3.3: 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.

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**.

Einstein's Relation Define a single-particle correlation function

$$G_S(\vec{r}, t) = \langle \delta(\vec{r}(t) - \vec{r}(0) - \vec{r}) \rangle \tag{3.3.1}$$

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

$$F_S(\vec{k}, t) = \langle \exp[-i\vec{k}(\vec{r}(t) - \vec{r}(0))] \rangle = \langle \rho_{s,k}(t) \rho_{s,k}(0) \rangle \tag{3.3.2}$$

All transport coefficients are defined for length and time scales when $k \to 0$ and $\omega \to 0$. 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:

$$\dot{\rho} = D\nabla^2 \rho \tag{3.3.3}$$

Therefore

$$\dot{\rho}_k = -Dk^2 \rho_k \tag{3.3.4}$$

and

$$F_S(\vec{k}, t) = e^{-k^2 Dt} \tag{3.3.5}$$

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

$$1 - k^2 Dt + \ldots = 1 - k^2 \frac{1}{2}(z(t) - z(0))^2 + \ldots \tag{3.3.6}$$

Then solve for D

$$D = \frac{1}{2t} \left\langle |z(t) - z(0)|^2 \right\rangle \Big|_{t=\infty} \tag{3.3.7}$$

This is Einstein's Relation.

The Green-Kubo Relation

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

$$\begin{aligned} \left\langle |z(t) - z(0)|^2 \right\rangle &= \left\langle \int_0^t \int_0^t v(t_1) v(t_2)\, dt_1 dt_2 \right\rangle \\ &= 2\int_0^t (t-\tau) C(\tau) d\tau \end{aligned}$$

where

$$C(t)=\langle v_z(t)v_z(0)\rangle=\frac{1}{3}\langle v(t)v(0)\rangle \tag{3.3.8}$$

Therefore

$$D=\lim_{t\to\infty}\frac{1}{2t}\left\langle|z(t)-z(0)|^2\right\rangle=\int_0^\infty C(\tau)d\tau \tag{3.3.9}$$

This is called the **Green-Kubo Relation**.

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

$$\int_0^\infty\langle\dot{A}(t)\dot{A}(0)\rangle dt=\lim_{t\to\infty}\frac{1}{2t}\left\langle|A(t)-A(0)|^2\right\rangle \tag{3.3.10}$$

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

$$S_s(k,\omega)=\int_{-\infty}^\infty e^{i\omega t}F_s(k,t)dt=\frac{2D^2k^2}{\omega^2+(Dk^2)^2} \tag{3.3.11}$$

Then solve this equation for D

$$D=\frac{1}{2}\lim_{\omega\to 0}\lim_{k\to 0}\frac{\omega^2}{k^2}S_s(k,\omega) \tag{3.3.12}$$

Therefore

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

This is the final expression for the diffusion constant.

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 $\omega\to 0$ and $k\to 0$. 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.

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 $(\omega\to 0$ and $k\to 0)$.

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

$$J_x=\sum_i v_{ix}(t)\delta(\vec{r}-\vec{r}_i(t)) \tag{3.3.13}$$

The Fourier transform is

$$J_k=\sum_i v_{ix}(t)\exp\left(-i\vec{k}\vec{r}_i(t)\right) \tag{3.3.14}$$

Therefore, the transverse current correlation function is

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

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

$$J_x - \nu_t \nabla^2 J_x = 0 \tag{3.3.15}$$

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

$$J_k + \nu_t k^2 J_k = 0 \tag{3.3.16}$$

which yields the solution

$$J_k(t) = J_k(0)e^{-\nu k^2 t} \tag{3.3.17}$$

Using this expression, the transverse current correlation function is

$$C_t(k,t) = \frac{1}{N}\langle J_k(t)J_{-k}(0)\rangle\, e^{-\nu k^2 t} = C_t(k,0)e^{-\nu k^2 t} \tag{3.3.18}$$

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

3. 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

$$\begin{aligned} C_t(k,0) &= \frac{1}{N}\left\langle \sum_i v_{ix}(0)\exp\left(-i\vec{k}\vec{r}_i(0)\right)\sum_j v_{jx}(0)\exp\left(-i\vec{k}\vec{r}_i(0)\right)\right\rangle \\ &= \frac{1}{N}\sum_{ij}\left\langle v_0^2\delta_{ij}\exp\left[-i\vec{k}\left(z_i-z_j\right)\right]\right\rangle \\ &= v_o^2 \end{aligned} \tag{3.3.19}$$

where

$$\langle v_{ix}v_{jx}\rangle = \delta_{ij}\langle v_{ix}v_{ix}\rangle = \delta_{ij}\frac{1}{\beta m} = \delta_{ij}v_o^2 \tag{3.3.20}$$

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 and solve for $C_t(k,0)$

$$C_t(k,t) = C_t(k,0)\left(1-\nu k^2 t\right) = \frac{1}{N}\sum_{ij}\left\langle v_i(t)v_j(0)\left[1-\frac{k^2}{2}\left(z_i(t)-z_j(0)\right)^2\right]\right\rangle \tag{3.3.21}$$

Then we have

$$C(k,0)\nu = \lim_{t\to\infty}\frac{1}{2tN}\sum_{ij}\left\langle v_i(t)v_j(0)\left[z_i(t)-z_j(0)\right]^2\right\rangle \tag{3.3.22}$$

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

$$\left\langle \sum_i v_i(t)z_i^2(t)\sum_j v_j(0)\right\rangle = \left\langle \sum_{ij} v_i(t)z_i^2(t)v_j(t)\right\rangle = \sum_i\left\langle v_i^2(t)z_i^2(t)\right\rangle \tag{3.3.23}$$

then the viscosity coefficient is given by

$$\eta = \lim_{t\to\infty}\frac{1}{vkT}\frac{1}{2t}\langle[A(t)-A(0)]^2\rangle \tag{3.3.24}$$

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

5. Define σ_{xz} as the time derivative of A

$$\dot{A}=\sigma_{xz}=\frac{d}{dt}\sum_i P_{ix}z_i \tag{3.3.25}$$

Then we can write the viscosity coefficient as

$$\eta=\frac{1}{Vm^2k_BT}\int_0^\infty\langle\sigma_{xz}(t)\sigma_{xz}(0)\rangle\,dt \tag{3.3.26}$$

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

$$C_t(\vec{k},t)=v_o^2e^{-\gamma k^2t}\Rightarrow C_t(\vec{k},\omega)=v_o^2\frac{2\nu_tk^2}{\omega^2+\nu_tk^2} \tag{3.3.27}$$

Therefore, the viscosity coefficient can be written as

$$\eta=\frac{\rho_om^2\beta}{2}\lim_{\omega\to0}\lim_{k\to0}\frac{\omega^2}{k^2}C_t(\vec{k},\omega) \tag{3.3.28}$$

7. In general, $\sigma_{\alpha\beta}$ denotes

$$\sigma_{\alpha\beta}=\frac{d}{dt}\sum_i P_{i\alpha}r_{i\beta} \tag{3.3.29}$$

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

$$\langle\sigma_{\alpha\beta}\rangle=\delta_{\alpha\beta}PV \tag{3.3.30}$$

The longitudinal current is given by

$$J_k(t)=J_k(0)e^{-bk^2t} \tag{3.3.31}$$

where

$$b=\frac{1}{m\rho_o}\left(\eta_B+\frac{4}{3}\eta\right) \tag{3.3.32}$$

Therefore, by analogy

$$\eta_B+\frac{4}{3}\eta=\frac{1}{Vk_bT}\int_0^\infty\langle\delta\sigma_{zz}(t)\delta\sigma_{zz}(0)\rangle\,dt \tag{3.3.33}$$

where

$$\delta\sigma_{zz}=\sigma_{zz}(t)-PV \tag{3.3.34}$$

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

$$D=\int_0^\infty v_z(t)v_z(0)dt \tag{3.3.35}$$

ii) Viscosity Coefficients

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

where

$$\sigma_{\alpha\beta} = \frac{d}{dt}\sum_i P_{i\alpha} r_{i\beta} \tag{3.3.36}$$

iii)

$$\lambda = \frac{1}{Vk_bT}\int_0^\infty \langle \dot{A}(t)\dot{A}(0)dt\rangle \tag{3.3.37}$$

where

$$A = \frac{d}{dt}\sum_i z_i\left[\frac{p_i^2}{2m} + \frac{1}{2}\sum_{ij} u_{ij} - \langle E\rangle\right] \tag{3.3.38}$$

3. 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

$$D = \int_0^\infty \left\langle v_z^2\right\rangle e^{-t/\tau_c} dt = \left\langle v_z^2\right\rangle \tau_c \tag{3.3.39}$$

and the viscosity coefficient is

$$\eta = \frac{1}{Vk_BT}\int_0^\infty \left\langle \left(\sum_i P_{xi} v_{zi}\right)^2\right\rangle e^{-t/\tau_c} dt = \frac{N}{Vk_BT}\left\langle P_{xi}^2 v_z^2\right\rangle \tau_c \tag{3.3.40}$$

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

$$\tau_c = \frac{\tau}{\bar{v}} = \frac{1}{\sqrt{2}\pi\sigma^2\rho}\left[\frac{\pi m}{8k_BT}\right]^{\frac{1}{2}} \tag{3.3.41}$$

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

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

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

Thermal Diffusion (Conduction)

Define the energy

$$E_k = \sum_i \delta e_i(t) e^{-i\vec{k}\vec{r}_i(t)} \tag{3.3.42}$$

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

$$C(k,t) = \sum_{ij}\left\langle \delta e_i e^{-i\vec{k}\vec{r}_i(t)}\, \delta e_j e^{-i\vec{k}\vec{r}_j(0)}\right\rangle \tag{3.3.43}$$

The initial value of this correlation function is

$$\begin{aligned} C(k,0) &= \sum_{ij} \langle \delta e_i \delta e_j \rangle \left\langle \exp\left[-i\vec{k}\vec{r_i} - \vec{r_j}\right]\right\rangle \\ &= \sum_{i} \langle \delta e_i \delta e_i \rangle = \langle E(0)E(0) \rangle = NC_V k_B T^2 \end{aligned}$$

where we have used the fact that $\langle \delta e_i \delta e_i \rangle = \delta_{ij} \left\langle (\delta e)^2 \right\rangle$. 2) Now, expand the correlation function to the order of k^2 :

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

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

$$A = \sum_i |e_i(t) - \langle e \rangle| \, z_i(t) \tag{3.3.44}$$

Conduction Equation

The conduction equation states that

$$\frac{\partial \rho e}{\partial t} - \nabla \lambda (\nabla T) = 0 \tag{3.3.45}$$

and therefore

$$\frac{\partial E}{\partial t} - \frac{\lambda}{C_V \rho} \nabla^2 E = 0 \tag{3.3.46}$$

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

$$E(t) = E(0) e^{-ak^2 t} \tag{3.3.47}$$

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

$$C(k,t) = \left\langle E^2(0) \right\rangle e^{-ak^2 t} = \left\langle E^2 \right\rangle \left[1 - ak^2 t + \ldots\right] \tag{3.3.48}$$

By equating the k^2 terms, we find that

$$ak^2 N C_V k_B T^2 = \frac{k^2}{2t} \left\langle |A(t) - A(0)|^2 \right\rangle \tag{3.3.49}$$

Therefore,

$$\lambda = \frac{1}{V k_b T^2} \int_0^\infty \langle \dot{A}(t) \dot{A}(0) dt \rangle = \lim_{t \to \infty} \frac{1}{V k_b T^2} \frac{1}{2t} \left\langle |A(t) - A(0)|^2 \right\rangle \tag{3.3.50}$$

where

$$e_i = \frac{p_i^2}{2m} + \frac{1}{2} \sum_{i=j} U_{ij} \tag{3.3.51}$$

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