o^2-\omega_o^2\Omega_L^2$$

3. Comparison to Self-intermediate Scattering Function With our results from the previous sections, we can write the short-time expansion of the intermediate scattering function as

$$F(\vec{k},t)=S(\vec{k})-\omega_o^2\frac{t^2}{2!}+\left[3\omega_o^2+\Omega_o^2-\Omega_L^2\right]\omega_o^2\frac{t^4}{4!}-\cdots$$

We can interpret $S(\vec{k})-\omega_o^2\frac{t^2}{2!}$ as the initial decay term and define the frequency $\omega_L^2=3\omega_o^2+\Omega_o^2-\Omega_L^2$.

For comparison, the self-intermediate scattering function is given by

$$F_s(\vec{k},t)=1-\omega_o^2\frac{t^2}{2!}+\left[3\omega_o^2+\Omega_o^2\right]\omega_o^2\frac{t^4}{4!}-\cdots$$

How do these compare in the long wavelength limit $k\to 0$? In the short-time limit, the scattering functions will be largely determined by the first terms in the expansions. We see that as

$$\lim_{k\to 0}S(\vec{k})=S(0)\leq 1$$

Therefore, in this limit, the intermediate scattering function $F(\vec{k},t)$ decays slower than the self-intermediate scattering function $F_s(\vec{k},t)$.

Transverse and Longitudinal Current Transverse and longitudinal current were introduced in chapter 3, where the Navier-Stokes equation was used to predict their rate of dissipation. Here, we will apply the short-time expansion to the current correlation functions to define the transverse and longitudinal speeds of sound and find their behavior in the free particle limit.

To review, the current is defined as

$$\vec{J}_k(t)=\sum_i\vec{v}_i(t)e^{-i\vec{k}\vec{r}_i}$$

Longitudinal current exists when the direction of motion of the particles (the velocity) is parallel with the direction of propagation of the waves. For waves propagating in the z-direction, the longitudinal current is given by

$$\vec{J}_L(k,t) = \sum_i \vec{\dot{z}}_i(t) e^{-i\vec{k}\vec{z}_i}$$

Transverse current exists when the direction of motion of the particles is perpendicular to the direction of propagation of the waves. For waves propagating in the z-direction, the transverse current is given by

$$\vec{J}_T(k,t) = \sum_i \vec{\dot{x}}_i(t) e^{-i\vec{k}\vec{z}_i}$$

The longitudinal current correlation function is given by

$$C_L = \frac{1}{N}\left\langle \vec{J}_L(\vec{k},t) | \vec{J}_L(\vec{k},t) \right\rangle$$

And the transverse current correlation function is given by

$$C_T = \frac{1}{N}\left\langle \vec{J}_T(\vec{k},t) | \vec{J}_T(\vec{k},t) \right\rangle$$

Using Eq.(4.2), we can write the short time expansion of each of these functions as

$$C_L(\vec{k},t) = v_o^2(1 - \omega_L^2 \frac{t^2}{2}) + \cdots$$

$$C_T(\vec{k},t) = v_o^2(1 - \omega_T^2 \frac{t^2}{2}) + \cdots$$

In the long wavelength limit the transverse and longitudinal frequencies ω_T and ω_L are related to the transverse and longitudinal speeds of sound by

$$\omega^2_{\frac{L}{T}} = k^2 c^2_{\frac{L}{T}}$$

And the transverse and longitudinal speeds of sound are given by

$$c_L^2 = 3v_o^2 + \frac{\rho_o}{2m}\int d\vec{r} g(\vec{r}) \partial_z^2 \phi \vec{z}$$

$$c_T^2 = v_o^2 + \frac{\rho_o}{2m}\int d\vec{r} g(\vec{r}) \partial_x^2 \phi \vec{z}$$

Therefore, in the long wavelength limit,

$$\omega_L^2 \backsim 3\omega_T^2$$

5. Free-Particle Limit In the free-particle limit, the forces between particles can be ignored. The longitudinal and transverse current correlation functions are then given by

$$C_L(\vec{k},t) = \left\langle v_z^2 e^{-i\vec{k}\vec{v}_z t} \right\rangle = v_o^2(1 - \omega_o^2 t^2) e^{-\frac{1}{2}(\omega_o t)^2}$$

$$C_T(\vec{k},t) = \left\langle v_x^2 e^{-i\vec{k}\vec{v}_z t} \right\rangle = v_o^2 e^{-\frac{1}{2}(\omega_o t)^2}$$

We can see that the Fourier transform of the transverse correlation function $\tilde{C}_T(\vec{k},\omega)$ is a Gaussian while the Fourier transform of the longitudinal correlation function $\tilde{C}_L(\vec{k},\omega)$ has poles at $\omega = \pm\sqrt{2}\omega_o$

4.2 Projection Operator Method

In chapter 3, we explored the long time behavior of time correlation functions, and in the previous section, we explored their short-time behavior. However, we are ultimately interested in finding expressions for the time correlation functions that apply at all time scales.

There are many different ways to approach this problem. In principle, we could simply calculate the position and velocity of each particle in the system at all times. Then, any other phase-space variable $A(t)$ could easily be determined. However, this is clearly not viable for macroscopic systems, which contain on the order of 10^{23} individual particles.

Another approach, and the one we will explore here, is to consider only that part of the system that we care about and treat all the rest as a statistical bath. This can be accomplished using projection operator techniques. To understand this method, it is useful to consider an analogy to a three dimensional vector space. Any three dimensional vector can be projected onto a vector of interest to find its component in that direction. Similarly, we can project the position and velocity information for the entire system onto $A(t)$, and treat the rest as a statistical bath.

To illustrate this idea, let $A(t)$ be the velocity of a Brownian particle. We could always calculate $A(t)$ by determining the positions and velocities of all the particles in the system. However, this would be very time consuming and generate much unnecessary information. Instead, we can project the system velocity onto the velocity of the Brownian particle and treat the rest of the system as a bath.

We have already solved this problem for one specific case: in chapter 1, we used the Langevin equation to describe the evolution of the velocity of a particle under the influence of friction and a random force. In this section, we will use the projection operator technique to derive the Generalized Langevin Equation. However, first we need to define some terms.

4.2.1 Definitions

1. The Projection Operator Given the column vectors A and B, the projection of B onto A is given by the expression

$$\mathcal{P}_A B = \frac{\langle B|A\rangle}{\langle A|A\rangle} A \tag{4.8}$$

By definition,

$$\mathcal{P}_A^2 = \mathcal{P}_A \tag{4.9}$$

For an equilibrium system, the operator product is

$$\langle B|A\rangle = Tr B A^{+} \rho_{eq} \tag{4.10}$$

or, in the phase space representation

$$\langle B|A\rangle = \int d\Gamma B(\Gamma) A^{+}(\Gamma) \rho_{eq} \tag{4.11}$$

Similarly, we can define the orthogonal operator $\mathcal{Q} = \mathcal{P} - 1$, which projects onto a subspace that is orthogonal to A.

2. Operator Identity If a and b are operators, the following are identities

$$\frac{1}{s-a-b} = \frac{1}{s-a} + \frac{1}{s-a-b} b \frac{1}{s+a} \tag{4.12}$$

$$e^{(a+b)t} = e^{at} + \int_0^t e^{(a+b)(t-\tau)} b e^{a\tau} d\tau \tag{4.13}$$

3. The Liouville Operator The time evolution of an operator A in a system with the Hamiltonian $\mathcal{H}$ is found using the Liouville operator $\mathcal{L}$

$$\frac{dA}{dt} = i\mathcal{L}A \tag{4.14}$$

The Liouville operator is a special form of operator called a "superoperator" because it acts upon other operators rather than on functions. In quantum mechanics, the Liouville operator for a system with the Hamiltonian $\mathcal{H}$ is defined as

$$i\mathcal{L}A \equiv \frac{1}{i\hbar} [A, \mathcal{H}] \tag{4.15}$$

where $[\ldots, \ldots]$ indicates the commutator. In the classical limit as $\hbar \to 0$, this becomes

$$i\mathcal{L}A \equiv i \{A, \mathcal{H}\} \tag{4.16}$$

where $\{\ldots, \ldots\}$ is the Poisson bracket. One important property of $\mathcal{L}$ is that it is Hermitian. This property is demonstrated in the following proof

$$\begin{aligned} \langle \mathcal{L}A | B \rangle &= Tr \left([A, \mathcal{H}] B^+ \rho \right) \qquad (4.17) \\ &= Tr \left(A\mathcal{H}B^+\rho - \mathcal{H}AB^+\rho \right) \\ &= Tr \left(A\mathcal{H}B^+\rho - AB^+\mathcal{H}\rho \right) \\ &= TrA \left[\mathcal{H}, B^+ \right] \rho \\ &= TrA \left[\mathcal{H}, B \right]^+ \rho \\ &= \langle A | \mathcal{H}B \rangle \end{aligned}$$

4.2.2 The Generalized Langevin Equation

The Liouville equation

$$\frac{d}{dt} A(t) = iLA(t) \tag{4.18}$$

has the formal solution

$$A(t) = e^{i\mathcal{L}t} A(0) \tag{4.19}$$

From this equation it is clear that the function $e^{i\mathcal{L}t}$ acts as a time propagator of A from an initial value $A(0)$. However, it is not very helpful in this form. We will use the projection operator to rewrite this equation in a more useful form. To simplify the notation, $A(t)$ will be written as A from now on. Start by writing the new equation of motion for $A(t)$

$$\frac{dA}{dt} = i\mathcal{L}e^{i\mathcal{L}t} A$$

Insert the identity, $I = (\mathcal{P} + \mathcal{Q})$

$$\frac{dA}{dt} = e^{i\mathcal{L}t}\left(\mathcal{P} + \mathcal{Q}\right) i\mathcal{L}A = e^{i\mathcal{L}t}Pi\mathcal{L}A + e^{i\mathcal{L}t}\mathcal{Q}i\mathcal{L}A$$

Begin by evaluating the first term. Using the definition of the projection operator, we can rewrite this as

$$\begin{aligned} e^{i\mathcal{L}t}Pi\mathcal{L}A &= e^{i\mathcal{L}t}\frac{\langle i\mathcal{L}A|A\rangle}{\langle A|A\rangle}A \qquad (4.20)\\ &= i\frac{\langle \mathcal{L}A|A\rangle}{\langle A|A\rangle}e^{i\mathcal{L}t}A \\ &= i\Omega A(t) \end{aligned}$$

where Ω is called the frequency matrix and is defined as

$$\Omega = \frac{\langle \mathcal{L}A|A\rangle}{\langle A|A\rangle}$$

To evaluate the second term, we will need to rewrite the time propagator in terms of $\mathcal{P}$ and $\mathcal{Q}$. Start by inserting the identity, and then rewrite the expression using the operator identity defined in section A.2, with $a = -i\mathcal{Q}\mathcal{L}$, $b = -iP\mathcal{L}$, and $(a + b) = -i\mathcal{L}$

$$e^{i\mathcal{L}t} = e^{i(\mathcal{P}+\mathcal{Q})\mathcal{L}t} \qquad (4.21)$$

$$= e^{i\mathcal{Q}\mathcal{L}t} + \int_0^t e^{i\mathcal{L}(t-\tau)}iP\mathcal{L}e^{i\mathcal{Q}\mathcal{L}t}d\tau \qquad (4.22)$$

Now, apply this expansion to $i\mathcal{Q}\mathcal{L}A$

$$e^{i\mathcal{L}t}i\mathcal{Q}\mathcal{L}A = e^{i\mathcal{Q}\mathcal{L}t}i\mathcal{Q}\mathcal{L}A + \int_0^t e^{i\mathcal{L}(t-\tau)}iP\mathcal{L}e^{i\mathcal{Q}\mathcal{L}t}(i\mathcal{Q}\mathcal{L}A)d\tau$$

To understand this expression, start by examining the first term. The operator $\mathcal{Q}$ projects the system into the solvent degrees of freedom, which are orthogonal to A. However, we are primarily interested in describing only the propagation in the A direction. Therefore, this term gives the random force or noise in the system, which we will denote $R(t)$

$$R(t) = e^{i\mathcal{Q}\mathcal{L}t}i\mathcal{Q}\mathcal{L}A$$

where $R(0) = i\mathcal{Q}\mathcal{L}A$ and $e^{i\mathcal{Q}\mathcal{L}t}$ describes the time propagation of $R(t)$. The second term in this expression describes the friction in the system. One interesting thing to note is that the expression for $R(t)$ appears in this term, indicating that the friction and noise of the system are related. This relation is called the fluctuation-dissipation theorem, and will be given more explicitly later. Using the definition of $R(t)$, we can rewrite the second term in the expression as

$$\int_0^t e^{i\mathcal{L}(t-\tau)}iP\mathcal{L}e^{i\mathcal{Q}\mathcal{L}t}(i\mathcal{Q}\mathcal{L}A)d\tau = \int_0^t e^{i\mathcal{L}(t-\tau)}iP\mathcal{L}R(t)d\tau$$

Then, use the definition of the projection operator $\mathcal{P}$ to write

$$\int_0^t e^{i\mathcal{L}(t-\tau)}\frac{\langle i\mathcal{L}R(t)|A\rangle}{\langle A|A\rangle}Ad\tau$$

Since the noise term $R(t)$ is already projected into the orthogonal space, we can always operate on it with $\mathcal{Q}$ without changing its value (recall that for any projection operator $\mathcal{P}$, $\mathcal{P}^2 = \mathcal{P}$)

$$\int_0^t e^{i\mathcal{L}(t-\tau)} \frac{\langle i\mathcal{L}\mathcal{Q}R(t)|A\rangle}{\langle A|A\rangle} A d\tau$$

Then, use the fact that $\mathcal{Q}$ and $\mathcal{L}$ are both Hermitian operators to rearrange the expression

$$-\int_0^t e^{i\mathcal{L}(t-\tau)} \frac{\langle R(t)|i\mathcal{Q}\mathcal{L}A\rangle}{\langle A|A\rangle} A d\tau$$

Finally, use the definition $R(0) = i\mathcal{Q}\mathcal{L}A$ and $e^{i\mathcal{L}(t-\tau)}A = A(t-\tau)$ to write the expression as

$$-\int_0^t \frac{\langle R(t)|R(0)\rangle}{\langle A|A\rangle} A(t-\tau) d\tau$$

Define the memory kernel $\kappa(t)$ as

$$\kappa(t) = \frac{\langle R(t)|R(0)\rangle}{\langle A|A\rangle}$$

This term gives the final fluctuation-dissipation theorem. The second term can then be written as simply

$$-\int_0^t \kappa(t) A(t-\tau) d\tau$$

With all of this in hand, we can finally write out the full Generalized Langevin equation

$$\frac{dA}{dt} = i\Omega A(t) - \int_0^t \kappa(t) A(t-\tau) d\tau + R(t) \tag{4.23}$$

where the frequency matrix is

$$\Omega = \frac{\langle \mathcal{L}A|A\rangle}{\langle A|A\rangle} \tag{4.24}$$

the random force is

$$R(t) = e^{i\mathcal{Q}\mathcal{L}t} i\mathcal{Q}\mathcal{L}A \tag{4.25}$$

and the memory kernel, which defines the fluctuation-dissipation theorem, is

$$\kappa(t) = \frac{\langle R(t)|R(0)\rangle}{\langle A|A\rangle} \tag{4.26}$$

Let's take a closer look at the frequency matrix and the memory kernel. For one-dimensional problems, the frequency matrix will evaluate to zero. To understand why, remember that $i\mathcal{L}A = \frac{dA}{dt}$. This allows us to rewrite the numerator of the frequency matrix as $\langle \frac{dA}{dt}|A\rangle$, which is simply the derivative of the correlation function $C(t) = \langle A(t)|A(0)\rangle$, evaluated at zero. Since all correlation functions are even in time, the derivative at zero must equal zero. This rule will apply to all of the problems that we address in this section.

As stated earlier, the definition of the memory kernel relates the fluctuation, or noise in the system, to the dissipation of A. The fluctuation term, $\langle R(t)|R(0)\rangle \langle A|A\rangle^{-1}$, will be zero when the noise in the system is zero. This indicates that in an isolated system with no noise, A will quickly decay to zero.

4.2.3 Applications of the GLE

1. GLE for Brownian Motion In chapter 1, we used the Langevin equation to explore the motion of a Brownian particle. Here, we will perform the same analysis using the Generalized Langevin equation. Recall that Brownian motion describes the discrete and random motion that is observed when a large particle is immersed in a fluid of smaller particles. We want to use the GLE to describe the velocity of the large particle without having to solve for the motion of the entire bath.

Begin by writing the GLE for the the velocity of the particle. For this system, the frequency matrix Ω is zero, so the full GLE is given by

$$\frac{dv}{dt} = -\int_0^t \gamma(t-\tau)v(\tau)d\tau + \frac{f(t)}{m}$$

where $\gamma(t)$ represents the memory kernel and $\frac{f(t)}{m} = R(t)$ represents the random force. For this system, the memory kernel is given by

$$\gamma(t) = \frac{\langle f(t)|f(0)\rangle}{m^2 \langle v|v\rangle}$$

The normalization factor $\langle v|v\rangle^{-1}$ is simply the average value of the squared velocity, $\left\langle v^2\right\rangle = v_o^2 = \frac{k_BT}{m}$. Therefore we can write this as

$$\gamma(t) = \frac{\beta}{m}\langle f(t)|f(0)\rangle$$

where $\beta = k_BT^{-1}$. The friction coefficient for the system is given by $\xi(t) = m\gamma(t)$. Using this, we can write the fluctuation-dissipation relation

$$\xi(t) = \beta\langle f(t)|f(0)\rangle$$

We can use the GLE to find the velocity autocorrelation function $C(t) = \langle v(t)v(0)\rangle$ for the Brownian particle. Begin by multiplying the GLE through by $v(0)$ and taking the thermal average.

$$\begin{aligned}
\frac{dv}{dt} &= -\int_0^t \gamma(t-\tau)v(\tau)d\tau + \frac{f(t)}{m} \\
\frac{dv}{dt}v(0) &= -\int_0^t \gamma(t-\tau)v(\tau)v(0)d\tau + \frac{f(t)}{m}v(0) \\
\left\langle \frac{dv}{dt}v(0)\right\rangle &= -\int_0^t \gamma(t-\tau)\langle v(\tau)v(0)\rangle d\tau + \frac{v(0)}{m}\langle f(t)\rangle \\
\frac{dC(t)}{dt} &= -\int_0^t \gamma(t-\tau)C(\tau)d\tau
\end{aligned}$$

Here we have used the fact that the thermal average over the random force $\langle f(t)\rangle = 0$. This gives us the equation of motion for $C(t)$, which can be solved using Laplace transformation. The Laplace transform of this equation gives

$$s\hat{C}(s) + \hat{\gamma}(s)\hat{C}(s) = C(0)$$

Using $C(0) = \langle v(0)v(0)\rangle = v_o^2$ and rearranging, we get the general Laplace transformed solution for $C(t)$

$$C\hat{(}s) = \frac{v_0^2}{s + \hat{\gamma}(s)} \tag{4.27}$$

which can be solved for specified values of $\gamma(t)$.

The Laplace transformed solution for $C(t)$ can be used to find an equation for the diffusion constant D. The Green-Kubo relation defines the diffusion constant as

$$D = \int_0^\infty C(t)d\tau = \hat{C}(s = 0)$$

Using the solution that we derived above

$$D = \frac{v_0^2}{\hat{\gamma}(0)} = \frac{k_BT}{m\hat{\gamma}(0)} \tag{4.28}$$

This is a generalized form of Einstein's relation, which we derived in chapter 1 for the Brownian particle.

The Brownian particle experiences white-noise, which can be modelled by making the memory function a delta function $\gamma(t) = \gamma_o\delta(t)$. Then the GLE simplifies to

$$\begin{aligned} \frac{dv}{dt} &= -\int_0^t \gamma_o\delta(t-\tau)v(\tau)d\tau + \frac{f(t)}{m} &(4.29)\\ &= -\gamma_o v(t) + \frac{f(t)}{m} &(4.30) \end{aligned}$$

which has the formal solution (chapter 1)

$$v(t) = v(0)e^{-\gamma t} + \frac{1}{m}\int_0^t e^{-\gamma(t-\tau)}f(t)d\tau \tag{4.31}$$

and the correlation function $C(t) = C(0)e^{-\gamma t}$. Using the white-noise memory function, we can also reproduce Einstein's relation from chapter 1. The Laplace transform of $\gamma(t) = \gamma_o\delta(t)$ is $\hat{\gamma}(s) = \gamma_o$. Substituting this for $\hat{\gamma}(0)$ in Eq.(4.28) and using the friction coefficient $\xi(t) = m\gamma_o$ gives the familiar Einstein relation

$$D = \frac{k_BT}{m\hat{\gamma}(0)} = \frac{k_BT}{\xi} \tag{4.32}$$

2. Exponential-decay memory In addition to the delta function memory kernel, which gives the dynamics of a Brownian particle, we can also consider a case in which the friction has the same overall strength γ_o but varies with time. We can model this with the exponential decay memory kernel

$$\gamma(t) = \gamma_o\alpha e^{-\alpha t}$$

This memory kernel has the special property that no matter the value of α, the integral of the function will always equal γ_o. In the limit as $\alpha \to \infty$, this function approaches $\gamma_o\delta(t^+)$.

The correlation function for this memory kernel is relatively easy to find because the Laplace transform of an exponential decay function is well defined. For the exponential decay $\gamma(t)$ defined above, the Laplace transform is

$$\hat{\gamma}(t) = \frac{\gamma_o \alpha}{s+\alpha}$$

Therefore, to solve the correlation function, we only need to find the value of γ_o. This can be estimated using the definition of the memory kernel

$$\gamma(0) = \frac{\langle iQ\mathcal{L}v | iQ\mathcal{L}v \rangle}{m^2 \langle v^2 \rangle}$$

Here, $i\mathcal{L}v = \frac{dv}{dt}$ is simply the acceleration. Using Newton's law, we can write $i\mathcal{L}v = \frac{F}{m} = \frac{-1}{m}\frac{\partial U}{\partial x}$, which is the gradient of the potential, or the non-random component of the force. Putting everything together, we find that the memory kernel evaluated at zero is

$$\gamma(0) = \frac{\left\langle \partial_x^2 U \right\rangle}{m} \equiv \Omega_o^2$$

This is the average curvature of the potential. For a harmonic oscillator, this is simply the average frequency.

We can now use the Laplace transform of the exponential decay memory kernel to find the correlation function.

$$\hat{C}(0) = \frac{v_o^2}{s + \frac{\Omega_o^2}{s+\alpha}} = v_o^2 \frac{s+\alpha}{s^2 + s\alpha + \Omega_o^2}$$

This is relatively easy to solve because it is quadratic. To generate the solutions, find the eigenvalues by solving the quadratic equation $s^2 + s\alpha + \Omega_o^2$ [1]. This gives the results

$$\lambda_{\pm} = -\frac{\alpha}{2} \pm \sqrt{\frac{\alpha - 4\Omega_o^2}{4}} \tag{4.33}$$

$$C(t) = v_o^2 \frac{1}{\lambda_+ + \lambda_-}\left(e^{-\lambda_+ t} - e^{-\lambda_- t}\right) \tag{4.34}$$

Some interesting results arise from this solution. We can see that if $\alpha < 2\Omega$, then $\lambda_{\pm}$ are complex numbers and $C(t)$ becomes oscillatory

$$C(t) = v_o^2 \frac{1}{\lambda_+ + \lambda_-}(\cos \Delta t)$$

We can examine these results for different relations between α and Ω_o.

1. Solids When $\alpha \ll \Omega$, the decay time is much longer than one oscillation period. The correlation function shows persistant oscillations at many frequencies. There is virtually no damping and the decay occurs primarily through dephasing (see Figure 4.1).

Physically, this represents a solid. In a solid, each individual particle is locked into position by strong bonding between itself and its neighbors. If it is disturbed from equilibrium, it can only vibrate within the small area allowed by these bonds.

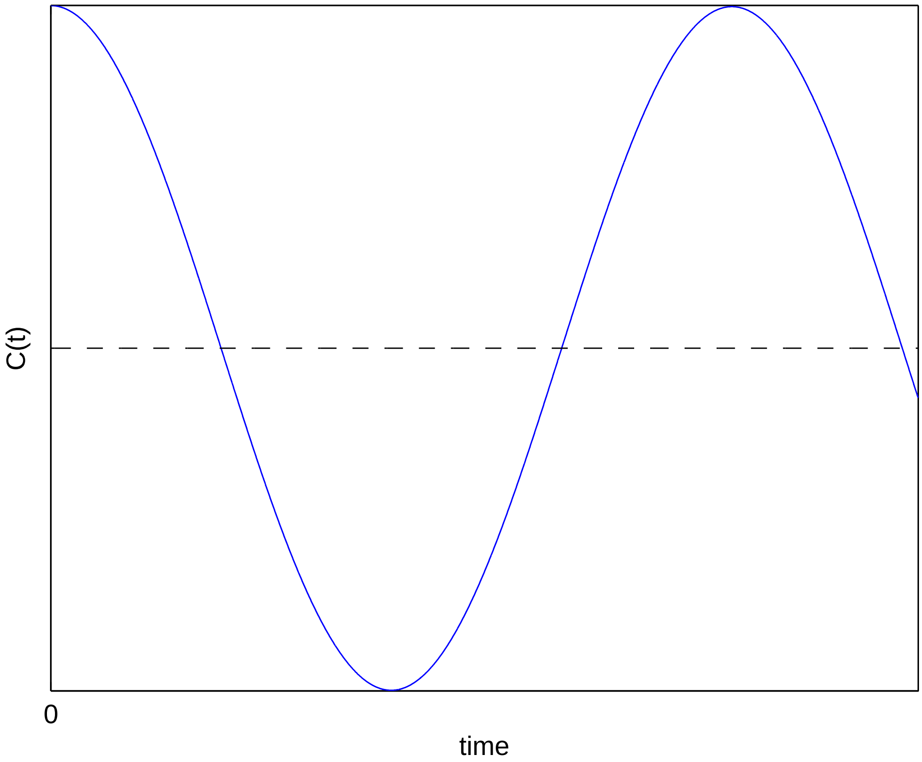

Figure 4.1: Velocity correlation function of a solid

2. Liquids When $\alpha l \Omega$, the decay time is longer than one oscillation period. The correlation function shows one or two oscillations which are quickly damped out and a long time decay tail (Figure 4.2).

Physically, this represents a liquid. At short times, a molecule in a liquid is “trapped” within a solvation shell formed by weak intermolecular bonds. When it is disturbed from equilibrium, it will initially vibrate within this shell. However, at longer times, this vibration will cause a rearrangement of the solvation shell, allowing the molecule to travel away from its initial position. This damps out the oscillations.

3. Gases When $\alpha \, \Omega$, the decay time is shorter than one oscillation period. The correlation function decays completely before undergoing an oscillation (Figure 4.3).

Physically, this represents a gas. In a gas, the molecules are not confined by intermolecular bonding, and the correlation function will decay without any oscillation.

3. Generalized Diffusion Constant We can use the GLE to derive the Green-Kubo relation for the generalized diffusion constant. Following a similar procedure as that used for the velocity correlation function, we can show that the equation of motion for the intermediate scattering function (which we have discussed in depth in Chapter 3 and in section IC of chapter 4) is given

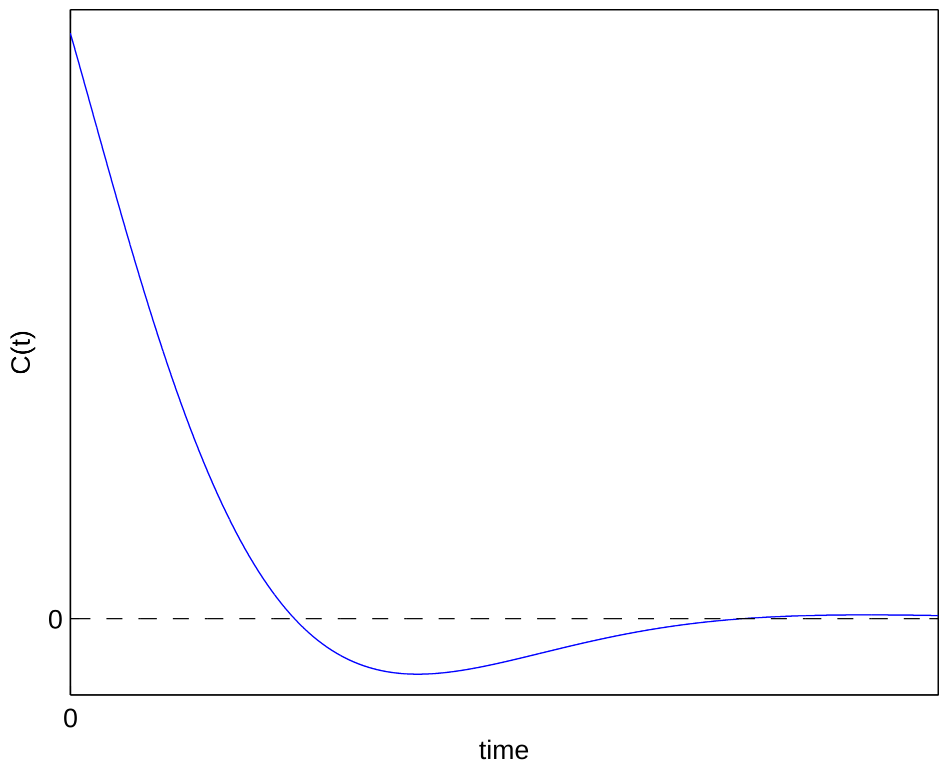

Figure 4.2: Velocity correlation function of a liquid

by

$$\dot{F}(\vec{k},t) = -\int_0^t \kappa(\vec{k},t)F(\vec{k},t-\tau)d\tau$$

where the memory kernel has its usual definition

$$\kappa(t) = \frac{\langle R(t)|R(0)\rangle}{\langle \rho_k|\rho_k\rangle}$$

Using the definition of the noise term for this system

$$R(t) = e^{i\mathcal{QL}t} i\mathcal{QL}\rho_k$$

We can rewrite the memory kernel

$$\begin{aligned}\kappa(t) &= \frac{\left\langle e^{i\mathcal{QL}t} i\mathcal{QL}\rho_k | i\mathcal{QL}\rho_k\right\rangle}{\langle \rho_k|\rho_k\rangle} \\ &= \left\langle \dot{\rho}_k | e^{i\mathcal{QL}t} | \dot{\rho}_k\right\rangle\end{aligned}$$

By evaluating $\dot{\rho}_k$ (section IC) we can write the memory kernel as

$$\kappa(t) = k^2 \left\langle \vec{v}e^{-i\vec{k}\vec{r}} | e^{i\mathcal{QL}t} | \vec{v}e^{-i\vec{k}\vec{r}}\right\rangle$$

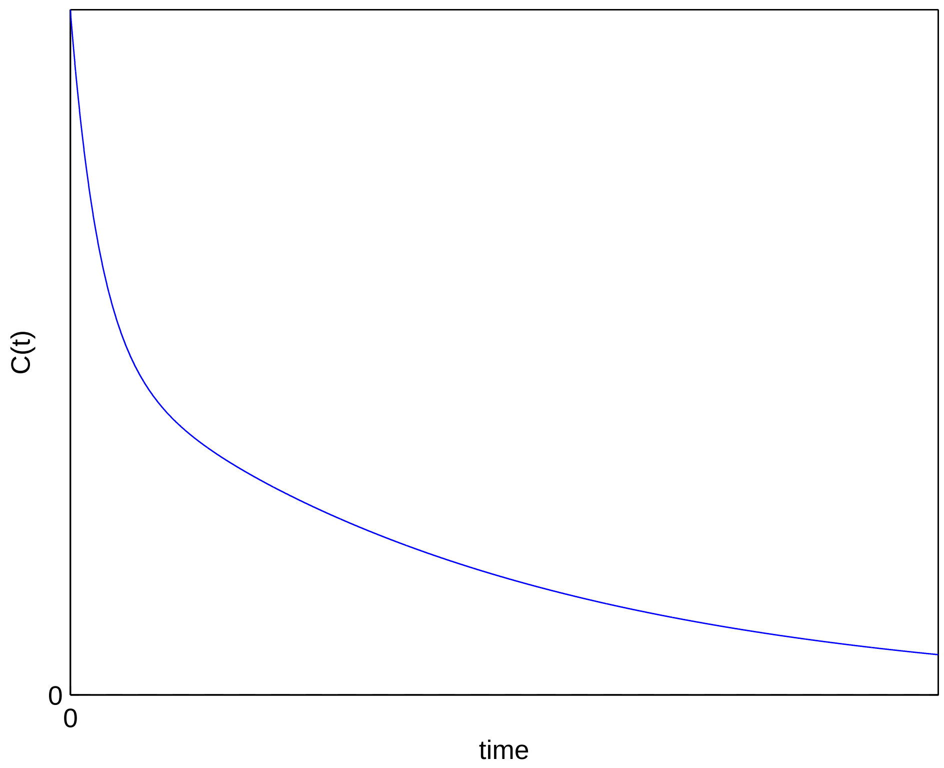

Figure 4.3: Velocity correlation function of a gas

However, this term is simply the diffusion constant $D(\vec{k},t)$multiplied by k^2. Therefore, the equation of motion for the intermediate scattering function can be written as

$$\dot{F}(\vec{k},t) = -k^2 \int_0^t D(\vec{k},\tau)F(\vec{k},t-\tau)d\tau$$

In the long time limit $t \to \infty$ and the long wavelength limit $k \to 0$, we find the Green-Kubo relation

$$D = \int_0^\infty D(0,t)dt = \int_0^\infty C(t)dt$$

4.3 Viscoelastic Model

4.3.1 Introduction

The Generalized Langevin Equation and Mode-Coupling theory are subsets of molecular hydrodynamics, the theory that was developed to bridge the gap between hydrodynamics and molecular dynamics. Hydrodynamics, which we discussed in chapter 3, describes the macroscopic, long time behavior of systems in the limit as $t \to \infty$ and $k \to 0$. It uses the transport coefficients D, λ, η, and η_B to predict long time fluctuations. Molecular dynamics, which we discussed in section I of chapter 4, describes the microscopic, short time behavior of systems in the limit as $t \to 0$ and $k \to \infty$. In this limit, systems behave as static liquid structures, and their dynamics are largely determined by the pairwise interaction potential.

In this section, we will use the GLE to derive the viscoelastic model for transverse current. By taking the appropriate limits, we can show that the results of the viscoelastic model are consistent with those of hydrodynamics and molecular dynamics, and that this model provides a successful bridge between the two limits.

4.3.2 Phenomenological Viscosity

Consider a constant shear force applied to a viscous liquid. At long times, the shear stress σ_{xz} in the liquid is related to the rate of strain $\partial_z \vec{v}_x + \partial_x \vec{v}_z$ by

$$\sigma_{xz} = -\eta \left(\partial_z \vec{v}_x + \partial_x \vec{v}_z\right)$$

Liquids behaving in this fashion do not support shear waves. However, if the force is applied instantaneously, the system does not have the time to relax like a liquid. Instead, it behaves like an elastic solid. The stress is now proportional to the strain rather than the rate of strain. The short term response is

$$\sigma_{xz} = -G \left(\partial_z \vec{x} + \partial_x \vec{z}\right)$$

where G is the modulus of rigidity. When the liquid is behaving like a solid, it supports shear waves propagating at a speed of $v_s = \sqrt{\frac{G}{\rho m}}$.

To determine the time scale on which the liquid behaves like an elastic solid, define the constant

$$\tau_M = \frac{\eta}{G}$$

This is the Maxwell relaxation time. For the timescales t when

$$\frac{t}{\tau_M} \ll 1$$

the system behaves like an elastic solid. For the timescales when

$$\frac{t}{\tau_M} \gg 1$$

the system behaves like a viscous liquid.

4.3.3 Viscoelastic Approximation

1. To interpolate between the two extremes, we can write

$$\left(\frac{1}{\eta} + \frac{1}{G}\frac{\partial}{\partial t}\right)\sigma_{xz} = -\left(\frac{\partial}{\partial z}\vec{v}_x + \frac{\partial}{\partial_x}\vec{v}_z\right)$$

The Laplace transform of this equation yields

$$\hat{\eta}(s) = \frac{G}{s + \frac{G}{\eta}} = \frac{G}{s + \frac{1}{\tau_M}}$$

In the steady-state limit, as $s \to 0$

$$\lim_{s\to 0} \hat{\eta} = \eta$$

and in the high-frequency limit, as $s \to \infty$

$$\lim_{s\to\infty} \hat{\eta} = \frac{G}{s}$$

2. Transverse Current Correlation Function We will use the transverse current correlation function to demonstrate the viscoelastic approximation. In Section I, we defined the transverse current as

$$J_T(\vec{k},t) = \sum_{j=1}^{N} \vec{x}_j e^{i\vec{k}\vec{z}_j}$$

and the transverse current correlation function as

$$C_T(\vec{k},t) = \frac{1}{N}\left\langle J_T(\vec{k},t)|J_T(\vec{k},0)\right\rangle$$

We have studied the transverse current in both the hydrodynamic limit ($k \to 0$, $\omega \to 0$) and the short-time expansion limit ($k \to \infty$, $\omega \to \infty$). In chapter 3, we used the Navier Stokes equation to find an equation of motion for the transverse correlation function in the hydrodynamic limit

$$\dot{C}_T(\vec{k},t) = -\nu k^2 C_T(\vec{k},t) \tag{4.35}$$

This has the solution

$$C_T(\vec{k},t) = C_T(\vec{k},0)e^{-\nu k^2 t} = v_o^2 e^{-\nu k^2 t}$$

where $\nu = \frac{\eta}{m\rho}$ is the shear viscosity. Therefore, in the hydrodynamic limit, transverse current fluctuations decay exponentially with a rate determined by the shear viscosity ν.

In section I of this chapter, we used the short-time expansion approximation to show that in the $k \to \infty$, $\omega \to \infty$ limit, the transverse current correlation function can be written as

$$C_T(\vec{k},t) = v_o^2(1 - \omega_T^2 \frac{t^2}{2}) + \cdots$$

where the transverse frequency ω_T is related to the transverse speed of sound $c_T(k)$ by

$$\omega_T^2 = k^2 c_T^2(k)$$

And the transverse speed of sound is given by

$$c_T^2(k) = v_o^2 + \frac{\rho}{m}\int g(\vec{r})\partial_x^2 U(\vec{r})\frac{[1-e^{ikz}]}{k^2}d\vec{r}$$

where $g(\vec{r})$ is the pairwise correlation function and $U(\vec{r})$ is the pairwise interaction potential. This frequency term can also be written as [3]

$$\omega_T^2 = \frac{(kv_o)^2}{nM}G_\infty(k)$$

where $G_\infty(k)$ is the shear modulus. This indicates that at short times and wavelengths, the dissipation effects are diminished and transverse current fluctuations can propagate through the material with speed $c_T(k)$.

Using the Generalized Langevin equation, we can generate a model for transverse current fluctuations that replicates the results of hydrodynamics and the short-time expansion when the appropriate limits are taken. Begin by writing the GLE for transverse current. Since the frequency matrix is zero, the GLE is written

$$\dot{J}_T(k,t) = -\int_0^t \kappa(t-\tau)J_T(k,\tau)d\tau + f(t)$$

where $\kappa(t)$ is the memory function and $f(t)$ is the noise term. Multiplying through by $J_T(k,0)$ and taking the average gives us the equation of motion for the transverse current correlation function

$$\dot{C}_T(k,t) = -\int_0^t \kappa(t-\tau)C_T(k,\tau)d\tau$$

Take a closer look at the memory kernel

$$\kappa(t) = \frac{\langle R(t)|R(0)\rangle}{\langle A|A\rangle} = \frac{\left\langle e^{i\mathcal{QL}t} i\mathcal{QL}J_T(k,0)|i\mathcal{QL}J_T(k,0)\right\rangle}{\langle J_T(k,0)|J_T(k,0)\rangle}$$

The normalization factor is simply $\frac{\beta m}{\rho}$. By writing the projection operator $\mathcal{Q}$ as $1-\mathcal{P}$ and eliminating terms, this can be written

$$\begin{aligned}\kappa(t) &= \frac{\beta m}{\rho}\left\langle e^{i(1-\mathcal{P})\mathcal{L}t} i\mathcal{L}J_T(k,0)|i\mathcal{L}J_T(k,0)\right\rangle \\ &= \frac{\beta m}{\rho}\left\langle \dot{J}_T(k,t)|e^{i(1-\mathcal{P})\mathcal{L}t}|\dot{J}_T(k,t)\right\rangle\end{aligned}$$

The equation of motion for the transverse current can be written as [5]

$$\dot{J}_T(\vec{k},t) = i\frac{k}{m}\sigma^{zx}(\vec{k},t)$$

where $\sigma^{zx}(\vec{k},t)$ is the zx-component of the microscopic stress tensor

$$\sigma^{zx}(\vec{k}) = \sum_i \left\{ m v_{i,z} v_{i,x} - \frac{1}{2}\sum_{j\neq i} \frac{z_{ij}x_{ij}}{r^2}\mathcal{P}_k(r_{ij}) \right\} e^{ikz_i}$$

Then the memory kernel becomes

$$\kappa(t) = k^2 \frac{\beta}{\rho m}\left\langle \sigma^{zx}(\vec{k},t)|e^{i(1-\mathcal{P})\mathcal{L}t}|\sigma^{zx}(\vec{k},t)\right\rangle = k^2\nu(k,t)$$

where $\nu(k,t)$ is defined as

$$\nu(k,t) = \frac{\beta}{\rho m}\left\langle \sigma^{zx}(\vec{k},t)e^{i(1-\mathcal{P})\mathcal{L}t}\sigma^{zx}(\vec{k},t)\right\rangle$$

This demonstrates that the memory kernel is proportional to k^2. Then the transverse current correlation function can be written

$$\dot{C}_T(k,t) = -k^2\int_0^t \nu(k,t-\tau)C_T(k,\tau)d\tau$$

The memory kernel is the key element that links the two limits. In general, the presence of the propagator $e^{i\mathcal{QL}t}$ makes it very difficult to evaluate $\nu(k,t)$ explicitly. However, the presence of $\mathcal{Q}$ indicates that we can separate out fast and slow motions and use this to construct a form for $\nu(k,t)$ that will bridge the short and long time limits. To find this form, the viscoelastic model starts my assuming that the memory kernel has an exponential form:

$$\nu(k,t) = \nu(k,0)\exp\left[\frac{-t}{\tau_M(k)}\right] \tag{4.36}$$

where $\tau_M(k)$ is the Maxwell relaxation time, discussed above. Before using this function, it is necessary to specify the values of the two parameters, $\nu(k,0)$ and $\tau_M(k)$. These can be found by taking the short and long time limits of the GLE and comparing them to the short-time expansion and hydrodynamic results, respectively.

3. The Short Time Limit The value of $\nu(k,t)$ at short times can be obtained by comparing the GLE at time $t=0$ to the short time expansion of the transverse correlation function. To find the GLE at time $t=0$, take its time derivative

$$\ddot{C}_T(k,t) = -k^2 \frac{d}{dt}\int_0^t \nu(k,t-\tau)C_T(k,\tau)d\tau$$
$$\ddot{C}_T(k,t) = -k^2\nu(k,0)C_T(k,t)$$
$$\ddot{C}_T(k,0) = -k^2\nu(k,0)C_T(k,0)$$
$$\ddot{C}_T(k,0) = -k^2\nu(k,0)v_o^2 \tag{4.37}$$

The first two terms of the short time expansion of the correlation function are

$$C_T(\vec{k},t) = v_o^2(1-\omega_T^2\frac{t^2}{2}) + \cdots$$

The second derivative of this expansion gives

$$\ddot{C}_T(k,0) = -k^2c_t^2(k)v_o^2 \tag{4.38}$$

Comparison of equations (4.38) and (4.35) shows that

$$\nu(k,0) = c_t^2(k) = \frac{G(k)}{\rho m}$$

Further, we see that in this limit the material supports propagating waves. The form of the waves can be found by solving the differential equation Eq.(4.38), and is given by

$$C_T(k,t) = v_o^2\cos(\omega_t t - kx)$$

where $\omega = kc_t(k)$ and the speed of the waves are $c_t = \sqrt{\frac{G(k)}{\rho m}}$.

4. The Hydrodynamic Limit The value of $\nu(k,t)$ at long times can be obtained by comparing the hydrodynamic equation to the long time limit of the GLE for $C_T(k,t)$:

$$\dot{C}_T(k,t) = -k^2\int_0^t \nu(k,t-\tau)C_T(k,\tau)d\tau$$

To take the long time limit of this equation, note that the memory function will generally be characterized by some relaxation time τ_κ. When the time t is much greater than this relaxation time, the major contribution to the integral will come when $t\sim\tau$. Therefore, we can approximate $C_T(k,\tau)\sim C_T(k,t)$. With this approximation, the correlation function can be taken out of the integral in the GLE:

$$\dot{C}_T(k,t) = -k^2C_T(k,t)\int_0^\infty \nu(k,t-\tau)d\tau$$

where the integration limit has been extended to ∞ to indicate that we are taking the long time limit.

This result should be identical to the hydrodynamic solution in the long time and long wavelength limit. By taking the long wavelength limit ($k\to 0$) and comparing to the hydrodynamic result (Eq.(4.35)), we see that this only holds when:

$$\int_0^\infty \nu(k,t-\tau)d\tau = \nu = \frac{\eta}{\rho m}$$

5. The Viscoelastic Solution We now have the information we need to construct the explicit form of the viscoelastic memory kernel.

$$\nu(k,t) = \nu(k,0)\left[\frac{-t}{\tau_M(k)}\right]$$

From the short time limit, we found that $\nu(k,0) = \frac{G(k)}{\rho m}$, which allows us to write

$$\nu(k,t) = \frac{G(k)}{\rho m}\exp\left[\frac{-t}{\tau_M(k)}\right]$$

From the long time limit, we know that

$$\int_0^\infty \nu(k,t-\tau)d\tau = \frac{\eta}{\rho m}$$

Now, plug in the exponential memory kernel for $k = 0$

$$\int_0^\infty \frac{G(0)}{\rho m}\exp\left[\frac{-t}{\tau_M(0)}d\tau = \frac{\eta}{\rho m}\right]$$

The elastic modulus has no time dependence, so it can be taken out of the integral

$$\frac{G(0)}{\rho m}\int_0^\infty \exp\left[\frac{-t}{\tau_M(0)}d\tau = \frac{\eta}{\rho m}\right]$$

Finally, evaluate the integral to find the Maxwell relaxation time at $k = 0$. It is reasonable to assume that the Maxwell relaxation time remains constant over all k values. Therefore, the Maxwell relaxation time can be written as the ratio of the shear viscosity coefficient of the liquid to the modulus of rigidity of the elastic solid at $k = 0$.

$$\tau_M = \frac{\eta}{G(0)}$$

When τ_M is small compared to the time t, the viscosity term dominates and the system will behave as a viscous liquid. However, when τ_M is large compared to the time t, the system does not have time to respond to a stimulus as a viscous liquid. The modulus of rigidity dominates, and the material will behave as an elastic solid, supporting propagating shear waves.

Finally, we can use the Maxwell relaxation time to write the explicit form of the viscoelastic memory kernel.

$$\nu(k,t) = \frac{G(k)}{\rho m}\exp\left[\frac{-\eta t}{G(0)}\right]$$

With this memory kernel in hand, we can now go on to find an explicit solution to the transverse current correlation function.

To find the equation for the viscoelastic wave, we first find the Laplace transform of the transverse current correlation function

$$\hat{C}_T(k,s) = \frac{C(k,t=0)}{s + k^2\hat{\nu}(k,s)} = \frac{v_o^2}{s + k^2\hat{\nu}(k,s)}$$

Now, solve this equation using the exponential memory kernel $\nu(k,t) = \frac{G(k)}{\rho m} \exp \frac{-t}{\tau_M}$. The Laplace transform of an exponential function is well defined

$$\mathcal{L}[\exp[-\alpha t u(t)]] = \frac{1}{s+\alpha}$$

Therefore, the Laplace transform of the viscoelastic memory kernel is

$$\hat{\nu}(k,s) = \frac{\nu(k,0)}{s+\tau_M^{-1}}$$

Plug this into the the Laplace transform of the transverse current correlation function

$$\hat{C}_T(k,s) = \frac{v_o^2}{s + k^2\left(\frac{\nu(k,0)}{s+\tau_M^{-1}}\right)}$$

$$\hat{C}_T(k,s) = \frac{v_o^2(s+\tau_M^{-1})}{s(s+\tau_M^{-1}) + k^2\nu(k,0)}$$

Since function is quadratic, it is relatively easy to find the reverse Laplace transform, using the same method as that presented in section 4.2.C.2, or reference [1].

$$C_T(k,t) = v_o^2 \frac{1}{\lambda_+ + \lambda_-}\left(e^{-\lambda_+ t} - e^{-\lambda_- t}\right)$$

where the eigenvalues $\lambda_\pm$ are given by the solutions to the quadratic equation $s^2 + \tau_M^{-1}s + k^2\nu(k,0)$:

$$\lambda_\pm = -\frac{-\tau_M^{-1}}{2} \pm \sqrt{\frac{\tau_M^{-2} - 4k^2\nu(k,0)}{4}}$$

Complex eigensolutions exist if

$$\frac{1}{\tau_M^2} < 4k^2\nu(k,0)$$

Recall that $\nu(k,0) = c_t^2(k)$. Then we can rewrite the above inequality in terms of the wavenumber

$$k > \frac{1}{2\tau_M c_t(k)}$$

Define the critical wavenumber, $k_c = (2\tau_M c_t(k))^{-1}$. For more information on the viscoelastic approximation and its application to transverse current, please see Chapter 6 of *Molecular Hydrodynamics* by Jean-Pierre Boon and Sidney Yip [3] and chapter 3 and chapter 6 of *Dynamics of the Liquid State* by Umberto Balucani [5].

4.4 Long-time Tails and Mode-coupling Theory

4.4.1 The Problem

From the Langevin equation $\frac{dv}{dt} = -\gamma v + \frac{f}{m}$, we found that the velocity correlation function should take the form of an exponential decay (see Figure 4.4)

$$C(t) = \langle v(t)v(0)\rangle = v_o^2 e^{-\gamma t}$$

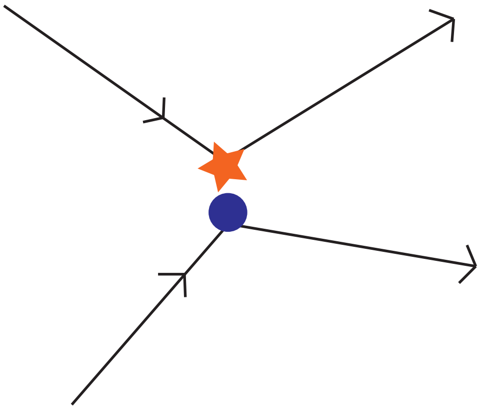

Figure 4.4: Uncorrelated collision of two particles in a fluid

where the memory kernel is related to the diffusion constant through Einstein's relation

$$\gamma = \frac{1}{mD\beta}$$

In 1967, Alder and Wainwright used computer simulations to calculate the velocity correlation function of hard-sphere gases [6]. They found that at long times, $C(t)$ exhibits a power-law decay rather than an exponential decay. That is, $C(t)$ decays according to $t^{-\frac{3}{2}}$

$$\lim_{t\to\infty} C(t) \propto \frac{1}{t^{\frac{3}{2}}}$$

This is the famous long-time tail problem in kinetic theory.

4.4.2 Memory Effects

The fundamental assumption underlying the exponential decay model of the velocity correlation function is that collisions between particles in a dilute hard-sphere gas are independent. This means that after each collision, a particle will lose memory of its original velocity until its motion has become completely randomized. This assumption leads to the exponential decay $C(t) = v_o^2 e^{-t/\tau_{coll}}$, where $\tau_{coll} = \frac{1}{\gamma}$ is the average collision time.

However, it is also possible that collisions are not completely independent but instead are correlated. A correlation would occur if, for example, two particles collide and then collide again after undergoing some number of other collisions (see Figures 4.5 and 4.6). This implies that there is a long term memory in the system which would lead to a decay that is slower than an exponential.

To estimate the form of this decay, we can consider the probability that, following a collision, a particle remains at or returns to its initial position after a time t, $P(r = 0, t)$. To make a rough estimate of this probability, imagine that at any moment in time we can draw a "probability sphere" for the particle. The probability of finding the particle inside the sphere is constant, and the probability of finding the particle outside the sphere is zero. At time $t = 0$, the particle has not had time to travel away from its initial position. Therefore, $P(r = 0, t) = \delta(r)$. As t increases, the particle begins to diffuse away from its initial position. The radius of the sphere increases linearly

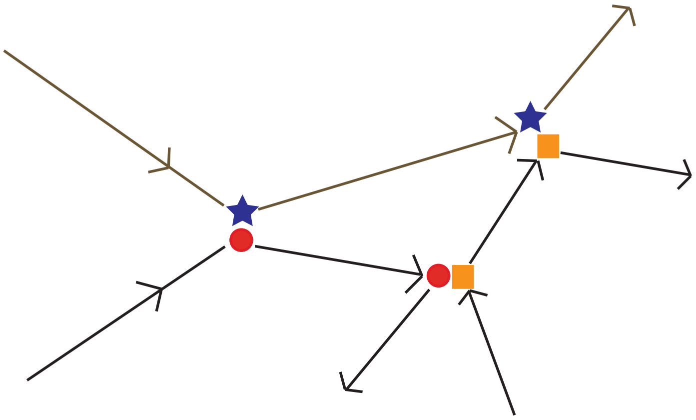

Figure 4.5: A test particle (blue star) collides with one particle (red circle), altering that particle's trajectory such that it collides with a third particle (yellow square). The subsequent collision of the third particle with the test particle is correlated with the initial collision.

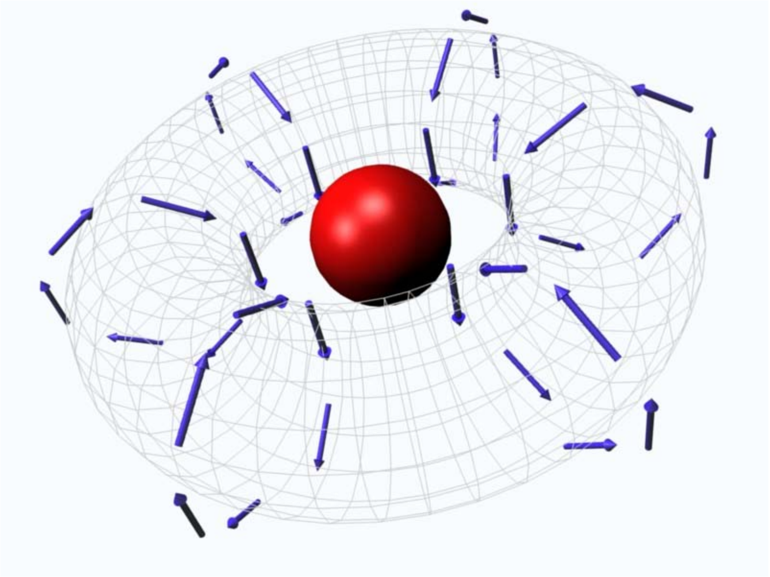

Figure 4.6: Vortex rings in the fluid around a hard sphere particle can contribute to the long-time tail of the velocity autocorrelation function [6].

with time according to $R = 2D^2t$, where D is the diffusion constant.

To estimate $P(r = 0, t)$ from probability sphere, note that the probability of finding the particle at any point in space must be unity:

$$\int P(r,t)dr = 1$$

We only need to integrate over the volume of the sphere, since the probability of finding the particle anywhere else is zero. Within the sphere, the probability is a constant, $P(r,t) = P(t)$. Therefore, this integral simplifies to

$$1 = \int_{sphere} P(t)dr \propto VP(t)$$

The volume of the sphere goes as $R^d = t^{\frac{d}{2}}$, where d is the spatial dimension. Therefore, the probability goes as

$$P(r = 0, t) = \frac{1}{V} \propto \frac{1}{R^d} \propto \frac{1}{t^{\frac{d}{2}}}$$

For a three dimensional system, we get a result consistent with Alder and Wainwright's predictions

$$P(r = 0, t) \propto \frac{1}{t^{\frac{3}{2}}}$$

This shows that memory effects may be the source of the power law decay.

We can construct a simple model of the behavior of a system for which memory effects are important. In this model, a particle with a velocity v_o creates a velocity field through its interactions with other particles. This velocity field can in turn influence the long time behavior of the particle.

We can start by getting a rough estimate of this velocity field from the transverse current

$$J_T(k,t) = J_T(k,0)e^{-\nu k^2 t}$$

where $\nu = \frac{\eta}{m\rho}$ is the diffusion constant, η is the shear viscosity, and $J_T(k,0) \propto v_o$. The transverse current is written in k-space. By transforming this into real space, we obtain an expression for the dissipation of the velocity field over time and space

$$v(r,t) \propto \frac{v_o}{\left(\sqrt{4\pi\nu t}\right)^3} e^{\frac{-r^2}{2\nu t}}$$

The velocity field dissipates due to friction. At short times, the decay has a Gaussian form. However, at long times the decay is dominated by the prefactor, which goes as $\tau^{-\frac{3}{2}}$.

4.4.3 Hydrodynamic Model

A simple way of deriving the above result would be to evaluate the velocity correlation function

$$C(t) = \langle v(t)v(0) \rangle$$

Using the hydrodynamic model, we can find this correlation function by taking the equilibrium average of the non-equilibrium average thermal velocity

$$C(t) = \langle v(t)v(0) \rangle = \int d\vec{r}_o \frac{1}{V} \int d\vec{v}_o f_B v_o \langle v(t) \rangle_{n.e.}$$

where f_B is the Boltzmann distribution and $\langle v(t)\rangle_{n.e.}$ is a non-equilibrium velocity field:

$$\langle v(t)\rangle_{n.e.} = \frac{\langle v_s(t)\delta\left(v_s - v_o\right)\delta\left(r_s - r_o\right)\rangle}{\langle \delta\left(v_s - v_o\right)\delta\left(v_s - v_o\right)\delta\left(r_s - r_o\right)\rangle}$$

Here, s describes the tagged particle.

The non-equilibrium velocity field can be represented as a coupling of the linear modes ρ^s and v_s.

$$\langle v(t)\rangle_{n.e.} = \int \rho^s\left(r,t\right) v_s\left(r,t\right) dr$$

$$= \frac{1}{\rho_o}\int \rho^s\left(r,t\right) J\left(r,t\right) dr$$

$$= \frac{\rho_o^{-1}}{\left(2\pi\right)^3}\int \rho^s\left(k,t\right) J\left(k,t\right) dk$$

We can solve this using the solutions of the hydrodynamic modes:

$$\rho_s\left(k,t\right) = \rho_s\left(k,0\right) e^{-k^2 Dt}$$

$$J_\perp\left(k,t\right) = J_\perp\left(k,0\right) e^{-k^2 \nu t}$$

$$J_L\left(k,t\right) = J_L\left(k,0\right) e^{-k^2 \frac{\Gamma}{2} t \pm i c_s k t}$$

For transverse modes,

$$v_o\langle v(t)\rangle_{n.e.} = \frac{1}{\left(2\pi\right)^3 \rho_o}\frac{2}{3}\int \rho^s\left(k,0\right) e^{-k^2 Dt} J_x\left(k,0\right) e^{-k^2 \nu t} v_x^s(0) dk$$

$$= \frac{1}{\left(2\pi\right)^3 \rho_o}\frac{2}{3}\int \rho^s\left(k,0\right) J_x\left(k,0\right) v_x^s(0) e^{-k^2 (D+\nu) t} dk$$

Then, take the equilibrium average

$$\langle \rho^s\left(k,0\right) J_x\left(k,0\right) v_x^s(0)\rangle = v_o^2$$

Finally,

$$C(t) = \frac{2}{3\rho_o} v_o^2 \frac{1}{\left(2\pi\right)^3}\int d\vec{k} e^{-k^2 (D+\nu) t}$$

$$= \frac{v_o^2}{12\rho_o}\frac{1}{\left[\pi t\left(D+\nu\right)\right]^{\frac{3}{2}}}$$

$$\propto \frac{1}{t^{\frac{3}{2}}}$$

4.4.4 Mode-Coupling Theory

As shown above, the correlation of a given dynamic quantity decays predominantly into pairs of hydrodynamic modes with conserved variables. Mode-Coupling Theory is the formalism that calculates their coupling.

From the discussion about, the velocity of the tagged particle is coupled to a bilinear mode, $A = \rho_s(k)J_x^*(k)$. then

$$C(t) = \left\langle v_x | e^{i\mathcal{L}t} | v_x \right\rangle \Rightarrow \left\langle v_x | P e^{i\mathcal{L}t} P | v_x \right\rangle$$

where P is the projection operator associated with A. By expanding the projection operator

$$C(t) = \langle v_s|A\rangle \langle A|A\rangle^{-1} \left\langle A|e^{i\mathcal{L}t}|A\right\rangle \langle A|A\rangle^{-1} \langle A|v_s\rangle$$

Now, use the linear hydrodynamic modes to evaluate the correlation function.

$$\rho_s = e^{-ikr_s}$$

$$J_x = \sum_i v_{xi} e^{-ikr_i}$$

Then

$$\langle v_s|A\rangle = \sum_i \left\langle v_{xs} | e^{-ikr_s} v_{xi} e^{ikr_i} \right\rangle = v_o^2$$

and

$$\langle A|A\rangle = N v_o^2$$

so that

$$\langle v_s|A\rangle \langle A|A\rangle^{-1} = \frac{1}{N}$$

Therefore,

$$\begin{aligned} C(t) &= \frac{1}{N^2} \sum_k \sum_{k'} \left\langle A(k)|e^{i\mathcal{L}t}|A(k')\right\rangle \\ &\approx \frac{1}{N^2} \sum_k \sum_{k'} \left\langle \rho_s(k,t)\,|\rho_s(k',0)\right\rangle \left\langle J_x(k,t)\,|J_x(k',0)\right\rangle \\ &= \frac{1}{N} \sum_k F_s(k,t)\, C_t(k,t) \\ &= \frac{V}{N} \frac{1}{(2\pi)^3} \int d\vec{k} F_s\left(\vec{k},t\right) C_t\left(\vec{k},t\right) \end{aligned}$$

Now,

$$F_s\left(\vec{k},t\right) = e^{-k^2 D t}$$

and

$$C_t\left(\vec{k},t\right) = v_o^2 e^{-k^2 \nu t}$$

Then

$$C(t) = \frac{1}{\rho} \frac{v_o^2}{(2\pi)^3} \int d\vec{k} e^{-k^2(D+\nu)t}$$

By incorporating the three-spatial components of J and v, we have

$$C(t) = \frac{1}{12\rho} v_o^2 \left[\frac{1}{\pi (D+\nu) t}\right]^{\frac{3}{2}}$$

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