4.1: Short-time Behavior

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

$$C(t) = \langle A(t)A(0)\rangle = \mathrm{Tr}\, A(t)A(0)\rho_{eq} \tag{4.1.1}$$

Where the equilibrium density matrix is given by

$$\rho_{eq} = \frac{e^{-\beta\mathcal{H}}}{Q} \tag{4.1.2}$$

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

$$A(t) = e^{i\mathcal{L}t}A(0) \tag{4.1.3}$$

or

$$\dot{A}(t) = i\mathcal{L}A(0) \tag{4.1.4}$$

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

$$i\mathcal{L} = \frac{1}{i\hbar}[\ldots,\mathcal{H}] \tag{4.1.5}$$

And for classical systems it is defined as the Poisson operator

$$i\mathcal{L} = \{\ldots,\mathcal{H}\} \tag{4.1.6}$$

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

$$C(t) = \langle A(t)A(0)\rangle \tag{4.1.7}$$

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

$$C(t) = \sum_{n=0}^{\infty}\frac{t^n}{n!}C^{(n)}(0) \tag{4.1.8}$$

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

$$C(t) = \sum_{n=0}^{\infty}\frac{t^{2n}}{(2n)!}C^{(2n)}(0) \tag{4.1.9}$$

The derivative of a correlation function can be written as

$$C^{(2n)}(t) = (-1)^n\left\langle A^{(2n)}(t)A(0)\right\rangle \tag{4.1.10}$$

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

$$C(t) = \sum_{n=0}^{\infty}(-1)^n\frac{t^{2n}}{(2n)!}\left\langle A^{(2n)}(0)A(0)\right\rangle \tag{4.1.11}$$

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

$$C(t) = \sum_{n=0}^{\infty}\frac{t^{2n}}{(2n)!}\left\langle A^{(n)}A^{(n)}\right\rangle \tag{4.1.12}$$

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

$$C^{(2n)} = \frac{1}{2\pi}\int_{-\infty}^{\infty} \tilde{C}(\omega)e^{-i\omega t}dt \tag{4.1.13}$$

the time derivatives can be evaluated easily as

$$C^{(2n)} = (-1)^{(n)}\left(\frac{\partial}{\partial t}\right)^{(2n)} C(t) = \frac{1}{2\pi}\int_{-\infty}^{\infty} \tilde{C}(\omega)\omega^{2n}dt = \langle \omega^{2n}\rangle \tag{4.1.14}$$

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

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

$$C(t) = \frac{1}{3}\langle \vec{v}(t)\vec{v}(0)\rangle = \langle \dot{z}(t)\dot{z}(0)\rangle \tag{4.1.15}$$

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

$$C(t) = \frac{1}{3}\langle \vec{v} \mid \vec{v}\rangle - \frac{t^2}{2}\frac{1}{3}\langle \dot{\vec{v}} \mid \vec{v}\rangle + \cdots \tag{4.1.16}$$

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

$$\frac{1}{3}\langle \vec{v} \mid \vec{v}\rangle = \frac{1}{\beta m} = v_o^2 \tag{4.1.17}$$

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

$$\frac{1}{3}\langle \dot{\vec{v}} \mid \dot{\vec{v}}\rangle = \frac{1}{3}\frac{\langle \nabla U \mid \nabla U\rangle}{m^2} \tag{4.1.18}$$

To evaluate this expression, write it in its explicit form

$$\frac{1}{3}\frac{\langle \nabla U \mid \nabla U\rangle}{m^2} = \frac{1}{3m^2}\int dz \partial_z U \partial_z U e^{-\beta U} \tag{4.1.19}$$

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:

$$\frac{1}{3m^2}\int dz \partial_z U\left(\frac{1}{\beta}\partial_z e^{-\beta U}\right) \tag{4.1.20}$$

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

$$\frac{1}{3\beta m^2}\int dz \partial_z^2 U e^{-\beta U} = \frac{1}{3\beta m}\left\langle \frac{\partial_z^2 U}{m}\right\rangle \tag{4.1.21}$$

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

$$\langle \nabla U A\rangle = \frac{1}{Q}\int d\mathbf{r} A \nabla U e^{-\beta U} = k_B T\langle \nabla A\rangle \tag{4.1.22}$$

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

$$\Omega_o^2 = \frac{1}{3m}\left\langle \nabla^2 U \right\rangle = \frac{\rho}{3m}\int d\mathbf{r} g(\mathbf{r}) \nabla^2 \phi \tag{4.1.23}$$

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

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

$$C(t) \simeq v_o^2 \left(1 - \frac{t^2}{2}\Omega_0^2\right) \tag{4.1.24}$$

3. 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

$$n_s(\mathbf{R}, t) = \delta(\mathbf{R} - r(t)) \tag{4.1.25}$$

Which has the Fourier transform

$$n_s(\vec{k}, t) = e^{-i\vec{k}\vec{r}(t)} \tag{4.1.26}$$

The self-intermediate scattering function is defined as

$$F_s(\vec{k}, t) = \left\langle n_s(\vec{k}, t) \mid n_s(\vec{k}, 0) \right\rangle = \left\langle e^{-i\vec{k}\vec{r}(t)} \mid e^{-i\vec{k}\vec{r}(0)} \right\rangle = \left\langle e^{-i\vec{k}(\vec{r}(t) - \vec{r}(0))} \right\rangle \tag{4.1.27}$$

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

$$C_0 = F_s(\vec{k}, 0) = \left\langle e^{-i\vec{k}(\vec{r}(0) - \vec{r}(0))} \right\rangle = 1 \tag{4.1.28}$$

The second order term is given by

$$C_2 = \left\langle \omega^2 \right\rangle = \left\langle \dot{n}_s \mid \dot{n}_s \right\rangle = \left\langle -i\vec{k}\dot{\vec{r}}(0) e^{-i\vec{k}\vec{r}(0)} \mid -i\vec{k}\ddot{\vec{r}}(0) e^{-i\vec{k}\vec{r}(0)} \right\rangle \tag{4.1.29}$$

This can be simplified to

$$C_2 = \left\langle (\vec{k}\vec{v}(0))^2 e^{-i\vec{k}(\vec{r}(0) - \vec{r}(0))} \right\rangle = k^2 v_o^2 \tag{4.1.30}$$

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

$$C_2 = \omega_o^2 \tag{4.1.31}$$

The fourth moment of this correlation function is given by

$$C_4 = \left\langle \omega^4 \right\rangle = \left\langle \ddot{n}_s \mid \ddot{n}_s \right\rangle = \left\langle -i\frac{d}{dt}\left(\vec{k}\dot{\vec{r}}(0) e^{-i\vec{k}\vec{r}(0)}\right) \mid -i\frac{d}{dt}\left(\vec{k}\dot{\vec{r}}(0) e^{-i\vec{k}\vec{r}(0)}\right) \right\rangle \tag{4.1.32}$$

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

$$C_4 = (\vec{k}\vec{v})^4 + \left\langle (\vec{k}\,\overrightarrow{\vec{v}}\,)^2 \right\rangle \tag{4.1.33}$$

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

$$\left\langle (\vec{k}\,\overrightarrow{\vec{v}}\,)^2 \right\rangle = \frac{1}{m^2} k^2 \left\langle \nabla_z V \nabla_z V \right\rangle \tag{4.1.34}$$

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

$$\frac{1}{m^2} k_B T k^2 \left\langle \nabla_z^2 V \right\rangle \tag{4.1.35}$$

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

$$\frac{k_BT}{m}k^2\left\langle\frac{\nabla_z^2V}{m}\right\rangle = k^2v_o^2\left\langle\frac{\nabla_z^2V}{m}\right\rangle = \omega_o^2\Omega_o^2 \tag{4.1.36}$$

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

$$F_s(\vec{k},t) = 1-\langle\omega^2\rangle\frac{t^2}{2!}+\langle\omega^4\rangle\frac{t^4}{4!}-\cdots \tag{4.1.37}$$

can be evaluated to

$$F_s(\vec{k},t) = 1-\omega_o^2\frac{t^2}{2!}+\left(3\omega_o^4+\omega_o^2\Omega_o^2\right)\frac{t^4}{4!}-\cdots \tag{4.1.38}$$

4. Free-Particle Limit (Ideal Fluid) We can use the short time expansion of the selfintermediate 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))

$$\Omega_o^2 = \frac{\rho}{3m}\int d\vec{r}g(\vec{r})\nabla^2\phi(\vec{r}) \tag{4.1.39}$$

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

$$F_s(\vec{k},t) = 1-\omega_o^2\frac{t^2}{2!}+\omega_o^4\frac{t^4}{8}-\cdots \tag{4.1.40}$$

This is simply the short time expansion for the function

$$F_s(\vec{k},t) = e^{-\frac{1}{2}\omega_o^2t^2} \tag{4.1.41}$$

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 $\omega_0^2\Omega_o^2$ is sufficiently smaller than $3\omega_0^4$ that it can be ignored. Therefore, the condition for ignoring collisions can be written as

$$\Omega_o^2 \ll 3\omega_o^2 \tag{4.1.42}$$

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

$$k \gg \frac{\Omega_o}{\sqrt{\frac{3k_BT}{m}}} \tag{4.1.43}$$

Now, define the parameter l as

$$l = \sqrt{\frac{3k_BT}{m}}\Omega_o \tag{4.1.44}$$

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

$$k \gg \frac{1}{l} \tag{4.1.45}$$

or

$$\lambda \ll l \tag{4.1.46}$$

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].

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

$$\rho(\vec{r}, t)=\sum_i \delta\left(\vec{r}-\vec{r}_i(t)\right) \tag{4.1.47}$$

We define the density fluctuation as

$$\delta \rho(\vec{r}, t)=\rho(\vec{r}, t)-\langle\rho\rangle \tag{4.1.48}$$

The Fourier transform of the density fluctuation is given by

$$\rho_k(t)=\sum_i e^{-i \vec{k} \vec{r}_i(t)}-(2 \pi)^3 \delta(\vec{k}) \rho_o \tag{4.1.49}$$

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

$$F(\vec{k}, t)=\frac{1}{N}\left\langle\rho_k(t) \mid \rho_k(0)\right\rangle=\frac{1}{N}\langle\rho(\vec{k}, t) \mid \rho(-\vec{k}, 0)\rangle \tag{4.1.50}$$

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 $F(k, t)$ by substituting in the definition of $\rho_k(t)$ and solving at time $t=0$.

$$C_0=F(\vec{k}, 0)=\frac{1}{N}\left\langle\sum_j e^{i \vec{k} \vec{r}_j(0)} \sum_i e^{-i \vec{k} \vec{r}_i(0)}\right\rangle \tag{4.1.51}$$

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

$$C_0=1+\frac{1}{N}\left\langle\sum_{i \neq j} e^{-i \vec{k} \vec{r}_{i j}}\right\rangle(2 \pi)^3 \delta(\vec{k}) \rho_o \tag{4.1.52}$$

where $\vec{r}_{i j}=\vec{r}_i(0)-\vec{r}_j(0)$. 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

$$C_0=1+\rho_o g(\vec{r})-(2 \pi)^3 \delta(\vec{k}) \rho_o=1+\rho_o \tilde{h}=S(\vec{k}) \tag{4.1.53}$$

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

$$S(0)=1+\rho_o k_B T \chi_T \leqslant 1 \tag{4.1.54}$$

where χ_T is the isothermal compressibility,

$$\chi_T=\frac{1}{\rho_o} \frac{\partial \rho}{\partial t} \tag{4.1.55}$$

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

$$G(\vec{r}, t)=\frac{1}{N}\left\langle\sum_{i, j} \vec{r}(0)-\vec{r}_{i j}(0)\right\rangle-\rho_o=\langle\delta \rho(\vec{r}, t) \rho(\vec{r}, 0)\rangle \tag{4.1.56}$$

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

$$G(\vec{r}, 0)=\delta(\vec{r})+\rho_o h(\vec{r}) \tag{4.1.57}$$

where $g=1+h$

3. 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

$$F(\vec{k}, t)=S(\vec{k})-\left\langle\omega^2\right\rangle \frac{t^2}{2!}+\left\langle\omega^4\right\rangle \frac{t^4}{4!}-\cdots \tag{4.1.58}$$

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 :

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

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

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

$$C_2 = \left\langle\omega^2\right\rangle = \frac{1}{N}\left\langle\dot{n}_k \mid \dot{n}_k\right\rangle = \left\langle(\vec{k}\,\vec{v})^2\right\rangle = \omega_o^2 \tag{4.1.59}$$

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

$$C_4 = \left\langle\omega^4\right\rangle = \frac{1}{N}\sum_{i,j}\left\langle\left[\left(\vec{k}\vec{v}_i\right)^2\left(\vec{k}\vec{v}_j\right)^2 + i\left(\vec{k}\,\vec{\dot{v}}_i\right)\left(\vec{k}\vec{v}_j\right)^2 - i\left(\vec{k}\,\vec{\dot{v}}_j\right)\left(\vec{k}\vec{v}_k\right)^2 + \left(\vec{k}\,\vec{\dot{v}}_i\right)\left(\vec{k}\,\vec{\dot{v}}_j\right)\right] e^{-i\vec{k}\vec{r}_{ij}}\right\rangle \tag{4.1.60}$$

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

$$C_4 = \left\langle\omega^4\right\rangle = \frac{1}{N}\left[\sum_{i=j}\langle\cdots\cdots\rangle + \sum_{i\neq j}\langle\cdots\cdots\rangle\right] \tag{4.1.61}$$

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

$$\frac{1}{N}\left\langle(\vec{k}\vec{v})^4\right\rangle + \frac{1}{N}\left\langle(\vec{k}\,\vec{\dot{v}})^2\right\rangle = 3\omega_o^4 + \omega_o^2\Omega_o^2 \tag{4.1.62}$$

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

$$= \frac{1}{N}\sum_{i\neq j}\left\langle\left(\vec{k}\vec{v}_i\right)^2\left(\vec{k}\vec{v}_j\right)^2 e^{-i\vec{k}\vec{r}_{ij}}\right\rangle = \left(k^2 v_o^2\right)^2 \frac{1}{N}\sum_{i\neq j}\left\langle e^{-i\vec{k}\vec{r}_{ij}}\right\rangle = \omega_o^4\tilde{g}\rho_o \tag{4.1.63}$$

The second and third term can be combined to give

$$\begin{aligned}\frac{1}{N}\sum_{i\neq j}&\left\langle\left[i\left(\vec{k}\ddot{\vec{v}}_i\right)\left(\vec{k}\vec{v}_j\right)^2 - i\left(\vec{k}\,\vec{\dot{v}}_j\right)\left(\vec{k}\vec{v}_k\right)^2\right] e^{-i\vec{k}\vec{r}_{ij}}\right\rangle \\ &= \frac{1}{N}\sum_{i\neq j}\left\langle(kv_o)^2\left[\vec{k}\dot{\vec{v}}_i - \vec{k}\,\vec{\dot{v}}_j\right] e^{-i\vec{k}\vec{r}_{ij}}\right\rangle \\ &= -2\omega_o^4\frac{1}{N}\sum_{i\neq j}\left\langle e^{-i\vec{k}\vec{r}_{ij}}\right\rangle = -2\omega_o^4\tilde{g}\rho_o\end{aligned}$$

And the fourth term gives

$$\frac{1}{N}\sum_{i\neq j}\left\langle\left(\vec{k}\,\vec{\dot{v}}_i\right)\left(\vec{k}\,\vec{\dot{v}}_j\right) e^{-i\vec{k}\vec{r}_{ij}}\right\rangle \tag{4.1.64}$$

$$= \frac{k^2}{m^2}\frac{1}{N}\sum_{i\neq j}\left\langle\nabla_{zi}U\nabla_{zj}Ue^{-i\vec{k}\vec{r}_{ij}}\right\rangle \tag{4.1.65}$$

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

$$\begin{aligned}\frac{k^2}{m^2}\frac{1}{N}\sum_{i\neq j}&\left\langle\left(-\frac{1}{\beta}\frac{\partial}{\partial z_i}\frac{\partial}{\partial z_j}U + \frac{k^2}{\beta^2}\right) e^{-i\vec{k}\vec{r}_{ij}}\right\rangle \\ &= -\omega_o^2\Omega_L^2 + \omega_o^4\tilde{g}\rho_o\end{aligned}$$

Then the distinct part of the fourth moment is given by

$$\omega_o^4\tilde{g}\rho_o - 2\omega_o^4\tilde{g}\rho_o + \omega_o^4\tilde{g}\rho_o - \omega_o^2\Omega_L^2 = -\omega_o^2\Omega_L^2 \tag{4.1.66}$$

where

$$\Omega_L^2 = \frac{1}{m}\left\langle \partial_z^2\phi e^{-i\vec{k}\vec{z}_{ij}}\right\rangle = \frac{\rho_o}{m}\int d\vec{r}e^{-i\vec{k}\vec{z}}\partial_z^2\phi g(\vec{r}) \tag{4.1.67}$$

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

$$C_4 = \left\langle \omega^4\right\rangle = 3\omega_o^4 + \omega_o^2\Omega_o^2 - \omega_o^2\Omega_L^2 \tag{4.1.68}$$

4. 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

$$F(\vec{k},t) = S(\vec{k}) - \omega_o^2\frac{t^2}{2!} + \left[3\omega_o^2 + \Omega_o^2 - \Omega_L^2\right]\omega_o^2\frac{t^4}{4!} - \cdots \tag{4.1.69}$$

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

$$F_s(\vec{k},t) = 1 - \omega_o^2\frac{t^2}{2!} + \left[3\omega_o^2 + \Omega_o^2\right]\omega_o^2\frac{t^4}{4!} - \cdots \tag{4.1.70}$$

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

$$\lim_{k\to 0} S(\vec{k}) = S(0) \leq 1 \tag{4.1.71}$$

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

$$\vec{J}_k(t) = \sum_i \vec{v}_i(t)e^{-i\vec{k}\vec{r}_i} \tag{4.1.72}$$

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

$$\vec{J}_L(k,t) = \sum_i \vec{z}_i(t)e^{-i\vec{k}\vec{z}_i} \tag{4.1.73}$$

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

$$\vec{J}_T(k,t) = \sum_i \vec{x}_i(t)e^{-i\vec{k}\vec{z}_i} \tag{4.1.74}$$

The longitudinal current correlation function is given by

$$C_L = \frac{1}{N}\left\langle \vec{J}_L(\vec{k},t) \mid \vec{J}_L(\vec{k},t)\right\rangle \tag{4.1.75}$$

And the transverse current correlation function is given by

$$C_T = \frac{1}{N}\left\langle \vec{J}_T(\vec{k},t) \mid \vec{J}_T(\vec{k},t)\right\rangle \tag{4.1.76}$$

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

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

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

$$\omega^2_{\frac{L}{T}} = k^2 c^2_{\frac{L}{T}} \tag{4.1.77}$$

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,

$$\omega_L^2 \backsim 3\omega_T^2 \tag{4.1.78}$$

6. 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

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

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 $\omega = \pm\sqrt{2}\omega_o$