

Chapter 3

Hydrodynamics and Light Scattering

Hydrodynamics describes the low-frequency, long-wavelength behavior of a system that is disturbed from equilibrium. When a system is disturbed from equilibrium, some quantities and parameters decay very quickly back to their equilibrium state, while others take a long time to relax [1]. Conserved quantities, such as particle number, momentum, and energy, take a long time to relax to equilibrium, while non-conserved quantities decay quickly [1]. Similarly, order parameters, such as average magnetization, take a long time to relax to equilibrium, while parameters which are not order parameters decay quickly [1]. Therefore, at long times, a non-equilibrium system can be completely described by order parameters and the densities of conserved quantities [1]. Hydrodynamic equations are the equations of motion for these quantities and parameters.

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

3.1 Scattering and Correlation Functions

A particle or light field propagating through space can be described by a wave vector \vec{k} . The direction of \vec{k} indicates the direction of propagation of the wave, and the magnitude of \vec{k} indicates the wave number, or inverse wavelength, of the wave. Scattering occurs when a propagating wave encounters a medium which alters the magnitude or direction of its wave vector. In this section, we will show that the behavior of light scattered from a medium is related to the density correlation functions of the medium. As a result, light scattering experiments can be used to probe the structure of a material.

3.1.1 Elastic Scattering

Neutron or Light Scattering In this section, we want to describe the behavior of a particle or light field that undergoes elastic scattering from a medium. This discussion could apply to x-ray, proton, neutron, or electron scattering, among others.

Elastic scattering occurs when there is no transfer of energy from the particle to the scattering medium. The direction of the particle's wave vector changes, but its wave number (or frequency) remains the same. A schematic of the scattering process is depicted in Figure 3.1 . The incident particle or light field with wave vector \vec{k}_o is scattered from the sample at point \vec{r} , changing its wave vector to \vec{k}_f . The vector \vec{k}_f has the same magnitude as \vec{k}_o , but a different direction. The scattered

light is detected at point \vec{r} .

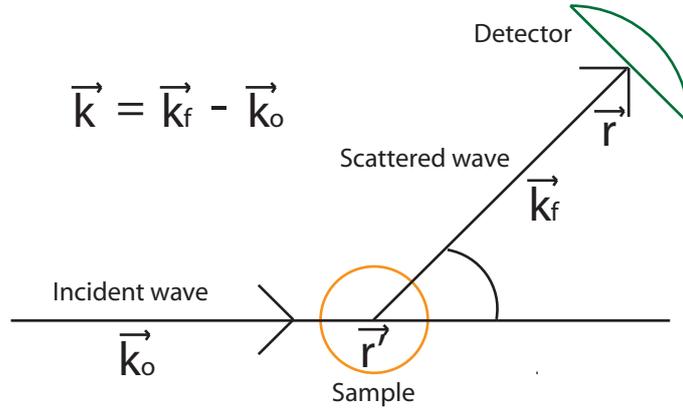


Figure 3.1: Elastic Scattering of a particle or light field from a medium

The scattered particle or light field can be modelled as a spherical wave. The quantum mechanical expression for this wave is

$$\Psi_s = \frac{i}{\hbar} \int \frac{e^{ik|\vec{r}-\vec{r}'|}}{|\vec{r}-\vec{r}'|} e^{i\vec{k}_o \cdot \vec{r}'} \rho(\vec{r}') d\vec{r}'$$

where $\rho(\vec{r}')$ is the density of scattering agents and the integral is carried out over all scattering agents.

In most light scattering experiments, the distance from the sample to the light detector is significantly larger than the size of the sample itself. In this case it is valid to make the assumption that $r \gg r'$. Then

$$e^{ik|\vec{r}-\vec{r}'|} \rightarrow e^{ikr - i\vec{k}_f \cdot \vec{r}'}$$

and the wavefunction can be written

$$\Psi_s = \frac{i}{\hbar} \frac{e^{ikr}}{r} \int \rho(\vec{r}') e^{-i(\vec{k}_f - \vec{k}_o) \cdot \vec{r}'} d\vec{r}' = \frac{i}{\hbar} \frac{e^{ikr}}{r} \int \rho(\vec{r}') e^{-i\vec{k} \cdot \vec{r}'} d\vec{r}'$$

where $\vec{k} = \vec{k}_f - \vec{k}_o$ is the difference between the initial and scattered wave vector.

We can also assume that the medium is composed of point particles, so the density is the sum over all points

$$\rho(\vec{r}) = \sum_{i=1}^N a_i \delta(\vec{r} - \vec{r}_i) = a \sum_{i=1}^N \delta(\vec{r} - \vec{r}_i)$$

Then the wavefunction simplifies to

$$\Psi_s = \frac{i}{\hbar} \frac{e^{ikr}}{r} a \sum_{i=1}^N e^{-i\vec{k} \cdot \vec{r}_i} \propto a \sum_{i=1}^N e^{-i\vec{k} \cdot \vec{r}_i}$$

In light scattering experiments the measured quantity is the intensity of scattered light over the angle spanned by the detector. This quantity is called the scattering cross section $\frac{d\sigma}{d\Omega}$, and it is proportional to the square of the wavefunction:

$$I(\vec{k}) = |\Psi_s|^2 \propto \frac{1}{r^2} \frac{d\sigma}{d\Omega} = \frac{a^2}{r^2} \langle |\sum_{i=1}^N e^{-i\vec{k}\cdot\vec{r}_i}|^2 \rangle = \frac{a^2}{r^2} N S(\vec{k})$$

where $S(\vec{k})$ is called the static structure factor, and is defined as:

$$S(\vec{k}) = \frac{1}{N} \langle |\sum_{i=1}^N e^{-i\vec{k}\cdot\vec{r}_i}|^2 \rangle$$

In order to find the scattering intensity, we must evaluate this term.

The Static Structure Factor The static structure factor can be rewritten as:

$$S(k) = \frac{1}{N} \langle \rho_k \rho_{-k} \rangle$$

where

$$\rho_k = \int e^{-i\vec{k}\cdot\vec{r}} \rho(\vec{r}) d\vec{r}$$

and $\rho(r)$ is the local number density. For a homogeneous liquid, $\langle \rho(r) \rangle = \rho_o$.

To model real systems, we can simplify the calculations by expressing the density correlations as a sum of the homogeneous density ρ_o and local fluctuations $\delta\rho$.

$$\rho(r) = \rho_o + \delta\rho$$

Using this separation, the scattering function can be written in two pieces:

$$S(k) = \frac{1}{N} \langle \rho_k \rho_{-k} \rangle = \rho_o (2\pi)^3 \delta(\vec{k}) + \frac{1}{N} \langle |\delta\rho_k \delta\rho_{-k}| \rangle$$

The first term arises from the homogeneous background and is called the forward scattering. The second term gives the scattering from the density fluctuations. In an ideal gas, there is no interaction between the particles $\delta\rho = 0$, and so there is only forward scattering.

The Density Correlation function It is also helpful to think about the scattering in real space. Define the density correlation function $G(\vec{r})$ as the Fourier transform of $S(k)$ into coordinate space.

$$\begin{aligned} G(\vec{r}) &= \frac{1}{(2\pi)^3} \int S(\vec{k}) e^{-i\vec{k}\cdot\vec{r}} d\vec{k} \\ &= \frac{1}{N} \frac{1}{(2\pi)^3} \int e^{-i\vec{k}\cdot\vec{r}} \langle \sum_i e^{i\vec{k}\cdot\vec{r}_i} \sum_j e^{-i\vec{k}\cdot\vec{r}_j} \rangle d\vec{k} \\ &= \frac{1}{N} \sum_{i,j} \langle \delta(\vec{r} - \vec{r}_{i,j}) \rangle \end{aligned}$$

From this, we can see that the Fourier transform of the structure factor gives probability of finding two particles separated by a vector \vec{r} .

We can also write the density correlation function in a slightly different form:

$$\begin{aligned} G(\vec{r}) &= \frac{1}{N} \sum_{i,j} \int d\vec{r}_o \langle \delta(\vec{r}_i - \vec{r}_o - \vec{r}) \delta(\vec{r}_j - \vec{r}_o) \rangle \\ &= \frac{1}{N} \int d\vec{r}_o \langle \rho(\vec{r}_o + \vec{r}) \rho(\vec{r}_o) \rangle = \frac{V}{N} \langle \rho(\vec{r}) \rho(0) \rangle = \frac{1}{\rho_o} \langle \rho(\vec{r}) \rho(0) \rangle \end{aligned}$$

The Pair Distribution Function To better understand the physical interpretation of the structure factor and the density correlation function, we can rewrite them in terms of the pair distribution function $g(r)$. The pair distribution function is given by:

$$g(r) = \frac{1}{N^2} \sum_{i \neq j} \langle \delta(\vec{r} - \vec{r}_{i,j}) \rangle$$

This gives the probability that, if I have a single particle i , I will be able to find another particle j at a distance \vec{r} away. It is defined only for terms with $i \neq j$. We can write $g(r)$ as:

$$g(r) = h(r) + 1$$

where $h(r)$ is the pair correlation function. The Fourier transform of the pair distribution function can be written:

$$\tilde{g}(\vec{k}) = \tilde{h}(\vec{k}) + (2\pi)^3 \delta(\vec{k})$$

This allows us to rewrite the structure factor and the density correlation function in terms of the interactions between individual pairs of particles.

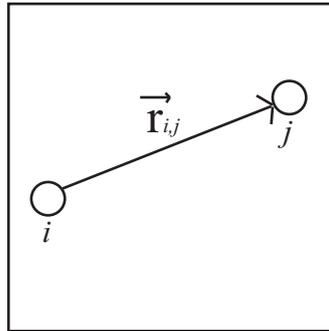


Figure 3.2: The pair distribution function

To write the structure factor $S(k)$ and the density correlation function $G(r)$ in terms of the pair distribution function, separate the summations into terms with $i = j$ and terms with $i \neq j$. The structure factor is written:

$$S(k) = \frac{1}{N} \sum_{i,j} \langle e^{-ikr_i} e^{ikr_j} \rangle$$

The terms with $i = j$ each contribute a value of $\frac{1}{N}$. After taking the summation over all N particles, this gives a value of 1.

$$S(k) = 1 + \sum_{i \neq j} \langle e^{-ik(r_i - r_j)} \rangle = 1 + \rho \tilde{g}(k) = 1 + \rho \tilde{h}(\vec{k}) + (2\pi)^3 \delta(\vec{k}) \rho$$

Now, the first two terms $1 + \rho \tilde{h}(\vec{k})$ give the scattering due to the molecular structure, or fluctuations. The third term gives the forward scattering, which as we discussed earlier is the scattering that we would expect in a system with no fluctuations (an ideal gas).

The density correlation function is written:

$$G(\vec{r}) = \frac{1}{N} \langle \sum_{i,j} \delta(r_{i,j} - r) \rangle$$

when $i = j$, we are discussing a single particle. Therefore, $r_{i,j} = 0$ and each term contributes $\frac{1}{N} \delta(\vec{r})$. After taking the summation over all N particles, the N cancels and we are left with $\delta(\vec{r})$.

$$\begin{aligned} G(\vec{r}) &= \delta(\vec{r}) + \frac{1}{N} \langle \sum_{i \neq j} \delta(r_{i,j} - r) \rangle \\ &= \delta(\vec{r}) + \rho g(\vec{r}) = \delta(\vec{r}) + \rho (h(\vec{r}) + 1) \end{aligned}$$

By writing the expressions for $S(\vec{k})$ and $G(\vec{r})$ in terms of $g(\vec{r})$, their physical interpretation becomes more clear. The pair distribution function for a typical liquid and a typical solid are shown in Figure 3.3 and Figure 3.4. If a particle has a radius d , then clearly no other particle can be closer than distance d . Therefore, for both the solid and the liquid, $g(\vec{r})$ has a value of 0 from a distance 0 to a distance d . At this point, the probability rapidly increases and begins oscillating around a value of 1. In a liquid, there is short range structure as weak intermolecular interactions form a series of solvation shells around a particle. However, these forces only act at short range, and as the distance increases the correlation decays to zero. In a solid, the structure persists throughout the sample, and therefore the oscillations do not decay.

3.1.2 Inelastic Scattering

The previous section described the behavior of a particle as it undergoes an elastic scattering event. In this section, we will address the phenomenon of inelastic scattering, which applies primarily to light fields. Inelastic scattering occurs when scattered light transfers some energy to the scattering material. While an elastic scattering event causes only a change in the direction of the wave vector, an inelastic scattering event causes both a change in the direction and the wavenumber of the scattered light. In other words, the scattered wave becomes frequency dispersed. Figure 3.5 gives a schematic of an inelastic scattering event.

1) Scattered Intensity To calculate the intensity of scattered light from an inelastic scattering event, we can follow a very similar process to that which we used for elastic scattering: model the scattered light as a spherical wave, and simplify it by assuming that the distance from the sample to the light detector is large compared with the size of the sample, and that the medium is composed of point particles. However, there is one major difference. Since the scattered light can transfer energy to the material, the position of the particles now depends on time. The scattered wavefunction is then:

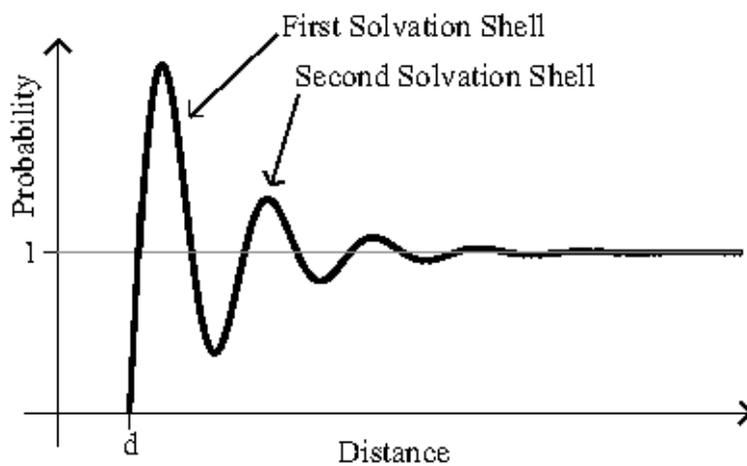


Figure 3.3: Pair Distribution Function for a Liquid

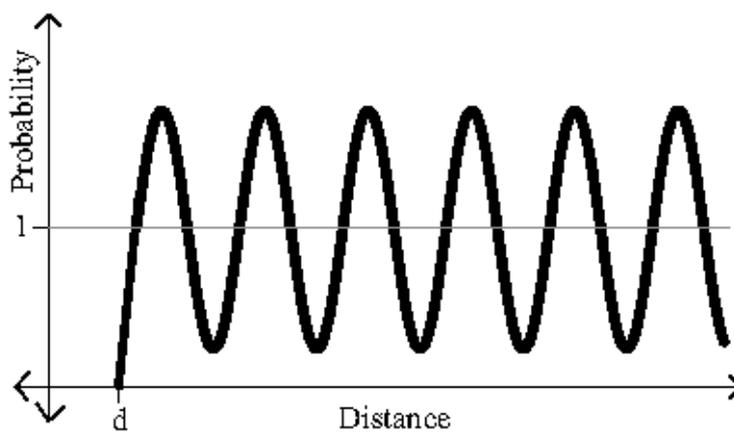


Figure 3.4: Pair Distribution Function for a Solid

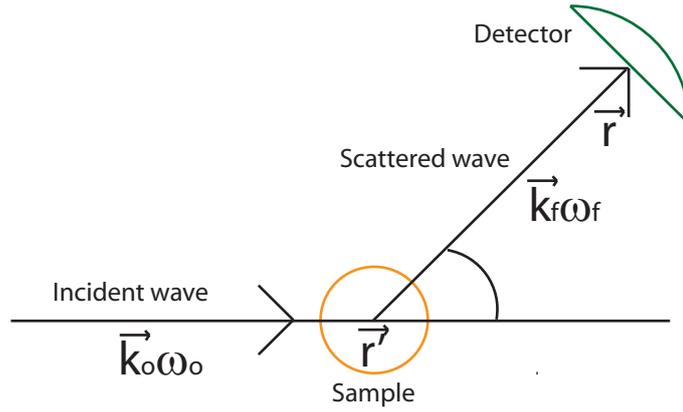


Figure 3.5: Schematic of an Inelastic Scattering Event

$$\Psi_s \propto \frac{a}{r} \sum_{i=1}^N e^{-i\vec{k} \cdot \vec{r}_i(t)}$$

which gives a differential cross-section of:

$$\frac{d\sigma}{d\Omega d\omega} = a^2 \left\langle \sum_i e^{-i\vec{k} \cdot \vec{r}_i(t)} \sum_j e^{-i\vec{k} \cdot \vec{r}_j(t)} \right\rangle$$

By taking the temporal Fourier transform, we can find the structure factor:

$$\begin{aligned} \frac{d\sigma}{d\Omega d\omega} &= a^2 \int e^{i\omega t} \left\langle \sum_i e^{-i\vec{k} \cdot \vec{r}_i(t)} \sum_j e^{-i\vec{k} \cdot \vec{r}_j(t)} dt \right\rangle \\ &= a^2 N S(\vec{k}, \omega) \end{aligned}$$

Note that the structure factor S is now dependent on both the wave vector \vec{k} and the frequency ω . Therefore, it is called the *Dynamic Structure Factor*.

2) The Intermediate Scattering Function The intermediate scattering function is defined as the Fourier transform of the dynamic structure factor into real time.

$$F(\vec{k}, t) = \frac{1}{2\pi} \int S(\vec{k}, \omega) e^{i\omega t} d\omega$$

$$S(\vec{k}, \omega) = \int F(\vec{k}, t) e^{-i\omega t} dt$$

It is called the *Intermediate scattering function* is because it has one variable, the spatial dimension \vec{k} , expressed in Fourier space, and the other variable, the time dimension t , expressed in real space. It can be expressed explicitly as:

$$F(\vec{k}, t) = \frac{1}{N} \langle \rho_{\vec{k}}(t) \rho_{-\vec{k}}(0) \rangle$$

where:

$$\rho_{\vec{k}}(t) = \sum_i e^{-i\vec{k}\cdot\vec{r}_i(t)}$$

Note that this function looks identical to the static structural factor from section 1, except that now the density is a function of time.

3) The Van Hove Function The Van Hove Function is defined as the Fourier transform of the intermediate scattering function into real space.

$$G(\vec{r}, t) = \frac{1}{(2\pi)^3} \int F(\vec{k}, t) e^{i\vec{k}\cdot\vec{r}} d\vec{k} = \frac{1}{N} \sum_{i,j} \langle \delta(\vec{r}_i(t) - \vec{r}_j(0) - \vec{r}) \rangle$$

The Van Hove Function can also be expressed as

$$\begin{aligned} G(\vec{r}, t) &= \frac{1}{N} \int d\vec{r}_o \left\langle \sum_i \delta(\vec{r}_i(t) - \vec{r} - \vec{r}_o) \sum_j \delta(\vec{r}_j(0) - \vec{r}_o) \right\rangle \\ &= \frac{1}{N} \int d\vec{r}_o \langle \rho(\vec{r} + \vec{r}_o, t) \rho(\vec{r}_o, 0) \rangle \\ &= \frac{V}{N} \langle \rho(\vec{r}, t) \rho(0, 0) \rangle \end{aligned}$$

where $\frac{V}{N} = \rho_o^{-1}$. The Van Hove function describes the fluctuation of densities at different times and positions.

It can be difficult to keep track of the many functions used to describe inelastic scattering. The following table summarizes these functions and their different spatial and temporal variables.

Name	Symbol	Spatial Dimension	Temporal Dimension
Dynamic Structure Factor	$S(\vec{k}, \omega)$	Fourier, \vec{k}	Fourier, ω
Intermediate Scattering Function	$F(\vec{k}, t)$	Fourier, \vec{k}	Real, t
Van Hove Function	$G(\vec{r}, t)$	Real, \vec{r}	Real, t

4) If we are only interested in the spatial structure, we can perform a sum over the temporal dimension:

$$S(\vec{k}) = \frac{1}{2\pi} \int S(\vec{k}, \omega) d\omega = F(\vec{k}, 0)$$

This gives the spatial structure.

5) The density can again be expressed as the sum of a constant background ρ_o and fluctuations $\delta\rho$:

$$\rho = \rho_o + \delta\rho$$

Then the dynamic structure factor can be expressed as

$$S(\vec{k}, \omega) = (2\pi)^4 \delta(\vec{k}) \delta(\omega) \rho_o + \int e^{i\omega t} \frac{1}{N} \langle \delta\rho_{\vec{k}}(t) \delta\rho_{-\vec{k}}(0) \rangle dt$$

In the first term, $\vec{k} = 0$ and $\omega = 0$. This is the forward, elastic, not scattered wave for an ideal gas. The second term gives the spectrum of density fluctuations in the fluid.

3.2 Navier-Stokes Hydrodynamic Equations

3.2.1 Basic Equations

Conservation of Mass Consider a fixed volume in space, such as that pictured in Figure 3.6

The total number of particles in the region at any point in time can be found by taking the sum over the density at all points:

$$N = \int_V \rho(\vec{r}) d\vec{r}$$

The change in N over time depends upon the flux, which can be found by integration over a surface or a volume

$$\frac{dN}{dt} = J_{in} - J_{out} = - \oint_{\partial V} \vec{J} \cdot d\vec{S} = - \int \vec{\nabla} \cdot \vec{J} dV$$

We can rewrite the change in the number of particles in terms of density:

$$\frac{dN}{dt} = \int \frac{d\rho}{dt} d\vec{r} = - \int \vec{\nabla} \cdot \vec{J} dV$$

Remove the spacial integration and rearrange

$$\frac{d\rho}{dt} + \vec{\nabla} \cdot \vec{J} = 0$$

To express the equation in terms of density and velocity, we rewrite the flux as $\vec{J} = \rho\vec{v}$, so that

$$\nabla \cdot \vec{J} = \vec{\nabla} \cdot (\rho\vec{v})$$

Then the conservation of mass is given by:

$$\frac{d\rho}{dt} + \vec{\nabla} \cdot (\rho\vec{v}) = 0$$

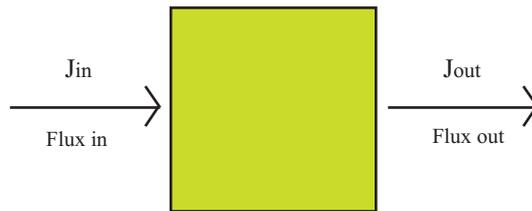


Figure 3.6: The flow of material into and out of a fixed region of space

Continuity Equations In general, for any dynamic quantity A , we can define a density ρ and write down a continuity equation.

This equation will be determined by the interaction between currents \vec{J} and sources σ .

$$\frac{\partial \rho A}{\partial t} + \vec{\nabla} \cdot \vec{J} = \sigma$$

The total current \vec{J} can be modelled as the sum of a conservative term $\vec{J}_V = \rho A \vec{v}$ and a dissipative term \vec{J}_D .

$$\vec{J} = \vec{J}_V + \vec{J}_D$$

The source σ can be written as the sum of external sources σ_{ext} and production sources σ_D

$$\sigma = \sigma_{ext} + \sigma_D$$

Therefore, the continuity equation for A can be written more explicitly as

$$\frac{\partial \rho A}{\partial t} + \vec{\nabla} \cdot (\rho A \vec{v}) + \vec{\nabla} \cdot \vec{J}_D = \sigma_{ext} + \sigma_D$$

In the physical world there are five conserved quantities: the density, the momentum (in three directions), and the energy (or entropy).

$$A = \{1, m\vec{v}, S\}$$

Therefore, we will find five continuity equations. We have already found the continuity equation for density, and in the next two sections we will find the equations for momentum and entropy.

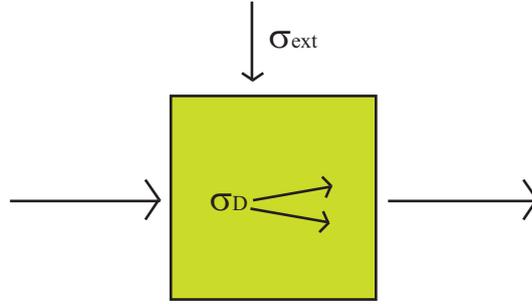


Figure 3.7: The flow and forces for a dynamic quantity

Momentum Equation (Navier-Stokes equations) To find the continuity equation for momentum, substitute $A = m\vec{v}$ into the general continuity equation.

$$\frac{\partial \rho m \vec{v}}{\partial t} + \vec{\nabla} \cdot (\rho m \vec{v} : \vec{v}) + \vec{\nabla} \cdot \vec{J}_D = \vec{\sigma}_{ext} + \vec{\sigma}_D$$

We assume that the production force is zero. The external force is pressure, which acts to create a net momentum or acceleration.

$$\vec{\sigma}_{ext} = \rho \vec{F} - \vec{\nabla} P$$

The terms representing conservative and dissipative current are both tensors. This is because momentum is a vector, and so the current, which represents the change in momentum, must be a tensor. The conservative current is given by

$$\vec{J}_V = (\rho m \vec{v} : \vec{v})$$

The dissipative current is the stress tensor $\vec{J}_D = -\vec{\Pi}$. The continuity equation for momentum can then be written as

$$m \frac{\partial \rho \vec{v}}{\partial t} + \vec{\nabla} \cdot (\rho m \vec{v} : \vec{v}) + \vec{\nabla} P = \rho \vec{F} + \vec{\nabla} \cdot \vec{\Pi}$$

Let's take a closer look at the stress tensor. For an isotropic medium, the stress tensor can be expressed as

$$\Pi_{i,j} = \eta_B (\vec{\nabla} \cdot \vec{v}) \delta_{i,j} + \eta (\partial_i v_j + \partial_j v_i - \frac{2}{3} (\vec{\nabla} \cdot \vec{v}) \delta_{i,j})$$

where η_B is the bulk viscosity. It gives the expected change in volume resulting from an applied stress. Likewise, η is the shear viscosity. This gives the expected amount of shearing, or change in shape, resulting from an applied stress. The final term $\partial_i v_j + \partial_j v_i - \frac{2}{3} \nabla \cdot \vec{v} \delta_{i,j}$ is a traceless symmetric component which changes the shape, but not the volume, of the medium.

We can express the change in the stress tensor as

$$(\vec{\nabla} \cdot \vec{\Pi})_i = \sum_j \nabla_j \Pi_{j,i} = (\frac{1}{3} \eta + \eta_B) \nabla_i (\vec{\nabla} \cdot \vec{v}) + \eta \nabla^2 v_i$$

With this, we can rewrite the momentum continuity equation as

$$m \frac{\partial \rho \vec{v}}{\partial t} + \vec{\nabla} \cdot (\rho m \vec{v} : \vec{v}) + \vec{\nabla} P = (\frac{1}{3} \eta + \eta_B) \vec{\nabla} (\vec{\nabla} \cdot \vec{v}) + \eta \nabla^2 \vec{v}$$

This is also called the Navier-Stokes equation.

Entropy Equation (heat-diffusion) To find the continuity equation for entropy, substitute $A = s$ in to the general continuity equation. In this case, we are thinking of the entropy for each particle and not the entire system, so a lowercase s is used.

$$\frac{\partial \rho s}{\partial t} + \vec{\nabla} \cdot (\rho s \vec{v}) + \vec{\nabla} \cdot \vec{J}_D = \sigma_{ext} + \sigma_D$$

We can simplify this expression by assuming that there are no forces that create or destroy entropy, so $\sigma_{ext} + \sigma_D = 0$. We also know that entropy flows from high temperatures to low temperatures, so

$$\vec{J}_D \propto -\vec{\nabla} \cdot \vec{T}$$

Write this explicitly using the constant λ

$$\vec{J}_D = -\frac{\lambda \vec{\nabla} T}{T}$$

Then, substitute this to get the continuity equation

$$\frac{\partial \rho s}{\partial t} + \vec{\nabla} \cdot (\rho s \vec{v}) - \lambda \vec{\nabla} \cdot \left(\frac{\vec{\nabla} T}{T} \right) = 0$$

We now have expressions for the 5 continuity equations for number of particles, momentum, and energy.

$$\frac{d\rho}{dt} + \vec{\nabla} \cdot (\rho \vec{v}) = 0 \quad (3.1)$$

$$m \frac{\partial \rho \vec{v}}{\partial t} + \vec{\nabla} \cdot (\rho m \vec{v} : \vec{v}) + \vec{\nabla} P = \vec{\nabla} \cdot \vec{\Pi} \quad (3.2)$$

$$\frac{\partial \rho s}{\partial t} + \vec{\nabla} \cdot (\rho s \vec{v}) - \lambda \vec{\nabla} \cdot \left(\frac{\vec{\nabla} T}{T} \right) = 0 \quad (3.3)$$

The solution to this set of equations gives $\rho(k, t)$. Though it is impossible to solve analytically, approximate solutions can be obtained by linearizing the equations.

3.2.2 Linearized Hydrodynamic Equations

The hydrodynamic equations are impossible to solve analytically. However, it is possible to obtain approximate solutions by linearizing the equations. Define the operator

$$\mathcal{L}(A) = \frac{\partial A}{\partial t}$$

For a time-independent quantity A_S ,

$$\mathcal{L}(A_S) = \frac{\partial A_S}{\partial t} = 0$$

We can construct any quantity A as the sum of a time-independent, “stable” part A_S and a fluctuating part δA

$$A = A_S + \delta A$$

Then we can write $\mathcal{L}(A)$ as an expansion. If we truncate the expansion at the first order, linear term, we find that

$$\mathcal{L}(A) = \mathcal{L}(A_S + \delta A) = \mathcal{L}(A_S) + \mathcal{L}(\delta A) = \frac{\partial \delta A}{\partial t}$$

For a homogeneous solution, ρ is a constant. There is no collective kinetic motion, only small Boltzmann motions which average to zero. Therefore, $\vec{v}_o = 0$. Entropy is also a constant. Therefore, we have three constants:

$$\rho_o, \vec{v}_o = 0, S_o$$

Since the density, velocity, and entropy are constants for a homogeneous solution, we can construct these quantities for a non-homogeneous solution by expanding around them:

$$\rho = \rho_o + \delta\rho$$

$$S = S_o + \delta S$$

$$\vec{v}$$

We can also expand around a constant temperature and pressure:

$$T = T_o + \delta T$$

$$P = P_o + \delta P$$

Start by substituting the density expansion into the density continuity equation

$$\frac{d}{dt}(\rho_o + \delta\rho) + \vec{\nabla} \cdot [(\rho_o + \delta\rho)\vec{v}] = 0$$

$$\frac{d\delta\rho}{dt} + \vec{\nabla} \cdot (\rho_o\vec{v}) = 0$$

This is the linearized number density continuity equation. To reach the final expression, we have used that $\frac{d\rho_o}{dt} = 0$. We have also ignored the term $\vec{\nabla} \cdot (\delta\rho\vec{v})$ because it is of quadratic order and we can assume that it is negligible.

In order to linearize the continuity equation for entropy, begin by expanding the original expression.

$$\rho \frac{\partial \delta s}{\partial t} + s_o \frac{\partial \rho}{\partial t} + s_o \vec{\nabla} \cdot (\rho \vec{v}) + \rho \vec{\nabla} \cdot (\delta s \vec{v}) - \lambda \vec{\nabla} \cdot \left(\frac{\vec{\nabla} T}{T} \right) = 0$$

The second and third term can be combined and will go to zero by conservation of mass. The fourth term is negligible. Then by substituting in the expansions and keeping only the linear terms, the expression simplifies to:

$$\rho_o \frac{\partial \delta s}{\partial t} - \frac{\lambda}{T_o} \nabla^2 \delta T = 0$$

Similarly we can linearize the momentum continuity equation, the solution is

$$m \rho_o \frac{\partial \vec{v}}{\partial t} + \vec{\nabla} \delta P = \left(\frac{1}{3} \eta + \eta_B \right) (\vec{\nabla} : \vec{\nabla}) \cdot \vec{v} + \eta \nabla^2 \vec{v}$$

In summary, the linearized hydrodynamic equations are given by

$$\frac{d\delta\rho}{dt} + \rho_o \vec{\nabla} \cdot \vec{v} = 0 \quad (3.4)$$

$$m \rho_o \frac{\partial \vec{v}}{\partial t} + \nabla \delta P = \left(\frac{1}{3} \eta + \eta_B \right) (\vec{\nabla} : \vec{\nabla}) \cdot \vec{v} + \eta \nabla^2 \vec{v} \quad (3.5)$$

$$\rho_o \frac{\partial \delta s}{\partial t} - \frac{\lambda}{T_o} \nabla^2 \delta T = 0 \quad (3.6)$$

3.2.3 Transverse Hydrodynamic Modes

In order to solve the eigenvalue equation, we need to decompose the velocity into its transverse and longitudinal components. Begin by rewriting the velocity in terms of its Fourier components

$$\vec{v}(r, t) = \frac{1}{(2\pi)^3} \int \vec{v}(k, t) e^{i\vec{k} \cdot \vec{r}} d\vec{k}$$

Through substitution, the momentum continuity equation becomes

$$m \rho_o \frac{\partial \vec{v}_k}{\partial t} + i\vec{k} P_k = \left(\frac{1}{3} \eta + \eta_B \right) (i\vec{k})(i\vec{k} \cdot \vec{v}_k) + \eta (i\vec{k})^2 \vec{v}_k$$

Now, decompose $\vec{v}(k, t)$ into its 3 components

$$v(k, t) = v_{xk}(t) \hat{x} + v_{yk}(t) \hat{y} + v_{zk}(t) \hat{z}$$

A longitudinal mode is one in which the velocity vector points parallel to the \vec{k} vector, and a transverse mode is one in which the velocity vector points perpendicular to the \vec{k} vector. We can decide arbitrarily that the \vec{k} vector points in the z direction. Therefore, $v_{zk}(t)$ is the longitudinal current and $v_{xk}(t)$ and $v_{yk}(t)$ are the transverse currents.

This decomposition is especially helpful in the transverse \hat{x} and \hat{y} directions because most of the terms in the continuity equation go to zero. The continuity equation for the transverse currents becomes (in Fourier space)

$$m \rho_o \frac{\partial \vec{v}_T}{\partial t} = -\eta k^2 \vec{v}_T$$

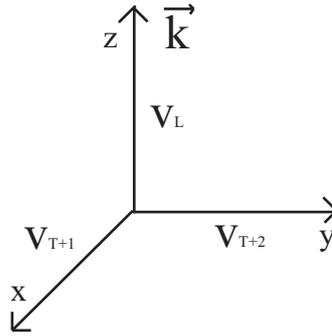


Figure 3.8: Velocity components in k-space

which is easy to solve, yielding the solution

$$v_{Tk}(t) = v_{Tk}(0)e^{-\gamma_T k^2 t}$$

where $\gamma_T = \frac{\eta}{m\rho_o}$ is the kinematic shear viscosity.

This result looks like a diffusion equation

$$\frac{\partial P_k}{\partial t} = -Dk^2 P_k$$

Therefore, γ_T can be interpreted as diffusion constant for velocity.

3.3 Longitudinal Hydrodynamic modes

3.3.1 Solving the Continuity Equations

It is much more difficult to solve for the longitudinal velocity component of the current because not as many terms go to zero.

Fourier Transform of the density Begin by writing the density in terms of its Fourier components

$$\vec{\rho}(r, t) = \frac{1}{(2\pi)^3} \int \vec{\rho}(k, t) e^{i\vec{k}\vec{r}} d\vec{k}$$

Using this expression, the linearized hydrodynamic equations can be written in terms of the Fourier components of the density. Note that hereafter, for brevity, we will drop the δ signs of the transformed variables. Readers should keep in mind that these k -space variables always refer to the Fourier transform of the fluctuations away from equilibrium.

$$\frac{d\rho_k}{dt} + ik\rho_o v_k = 0 \quad (3.7)$$

$$m\rho_o \frac{\partial v_k}{\partial t} + ikP_k + \left(\frac{4}{3}\eta + \eta_B\right)k^2 v_k = 0 \quad (3.8)$$

$$\rho_o \frac{\partial s_k}{\partial t} + \frac{\lambda}{T_o} k^2 T_k = 0 \quad (3.9)$$

Also we denote the velocity as v_k for simplicity. However, it is important to remember that this only refers to the longitudinal velocity, $v_{z,k}$.

Choosing independent variables As written, the three continuity equations have five variables: ρ_k , v_k , T_k , P_k , and S_k . Luckily, these variables are not all independent. Let ρ_k , v_k , and T_k be the three independent variables. We can use thermodynamic relations to rewrite P_k and S_k in terms of these variables.

The Helmholtz free energy is a function of temperature and density, $F(T, \rho)$. We can write this in differential form:

$$dF = -SdT + Pd\rho$$

This is a total differential of the form:

$$dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy$$

Using this, we can write the entropy S and the pressure P in differential form

$$S = -\left(\frac{\partial F}{\partial T}\right)_\rho$$

$$P = \left(\frac{\partial F}{\partial \rho}\right)_T$$

Define the variable α as

$$\alpha = \left(\frac{\partial P}{\partial T}\right)_\rho = \frac{\partial}{\partial T} \left(\frac{\partial F}{\partial \rho}\right)_T = \frac{\partial}{\partial \rho} \left(\frac{\partial F}{\partial T}\right)_\rho = -\left(\frac{\partial S}{\partial \rho}\right)_T$$

Here we have used the property that for continuous functions, the mixed partial second derivatives are equal. This gives one of the Maxwell relations.

We will also use a couple of well known relations, the isothermal speed of sound:

$$c_T = \sqrt{\frac{1}{m} \left(\frac{\partial P}{\partial \rho}\right)_T}$$

and the specific heat:

$$C_V = T \left(\frac{\partial S}{\partial T}\right)_\rho$$

With these relations in hand, we can rewrite the pressure P and the entropy S in terms of temperature T and density ρ :

$$dP = \left(\frac{\partial P}{\partial \rho}\right)_T d\rho + \left(\frac{\partial P}{\partial T}\right)_\rho dT = mC_T^2 d\rho + \alpha dT$$

$$T_o dS = T_o \left(\frac{\partial S}{\partial \rho}\right)_T d\rho + T_o \left(\frac{\partial S}{\partial T}\right)_\rho dT = -T_o \alpha d\rho + C_V dT$$

The Condensed Equations With these substitutions, we can rewrite the continuity equations in terms of the independent variables ρ_k , v_k , and T_k .

$$\frac{d\rho_k}{dt} + ik\rho_0 v_k = 0 \quad (3.10)$$

$$v_k + \frac{ik}{m\rho_0} [C_T^2 m\rho_k + \alpha T_k] + bk^2 v_k = 0 \quad (3.11)$$

$$\dot{T}_k + ik \left(\frac{T_0 \alpha \rho_0}{C_V} \right) v_k + ak^2 T_k = 0 \quad (3.12)$$

where we have defined the constants a and b

$$a = \frac{\lambda}{\rho_0 C_V}$$

$$b = \left(\eta_B + \frac{4}{3}\eta \right) \frac{1}{m\rho_0}$$

and $\dot{\rho}_k = -ik\rho_0 v_k$ is used to simplify the last equation.

The Laplace Transform To further simplify the equations, use the Laplace transform of each variable:

$$\hat{\rho}_k(z) = \int_0^\infty e^{-zt} \rho_k(t) dt \quad \text{and} \quad \rho_k(t) = \frac{1}{2\pi i} \int_{\delta-i\infty}^{\delta+i\infty} e^{zt} \hat{\rho}_k(z) dz$$

$$\hat{v}_k(z) = \int_0^\infty e^{-zt} v_k(t) dt \quad \text{and} \quad v_k(t) = \frac{1}{2\pi i} \int_{\delta-i\infty}^{\delta+i\infty} e^{zt} \hat{v}_k(z) dz$$

$$\hat{T}_k(z) = \int_0^\infty e^{-zt} T_k(t) dt \quad \text{and} \quad T_k(t) = \frac{1}{2\pi i} \int_{\delta-i\infty}^{\delta+i\infty} e^{zt} \hat{T}_k(z) dz$$

Using this transform, the continuity equations can be rewritten (in matrix form):

$$\begin{bmatrix} z & ik\rho_0 & 0 \\ ik\frac{C_T^2}{\rho_0} & z + bk^2 & \frac{ik}{m\rho_0}\alpha \\ 0 & \frac{ik}{C_V}\alpha T_0\rho_0 & z + ak^2 \end{bmatrix} = \begin{bmatrix} \hat{\rho}_k \\ \hat{v}_k \\ \hat{T}_k \end{bmatrix} = \begin{bmatrix} \rho_k(0) \\ v_k(0) \\ T_k(0) \end{bmatrix}.$$

3.3.2 Thermodynamic Identities

1) Isothermal and Adiabatic Speed of Sound The adiabatic c_s and isothermal c_T speeds of sound are given by:

$$c_s^2 = \frac{1}{m} \left(\frac{\partial P}{\partial \rho} \right)_S$$

$$c_T^2 = \frac{1}{m} \left(\frac{\partial P}{\partial \rho} \right)_T$$

We can rewrite these quantities using:

$$\left(\frac{\partial P}{\partial \rho} \right)_T = \frac{\left(\frac{\partial P}{\partial S} \right)_T}{\left(\frac{\partial \rho}{\partial S} \right)_T} = \frac{\left(\frac{\partial P}{\partial T} \right)_S \left(\frac{\partial T}{\partial S} \right)_P}{\left(\frac{\partial \rho}{\partial T} \right)_S \left(\frac{\partial T}{\partial S} \right)_\rho} = \frac{C_V}{C_P} \left(\frac{\partial P}{\partial \rho} \right)_S$$

Here, we have used the constant volume C_V and constant pressure C_P heat capacities:

$$C_V = T \left(\frac{\partial S}{\partial T} \right)_\rho$$

$$C_P = T \left(\frac{\partial S}{\partial T} \right)_P$$

and the identity for differentials:

$$\left(\frac{\partial x}{\partial y} \right)_z = \left(\frac{\partial x}{\partial z} \right)_y \left(\frac{\partial z}{\partial y} \right)_x$$

Now, we can show that the ratio is equal to:

$$\frac{c_T^2}{c_S^2} = \frac{\frac{1}{m} \frac{C_V}{C_P} \left(\frac{\partial P}{\partial \rho} \right)_S}{\frac{1}{m} \left(\frac{\partial P}{\partial \rho} \right)_S} = \frac{C_V}{C_P} = \frac{1}{\gamma}$$

2) Thermodynamic identities can be used to rewrite the quantity

$$mC_T^2 (C_P - C_V)$$

Start by writing the expression explicitly in terms of thermodynamic variables:

$$mC_T^2 (C_P - C_V) = T \left(\frac{\partial P}{\partial \rho} \right)_T \left[\left(\frac{\partial S}{\partial T} \right)_P - \left(\frac{\partial S}{\partial T} \right)_\rho \right]$$

In order to simplify this expression, we will use another identity for differentials:

$$\left(\frac{\partial x}{\partial y} \right)_z = \left(\frac{\partial x}{\partial y} \right)_w + \left(\frac{\partial x}{\partial w} \right)_y \left(\frac{\partial w}{\partial y} \right)_z$$

Using this identity, combined with the identity introduced in the previous section, we can rewrite the first term in the expression:

$$\left(\frac{\partial S}{\partial T} \right)_P = \left(\frac{\partial S}{\partial T} \right)_\rho + \left(\frac{\partial S}{\partial \rho} \right)_T \left(\frac{\partial \rho}{\partial T} \right)_P = \left(\frac{\partial S}{\partial T} \right)_\rho - \left(\frac{\partial S}{\partial \rho} \right)_T \left(\frac{\partial \rho}{\partial P} \right)_T \left(\frac{\partial P}{\partial T} \right)_\rho$$

Now, plug this into the expression above and cancel terms, to obtain the new identity:

$$mC_T^2 (C_P - C_V) = -T_o \left(\frac{\partial S}{\partial \rho} \right)_T \left(\frac{\partial P}{\partial T} \right)_\rho$$

3) Adiabatic and Isothermal Compressibility The adiabatic χ_S and isothermal χ_T compressibilities are given by:

$$\chi_S = \frac{1}{\rho} \left(\frac{\partial \rho}{\partial P} \right)_S$$

$$\chi_T = \frac{1}{\rho} \left(\frac{\partial \rho}{\partial P} \right)_T$$

Therefore,

$$\gamma = \frac{C_P}{C_V} = \frac{\chi_T}{\chi_S} = \frac{c_S^2}{c_T^2}$$

3.3.3 Eigensolution

1) Now, we can solve the set of continuity equations for the density. The density can be found from:

$$\hat{\rho}(z) = \frac{Det'M(1|1)}{DetM} = (M^{-1})_{11} \rho(0)$$

Note that the Laplace transform of the intermediate scattering function is:

$$\hat{F}(\vec{k}, z) = (M^{-1})_{11} \langle |\rho_k|^2 \rangle$$

To solve for $\hat{\rho}(z)$, find $Det'M(1|1)$ and $DetM$.

$$\begin{aligned} Det'M(1|1) &= (z + ak^2)(z + bk^2) + \frac{k^2 T_o \alpha^2}{m C_V} \\ &= (z + ak^2)(z + bk^2) + k^2 C_T^2 (\gamma - 1) \end{aligned}$$

and

$$DetM = z(z + ak^2)(z + bk^2) + zk^2 c_S^2 + zk^4 c_T^2$$

where we have used some of the thermodynamic identities defined in the previous section.

2) The eigenfrequencies can be obtained from $DetM(z) = 0$. The eigenvalues can be solved using perturbation $z = s_o + s_1 k + s_2 k^2 + \dots$. The solutions are

$$z_{\pm} = -a \frac{c_T^2}{c_S^2} k^2 = -\frac{a}{T} k^2$$

$$z_{\pm} = \pm i c_S k - \Gamma k^2$$

where

$$\Gamma = \frac{1}{2} \left[(a + b) - \frac{a}{\gamma} \right]$$

3) To first order in k , we have

$$(M^{-1})_{11} = \frac{Det'M(1|1)}{DetM} \approx \frac{z^2 + \left(1 - \frac{1}{\gamma}\right) c_S^2 k^2}{z^3 + zk^2 c_S^2} = \left(1 - \frac{1}{\gamma}\right) \frac{1}{z} + \frac{1}{\gamma} \frac{1}{z^2 + k^2 c_S^2}$$

Then, to second order in k , we have

$$\hat{\rho}_k(t) = \hat{\rho}_k(0) \left[\left(1 - \frac{1}{\gamma}\right) e^{-\frac{a}{\gamma} k^2 t} + \frac{1}{\gamma} \cos(c_S k t) e^{-\Gamma k^2 t} \right]$$

The first term gives the contributions from thermal fluctuations, while the second term gives the solution for a damped acoustic wave. Notice that the integrated intensity of the first term is $\left(1 - \frac{1}{\gamma}\right)$ and the integrated intensity of the second term is $\frac{1}{\gamma}$.

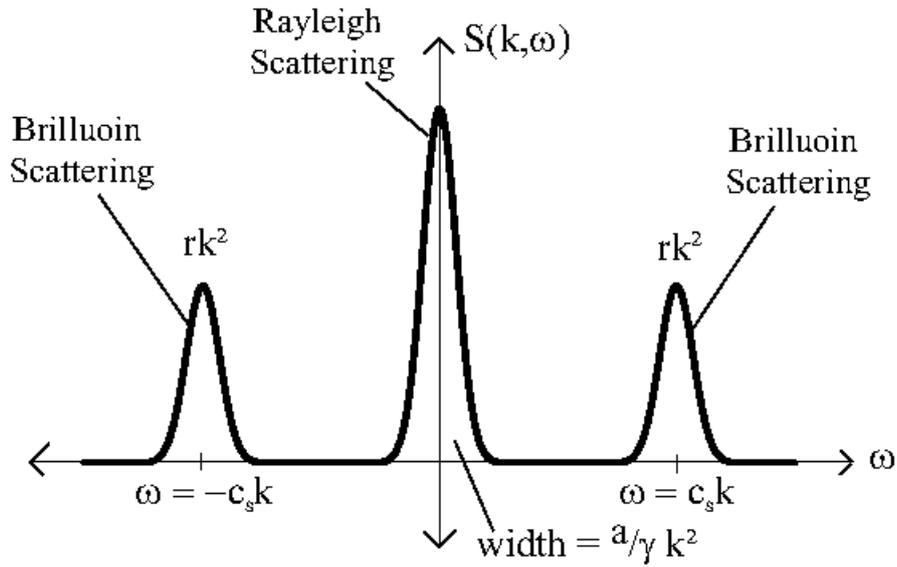


Figure 3.9: Light Scattering Spectrum

Light Scattering

The Landau-Placzek ratio gives the ratio between the intensity of thermal and acoustic scattering

$$\frac{I_{thermal}}{I_{acoustic}} = \frac{\langle (\delta\rho)^2 \rangle_{thermal}}{\langle (\delta\rho)^2 \rangle_{mech}} = \frac{\left(\frac{\partial\rho}{\partial S}\right)_P^2 \langle \Delta S^2 \rangle}{\left(\frac{\partial\rho}{\partial P}\right)_S^2 \langle \Delta P^2 \rangle} = \frac{C_P - C_V}{C_V} = \gamma - 1$$

Note that the dynamic structure factor is twice the real part of the Laplace transform of the intermediate scattering function (Figure 3.9):

$$S(\vec{k}, \omega) = \int_{-\infty}^{\infty} F(\vec{k}, t) e^{-i\omega t} dt = 2\text{Re}\hat{F}(z = -i\omega)$$

The initial value of this function is

$$F(k, 0) = \frac{1}{N} \langle |\delta\rho_k|^2 \rangle = \rho_o h + 1 = \frac{\rho_o \chi T}{\beta}$$

Acoustic Scattering

By ignoring the coupling to entropy flow, we have

$$dP = \left(\frac{\partial P}{\partial \rho}\right)_S d\rho$$

so that

$$\frac{d\delta\rho_k}{dt} + ik\rho_o v_k = 0 \quad (3.13)$$

$$v_k + ic_S^2 k \rho_k + bk^2 v_k = 0 \quad (3.14)$$

For an ideal gas, $b = 0$, and so we get a propagating sound wave

$$z = \pm ic_s k$$

In a viscous liquid, $b \neq 0$, and so we get a propagating acoustic wave with a damping term

$$z = \pm ic_s k - \frac{1}{2} b k^2$$

3.4 Transport Coefficients

Before we jump into the next section on transport equations, let's take a moment to briefly summarize what we have seen in this chapter and where we are going:

- 1) The response of a liquid to an external probe $\frac{d^2\sigma}{d\omega d\Omega}$ is given by spontaneous time-dependent fluctuations, described in $G(\vec{r}, t)$ or $S(\vec{k}, \omega)$.
- 2) Hydrodynamic equations describe the decay of spontaneous fluctuations.
- 3) Hydrodynamic modes can be used to find transport coefficients.

3.4.1 Diffusion Constant

We will begin our exploration of transport coefficients with the diffusion constant. We will use the concepts developed in this chapter to find three different expressions for the diffusion constant. These expressions are called Einstein's relation, the Green-Kubo relation, and the Scattering function in the hydrodynamic limit.

- 1) **Einstein's Relation** Define a single-particle correlation function

$$G_S(\vec{r}, t) = \langle \delta(\vec{r}(t) - \vec{r}(0) - \vec{r}) \rangle$$

Taking the Fourier transform into \vec{k} space gives the self-intermediate scattering function

$$F_S(\vec{k}, t) = \left\langle \exp[-i\vec{k}(\vec{r}(t) - \vec{r}(0))] \right\rangle = \langle \rho_{s,k}(t) \rho_{s,k}(0) \rangle \quad (3.15)$$

All transport coefficients are defined for length and time scales when $k \rightarrow 0$ and $\omega \rightarrow 0$. In real space, they apply to relatively long length and time scales. Therefore, hydrodynamics theory applies. Recall that hydrodynamics theory applies on the coarse-grained scale much larger and longer than characteristic molecular interactions.

Apply Fick's law to the problem:

$$\dot{\rho} = D\nabla^2 \rho$$

Therefore

$$\dot{\rho}_k = -Dk^2 \rho_k$$

and

$$F_S(\vec{k}, t) = e^{-k^2 D t} \quad (3.16)$$

We now have two equations for $F_S(\vec{k}, t)$. Expand both of them to k^2 and set them equal

$$1 - k^2 Dt + \dots = 1 - k^2 \frac{1}{2} (z(t) - z(0))^2 + \dots$$

Then solve for D

$$D = \frac{1}{2t} \langle |z(t) - z(0)|^2 \rangle |_{t=\infty}$$

This is *Einstein's Relation*.

2) The Green-Kubo Relation To find the Green-Kubo relation, use time-invariance to rewrite the thermal average in Einstein's relation

$$\begin{aligned} \langle |z(t) - z(0)|^2 \rangle &= \left\langle \int_0^t \int_0^t v(t_1)v(t_2)dt_1dt_2 \right\rangle \\ &= 2 \int_0^t (t - \tau)C(\tau)d\tau \end{aligned}$$

where

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

Therefore

$$D = \lim_{t \rightarrow \infty} \frac{1}{2t} \langle |z(t) - z(0)|^2 \rangle = \int_0^\infty C(\tau)d\tau$$

This is called the *Green-Kubo Relation*.

In general, for any variable $A(t)$ we have

$$\int_0^\infty \langle \dot{A}(t)\dot{A}(0) \rangle dt = \lim_{t \rightarrow \infty} \frac{1}{2t} \langle |A(t) - A(0)|^2 \rangle$$

3) Relation to Scattering We can also relate the diffusion constant to scattering, such as incoherent neutron scattering. The dynamic structure factor is related to the diffusion constant through

$$S_s(k, \omega) = \int_{-\infty}^\infty e^{i\omega t} F_s(k, t) dt = \frac{2D^2 k^2}{\omega^2 + (Dk^2)^2}$$

Then solve this equation for D

$$D = \frac{1}{2} \lim_{\omega \rightarrow 0} \lim_{k \rightarrow 0} \frac{\omega^2}{k^2} S_s(k, \omega)$$

Therefore

$$\begin{aligned} D &= \frac{1}{2} \lim_{\omega \rightarrow 0} \lim_{k \rightarrow 0} \frac{1}{k^2} \int \ddot{F}_s(k, t) e^{i\omega t} dt = \lim_{\omega \rightarrow 0} \int_0^\infty C(t) e^{i\omega t} dt \\ &= \int_0^\infty \langle v(t)v(0) \rangle dt \end{aligned}$$

This is the final expression for the diffusion constant.

4) In this section we showed how there are three different methods for finding the diffusion constant. These are *Einstein's Relation*, the *Green-Kubo Relation*, and the *Scattering Function*, as $\omega \rightarrow 0$ and $k \rightarrow 0$. This process can be generalized for different types of transport coefficients. In the next two sections, we will evaluate the viscosity coefficients and the thermal transport coefficients using these three methods.

3.4.2 Viscosity Coefficients

In this section, we will evaluate the viscosity coefficients η and η_B using Einstein's relation, the Green-Kubo relation, and the scattering function in the hydrodynamic limit ($\omega \rightarrow 0$ and $k \rightarrow 0$).

1) The Transverse Current Define the transverse current as the sum of the velocity components in the x-direction

$$J_x = \sum_i v_{ix}(t) \delta(\vec{r} - \vec{r}_i(t))$$

The Fourier transform is

$$J_k = \sum_i v_{ix}(t) \exp(-i\vec{k}\vec{r}_i(t))$$

Therefore, the transverse current correlation function is

$$\begin{aligned} C_t(k, t) &= \frac{1}{N} \langle J_k(t) J_{-k}(0) \rangle \\ &= \frac{1}{N} \sum_{ij} \left\langle v_i(t) v_j(0) \exp[-i\vec{k}(\vec{r}_i(t) - \vec{r}_j(0))] \right\rangle \end{aligned}$$

On the other hand, the Navier-Stokes equation predicts that

$$J_x - \nu_t \nabla^2 J_x = 0$$

where $\nu_t = \frac{\eta}{m\rho_0}$ is the kinematic shear viscosity. The Fourier transform of this relation is

$$J_k + \nu_t k^2 J_k = 0$$

which yields the solution

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

Using this expression, the transverse current correlation function is

$$C_t(k, t) = \frac{1}{N} \langle J_k(t) J_{-k}(0) \rangle e^{-\nu k^2 t} = C_t(k, 0) e^{-\nu k^2 t}$$

Now, we have two different expressions for the transverse current correlation function.

2) To complete the expression for the transverse current correlation function, we must find $C_t(k, 0)$. Using the first expression for $C_t(k, t)$, we find that

$$C_t(k, 0) = \frac{1}{N} \left\langle \sum_i v_{ix}(0) \exp(-i\vec{k}\vec{r}_i(0)) \sum_j v_{jx}(0) \exp(-i\vec{k}\vec{r}_j(0)) \right\rangle$$

$$= \frac{1}{N} \sum_{ij} \left\langle v_0^2 \delta_{ij} \exp \left[-i\vec{k} \cdot (z_i - z_j) \right] \right\rangle$$

$$= v_o^2$$

where

$$\langle v_{ix} v_{jx} \rangle = \delta_{ij} \langle v_{ix} v_{ix} \rangle = \delta_{ij} \frac{1}{\beta m} = \delta_{ij} v_o^2$$

Note that $C_t(k, 0)$ is independent of k . Now, expand the two expressions for the transverse current to the order of k^2 . Set them equal and solve for $C_t(k, 0)$

$$C_t(k, t) = C_t(k, 0) (1 - \nu k^2 t) = \frac{1}{N} \sum_{ij} \left\langle v_i(t) v_j(0) \left[1 - \frac{k^2}{2} (z_i(t) - z_j(0))^2 \right] \right\rangle$$

Then we have

$$C(k, 0)\nu = \lim_{t \rightarrow \infty} \frac{1}{2tN} \sum_{ij} \left\langle v_i(t) v_j(0) [z_i(t) - z_j(0)]^2 \right\rangle$$

3) To simplify this equation, use the momentum conservation condition $\sum_i v_i(t) = \sum_i v_i(0)$. Then we can write that

$$\left\langle \sum_i v_i(t) z_i^2(t) \sum_j v_j(0) \right\rangle = \left\langle \sum_{ij} v_i(t) z_i^2(t) v_j(t) \right\rangle = \sum_i \langle v_i^2(t) z_i^2(t) \rangle$$

then the viscosity coefficient is given by

$$\eta = \lim_{t \rightarrow \infty} \frac{1}{\nu k T} \frac{1}{2t} \langle [A(t) - A(0)]^2 \rangle$$

where $A = \sum_i P_{ix} z_i$. This is Einstein's expression for the viscosity coefficient.

4) Define σ_{xz} as the time derivative of A

$$\dot{A} = \sigma_{xz} = \frac{d}{dt} \sum_i P_{ix} z_i$$

Then we can write the viscosity coefficient as

$$\eta = \frac{1}{V m^2 k_B T} \int_0^\infty \langle \sigma_{xz}(t) \sigma_{xz}(0) \rangle dt$$

5) Define the Fourier transform of $C_t(\vec{r}, t)$ as $C_t(\vec{k}, \omega)$

$$C_t(\vec{k}, t) = v_o^2 e^{-\gamma k^2 t} \Rightarrow C_t(\vec{k}, \omega) = v_o^2 \frac{2\nu_t k^2}{\omega^2 + \nu_t k^2}$$

Therefore, the viscosity coefficient can be written as

$$\eta = \frac{\rho_o m^2 \beta}{2} \lim_{\omega \rightarrow 0} \lim_{k \rightarrow 0} \frac{\omega^2}{k^2} C_t(\vec{k}, \omega)$$

6) In general, $\sigma_{\alpha\beta}$ denotes

$$\sigma_{\alpha\beta} = \frac{d}{dt} \sum_i P_{i\alpha} r_{i\beta}$$

From the virial theorem, the thermal average of $\sigma_{\alpha\beta}$ is

$$\langle \sigma_{\alpha\beta} \rangle = \delta_{\alpha\beta} PV$$

The longitudinal current is given by

$$J_k(t) = J_k(0)e^{-bk^2t}$$

where

$$b = \frac{1}{m\rho_0} \left(\eta_B + \frac{4}{3}\eta \right)$$

Therefore, by analogy

$$\eta_B + \frac{4}{3}\eta = \frac{1}{Vk_bT} \int_0^\infty \langle \delta\sigma_{zz}(t)\delta\sigma_{zz}(0) \rangle dt$$

where

$$\delta\sigma_{zz} = \sigma_{zz}(t) - PV$$

Evaluation of the Thermal Transport Coefficients

1) Summary of the Transport Coefficients Before we enter the topic of thermal transport, let's briefly review the transport coefficients we have defined in this chapter.

i) Diffusion Constant

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

ii) Viscosity Coefficients

$$\eta = \frac{1}{Vk_B T} \int_0^\infty \sigma_{xz}(t)\sigma_{xz}(0)dt$$

$$\eta_B + \frac{4}{3}\eta = \frac{1}{Vk_bT} \int_0^\infty [\sigma_{zz}(t) - PV][\sigma_{zz}(0) - PV] dt$$

where

$$\sigma_{\alpha\beta} = \frac{d}{dt} \sum_i P_{i\alpha} r_{i\beta}$$

iii)

$$\lambda = \frac{1}{Vk_bT} \int_0^\infty \langle \dot{A}(t)\dot{A}(0)dt \rangle$$

where

$$A = \frac{d}{dt} \sum_i z_i \left[\frac{p_i^2}{2m} + \frac{1}{2} \sum_{ij} u_{ij} - \langle E \rangle \right]$$

2) Mean Free Path Approximation The mean free path approximation can be used to approximate the value of the diffusion constant and the viscosity coefficients. The mean free path approximation states that the motion of molecules is described by collisions. The behavior of these collisions is governed by two main assumptions:

i) The collisions are *Markovian*. In other words, the velocity of a particle after a collision is random and is not correlated with the velocity before the collision.

ii) The distribution of collisions is a Poisson process e^{-t/τ_c} .

Using this approximation, the diffusion constant is

$$D = \int_0^\infty \langle v_z^2 \rangle e^{-t/\tau_c} dt = \langle v_z^2 \rangle \tau_c$$

and the viscosity coefficient is

$$\eta = \frac{1}{Vk_B T} \int_0^\infty \left\langle \left(\sum_i P_{xi} v_{zi} \right)^2 \right\rangle e^{-t/\tau_c} dt = \frac{N}{Vk_B T} \langle P_{xi}^2 v_z^2 \rangle \tau_c$$

3) Hard-Sphere gas For a hard sphere gas, the average collision time τ_c is given by

$$\tau_c = \frac{\tau}{\bar{v}} = \frac{1}{\sqrt{2}\pi\sigma^2\rho} \left[\frac{\pi m}{8k_B T} \right]^{\frac{1}{2}}$$

where σ is the radius of the particles. Then, substituting this expression for τ_c into D and η gives

$$D = \frac{1}{4\sigma^2\rho} \left[\frac{kT}{\pi m} \right]^{\frac{1}{2}}$$

$$\eta = \frac{1}{4\sigma^2} \left[\frac{mkT}{\pi} \right]^{\frac{1}{2}}$$

3.4.3 Thermal Diffusion (Conduction)

1) Define the energy

$$E_k = \sum_i \delta e_i(t) e^{-i\vec{k}\vec{r}_i(t)}$$

where $\delta e = e - \langle e \rangle$. The correlation function is

$$C(k, t) = \sum_{ij} \left\langle \delta e_i e^{-i\vec{k}\vec{r}_i(t)} \delta e_j e^{-i\vec{k}\vec{r}_j(0)} \right\rangle$$

The initial value of this correlation function is

$$C(k, 0) = \sum_{ij} \langle \delta e_i \delta e_j \rangle \left\langle \exp \left[-i\vec{k}\vec{r}_i - \vec{r}_j \right] \right\rangle = \sum_i \langle \delta e_i \delta e_i \rangle = \langle E(0)E(0) \rangle = NC_V k_B T^2$$

where we have used the fact that $\langle \delta e_i \delta e_i \rangle = \delta_{ij} \langle (\delta e)^2 \rangle$.

2) Now, expand the correlation function to the order of k^2 :

$$\begin{aligned} C(k, t) &= C(k, 0) - \frac{k^2}{2} \sum_{ij} \left\langle \delta e_i(t) \delta e_j(0) (z_i(t) - z_j(0))^2 \right\rangle + \dots \\ &= C(k, 0) - \frac{k^2}{2} \left\langle \left| \sum_i \delta e_i(t) z_i(t) - \sum_i \delta e_i(0) z_i(0) \right|^2 \right\rangle + \dots \end{aligned}$$

where we have used the conservation of energy to rewrite the expression. This allows us to write

$$A = \sum_i |e_i(t) - \langle e \rangle| z_i(t)$$

3) Conduction Equation The conduction equation states that

$$\frac{\partial \rho e}{\partial t} - \nabla \lambda (\nabla T) = 0$$

and therefore

$$\frac{\partial E}{\partial t} - \frac{\lambda}{C_V \rho} \nabla^2 E = 0$$

We can solve this equation for $E(t)$

$$E(t) = E(0) e^{-ak^2 t}$$

where $a = \frac{\lambda}{C_V \rho}$. Use this expression to write the correlation function

$$C(k, t) = \langle E^2(0) \rangle e^{-ak^2 t} = \langle E^2 \rangle [1 - ak^2 t + \dots]$$

By equating the k^2 terms, we find that

$$ak^2 N C_V k_B T^2 = \frac{k^2}{2t} \langle |A(t) - A(0)|^2 \rangle$$

Therefore,

$$\lambda = \frac{1}{V k_b T^2} \int_0^\infty \langle \dot{A}(t) \dot{A}(0) dt \rangle = \lim_{t \rightarrow \infty} \frac{1}{V k_b T^2} \frac{1}{2t} \langle |A(t) - A(0)|^2 \rangle$$

where

$$e_i = \frac{p_i^2}{2m} + \frac{1}{2} \sum_{i=j} U_{ij}$$

References

- [1] L.E. Reichl. *A Modern Course in Statistical Physics*. New York: Wiley-Interscience, 1998.
- [2] Jean Pierre Hansen and Ian R. McDonald. *Theory of Simple Liquids*. Burlington, MA: Elsevier Academic Press, 2006.
- [3] Donald A. McQuarrie. *Statistical Mechanics*. Sausalito: University Science Books, 2000.

MIT OpenCourseWare
<http://ocw.mit.edu>

5.72 Statistical Mechanics
Spring 2012

For information about citing these materials or our Terms of Use, visit: <http://ocw.mit.edu/terms>.