NON-EQUILIBRIUM STATISTICAL MECHANICS

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CHAPTER OVERVIEW

1: Stochastic Processes and Brownian Motion

Equilibrium thermodynamics and statistical mechanics are widely considered to be core subject matter for any practicing chemist [1]. There are plenty of reasons for this:

- A great many chemical phenomena encountered in the laboratory are well described by equilibrium thermodynamics.
- The physics of chemical systems at equilibrium is generally well understood and mathematically tractable.
- Equilibrium thermodynamics motivates our thinking and understanding about chemistry away from equilibrium.

This last point, however, raises a serious question: how well does equilibrium thermodynamics really motivate our understanding of nonequilibrium phenomena? Is it reasonable for an organometallic chemist to analyze a catalytic cycle in terms of rate-law kinetics, or for a biochemist to treat the concentration of a solute in an organelle as a bulk mixture of compounds? Under many circumstances, equilibrium thermodynamics suffices, but a growing number of outstanding problems in chemistry - from electron transfer in light-harvesting complexes to the chemical mechanisms behind immune system response- concern processes that are fundamentally out of equilibrium.

This course endeavors to introduce the key ideas that have been developed over the last century to describe nonequilibrium phenomena. These ideas are almost invariably founded upon a statistical description of matter, as in the equilibrium case. However, since nonequilibrium phenomena contain a more explicit time-dependence than their equilibrium counterparts (consider, for example, the decay of an NMR signal or the progress of a reaction), the probabilistic tools we develop will require some time-dependence as well.

In this chapter, we consider systems whose behavior is inherently nondeterministic, or stochastic, and we establish methods for describing the probability of finding the system in a particular state at a specified time.

Thumbnail: This is a simulation of the Brownian motion of a big particle (dust particle) that collides with a large set of smaller particles (molecules of a gas) which move with different velocities in different random directions. (CC BY-SA 3.0; Lookang via Wikipedia)

1.1: Markov Processes

Probability Distributions and Transitions

Suppose that an arbitrary system of interest can be in any one of N distinct states. The system could be a protein exploring different conformational states; or a pair of molecules oscillating between a "reactants" state and a "products" state; or any system that can sample different states over time. Note here that N is finite, that is, the available states are discretized. In general, we could consider systems with a continuous set of available states (and we will do so in section 1.3), but for now we will confine ourselves to the case of a finite number of available states. In keeping with our discretization scheme, we will also (again, for now) consider the time evolution of the system in terms of discrete timesteps rather than a continuous time variable.

Let the system be in some unknown state m at timestep s, and suppose we're interested in the probability of finding the system in a specific state n, possibly but not necessarily the same as state m, at the next timestep $s+1$. We will denote this probability by

$$P(n, s+1) \tag{1.1.1}$$

If we had knowledge of m, then this probability could be described as the probability of the system being in state n at timestep $s+1$ given that the system was in state m at timestep s. Probabilities of this form are known as conditional probabilities, and we will denote this conditional probability by

$$Q(m, s \mid n, s+1) \tag{1.1.2}$$

In many situations of physical interest, the probability of a transition from state m to state n is time-independent, depending only on the nature of m and n, and so we drop the timestep arguments to simplify the notation,

$$Q(m, s \mid n, s+1) \equiv Q(m, n) \tag{1.1.3}$$

This observation may seem contradictory, because we are interested in the time-dependent probability of observing a system in a state n while also claiming that the transition probability described above is time-independent. But there is no contradiction here, because the transition probability Q - a conditional probability - is a different quantity from the time-dependent probability P we are interested in. In fact, we can express $P(n, s+1)$ in terms of $Q(m, n)$ and other quantities as follows:

Since we don't know the current state m of the system, we consider all possible states m and multiply the probability that the system is in state m at timestep s by the probability of the system being in state n at timestep $s+1$ given that it is in state m at timestep s. Summing over all possible states m gives $P\left(n, s_1\right)$ at timestep $s+1$ in terms of the corresponding probabilities at timestep s.

Mathematically, this formulation reads

$$P(n, s+1) = \sum_m P(m, s) Q(m, n) \tag{1.1.4}$$

We've made some progress towards a practical method of finding $P(n, s+1)$, but the current formulation Eq.(1.1) requires knowledge of both the transition probabilities $Q(m, n)$ and the probabilities $P(m, s)$ for all states m. Unfortunately, $P(m, s)$ is just as much a mystery to us as $P(n, s+1)$. What we usually know and control in experiments are the initial conditions; that is, if we prepare the system in state k at timestep $s=0$, then we know that $P(k, 0)=1$ and $P(n, 0)=0$ for all $n \neq k$. So how do we express $P(n, s+1)$ in terms of the initial conditions of the experiment?

We can proceed inductively: if we can write $P(n, s+1)$ in terms of $P(m, s)$, then we can also write $P(m, s)$ in terms of $P(l, s-1)$ by the same approach:

$$P(n, s+1) = \sum_{l,m} P(l, s-1) Q(l, m) Q(m, n) \tag{1.1.5}$$

Note that Q has two parameters, each of which can take on N possible values. Consequently we may choose to write Q as an $N \times N$ matrix $\mathbf{Q}$ with matrix elements $(\mathbf{Q})_{mn} = Q(m, n)$. Rearranging the sums in Eq.(1.2) in the following manner,

$$P(n, s+1) = \sum_l P(l, s-1) \sum_m Q(l, m) Q(m, n) \tag{1.1.6}$$

we recognize the sum over m as the definition of a matrix product,

$$\sum_m (\mathbf{Q})_{lm}(\mathbf{Q})_{mn} = \left(\mathbf{Q}^2\right)_{ln} \tag{1.1.7}$$

Hence, Eq.(1.2) can be recast as

$$P(n, s+1) = \sum_l P(l, s-1)\left(\mathbf{Q}^2\right)_{ln} \tag{1.1.8}$$

This process can be continued inductively until $P(n, s+1)$ is written fully in terms of initial conditions. The final result is:

$$\begin{aligned} P(n, s+1) &= \sum_m P(m, 0)\left(\mathbf{Q}^{s+1}\right)_{mn} \\ &= P(k, 0)\left(\mathbf{Q}^{s+1}\right)_{mn} \end{aligned}$$

where k is the known initial state of the system (all other m do not contribute to the sum since $P(m, 0) = 0$ for $m \neq k$). Any process that can be described in this manner is called a Markov process, and the sequence of events comprising the process is called a Markov chain.

A more rigorous discussion of the origins and nature of Markov processes may be found in, e.g., de Groot and Mazur [2].

The Transition Probability Matrix

We now consider some important properties of the transition probability matrix $\mathbf{Q}$. By virtue of its definition, Q is not necessarily Hermitian: if it were Hermitian, every conceivable transition between states would have to have the same forward and backward probability, which is often not the case.

Example: Consider a chemical system that can exist in either a reactant state A or a product state B, with forward reaction probability p and backward reaction probability $q = 1 - p$,

$$\mathrm{A} \underset{q}{\overset{p}{\rightleftharpoons}} \mathrm{B} \tag{1.1.9}$$

The transition probability matrix $\mathbf{Q}$ for this system is the 2×2 matrix

$$\mathbf{Q} = \begin{pmatrix} q & p \\ q & p \end{pmatrix} \tag{1.1.10}$$

To construct this matrix, we first observe that the given probabilities directly describe the off-diagonal elements Q_{AB} and Q_{BA}; then we invoke conservation of probability. For example, if the system is in the reactant state A, it can only stay in A or react to form product B; there are no other possible outcomes, so we must have $Q_{AA} + Q_{AB} = 1$. This forces the value $1 - p = q$ upon Q_{AA}, and a similar argument yields Q_{BB}.

Clearly this matrix is not symmetric, hence it is not Hermitian either, thus demonstrating our first general observation about $\mathbf{Q}$.

The non-Hermiticity of $\mathbf{Q}$ implies also that its eigenvalues λ_i are not necessarily real-valued. Nevertheless, $\mathbf{Q}$ yields two sets of eigenvectors, a left set χ_i and a right set ϕ_i, which satisfy the relations

$$\begin{aligned} \chi_i \mathbf{Q} &= \lambda_i \chi_i \\ \mathbf{Q} \phi_i &= \lambda_i \phi_i \end{aligned}$$

The left- and right-eigenvectors of $\mathbf{Q}$ are orthonormal,

$$\langle \chi_i \mid \phi_j \rangle = \delta_{ij} \tag{1.1.11}$$

and they form a complete set, hence there is a resolution of the identity of the form

$$\sum_i |\phi_i\rangle \langle \chi_i| = 1 \tag{1.1.12}$$

Conservation of probability further restricts the elements of $\mathbf{Q}$ to be nonnegative with $\sum_n \mathbf{Q}_{mn} = 1$. It can be shown that this condition guarantees that all eigenvalues of $\mathbf{Q}$ are bounded by the unit circle in the complex plane,

$$|\lambda_i| \leq 1, \forall i \tag{1.1.13}$$

Proof of Eq. (1.12): The i^{th} eigenvalue of Q satisfies

$$\lambda_i\phi_i(n)=\sum_m Q_{nm}\phi_i(m) \tag{1.1.14}$$

for each n. Take the absolute value of this relation,

$$|\lambda_i\phi_i(n)|=\left|\sum_m Q_{nm}\phi_i(m)\right| \tag{1.1.15}$$

Now we can apply the triangle inequality to the right hand side of the equation:

$$\left|\sum_m Q_{nm}\phi_i(m)\right|\leq\sum_m |Q_{nm}\phi_i(m)| \tag{1.1.16}$$

Also, since all elements of **Q** are nonnegative,

$$|\lambda_i\phi_i(n)|\leq\sum_m Q_{nm}\,|\phi_i(m)| \tag{1.1.17}$$

Now, the $\phi_i(n)$ are finite, so there must be some constant c such that

$$|\phi_i(n)|\leq c \tag{1.1.18}$$

for all n. Then our triangle inequality relation reads

$$c\,|\lambda_i|\leq c\sum_m Q_{nm} \tag{1.1.19}$$

Finally, since $\sum_m Q_{nm}=1$, we have the desired result,

$$|\lambda_i|\leq 1 \tag{1.1.20}$$

Another key feature of the transition probability matrix **Q** is the following claim, which is intimately connected with the notion of an equilibrium state:

$$\text{Q always has the eigenvalue } \lambda=1 \tag{1.1.21}$$

Proof of Eq.(1.13): We refer now to the left eigenvectors of $\mathbf{Q}:$ a given left eigenvector χ_i satisfies

$$\chi_i(n)\lambda_i=\sum_m \chi_i(m)Q_{mn} \tag{1.1.22}$$

Summing over n, we find

$$\sum_n \chi_i(n)\lambda_i=\sum_n\sum_m \chi_i(m)Q_{mn}=\sum_m \chi_i(m) \tag{1.1.23}$$

since $\sum_m Q_{nm}=1$. Thus, we have the following secular equation:

$$(\lambda_i-1)\sum_n \chi_i(n)=0 \tag{1.1.24}$$

Clearly, $\lambda=1$ is one of the eigenvalues satisfying this equation.

The decomposition of the secular equation in the preceding proof has a direct physical interpretation: the eigenvalue $\lambda_1=1$ has a corresponding eigenvector which satisfies $\sum_n \chi_1(n)=1$; this stationary-state eigensolution corresponds to the steady state of a system $\chi_1(n)=P_{\text{st}}(n)$. It then follows from the normalization condition that $\phi_1(n)=1$. The remaining eigenvalues $|\lambda_j|<1$ each satisfy $\sum_n \chi_j(n)=0$ and hence correspond to zero-sum fluctuations about the equilibrium state.

In light of these properties of **Q**, we can define the time-dependent evolution of a system in terms of the eigenstates of **Q**; this representation is termed the spectral decomposition of $P(n,s)$ (the set of eigenvalues of a matrix is also known as the spectrum of that matrix). In the basis of left and right eigenvectors of **Q**, the probability of being in state n at timestep s, given the initial state as n_0, is

$$P(n,s)=\langle n_0\,|\mathbf{Q}^s|\,n\rangle=\sum_i \langle n_0\mid\phi_i\rangle\,\lambda_i^s\,\langle\chi_i\mid n\rangle \tag{1.1.25}$$

If we (arbitrarily) assign the stationary state to $i=1$, we have $\lambda_1=1$ and $\chi_1=P_{st}$, where P_{st} is the steady-state or equilibrium probability distribution. Thus,

$$P(n, s)=P_{st}(n)+\sum_{i \neq 1} \phi_i\left(n_0\right) \lambda_i^s \chi_i(n) \tag{1.1.26}$$

The spectral decomposition proves to be quite useful in the analysis of more complicated probability distributions, especially those that have sufficiently many states as to require computational analysis.

Example: Consider a system which has three states with transition probabilities as illustrated in Figure 1.1. Notice that counterclockwise and clockwise transitions have differing probabilities, which allows this system to exhibit a net current or flux. Also, suppose that $p+q=1$ so that the system must switch states at every timestep.

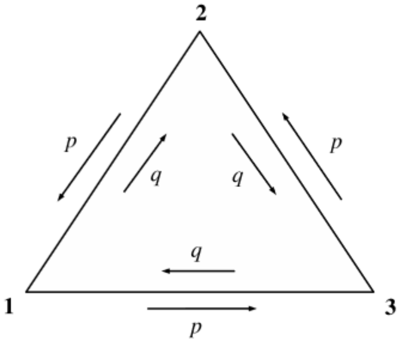

Figure 1.1: A simple three-state system with nonzero flux

The transition probability matrix for this system is

$$\mathbf{Q}=\begin{pmatrix} 0 & p & q \\ q & 0 & p \\ p & q & 0 \end{pmatrix} \tag{1.1.27}$$

To determine $P(s)$, we find the eigenvalues and eigenvectors of this matrix and use the spectral decomposition, Eq.(1.14). The secular equation is

$$\operatorname{Det}(\mathbf{Q}-\lambda \mathbf{I})=\mathbf{0} \tag{1.1.28}$$

and its roots are

$$\lambda_1=1, \quad \lambda_{\pm}=-\frac{1}{2} \pm \frac{1}{2} \sqrt{3(4 p q-1)} \tag{1.1.29}$$

Notice that the nonequilibrium eigenvalues are complex unless $p=q=\frac{1}{2}$, which corresponds to the case of vanishing net flux. If there is a net flux, these complex eigenvalues introduce an oscillatory behavior to $P(s)$.

In the special case $p=q=\frac{1}{2}$, the matrix $\mathbf{Q}$ is symmetric, so the left and right eigenvectors are identical,

$$\begin{aligned} \chi_1 &=\phi_1^T=\frac{1}{\sqrt{3}}(1,1,1) \\ \chi_2 &=\phi_2^T=\frac{1}{\sqrt{6}}(1,1,-2) \\ \chi_3 &=\phi_3^T=\frac{1}{\sqrt{2}}(1,-1,0) \end{aligned}$$

where T denotes transposition. Suppose the initial state is given as state 1 , and we're interested in the probability of being in state 3 at timestep $s, P_{1 \rightarrow 3}(s)$. According to the spectral decomposition formula $\mathrm{Eq} \cdot(1.14)$

$$\begin{aligned}P_{1\to 3}(s) &= \sum_i \phi_i(1)\lambda_i^s \chi_i(3)\\ &= \left(\frac{1}{\sqrt{3}}\right)(1^s)\left(\frac{1}{\sqrt{3}}\right)\\ &\quad+\left(\frac{1}{\sqrt{6}}\right)(1)\left(-\frac{1}{2}\right)^s\left(\frac{1}{\sqrt{6}}\right)(-2)\\ &\quad+\left(\frac{1}{\sqrt{2}}\right)(1)\left(-\frac{1}{2}\right)^s\left(\frac{1}{\sqrt{2}}\right)(0)\\ P_{1\to 3}(s) &= \frac{1}{3}-\frac{1}{3}\left(-\frac{1}{2}\right)^s\end{aligned}$$

Note that in the evaluation of each term, the first element of each left eigenvector χ and the third element of each right eigenvector ϕ was used, since we're interested in the transition from state 1 to state 3 . Figure 1.2 is a plot of $P_{1\to 3}(s)$; it shows that the probability oscillates about the equilibrium value of $\frac{1}{3}$, approaching the equilibrium value asymptotically.

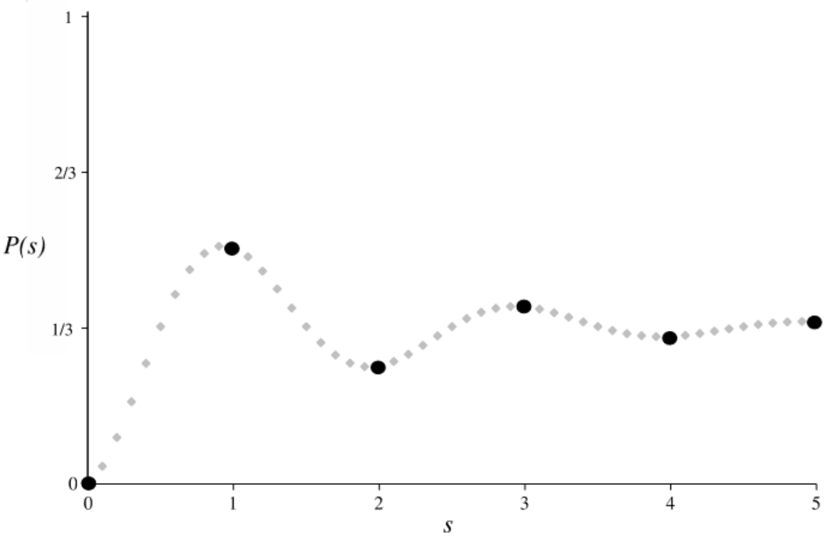

Figure 1.2: Probability of a transition from state 1 to state 3 vs. number of timesteps. Black points correspond to actual timesteps; grey points have been interpolated to emphasize the oscillatory nature of $P(s)$.

Detailed Balance

Our last topic of consideration within the subject of Markov processes is the notion of detailed balance, which is probably already somewhat familiar from elementary kinetics. Formally, a Markov process with transition probability matrix $\mathbf{Q}$ satisfies detailed balance if the following condition holds:

$$P_{\text{st}}(n)Q_{nm} = P_{\text{st}}(m)Q_{mn} \tag{1.1.30}$$

And this steady state defines the equilibrium distribution:

$$P_{\text{eq}}(n) = P_{\text{st}}(n) = \lim_{t\to\infty} P(n,t) \tag{1.1.31}$$

This relation generalizes the notion of detailed balance from simple kinetics that the rates of forward and backward processes at equilibrium should be equal: here, instead of considering only a reactant state and a product state, we require that all pairs of states be related by Eq.(1.16).

Note also that this detailed balance condition is more general than merely requiring that $\mathbf{Q}$ be symmetric, as the simpler definition from elementary kinetics would imply. However, if a system obeys detailed balance, we can describe it using a symmetric matrix via the following transformation: let

$$V_{nm} = \frac{\sqrt{P_{\text{st}}(n)}}{\sqrt{P_{\text{st}}(m)}}Q_{nm} \tag{1.1.32}$$

If we make the substitution $P(n,s)=\sqrt{P_{\text{st}}(n)}\cdot\tilde{P}(n,s)$, some manipulation using equations (1.1) and (1.17) yields

$$\frac{d\tilde{P}(n,t)}{dt}=\sum_m \tilde{P}(m,t)V_{mn} \tag{1.1.33}$$

The derivative $\frac{d\tilde{P}(n,s)}{dt}$ here is really the finite difference $\tilde{P}(n,s+1)-\tilde{P}(n,s)$ since we are considering discrete-time Markov processes, but we have introduced the derivative notation for comparison of this formula to later results for continuous-time systems.

As we did for $\mathbf{Q}$, we can set up an eigensystem for $\mathbf{V}$, which yields a spectral decomposition similar to that of $\mathbf{Q}$ with the exception that the left and right eigenvectors ψ of $\mathbf{V}$ are identical since $\mathbf{V}$ is symmetric; in other words, $\langle\psi_i\mid\psi_j\rangle=\delta_{ij}$. Furthermore, it can be shown that all eigenvalues not corresponding to the equilibrium state are either negative or zero; in particular, they are real. The eigenvectors of $\mathbf{V}$ are related to the left and right eigenvectors of $\mathbf{Q}$ by

$$|\phi_i\rangle=\frac{1}{\sqrt{P_{\text{st}}}}|\psi_i\rangle \quad \text{and} \quad \langle\chi_i|=\sqrt{P_{\text{st}}}\,\langle\psi_i| \tag{1.1.34}$$

Example: Our final model Markovian system is a linear three-state chain (Figure 1.3) in which the system must pass through the middle state in order to get from either end of the chain to the other. Again we require that $p+q=1$. From this information, we can construct $\mathbf{Q}$,

$$\mathbf{Q}=\begin{pmatrix} q & p & 0\\ q & 0 & p\\ 0 & q & p\end{pmatrix} \tag{1.1.35}$$

Notice how the difference between the three-site linear chain and the three-site ring of the previous example is manifest in the structure of $\mathbf{Q}$, particularly in the direction of the zero diagonal. This structural difference carries through to general N-site chains and rings.

To determine the equilibrium probability distribution P_{st} for this system, one could multiply $\mathbf{Q}$ by itself many times over and hope to find an analytic formula for $\lim_{s\to\infty}\mathbf{Q}^s$; however, a less tedious and more intuitive approach is the following:

Noticing that the system cannot stay in state 2 at time s if it is already in state 2 at time $s-1$, we conclude that $P(1,s+2)$ depends only on $P(1,s)$ and $P(3,s)$. Also, the conditional probabilities $P(1,s+2\mid 1,s)$ and $P(1,s+2\mid 3,s)$ are both equal to q^2. Likewise, $P(3,s+2\mid 1,s)$ and $P(3,s+2\mid 3,s)$ are both equal to p^2. Finally, if the system is in state 2 at time s, it can only get back to state 2 at time $s+2$ by passing through either state 1 or state 3 at time $s+1$. The probability of either of these occurrences is pq.

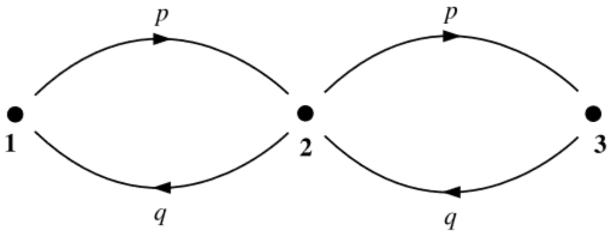

Figure 1.3: A three-state system in which sites are no longer identical

So the ratio $P_{\text{st}}(1):P_{\text{st}}(2):P_{\text{st}}(3)$ in the equilibrium limit is $q^2:qp:p^2$. We merely have to normalize these probabilities by noting that $q^2+qp+p^2=(q+p)^2-qp=1-qp$. Thus, the equilibrium distribution is

$$P(s)=\frac{1}{1-qp}\left(q^2,qp,p^2\right) \tag{1.1.36}$$

Plugging each pair of states into the detailed balance condition, we verify that this system satisfies detailed balance, and hence all of its eigenvalues are real, even though $\mathbf{Q}$ is not symmetric.

1.2: Master Equations

Motivation and Derivation

The techniques developed in the basic theory of Markov processes are widely applicable, but there are of course many instances in which the discretization of time is either inconvenient or completely unphysical. In such instances, a master equation (more humbly referred to as a rate equation) may provide a continuous-time description of the system that is in keeping with all of our results about stochastic processes.

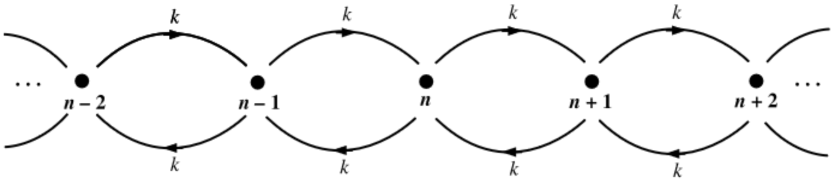

Figure 1.4: Infinite lattice with transition rate *[Math Processing Error]* between all contiguous states

Eq. *[Math Processing Error]* is a master equation. As the derivation suggests, *[Math Processing Error]* plays the role of a transition probability matrix in this formulation. You may notice that the master equation looks structurally very similar to rate equations in elementary kinetics; in fact, the master equation is a generalization of such rate equations, and the derivation above provides some formal justification for the rules we learn in kinetics for writing them down. The matrix *[Math Processing Error]* is analogous to the set of rate constants indicating the relative rates of reaction between species in the system, and the probabilities *[Math Processing Error]* are analogous to the relative concentrations of these species.

Example: Consider a random walk on a one-dimensional infinite lattice (see Figure 1.4). As indicated in the figure, the transition probability between a lattice point and either adjacent lattice point is *[Math Processing Error]*, and all other transition probabilities are zero (in other words, the system cannot "hop" over a lattice point without first occupying it). We can write down a master equation to describe the flow of probability among the lattice sites in a manner analogous to writing down a rate law. For any given site *[Math Processing Error]* on the lattice, probability can flow into *[Math Processing Error]* from either site *[Math Processing Error]* or site *[Math Processing Error]*, and both of these occur at rate *[Math Processing Error]*; likewise, probability can flow out of state *[Math Processing Error]* to either site *[Math Processing Error]* or site *[Math Processing Error]*, both of which also happen at rate *[Math Processing Error]*. Hence, the master equation for all sites *[Math Processing Error]* on the lattice is

[Math Processing Error]

Now we define the average site of occupation as a sum over all sites, weighted by the probability of occupation at each site,

[Math Processing Error]

Then we can compute, for example, how this average site evolves with time,

[Math Processing Error]

Hence the average site of occupation does not change over time in this model, so if we choose the initial distribution to satisfy *[Math Processing Error]*, then this will always be the average site of occupation.

However, the mean square displacement *[Math Processing Error]* is not constant; in keeping with our physical interpretation of the model, the mean square displacement increases with time. In particular,

[Math Processing Error]

If the initial probability distribution is a delta function on site *[Math Processing Error]*, then it turns out that Fourier analysis provides a route towards a closed-form expression for the long-time limit of *[Math Processing Error]* :

[Math Processing Error]

[Math Processing Error]

In the above manipulations, we have replaced *[Math Processing Error]* with the diffusion constant *[Math Processing Error]*, the long-time limit of the rate constant (in this case, the two are identical). Thus the probability distribution for occupying the various sites becomes Gaussian at long times.

Mean First Passage Time

One of the most useful quantities we can determine from the master equation for a random walk is the average time it takes for the random walk to reach a particular site *[Math Processing Error]* for the first time. This quantity, called the mean first passage time, can be determined via the following trick: we place an absorbing boundary condition at *[Math Processing Error]*. Whenever the walk reaches site *[Math Processing Error]*, it stays there for all later times. One then calculates the survival probability *[Math Processing Error]*, that is, the probability that the walker has not yet visited *[Math Processing Error]* at time *[Math Processing Error]*,

[Math Processing Error]

The mean first passage time *[Math Processing Error]* then corresponds to the time-averaged survival probability,

[Math Processing Error]

Sometimes it is more convenient to write the mean first passage time in terms of the probability density of reaching site *[Math Processing Error]* at time *[Math Processing Error]*. This quantity is denoted by *[Math Processing Error]* and satisfies

[Math Processing Error]

In terms of *[Math Processing Error]*, the mean first passage time is given by

[Math Processing Error]

The mean first passage time is a quantity of interest in a number of current research applications. Rates of fluorescence quenching, electron transfer, and exciton quenching can all be formulated in terms of the mean first passage time of a stochastic process.

Example: Let's calculate the mean first passage time of the three-site model introduced in Figure *[Math Processing Error]*, with all transition rates having the same value *[Math Processing Error]*. Suppose the system is prepared in state 1 , and we're interested in knowing the mean first passage time for site 3 . Applying the absorbing boundary condition at site 3 , we derive the following master equations:

[Math Processing Error]

The transition matrix *[Math Processing Error]* corresponding to this system would have a zero column since *[Math Processing Error]* does not occur on the right hand side of any of these equations; hence the sink leads to a zero eigenvalue that we can ignore. The relevant submatrix

[Math Processing Error]

has eigenvalues *[Math Processing Error]*. Using the spectral decomposition formula, we find that the survival probability is

[Math Processing Error]

Hence, the previously defined probability density *[Math Processing Error]* is given by *[Math Processing Error]*, and the mean first passage time for site 3 is

[Math Processing Error]

1.3: Fokker-Planck Equations

Fokker-Planck Equations and Diffusion

We have already generalized the equations governing Markov processes to account for systems that evolve continuously in time, which resulted in the master equations. In this section, we adapt these equations further so that they may be suitable for the description of systems with a continuum of states, rather than a discrete, countable number of states.

Motivation and Derivation

Consider once again the infinite one-dimensional lattice, with lattice spacing Δx and timestep size Δt. In the previous section, we wrote down the master equation (discrete sites, continuous time) for this system, but here we will begin with the Markov chain expression (discrete sites, discrete time) for the system,

$$P(n, s+1) = \frac{1}{2}(P(n+1, s) + P(n-1, s)) \tag{1.3.1}$$

In terms of Δx and Δt, this equation is

$$P(x, t+\Delta t) = \frac{1}{2}[P(x+\Delta x, t) + P(x-\Delta x, t)] \tag{1.3.2}$$

Rearranging the previous equation as a finite difference, as in

$$\frac{P(x, t+\Delta t) - P(x, t)}{\Delta t} = \frac{(\Delta x)^2}{2\Delta t} \cdot \frac{P(x+\Delta x, t) + P(x-\Delta x, t) - 2P(x, t)}{(\Delta x)^2} \tag{1.3.3}$$

and taking the limits $\Delta x \rightarrow 0, \Delta t \rightarrow 0$, we arrive at the following differential equation:

$$\frac{\partial}{\partial t} P(x, t) = D \frac{\partial^2}{\partial x^2} P(x, t) \tag{1.3.4}$$

where $D = \frac{(\Delta x)^2}{2\Delta t}$. This differential equation is called a diffusion equation with diffusion constant D, and it is a special case of the Fokker-Planck equation, which we will introduce shortly. The most straightforward route to the solution of the diffusion equation is via spatial Fourier transformation,

$$\tilde{P}(k, t) = \int_{-\infty}^{\infty} P(x, t) e^{ikx} dx \tag{1.3.5}$$

In Fourier space, the diffusion equation reads

$$\frac{\partial}{\partial t} \tilde{P}(k, t) = -Dk^2 \tilde{P}(k, t) \tag{1.3.6}$$

and its solution is

$$\tilde{P}(k, t) = \tilde{P}(k, 0) e^{-Dk^2 t} \tag{1.3.7}$$

If we take a delta function $P(x, 0) = \delta\left(x - x_0\right)$ centered at x_0 as the initial condition, the solution in x-space is

$$P(x, t) = \frac{1}{\sqrt{4\pi Dt}} e^{-\frac{\left(x-x_0\right)^2}{4Dt}} \tag{1.3.8}$$

Thus the probability distribution is a Gaussian in x that spreads with time. Notice that this solution is essentially the same as the long-time solution to the spatially discretized version of the problem presented in the previous example.

We are now in a position to consider a generalization of the diffusion equation known as the Fokker-Planck equation. In addition to the diffusion term $D\frac{\partial^2}{\partial x^2}$, we introduce a term linear in the first derivative with respect to x, which accounts for drift of the center of the Gaussian distribution over time.

Consider a diffusion process on a three-dimensional potential energy surface $U(\mathbf{r})$. Conservation of probability requires that

$$\dot{P}(\mathbf{r}, t) = -\nabla \cdot \mathbf{J} \tag{1.3.9}$$

where $\mathbf{J}$ is the probability current, $\mathbf{J} = -D\nabla P + \mathbf{J}_U$, and $\mathbf{J}_U$ is the current due to the potential $U(\mathbf{r})$. At equilibrium, we know that the probability current $\mathbf{J} = 0$ and that the probability distribution should be Boltzmann-weighted according to energy, $P_{\text{eq}}(\mathbf{r}) \propto e^{-\beta U(\mathbf{r})}$. Therefore, at equilibrium,

$$-D\beta\nabla U(\mathbf{r})P(\mathbf{r})_{\text{eq}} + \mathbf{J}_U = 0 \tag{1.3.10}$$

Solving Eq.(1.36) for $\mathbf{J}_U$ and plugging the result into Eq.(1.35) yields the Fokker-Planck equation,

$$\dot{P}(\mathbf{r}, t) = D\nabla[\nabla P(\mathbf{r}, t) + \beta\nabla U(\mathbf{r})P(\mathbf{r}, t)] \tag{1.3.11}$$

Properties of Fokker-Planck Equations

Let’s return to one dimension to discuss some salient features of the Fokker-Planck equation.

- First, the Fokker-Planck equation gives the expected results in the long-time limit:

$$\lim_{t\to\infty} P = P_{\text{eq}} \text{ with } \dot{P} = 0 \tag{1.3.12}$$

- Also, if we define the average position $\bar{x} = \int_{-\infty}^{\infty} xP(x)dx$, then the differential form of the Fokker-Planck equation can be used to verify that

$$\dot{\bar{x}} = D\beta\left(-\frac{\partial}{\partial x}\overline{U(x)}\right) \tag{1.3.13}$$

Since the quantity in parentheses is just the average force $\bar{F}$, Eq. (1.39) can be combined with the Einstein relation $D\beta\zeta = 1$ (see section 1.4) to justify that $\zeta\bar{v} = \bar{F}$; the meaning and significance of this equation, including the definition of ζ, will be discussed in section 1.4.

- The Fokker-Planck equation is linear in the first and second derivatives of P with respect to x; it turns out that any spatial operator that is a linear combination of $\frac{\partial}{\partial x}$, $x\frac{\partial}{\partial x}$, and $\frac{\partial^2}{\partial x^2}$ will define a Gaussian process when used to describe the time evolution of a probability density. Thus, both the diffusion equation and the more general Fokker-Planck equation will generally always describe a Gaussian process. - One final observation about the Fokker-Planck equation is that it is only analytically solvable in a small number of special cases. This situation is exacerbated by the fact that it is not of Hermitian (self-adjoint) form. However, we can introduce the change of variable $P = e^{-\frac{\beta U}{2}}\Phi$; in terms of Φ, the Fokker-Planck equation is Hermitian,

$$\frac{\partial\Phi}{\partial t} = D\left[\nabla^2\Phi - U_{\text{eff}}\Phi\right] \tag{1.3.14}$$

where $U_{\text{eff}} = \frac{(\beta\nabla U)^2}{4} - \frac{\beta\nabla^2 U}{2}$. This transformed Fokker-Planck equation now bears the same functional form as the time-dependent Schrödinger equation, so all of the techniques associated with its solution can likewise be applied to Eq.(1.40).

Example: One of the simplest, yet most useful, applications of the Fokker-Planck equation is the description of the diffusive harmonic oscillator, which can be treated analytically. Here we solve the Fokker-Planck equation for the one-dimensional diffusive oscillator with frequency ω. The differential equation is

$$\frac{\partial P}{\partial t} = D\frac{\partial^2}{\partial x^2}P + \gamma\frac{\partial}{\partial x}(xP) \tag{1.3.15}$$

where $\gamma = m\omega^2 D\beta$. We can solve this equation in two steps: first, solve for the average position using Eq. (1.39),

$$\dot{\bar{x}} = -\gamma\bar{x} \tag{1.3.16}$$

Given the usual delta function initial condition $P(x, 0) = \delta\left(x - x_0\right)$, the average position is given by

$$\bar{x}(t) = x_0 e^{-\gamma t} \tag{1.3.17}$$

Thus, memory of the initial conditions decays exponentially for the diffusive oscillator.

Then, since the Fokker-Planck equation is linear in P and bilinear in x and $\frac{\partial}{\partial x}$, the full solution must take the form of a Gaussian, so we can write

$$P\left(x_0, x, t\right)=\frac{1}{\sqrt{2 \pi \alpha(t)}} \exp \left[-\frac{(x-\bar{x}(t))^2}{2 \alpha(t)}\right] \tag{1.3.18}$$

where $\bar{x}(t)$ is the time-dependent mean position and $\alpha(t)$ is the time-dependent standard deviation of the distribution. But we've already found $\bar{x}(t)$, so we can substitute it into the solution,

$$P\left(x_0, x, t\right)=\frac{1}{\sqrt{2 \pi \alpha(t)}} \exp \left[-\frac{\left(x-x_0 e^{-\gamma t}\right)^2}{2 \alpha(t)}\right] \tag{1.3.19}$$

Finally, from knowledge that the equilibrium distribution must satisfy the stationary condition

$$P_{\text{eq}}(x)=\int_{-\infty}^{\infty} P\left(x_0, x, t\right) P_{\text{eq}}\left(x_0\right) d x_0 \tag{1.3.20}$$

we can determine that

$$\alpha(t)=\frac{1-e^{-2 \gamma t}}{m \omega^2 \beta} \tag{1.3.21}$$

Thus the motion of the diffusive oscillator is fully described.

The long and short-time limits of $P\left(x_0, x, t\right)$ are both of interest to us. At short times,

$$\lim _{t \rightarrow 0} P\left(x_0, x, t\right)=\sqrt{\frac{1}{4 \pi D t}} \exp \left[-\frac{\left(x-x_0\right)^2}{4 D t}\right] \tag{1.3.22}$$

and the evolution of the probability looks like that of a random walk. In the long-time limit, on the other hand, we find the equilibrium probability distribution

$$\lim _{t \rightarrow \infty} P\left(x_0, x, t\right)=\sqrt{\frac{m \omega^2 \beta}{2 \pi}} \exp \left[-\frac{1}{2} m \omega^2 \beta x^2\right] \tag{1.3.23}$$

which is Gaussian with no mean displacement and with variance determined by a thermal parameter and a parameter describing the shape of the potential. A Gaussian, Markovian process that exhibits exponential memory decay, such as this diffusive oscillator, is called an Ornstein-Uhlenbeck process.

1.4: The Langevin Equation

Our focus in this chapter has been on the description of purely stochastic processes. However, a variety of interesting and important phenomena are subject to combinations of deterministic and stochastic processes. We concern ourselves now with a particular class of such phenomena which are described by Langevin equations. In its simplest form, a Langevin equation is an equation of motion for a system that experiences a particular type of random force. The archetypal system governed by a Langevin equation is a Brownian particle, that is, a particle undergoing Brownian motion. (For a brief description of the nature and discovery of Brownian motion, see the Appendix).

The Langevin equation for a Brownian particle in a one-dimensional fluid bath is

$$m\dot{v}(t)+\zeta v(t)=f(t) \tag{1.4.1}$$

where $v(t)=\dot{x}(t)$ is the velocity of the Brownian particle, ζ is a coefficient describing friction between the particle and the bath, m is the mass of the Brownian particle, and $f(t)$ is a random force. Though it is random, we can make a couple of useful assumptions about $f(t)$:

- The random force is equally likely to push in one direction as it is in the other, so the average over all realizations of the force is zero,

$$\langle f(t)\rangle_f=0 \tag{1.4.2}$$

- The random force exhibits no time correlation but has a characteristic strength factor g that does not change over time,

$$\langle f\left(t_1\right) f\left(t_2\right)\rangle_f=g\delta\left(t_1-t_2\right) \tag{1.4.3}$$

Random forces that obey these assumptions are called white noise, or more precisely, Gaussian white noise. In this case, all odd moments of f will vanish, and all even moments can be expressed in terms of two-time correlation functions: for example, the fourth moment is given by

$$\begin{aligned}\langle f\left(t_1\right) f\left(t_2\right) f\left(t_3\right) f\left(t_4\right)\rangle_f= & \langle f\left(t_1\right) f\left(t_2\right)\rangle_f\langle f\left(t_3\right) f\left(t_4\right)\rangle_f \\ & +\langle f\left(t_1\right) f\left(t_3\right)\rangle_f\langle f\left(t_2\right) f\left(t_4\right)\rangle_f \\ & +\langle f\left(t_1\right) f\left(t_4\right)\rangle_f\langle f\left(t_2\right) f\left(t_3\right)\rangle_f\end{aligned}$$

In general, complex systems may exhibit time-dependent strength factors $g(t)$, but we will work with the more mathematically tractable white noise assumption for the random force.

The formal solution to the Langevin equation Eq.(1.41) is

$$v(t)=v(0)e^{-\frac{\zeta}{m}t}+\frac{1}{m}\int_0^t e^{-\frac{\zeta}{m}(t-\tau)} f(\tau)d\tau \tag{1.4.4}$$

In computing the average velocity under the white noise assumption, the second term of Eq.(1.42) vanishes thanks to the condition $\langle f(t)\rangle_f=0$. So the average velocity is simply

$$\langle v(t)\rangle_f=v(0)e^{-\frac{\zeta}{m}t} \tag{1.4.5}$$

Of special interest is the velocity-velocity correlation function

$$C\left(t_1-t_2\right)=\left\langle v\left(t_1\right) v\left(t_2\right)\right\rangle_f \tag{1.4.6}$$

which can also be computed from Eq.(1.42). Invoking the white noise condition for $\langle f\left(t_1\right) f\left(t_2\right)\rangle_f$, we find that

$$\left\langle v\left(t_1\right) v\left(t_2\right)\right\rangle_f=\left(v(0)^2-\frac{g}{2m\zeta}\right)e^{-\frac{\zeta}{m}\left(t_1+t_2\right)}+\frac{g}{2m\zeta}e^{-\frac{\zeta}{m}\left(t_2-t_1\right)} \tag{1.4.7}$$

So far, we have only performed an average over realizations of the random force, denoted by $\langle\ldots\rangle_f$; to proceed, we may also take a thermal average $\langle\ldots\rangle_\beta$, that is, the average over realizations of different initial velocities at inverse temperature β. Equipartition tells us that $\left\langle v_0^2\right\rangle_\beta=\frac{1}{m\beta}$; if we use Eq.(1.45) to write down an expression for $\left\langle\left\langle v\left(t_1\right) v\left(t_2\right)\right\rangle_f\right\rangle_\beta$ and apply equipartition, we arrive at the conclusion that

$$g=\frac{2\zeta}{\beta} \tag{1.4.8}$$

which is a manifestation of the fluctuation-dissipation theorem (the fluctuations in the random force, described by g, are proportional to the dissipation of energy via friction, described by ζ).

The properties of the velocity variable v enumerated above imply that the distribution of velocities is Gaussian with exponential memory decay, like the diffusive oscillator in section 1.3, and so we can also think of this type of Brownian motion as an Ornstein-Uhlenbeck process. In particular, the probability distribution for the velocity is

$$P\left(v_0, v, t\right)=\sqrt{\frac{m \beta}{2 \pi\left(1-e^{-2 \gamma t}\right)}} \exp \left[-\frac{m \beta\left(v-v_0 e^{-\gamma t}\right)^2}{2\left(1-e^{-2 \gamma t}\right)}\right] \tag{1.4.9}$$

We now have a thorough description of the Brownian particle's velocity, but what about the particle's diffusion? We'd like to know how far away the Brownian particle can be expected to be found from its initial position as time passes. To proceed, we calculate the mean square displacement of the particle from its initial position,

$$\begin{aligned} R^2(t) & =\left\langle(x(t)-x(0))^2\right\rangle \\ & =\int_0^t \int_0^t\left\langle v\left(\tau_1\right) v\left(\tau_2\right)\right\rangle d \tau_2 d \tau_1 \\ & =2 \int_0^t(t-\tau) C(\tau) d \tau \end{aligned}$$

At long times, the mean square displacement behaves as

$$R^2(t)=2 t \int_0^{\infty} C(t) d t \tag{1.4.10}$$

This linear scaling with time is the experimentally observed behavior of Brownian particles, where the proportionality constant is called the diffusion constant D; hence, we have found an expression for the macroscopic diffusion constant D in terms of the correlation function,

$$D=\int_0^{\infty} C(t) d t \tag{1.4.11}$$

Eq. (1.52) is known as the Green-Kubo relation, and it implies that the mean square displacement at long times is simply

$$\lim _{t \gg 1} R^2(t)=2 D t \tag{1.4.12}$$

This result for the mean square displacement also scales linearly with the dimensionality of the system (i.e. in three dimensions, $R^2(t)=6 D t$).

To determine the behavior of $R^2(t)$ at short times, note that $v(t) \approx v(0)$ for short times, so that $R^2(t)=\left(\int v(t) d t\right)^2 \approx\left\langle v_0^2\right\rangle t^2$. Therefore, the short-time limit of the mean square displacement is

$$\lim _{t \ll 1} R^2(t)=\frac{1}{m \beta} t^2 \tag{1.4.13}$$

For times in between these extremes, the formal solution to the Langevin equation for the velocity would have to be integrated. This can be done; sparing the details, the result after thermal averaging is

$$R^2(t)=\frac{2}{\beta \zeta}\left[t-\frac{1}{\gamma}\left(1-e^{-t}\right)\right] \tag{1.4.14}$$

where $\gamma=\frac{\zeta}{m}$.

As a final note, the Langevin equation as presented in this section is often modified to describe more complex systems. The most common modifications to the Langevin equation are:

- The replacement of the friction coefficient ζ with a memory kernel $\gamma(t)$ that allows the system to have some memory of previous interactions.

- The addition of a deterministic mean force $F = -\nabla U$, which permits the system to respond to forces beyond those due to interactions with the bath.

Such modified Langevin equations, also known as Generalized Langevin equations or GLEs, will be explored in further detail in Chapter 4. The Langevin equation and its generalized counterparts provide the basis for a number of successful models of stochastic processes in chemical physics. [3]

1.5: Appendix: Applications to Brownian Motion

Brownian motion is one of the simplest physical examples of a system whose description necessitates a nonequilibrium statistical description. As such, it is the token example that unifies all of the topics in this course, from Markov processes (Ch. 1) and response functions (Ch. 2) to diffusion constants (Ch. 3) and generalized Langevin equations (Ch. 4). In this appendix, the salient features of Brownian motion and the key results about Brownian motion that will be developed during the course are exposited together as a handy reference. Some basic properties of relevant integral transformations are also included in this Appendix.

The discovery of Brownian motion predates the development of statistical mechanics and provided important insight to physicists of the early twentieth century in their first formulations of an atomic description of matter. A fine example of the importance of keeping an eye open for the unexpected in experimental science, Brownian motion was discovered somewhat serendipitously in 1828 by botanist Robert Brown while he was studying pollen under a microscope. Though many others before him had observed the jittery, random motion of fine particles in a fluid, Brown was the first to catalogue his observations [4] and use them to test hypotheses about the nature of the motion.

Interest in the phenomenon was revived in 1905 by Albert Einstein, who successfully related observations about Brownian motion to underlying atomic properties. Einstein’s work on Brownian motion [5] is perhaps the least well known of the four paradigm-shifting papers he published in his "Miracle Year" of 1905, which goes to show just how extraordinary his early accomplishments were (the other three papers described the photoelectric effect, special relativity, and mass-energy equivalence)! Einstein determined that the diffusion of a Brownian particle in a fluid is proportional to the system temperature and inversely related to a coefficient of friction ζ characteristic of the fluid,

$$D=\frac{1}{\beta\zeta} \tag{1.5.1}$$

Any physical description of Brownian motion will boil down to an equation of motion for the Brownian particle. The simplest way, conceptually, to model the system is to perform Newtonian dynamics on the Brownian particle and N particles comprising the fluid, with random initial conditions (positions and velocities) for the fluid particles. By performing such calculations for all possible initial configurations of the fluid and averaging the results, we can obtain the correct picture of the stochastic dynamics. This procedure, however, is impossibly time-consuming in practice, and so a number of statistical techniques, such as Monte Carlo simulation, have been developed to make such calculations more practical.

Alternatively, we can gain qualitative insight into Brownian dynamics by mean-field methods; that is, instead of treating each particle in the fluid explicitly, we can devise a means to describe their average influence on the Brownian particle, circumventing the tedium of tracking each particle’s trajectory independently. This approach gives rise to the Langevin equation of section 1.4, under the assumption that the fluid exerts a random force $f(t)$ on the Brownian particle that obeys the conditions of Gaussian white noise.

For instantaneous (gas-phase) collisions of the fluid and Brownian particle, a Langevin equation with constant frictional coefficient ζ suffices,

$$m\dot{v}(t)+\zeta v(t)=f(t) \tag{1.5.2}$$

However, if fluid-particle collisions are correlated, which is the case for any condensed-phase system, this correlation must be taken into account by imbuing the Brownian particle with memory of its previous interactions, embodied by a memory kernel γ,

$$m\dot{v}(t)+m\int_0^t \gamma(t-\tau)v(\tau)d\tau=f(t) \tag{1.5.3}$$

where $\gamma(t)\rightarrow\zeta\delta(t)$ in the limit of uncorrelated collisions.

We now present some of the key features of Brownian motion. Some of these results are derived in section 1.4; others are presented here for reference. Please consult the references at the end of this chapter for further details about the derivation of these properties.

- Fick’s Law: The spreading of the Brownian particle’s spatial probability distribution over time is governed by Fick’s Law,

$$\frac{\partial}{\partial t}P(\mathbf{r},t)=-D\nabla^2P(\mathbf{r},t) \tag{1.5.4}$$

- Green-Kubo relation: The diffusion constant D is tied to the particle's velocity-velocity correlation function $C(t)$ by the Green-Kubo relation,

$$D=\int_{0}^{\infty} C(t) d t \tag{1.5.5}$$

This essentially means that the diffusion constant is the area under the velocity-velocity correlation curve across all times $t>0$.

- Solution of the Langevin Equation: All of the information we require from the Langevin equation is contained in the correlation function. Multiplication of the Langevin equation for $v\left(t_{1}\right)$ by the velocity $v\left(t_{2}\right)$ yields a differential equation for the correlation function,

$$\dot{C}+\int_{0}^{t} \gamma(t-\tau) C(\tau) d \tau=0 \tag{1.5.6}$$

The Laplace transform of this equation,

$$s \hat{C}(s)-C(0)+\hat{\gamma}(s) \hat{C}(s)=0 \tag{1.5.7}$$

has as its solution

$$\hat{C}(s)=\frac{C(0)}{s+\hat{\gamma}(s)} \tag{1.5.8}$$

where $C(0)$ is the non-transformed velocity-velocity correlation function at $t=0$ and s is the Laplace variable. - Einstein relation: The solution to the Langevin equation tells us that

$$\hat{C}(0)=\frac{C(0)}{\hat{\gamma}(0)} \tag{1.5.9}$$

Additionally, a comparison of the Green-Kubo relation to the formula for the Laplace transform indicates that $C(0)=D$. Finally, we can conclude from the equipartition theorem that $C(0)=\frac{1}{m \beta}$. Combining this information together, we arrive at Einstein's relation,

$$D=\frac{1}{m \beta \hat{\gamma}(0)} \tag{1.5.10}$$

In Chapter 4, the behavior of the velocity-velocity correlation function is explored for the cases in which the fluid is a bath of harmonic oscillators, a simple liquid, and an elastic solid. Their general functional forms are summarized here; further details can be found in Chapter 4 .

- Harmonic oscillators: $C(t)$ is periodic with amplitude $C(0)$ and frequency Ω_{0} (the Einstein frequency), where $\Omega_{0}^{2}=\gamma(0)$.
- Liquids: $C(t)$ exhibits a few oscillations while decaying, eventually leveling out to zero.
- Solids: Like a liquid, $C(t)$ will be damped, but like the harmonic oscillator model, the periodic structure of the solid will prevent $C(t)$ from decaying to zero; some oscillation at the Einstein frequency will continue indefinitely.

Finally, we summarize the response of a Brownian particle to an external force F. The modified Langevin equation for this situation is

$$\dot{v}(t)+\gamma v(t)=\frac{f(t)}{m}+\frac{F(t)}{m} \tag{1.5.11}$$

In general, this Langevin equation is difficult to work with, but many forces of interest (such as EM fields) are oscillatory, so we assume an oscillatory form for the external force,

$$F(t)=F_{\omega} e^{-i \omega t} \tag{1.5.12}$$

Then we can use the techniques developed in Chapter 2 to determine that the velocity in Fourier space is given by

$$\tilde{v}(\omega)=\chi(\omega) \tilde{F}(\omega) \tag{1.5.13}$$

Finally, from this information it can be determined that the response function $K(t)$ is (see Chapter 2)

$$K(t)=\frac{1}{2\pi}\int_0^\infty \frac{e^{-i\omega t}}{-i\omega+\gamma}d\omega=e^{t}\theta(t) \tag{1.5.14}$$

These formulas are the basis for the Debye theory of dipole reorganization in a solvent, in the case where F corresponds to the force due to the electric field $E(\omega)$ generated by the oscillating dipoles.

Integral Transformations: We conclude with a summary of the Laplace and Fourier transforms, which are used regularly in this course and in chemical physics generally to solve and analyze differential equations. 1. Laplace transform: The Laplace transform of an arbitrary function $f(t)$ is

$$\hat{f}(s)=\int_0^\infty e^{-st}f(t)dt \tag{1.5.15}$$

Both the Laplace and Fourier transforms convert certain types of differential equations into algebraic equations, hence their utility in solving differential equations. Consequently, it is often useful to have expressions for the first and second derivatives of $\hat{f}(s)$ on hand:

$$\hat{f}^{(1)}(s)=s\hat{f}(s)-f(0)$$
$$\hat{f}^{(2)}(s)=s^2\hat{f}(s)-sf(0)-\hat{f}^{(1)}(0)$$

A convolution of two functions

$$F(t)=\int_0^t f(t)g(t-\tau)d\tau \tag{1.5.16}$$

is also simplified by Laplace transformation; in Laplace space, it is just a simple product,

$$\hat{F}(s)=\hat{f}(s)\hat{g}(s) \tag{1.5.17}$$

3. Fourier transform: The Fourier transform of an arbitrary function $f(t)$ is

$$\tilde{f}(\omega)=\int_{-\infty}^\infty e^{i\omega t}f(t)dt \tag{1.5.18}$$

Its derivatives are even simpler in structure than those of the Laplace transform:

$$\tilde{f}^{(1)}(\omega)=-i\omega\tilde{f}(\omega)$$
$$\tilde{f}^{(2)}(\omega)=-\omega^2\tilde{f}(\omega)$$

For an even function $f(t)$, the relationship between the Fourier and Laplace transforms can be determined by taking a Laplace transform of f at $s=i\omega$, from which we discover that

$$\tilde{f}(\omega)=2\,\mathrm{Re}\,\hat{f}(-i\omega) \tag{1.5.19}$$

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CHAPTER OVERVIEW

2: Non-equilibrium Thermodynamics

2.1: Response, Relaxation, and Correlation

At the beginning of the 21st century, the thermodynamics of systems far from equilibrium remains poorly understood. However, it turns out that many nonequilibrium phenomena can be described rather well in terms of equilibrium fluctuations; this is especially true of systems near equilibrium $[1, 2]$.

By designating a system as "near equilibrium", we mean that the system is perturbed from its equilibrium state by some time-dependent external force $f(t)$. The external force is deterministic, not random; typical examples include mechanical forces and forces due to an applied electric or magnetic field. This force drives the expectation values of some of the system's observables away from their equilibrium values. For example, a typical observable A affected by the external force might be the system's velocity or its magnetic moment. If the response of the observable A to the external force $f(t)$ satisfies the linearity property

$$\delta A(\lambda f(t), t) = \lambda \delta A(f(t), t) \tag{2.1.1}$$

where $\delta A = A - \langle A \rangle_{eq}$ and λ describes the strength of the force, then we call the time-dependent behavior of A the linear response of A to the external force $f(t)$. The linearity property Eq.(2.1) implies that the shape of the response curve A vs. t is independent of the value of λ in the case of linear response.

After achieving a short-lived nonequilibrium steady state (between t_2 and t_3 in Figure 2.1), the system is allowed to relax back to equilibrium. This process is also known as regression. Linear response and regression of a system driven from equilibrium are both described in terms of the **time correlation function** of the observable A, and so we turn first to the definition and properties of the time correlation function $[3, 4]$.

The time correlation function $C_{AA}\left(t, t'\right)$ of the observable A is defined by

$$C_{AA}\left(t, t'\right) = \langle A(t) A\left(t'\right)\rangle = \frac{\operatorname{Tr}\left[A(t) A\left(t'\right) \rho_{eq}\right]}{\operatorname{Tr}\left[\rho_{eq}\right]} \tag{2.1.2}$$

Here, ρ_{eq} denotes the equilibrium density matrix of the system; hence the average denoted by $\langle\rangle$ is the ensemble average. This function describes how the value of A at time t is correlated to its

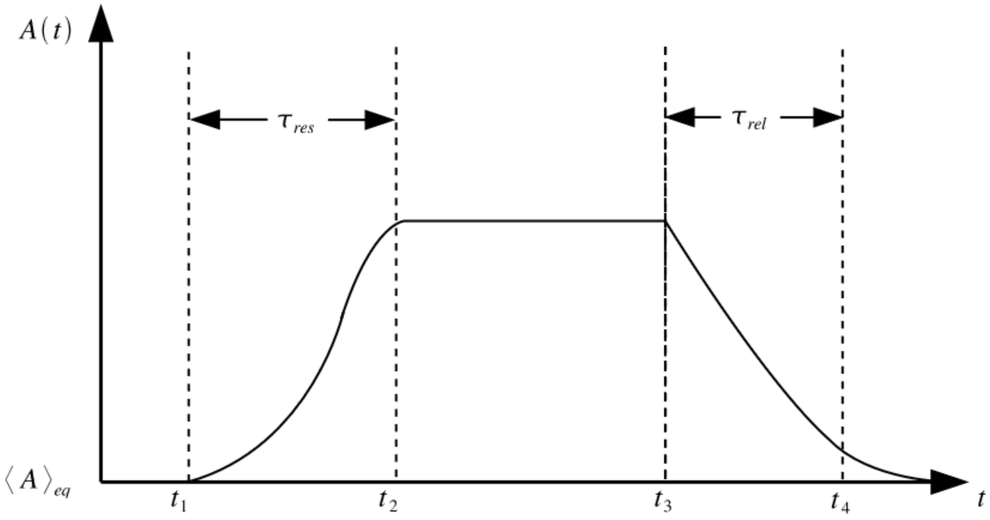

Figure 2.1: Response, nonequilibrium steady state, and relaxation

value at time t'; it is sometimes referred to as the autocorrelation function of A to distinguish it from correlation functions between A and other observables.

For a system which is time-translational invariant, we often choose for convenience to set $t' = 0$ and to drop the subscript on C_{AA}, so that the time correlation function becomes simply

$$C(t) = \langle A(t) A(0) \rangle \tag{2.1.3}$$

The correlation function may in general take on complex values. This result is in keeping with our phenomenological understanding of quantum mechanics in the following way. In order to measure the correlation function of an observable A, the quantity A must be measured twice (first at time zero, then again at time t). However, the first measurement at $t=0$ collapses the system wavepacket, and the state that would have been exhibited by the unperturbed system at time t becomes irrecoverable.

We now identify some important features and properties of correlation functions.

1. All inner products $\langle X \mid Y\rangle$ satisfy the Schwarz inequality

$$|\langle X \mid Y\rangle|^2 \leq \left\langle X^2\right\rangle\left\langle Y^2\right\rangle \tag{2.1.4}$$

Thus the correlation function for any relaxation process has the property

$$C^2(t)=|\langle A(t) \mid A(0)\rangle|^2 \leq\left\langle A^2(t) A^2(0)\right\rangle \leq\left\langle A^2(0)\right\rangle^2=C^2(0) \tag{2.1.5}$$

The second inequality above arises from the fact that $A^2(t)<A^2(0)$ for relaxation processes when $t>0$. More concisely, the Schwarz inequality implies that

$$|C(t)| \leq C(0) \tag{2.1.6}$$

3. Correlation functions are time-invariant, that is, their value depends only on the time interval between the two measurements of the observable:

$$\langle A(t) A(0)\rangle=\left\langle A\left(t-t_0\right) A\left(t_0\right)\right\rangle=\langle A(0) A(-t)\rangle \tag{2.1.7}$$

4. Time-invariance imparts the following identities on the time derivative of a time correlation function:

$$\dot{C}(t)=\langle\dot{A}(t) A(0)\rangle=-\langle A(0) \dot{A}(-t)\rangle=-\langle A(t) \dot{A}(0)\rangle \tag{2.1.8}$$

5. If the equilibrium value of A is $\langle A\rangle_{eq}=0$, then the long-time limit of the correlation function is zero,

$$\lim_{t \rightarrow \infty}\langle A(t) A(0)\rangle=\langle A\rangle_{eq}\langle A(0)\rangle=0 \tag{2.1.9}$$

6. For quantum systems, the time-invariance properties imply that $C(-t)=C^*(t)$. In the classical limit, the correlation function is always real-valued, so this relation becomes $C(-t)=C(t)$ and $C(t)$ is thus even. The fact that classical correlation functions are real-valued should seem sensible because we can (and do) measure correlation functions every day for classical systems, for example, when we try to steady a cord dangling from the ceiling. In this case, we determine the appropriate time and place to apply an external steadying force by looking for time correlations between the various motions the cord undergoes. Note that $C(t)$ is odd with $C(0)=0$ for classical time correlation functions.
7. For ergodic systems, the time correlation function can be calculated as a time average instead of an ensemble average:

$$\langle A(t) A(0)\rangle=\lim_{\tau \rightarrow \infty} \frac{1}{\tau} \int_0^\tau A\left(t+\tau^{\prime}\right) A\left(\tau^{\prime}\right) d \tau^{\prime} \tag{2.1.10}$$

Since most systems amenable to analysis by the methods of statistical mechanics are inherently ergodic, we are generally free to choose whichever formulation is easier to work with. The time average is often easier to implement experimentally because it only requires integration along a trajectory rather than a simultaneous sampling of every state accessible to the system.

Example: The classical linear harmonic oscillator with mass m and frequency ω obeys the equation of motion

$$\ddot{x}+\omega^2 x=0 \tag{2.1.11}$$

If we provide initial conditions $x(0)$ and $\dot{x}(0)=v(0)$, then this equation of motion has the closed-form solution

$$x(t)=x(0) \cos \omega t+\frac{v(0)}{\omega} \sin \omega t \tag{2.1.12}$$

Taking the inner product of $x(t)$ with the initial value $x(0)$, we find

$$\langle x(t) x(0)\rangle=\left\langle x^2(0)\right\rangle \cos \omega t+\frac{\langle v(0) x(0)\rangle}{\omega} \sin \omega t \tag{2.1.13}$$

The second term is zero because $\langle x(0)\rangle=0$, so the time correlation function is just

$$C(t)=\left\langle x^2(0)\right\rangle \cos \omega t \tag{2.1.14}$$

Finally, invoking the equipartition result $\left\langle x^{2}(0)\right\rangle=\frac{kT}{m\omega^{2}}$, where k is the Boltzmann constant, the correlation function for the classical linear harmonic oscillator is

$$C(t)=\frac{kT}{m\omega^{2}}\cos\omega t \tag{2.1.15}$$

2.2: Onsager Regression Theory

At first glance, the relaxation of macroscopic non-equilibrium disturbances in a system might seem completely unrelated to the regression of microscopic fluctuations in the corresponding equilibrium system. However, they are intimately related by so-called **fluctuation-dissipation theorems**. The existence of this link between microscopic fluctuations and macroscopic relaxation was conjectured by Lars Onsager in 1931, some twenty years before it was finally proven to be true; hence it is often referred to as the **Onsager regression hypothesis**.

To formulate the hypothesis, we consider an observable A with $\langle A\rangle_{eq} = 0$ that takes on a nonequilibrium average value ΔA due to an applied external force f which acts during the time interval $t \leq 0$ but becomes identically zero for $t > 0$.

For $t \leq 0$, the ensemble average of ΔA can be expressed as

$$\Delta A = \frac{\left\langle A e^{-\beta(H-fA)}\right\rangle}{\left\langle e^{-\beta(H-fA)}\right\rangle} \approx \beta f\left[\langle A(0)A(0)\rangle - \langle A(0)\rangle^2\right] = \beta f C(0) \tag{2.2.1}$$

where the approximation being made is truncation of the Taylor series for each exponential to first order.

For $t > 0$, the system evolves according to H instead of $H - fA$, so ΔA is no longer stationary, but acquires a time-dependence:

$$\Delta A = \frac{\left\langle A(t) e^{-\beta(H-fA)}\right\rangle}{\left\langle e^{-\beta(H-fA)}\right\rangle} \approx \beta f\left[\langle A(t)A(0)\rangle - \langle A(0)\rangle^2\right] = \beta f C(t) \tag{2.2.2}$$

Onsager’s hypothesis states that the relaxation of the non-equilibrium value of ΔA is related to its value at $t = 0$ in the same way that the time correlation function for a spontaneous fluctuation is related to its value at $t = 0$:

$$\frac{\Delta A(t)}{\Delta A(0)} = \frac{C(t)}{C(0)} \tag{2.2.3}$$

Example 2.2.1

The transition state theory of chemical kinetics can be formulated through the Onsager relation we’ve just presented. Consider a chemical equilibrium established between two species A and B,

$$\mathrm{A} \underset{k_b}{\overset{k_f}{\rightleftharpoons}} \mathrm{B} \tag{2.2.4}$$

with forward rate constant k_f and backward rate constant k_b.

Equilibrium populations

We can describe the population dynamics of A and B deterministically in the macroscopic limit through a pair of coupled differential equations,

$$\begin{cases} \dot{P}_\mathrm{A} = -k_f P_\mathrm{A} + k_b P_\mathrm{B} \\ \dot{P}_\mathrm{B} = k_f P_\mathrm{A} - k_b P_\mathrm{B} \end{cases} \tag{2.2.5}$$

The equilibrium state of this system satisfies the detailed balance condition

$$k_f \langle P_\mathrm{A}\rangle = k_b \langle P_\mathrm{B}\rangle \tag{2.2.6}$$

where the angle brackets denote the equilibrium values of the populations. Taking the populations to be normalized to unity, $\langle P_\mathrm{A}\rangle + \langle P_\mathrm{B}\rangle = 1$, we can express $\langle P_\mathrm{A}\rangle$ in terms of the rate constants:

$$\langle P_\mathrm{A}\rangle = \frac{\langle P_\mathrm{A}\rangle}{\langle P_\mathrm{A}\rangle + \langle P_\mathrm{B}\rangle} = \frac{k_b}{k_f + k_b} \tag{2.2.7}$$

For notational simplicity, we introduce $k = k_f + k_b$ and refer to the equilibrium populations $\langle P_\mathrm{A}\rangle$ and $\langle P_\mathrm{B}\rangle$ by q_A and q_B, respectively. With this new notation, we can express the equilibrium populations of A and B as

$$\begin{cases} q_{\mathrm{A}} = \frac{k_b}{k} \\ q_{\mathrm{B}} = \frac{k_f}{k} \end{cases} \tag{2.2.8}$$

If the initial state is all species A, the solution to the coupled differential equations indicates a decay to equilibrium with rate constant k, which we can write in terms of $\Delta P_{\mathrm{A}}(t) = P_{\mathrm{A}}(t) - q_{\mathrm{A}}$ as

$$\Delta P_{\mathrm{A}}(t) = \Delta P_{\mathrm{A}}(0) e^{-kt} \tag{2.2.9}$$

Setting this result aside for a moment, note that if we consider the energies of species A and B to be potential wells connected along a reaction coordinate x, then we can write down an expression for the fluctuation in occupation number n for each species as a function of x. The barrier between the A and B potential wells is a maximum at $x = x_b$; see Figure 2.2.

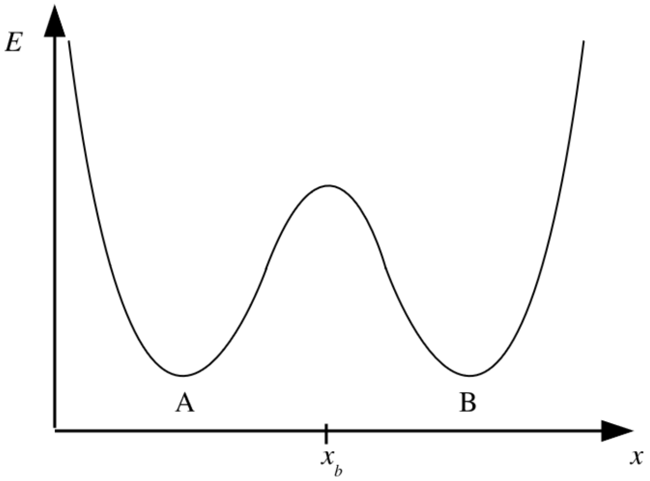

Figure 2.2: Projection of the potential energy surface connecting species A and B along reaction coordinate x

Application of Onsager Regression hypothesis

To reflect the fact that a particle to the left of the barrier is species A and a particle to the right is species B, we write the occupation numbers in terms of the Heaviside step function,

$$\begin{cases} n_{\mathrm{A}} = \theta(x_b - x) \\ n_{\mathrm{B}} = \theta(x - x_b) \end{cases} \tag{2.2.10}$$

where $\langle n_{\mathrm{A}} \rangle = q_{\mathrm{A}}$ and $\langle n_{\mathrm{B}} \rangle = q_{\mathrm{B}}$. Applying Onsager's regression hypothesis to this example, we can relate the dissipation of P_{A} to the fluctuations in occupation number as follows:

$$\frac{C(t)}{C(0)} = \frac{\langle \delta n_{\mathrm{A}}(t) \delta n_{\mathrm{A}}(0) \rangle}{\langle \delta n_{\mathrm{A}}^2(0) \rangle} = \frac{\Delta P_{\mathrm{A}}(t)}{\Delta P_{\mathrm{A}}(0)} = e^{-kt} \tag{2.2.11}$$

The second equality arises from our integrated rate equation for the dissipation of P_{A}. Also note that

$$\langle \delta n_{\mathrm{A}}^2 \rangle = \langle n_{\mathrm{A}}^2 \rangle - \langle n_{\mathrm{A}} \rangle^2 = q_{\mathrm{A}} - q_{\mathrm{A}}^2 = q_{\mathrm{A}} - q_{\mathrm{A}}(1 - q_{\mathrm{B}}) = q_{\mathrm{A}} q_{\mathrm{B}} \tag{2.2.12}$$

Differentiating the fluctuation-dissipation relation above with respect to t and invoking the identity just shown, we find

$$ke^{-kt} = -\frac{\langle \delta \dot{n}_{\mathrm{A}}(t) \delta n_{\mathrm{A}}(0) \rangle}{\langle \delta n_{\mathrm{A}}^2(0) \rangle} = \frac{\langle n_{\mathrm{A}}(t) \dot{n}_{\mathrm{A}}(0) \rangle}{q_{\mathrm{A}} q_{\mathrm{B}}} \tag{2.2.13}$$

Recasting this equation in terms of the reaction coordinate x, we arrive at an expression for the time dependence of the forward rate constant $k_f(t)$,

$$k_f(t) = k_f e^{-kt} = \frac{\langle \theta(x(t) - x_b) \delta(x_b - x(0)) v \rangle}{\langle \theta(x_b - x(t)) \rangle} \tag{2.2.14}$$

where $v = \dot{n}_{\mathrm{A}}(0)$ is the initial rate of reaction.

Expression for the TST rate constant

Finally, to determine the transition state theory (TST) rate constant, we consider our time-dependent expression for k_f in the short-time limit, since transition states typically only survive a few molecular vibrations. In this limit,

$$\lim_{t\to 0^+} k_f(t) = \frac{\langle \theta\left(x\left(0^+\right)-x_b\right)\delta\left(x_b-x(0)\right)v\rangle}{\langle n_{\mathrm{A}}\rangle} = \frac{\langle \theta(v)\delta\left(x_b-x(0)\right)v\rangle}{\langle n_{\mathrm{A}}\rangle} \tag{2.2.15}$$

From the kinetic theory of gases, we recognize that

$$\langle \theta(v)v\rangle = \sqrt{\frac{k_B T}{2\pi m}} = (2\pi m\beta)^{-1/2} \tag{2.2.16}$$

If we stipulate now that the height of the barrier is E_b, some rearrangement of the preceding formulas reveals that

$$\frac{\langle \delta\left(x_b-x\right)\rangle}{\langle \theta\left(x_b-x\right)\rangle} = \sqrt{\frac{m\omega^2\beta}{2\pi}}e^{-\beta E_b} \tag{2.2.17}$$

where ω is the fundamental frequency of the left potential well. It follows that the TST rate constant takes on the simple form

$$k_{TST} = \frac{\omega}{2\pi}e^{-\beta E_b} \tag{2.2.18}$$

To conclude our excursion into TST kinetics, note that the ratio

$$\frac{k(t)}{k_{TST}} = \frac{\langle \theta\left(x(t)-x_b\right)\delta\left(x(0)-x_b\right)v\rangle}{\langle \theta\left(x\left(0^+\right)-x_b\right)\delta\left(x(0)-x_b\right)v\rangle} \tag{2.2.19}$$

is always less than or equal to one. This result indicates that the TST flux is partially trapped in the product well while part of the TST flux recrosses back to the reactant state. This result is in keeping with our intuition of chemical dynamics in that every macroscopic reaction is, to some degree, a process of establishing equilibrium rather than a perfect flow from all reactants to all products.

2.3: Linear Response Theory and Causality

The concept of linear response was introduced in section 2.1. Here, we explore further how the linear response of a system is quantified by considering the important relations regularly invoked by practitioners of linear response theory.

Response Functions

The motivating idea behind linear response is that the response of a system to an external force depends on the strength of that force at all times during which the force acts on the system. That is, the response at time t depends on the history of the force's action on the system. An appropriately weighted sum of the strength of the external force at each moment during the interaction will describe the overall response. Mathematically, therefore, we express the response as an integral over the history of the interaction,

$$\Delta A(t) = \int_{-\infty}^{\infty} K(t,\tau) f(\tau) d\tau \tag{2.3.1}$$

The kernel $K(t,\tau)$ in this expression, which provides the weight for the strength of the external force at each time, is called the response function. The response function has two very important properties:

- **Time invariance**: K depends only on the time interval between τ and t, not on the two times independently. More succinctly,
$$K(t,\tau) = K(t-\tau) \tag{2.3.2}$$
- **Causality**: The system cannot respond until the force has been applied. This places an upper limit of t on the integration over the history of the external force.

With these observations in place, we arrive at the standard formula describing the linear response of an observable A to an external force $f(t)$,

$$\Delta A(t) = \int_{-\infty}^{t} K(t-\tau) f(\tau) d\tau \tag{2.3.3}$$

Linear response - described by the response function $K(t)$ - and linear regression - described by the time correlation function $C(t)$ - are directly related to one another. To see the connection, consider a force $f(t)$ which is constant with strength f for $t \leq 0$ and is zero for $t > 0$. We have established two ways to describe the response of an observable A to this force:

- **Linear regression**: $\Delta A(t) = \beta f C(t)$
- **Linear response**: $\Delta A(t) = \int_{-\infty}^{0} K(t-\tau) f(\tau) d\tau$

From this information, we conclude that the correlation function and response function are related by

$$K(t) = -\beta \dot{C}(t) \theta(t) \tag{2.3.4}$$

where $\theta(t)$ is the Heaviside function.

Sometimes the linear response function is more conveniently expressed in the frequency domain, in which case it is called the frequency-dependent response function. In many physical situations, it plays the role of a susceptibility to a force and consequently is denoted by $\chi(\omega)$,

$$\chi(\omega) = \int_{0}^{\infty} e^{i\omega t} K(t) dt \tag{2.3.5}$$

This response function is often partitioned into real and imaginary parts, which can also be thought of as even and odd parts, respectively,

$$\chi(\omega) = \chi'(\omega) + i\chi''(\omega) \tag{2.3.6}$$

Example: The response function for the classical linear harmonic oscillator can be quickly deduced from its time correlation function. Recall from the first example in this chapter that the time correlation function for the classical linear harmonic oscillator is

$$C(t) = \frac{k_B T}{m\omega^2} \cos \omega t \tag{2.3.7}$$

Applying Eq.(2.17), we differentiate with respect to t and multiply by $\beta = \frac{1}{k_B T}$ to determine that

$$K(t) = \frac{1}{m\omega}\sin(\omega t)\theta(t) \tag{2.3.8}$$

This is the response function for the classical linear harmonic oscillator.

Absorption Power Spectra

The frequency-dependent response function is directly related to the absorption spectrum: in fact, knowledge of $\chi(\omega)$ and the time-dependent external force $f(t)$ is sufficient to fully describe the absorption spectrum.

The rate at which work is done on a system by a generalized external force $f(t)$ is $f(t)\dot{A}(t)$, where A is the observable corresponding to the generalized force f. This quantity has units of power, so we can calculate the total absorption energy by integrating this power over time,

$$\int P(t)dt = \int f(t)\dot{A}(t)dt \tag{2.3.9}$$

To recast this result in terms of $\chi(\omega)$, we first consider the Fourier transform of the time-dependent observable A,

$$\tilde{A}(\omega) = \int e^{it} A(t)dt \tag{2.3.10}$$

Applying Eq.(2.16), we have

$$\tilde{A}(\omega) = \int e^{i\omega t} \int K(t-\tau)f(\tau)d\tau dt \tag{2.3.11}$$

The following rearrangements allow us to express $\tilde{A}(\omega)$ entirely in terms of frequency-dependent functions:

$$\begin{aligned}\tilde{A}(\omega) &= \iint e^{i\omega(t-\tau)} e^{i\tau} K(t-\tau)f(\tau)d\tau dt \\ &= \int e^{i\omega(t-\tau)} K(t-\tau)d(t-\tau) \int e^{i\omega\tau} f(\tau)dt \\ &= \chi(\omega)\tilde{f}(\omega)\end{aligned}$$

where $\tilde{f}(\omega)$ is the Fourier transform of $f(t)$. Returning to Eq. (2.20) for the absorption energy,

$$\int P(t)dt = \int f(t)\dot{A}(t)dt = \frac{1}{2\pi}\int \tilde{f}(-\omega)\tilde{\dot{A}}(\omega)d\omega \tag{2.3.12}$$

Rearranging the expression once again and evaluating the integral over time yields

$$\begin{aligned}\int P(t)dt &= \frac{1}{2\pi}\int(-i\omega)\tilde{f}(-\omega)\tilde{A}(\omega)d\omega \\ &= \frac{1}{2\pi}\int(-i\omega)\chi(\omega)|\tilde{f}(\omega)|^2 d\omega \\ &= \frac{1}{2\pi}\int \omega\chi''(\omega)|\tilde{f}(\omega)|^2 d\omega\end{aligned}$$

Hence the absorption power spectrum $P(\omega)$ has the form

$$P(\omega) = \omega\chi''(\omega)|\tilde{f}(\omega)|^2 \tag{2.3.13}$$

Example: For a monochromatic force $F(t) = F\cos\omega_0 t$, the Fourier transform of $F(t)$ is given by

$$\tilde{F}(\omega) = F\pi\left[\delta(\omega-\omega_0) + \delta(\omega+\omega_0)\right] \tag{2.3.14}$$

Hence our expression for the absorption power spectrum Eq.(2.30) tells us that the absorption rate (i.e. the time average of $P(t)$) for such a system is

$$\lim_{\tau\to\infty}\frac{1}{\tau}\int_0^\tau P(t)dt = \frac{\omega}{2}\chi''(\omega)|F|^2 \tag{2.3.15}$$

Furthermore, using Eq. (2.17) and the fact that $\chi''(\omega)$ is odd, we find that

$$\begin{aligned}\chi''(\omega) &= \int_0^\infty \sin\omega t K(t)dt \\ &= \int_0^\infty \sin\omega t(-\beta\dot{C}(t))dt \\ &= \beta\omega\int_0^\infty C(t)\cos\omega t dt \\ &= \frac{\beta\omega}{2}\int_{-\infty}^\infty e^{i\omega t}C(t)dt \\ &= \frac{\beta\omega}{2}\tilde{C}(\omega)\end{aligned}$$

This simple relationship illustrates the close connection between frequency-dependent response functions (or susceptibilities) and time correlation functions.

Causality and the Kramers-Kronig Relations

Our final consideration in this chapter is the relationship between the real and imaginary parts of the frequency-dependent response function as defined in Eq.(2.19). The equations relating these two functions are known as the **Kramers-Kronig relations**. In their most general form, they govern the response function as a function of the complex frequency $z = \omega + i\epsilon$, though under most physical circumstances of interest they can be expressed in terms of real-valued frequencies alone.

The relations arise from the causality requirement, which we originally expressed by requiring $K(t) = 0, \forall t < 0$. It turns out that this requirement, along with the assumption that $\int_0^\infty K(t)dt$ converges, implies that the response function $\chi(z)$ is analytic on the upper half of the complex plane.

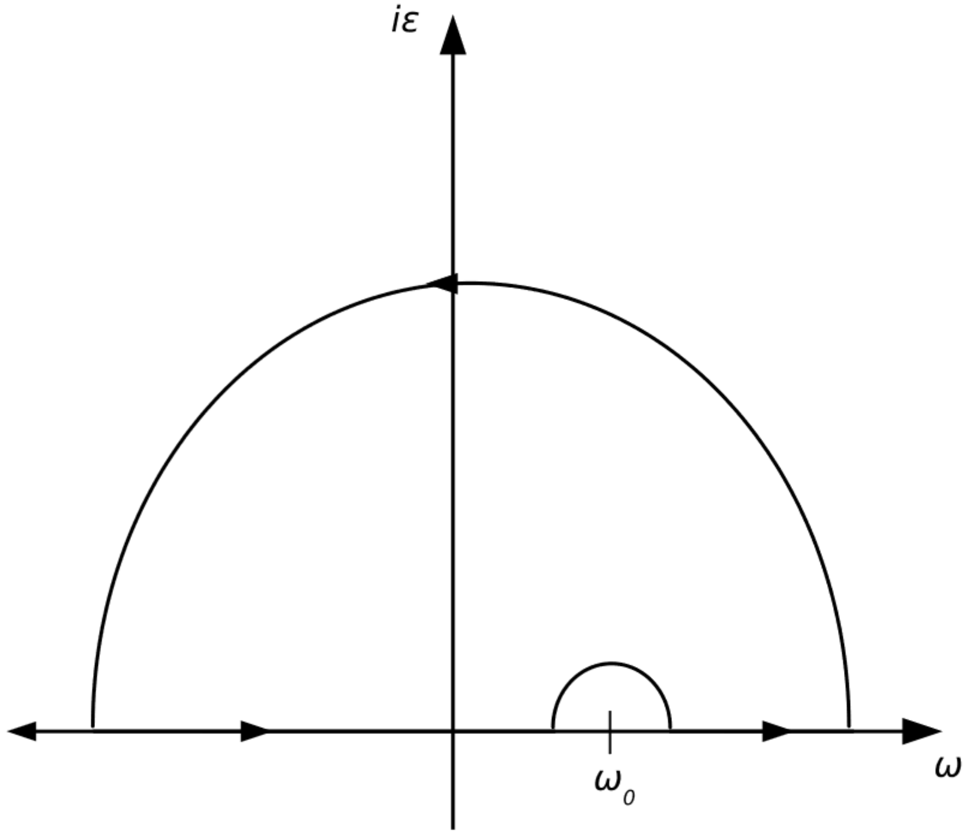

Figure 2.3: Contour in the complex frequency plane used to motivate the Kramers-Kronig relations

We can also, however, integrate piecewise over each part of the contour; some manipulation with the residue theorem is required, but the final result is

$$\oint \frac{\chi(z)}{z-\omega_0} dz = \mathcal{P} \int_{-\infty}^{\infty} \frac{\chi(z)}{z-\omega_0} dz - i\pi\chi\left(\omega_0\right) \tag{2.3.16}$$

where $\mathcal{P}$ denotes the Cauchy principal value of the integral. Setting the two results above equal and solving for the response function,

$$\chi(\omega) = \frac{1}{i\pi} \mathcal{P} \int_{-\infty}^{\infty} \frac{\chi(z)}{z-\omega} dz \tag{2.3.17}$$

The decomposition of Eq.(2.33) into real and imaginary parts yields the Kramers-Kronig relations,

$$\begin{aligned} \chi'(\omega) &= \frac{1}{\pi} \mathcal{P} \int_{-\infty}^{\infty} \frac{\chi''(z)}{z-\omega} dz \\ \chi''(\omega) &= -\frac{1}{\pi} \mathcal{P} \int_{-\infty}^{\infty} \frac{\chi'(z)}{z-\omega} dz \end{aligned}$$

As promised, this pair of equations provides a concise relationship between the real and imaginary parts of any response function $\chi(\omega)$.

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CHAPTER OVERVIEW

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].

Thumbnail: Scheme of Rayleigh scattering.

3.1: Light Scattering

Scattering and Correlation Functions

A particle or light field propagating through space can be described by a wave vector $\vec{k}$. The direction of k indicates the direction of propagation of the wave, and the magnitude of 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.

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 $\overrightarrow{k_o}$ is scattered from the sample at point $\vec{r}$, changing its wave vector to $\overrightarrow{k_f}$. The vector $\overrightarrow{k_f}$ has the same magnitude as $\overrightarrow{k_o}$, but a different direction. The scattered light is detected at point $\overrightarrow{r'}$.

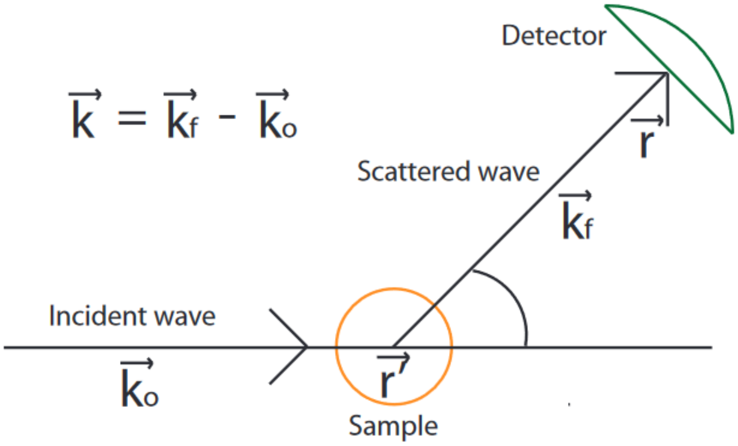

Figure 3.1: Elastic Scattering of a particle or light field from a medium

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

$$\Psi_s = \frac{i}{\hbar} \int \frac{e^{ik\left|\vec{r}-\overrightarrow{r'}\right|}}{\left|\vec{r}-\overrightarrow{r'}\right|} e^{i\overrightarrow{k_o}\cdot\overrightarrow{r'}} \rho\left(\overrightarrow{r'}\right) d\overrightarrow{r'} \tag{3.1.1}$$

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 $r >> r'$. Then

$$e^{ik\left|\vec{r}-\vec{r}'\right|} \rightarrow e^{ikr-i\overrightarrow{k_f}\cdot\overrightarrow{r'}} \tag{3.1.2}$$

and the wavefunction can be written

$$\Psi_s = \frac{i}{\hbar} \frac{e^{ikr}}{r} \int \rho\left(\overrightarrow{r'}\right) e^{-i\left(\overrightarrow{k_f}-\overrightarrow{k_o}\right)\cdot\overrightarrow{r'}} d\overrightarrow{r'} = \frac{i}{\hbar} \frac{e^{ikr}}{r} \int \rho\left(\overrightarrow{r'}\right) e^{-i\vec{k}\cdot\vec{r}'} d\overrightarrow{r'} \tag{3.1.3}$$

where $\vec{k}=\overrightarrow{k_f}-\overrightarrow{k_o}$ 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

$$\rho(\vec{r})=\sum_{i=1}^{N} a_i \delta\left(\vec{r}-\vec{r}_i\right)=a \sum_{i=1}^{N} \delta\left(\vec{r}-\vec{r}_i\right) \tag{3.1.4}$$

Then the wavefunction simplifies to

$$\Psi_s=\frac{i}{\hbar} \frac{e^{ikr}}{r} a \sum_{i=1}^{N} e^{-i\vec{k}\cdot\overrightarrow{r_i}} \propto a \sum_{i=1}^{N} e^{-i\vec{k}\cdot\overrightarrow{r_i}} \tag{3.1.5}$$

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:

$$I(\vec{k})=\left|\Psi_s\right|^2 \propto \frac{1}{r^2} \frac{d\sigma}{d\Omega}=\frac{a^2}{r^2}\left\langle\sum_{i=1}^{N} e^{-i\vec{k}\cdot\vec{r}_i}\right|^2\right\rangle=\frac{a^2}{r^2} N S(\vec{k}) \tag{3.1.6}$$

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

$$S(\vec{k})=\frac{1}{N}\left\langle\left|\sum_{i=1}^{N} e^{-i\vec{k}\cdot\vec{r}_i}\right|^2\right\rangle \tag{3.1.7}$$

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

The Static Structure Factor

The static structure factor can be rewritten as:

$$S(k)=\frac{1}{N}\left\langle\rho_k \rho_{-k}\right\rangle \tag{3.1.8}$$

where

$$\rho_k=\int e^{-i\vec{k}\cdot\vec{r}} \rho(\vec{r}) d\vec{r} \tag{3.1.9}$$

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 $\delta\rho$.

$$\rho(r)=\rho_o+\delta\rho \tag{3.1.10}$$

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

$$S(k)=\frac{1}{N}\left\langle\rho_k \rho_{-k}\right\rangle=\rho_0(2\pi)^3 \delta(\vec{k})+\frac{1}{N}\left\langle\delta\rho_k \delta\rho_{-k} \mid\right\rangle \tag{3.1.11}$$

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.

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

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:

$$\begin{aligned} G(\vec{r}) &= \frac{1}{N}\sum_{i,j}\int d\overrightarrow{r_o}\left\langle\delta\left(\overrightarrow{r_i}-\overrightarrow{r_o}-\vec{r}\right)\delta\left(\overrightarrow{r_j}-\overrightarrow{r_o}\right)\right\rangle \\ &= \frac{1}{N}\int d\overrightarrow{r_o}\left\langle\rho\left(\overrightarrow{r_o}+\vec{r}\right)\rho\left(\overrightarrow{r_o}\right)\right\rangle = \frac{V}{N}\langle\rho(\vec{r})\rho(0)\rangle = \frac{1}{\rho_o}\langle\rho(\vec{r})\rho(0)\rangle \end{aligned}$$

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:

$$g(r) = \frac{1}{N^2}\sum_{i\neq j}\left\langle\delta\left(\vec{r}-\vec{r}_{i,j}\right)\right\rangle \tag{3.1.12}$$

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:

$$g(r) = h(r)+1 \tag{3.1.13}$$

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

$$\tilde{g}(\vec{k}) = \tilde{h}(\vec{k})+(2\pi)^3\delta(\vec{k}) \tag{3.1.14}$$

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

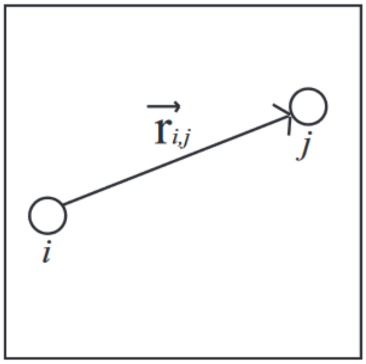

Figure 3.2: The pair distribution function

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:

$$S(k) = \frac{1}{N}\sum_{i,j}\left\langle e^{-ikr_i}e^{ikr_j}\right\rangle \tag{3.1.15}$$

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 .

$$S(k)=1+\sum_{i\neq j}\left\langle e^{-ik(r_i-r_j)}\right\rangle=1+\rho\tilde{g}(k)=1+\rho\tilde{h}(\vec{k})+(2\pi)^3\delta(\vec{k})\rho \tag{3.1.16}$$

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:

$$G(\vec{r})=\frac{1}{N}\left\langle\sum_{i,j}\delta\left(r_{i,j}-r\right)\right\rangle \tag{3.1.17}$$

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 $\delta(\vec{r})$.

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

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.

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.

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:

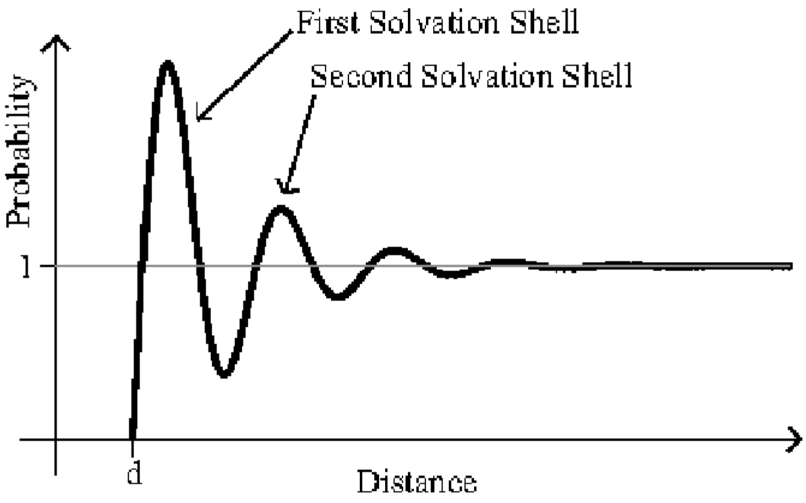

Figure 3.3: Pair Distribution Function for a Liquid

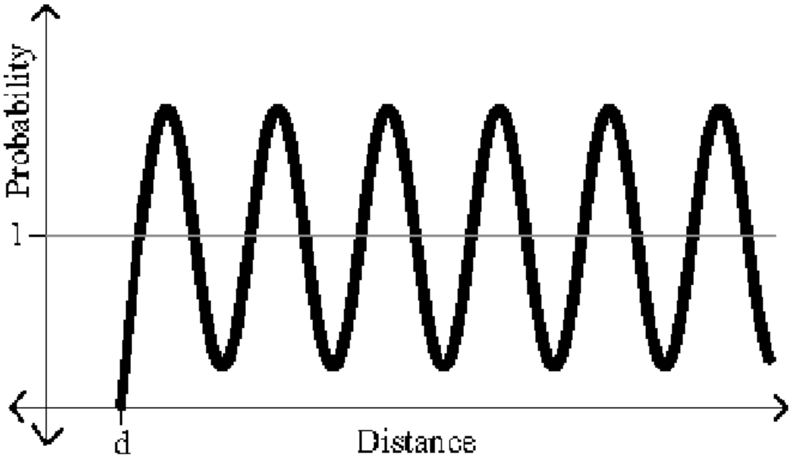

Figure 3.4: Pair Distribution Function for a Solid

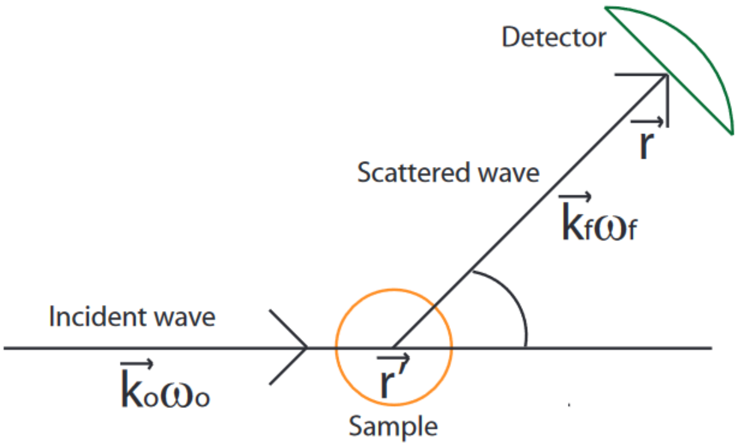

Figure 3.5: Schematic of an Inelastic Scattering Event

$$\Psi_s \propto \frac{a}{r}\sum_{i=1}^{N} e^{-i\vec{k}\cdot\vec{r}_i(t)} \tag{3.1.18}$$

which gives a differential cross-section of:

$$\frac{d\sigma}{d\Omega d\omega} = a^2 \left\langle \sum_i e^{-i\vec{k}\cdot\overrightarrow{r_i}(t)} \sum_j e^{-i\vec{k}\cdot\overrightarrow{r_j}(t)} \right\rangle \tag{3.1.19}$$

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

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

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.

The Intermediate Scattering Function

The intermediate scattering function is defined as the Fourier transform of the dynamic structure factor into real time.

$$\begin{aligned}F(\vec{k}, t) &= \frac{1}{2\pi} \int S(\vec{k}, \omega) e^{i\omega t} d\omega \\ S(\vec{k}, \omega) &= \int F(\vec{k}, t) e^{-i\omega t} dt\end{aligned}$$

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

$$F(\vec{k}, t) = \frac{1}{N} \langle \rho_k(t) \rho_{-k}(0) \rangle \tag{3.1.20}$$

where:

$$\rho_k(t) = \sum_i e^{-i\vec{k}\cdot\overrightarrow{r_i}(t)} \tag{3.1.21}$$

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

The Van Hove Function

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

$$G(\vec{r}, t) = \frac{1}{(2\pi)^3} \int F(\vec{k}, t) e^{i\vec{k}\cdot\vec{r}} d\vec{k} = \frac{1}{N} \sum_{i,j} \left\langle \delta\left(\vec{r}_i(t) - \overrightarrow{r_j}(0) - \vec{r}\right) \right\rangle \tag{3.1.22}$$

The Van Hove Function can also be expressed as

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

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

Name	Symbol	Spatial Dimension	Temporal Dimension
Van Hove Function	$G(\vec{r}, t)$	Real, $\vec{r}$	Real, t

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

$$S(\vec{k}) = \frac{1}{2\pi}\int S(\vec{k}, \omega)d\omega = F(\vec{k}, 0) \tag{3.1.23}$$

This gives the spatial structure.

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

$$\rho = \rho_o + \delta\rho \tag{3.1.24}$$

Then the dynamic structure factor can be expressed as

$$S(\vec{k}, w) = (2\pi)^4\delta(\vec{k})\delta(\omega)\rho_o + \int e^{i\omega t}\frac{1}{N}\langle\delta\rho_k(t)\delta\rho_{-k}(0)\rangle\, dt \tag{3.1.25}$$

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

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:

$$N=\int_V \rho(\vec{r})d\vec{r} \tag{3.2.1}$$

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

$$\frac{dN}{dt}=J_{in}-J_{out}=-\oint_{\partial V}\vec{J}\cdot d\vec{S}=-\int\vec{\nabla}\cdot\vec{J}\,dV \tag{3.2.2}$$

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

$$\frac{dN}{dt}=\int\frac{d\rho}{dt}d\vec{r}=-\int\vec{\nabla}\cdot\vec{J}\,dV \tag{3.2.3}$$

Remove the spacial integration and rearrange

$$\frac{d\rho}{dt}+\vec{\nabla}\cdot\vec{J}=0 \tag{3.2.4}$$

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

$$\nabla\vec{J}=\vec{\nabla}\cdot(\rho\vec{v}) \tag{3.2.5}$$

Then the conservation of mass is given by:

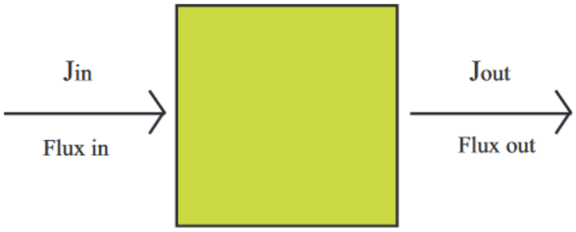

Figure 3.6: The flow of material into and out of a fixed region of space

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.

$$\frac{\partial\rho A}{\partial t}+\vec{\nabla}\cdot\vec{J}=\sigma \tag{3.2.6}$$

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 $\vec{J}_D$.

$$\vec{J}=\vec{J}_V+\vec{J}_D \tag{3.2.7}$$

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

$$\sigma=\sigma_{\text{ext}}+\sigma_D \tag{3.2.8}$$

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

$$\frac{\partial\rho A}{\partial t}+\vec{\nabla}\cdot(\rho A\vec{v})+\vec{\nabla}\cdot\vec{J}_D=\sigma_{ext}+\sigma_D \tag{3.2.9}$$

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

$$A=\{1,m\vec{v},S\} \tag{3.2.10}$$

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.

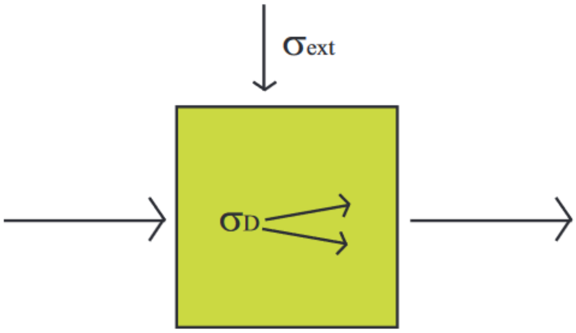

Figure 3.7: The flow and forces for a dynamic quantity

Momentum Equation (Navier-Stokes equations)

To find the continuity equation for momentum, substitute $A=m\vec{v}$ into the general continuity equation.

$$\frac{\partial \rho m\vec{v}}{\partial t}+\vec{\nabla}\cdot(\rho m\vec{v}:\vec{v})+\vec{\nabla}\cdot\overrightarrow{J}_{D}=\vec{\sigma}_{ext}+\vec{\sigma}_{D} \tag{3.2.11}$$

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

$$\vec{\sigma}_{\text{ext}}=\rho\vec{F}-\vec{\nabla}P \tag{3.2.12}$$

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

$$\overrightarrow{J}_{V}=(\rho m\vec{v}:\vec{v}) \tag{3.2.13}$$

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

$$m\frac{\partial\rho\vec{v}}{\partial t}+\vec{\nabla}\cdot(\rho m\vec{v}:\vec{v})+\vec{\nabla}P=\rho\vec{F}+\vec{\nabla}\cdot\overrightarrow{\Pi} \tag{3.2.14}$$

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

$$\Pi_{i,j}=\eta_B(\vec{\nabla}\cdot\vec{v})\delta_{i,j}+\eta\left(\partial_i v_j+\partial_j v_i-\frac{2}{3}(\vec{\nabla}\cdot\vec{v})\delta_{i,j}\right) \tag{3.2.15}$$

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 $\partial_i v_j+\partial_j v_i-\frac{2}{3}\nabla\vec{v}\delta_{i,j}$ 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

$$(\vec{\nabla}\cdot\overrightarrow{\Pi})_i=\sum_j\nabla_j\Pi_{j,i}=\left(\frac{1}{3}\eta+\eta_B\right)\nabla_i(\vec{\nabla}\cdot\vec{v})+\eta\nabla^2 v_i \tag{3.2.16}$$

With this, we can rewrite the momentum continuity equation as

$$m\frac{\partial\rho\vec{v}}{\partial t}+\vec{\nabla}\cdot(\rho m\vec{v}:\vec{v})+\vec{\nabla}P=\left(\frac{1}{3}\eta+\eta_B\right)\vec{\nabla}(\vec{\nabla}\cdot\vec{v})+\eta\nabla^2\vec{v} \tag{3.2.17}$$

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.

$$\frac{\partial \rho s}{\partial t}+\vec{\nabla}\cdot(\rho s\vec{v})+\vec{\nabla}\cdot\vec{J}_D=\sigma_{ext}+\sigma_D \tag{3.2.18}$$

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

$$\vec{J}_D\propto-\vec{\nabla}\cdot\vec{T} \tag{3.2.19}$$

Write this explicitly using the constant λ

$$\vec{J}_D=-\frac{\lambda\vec{\nabla}T}{T} \tag{3.2.20}$$

Then, substitute this to get the continuity equation

$$\frac{\partial \rho s}{\partial t}+\vec{\nabla}\cdot(\rho s\vec{v})-\lambda\vec{\nabla}\cdot\left(\frac{\vec{\nabla}T}{T}\right)=0 \tag{3.2.21}$$

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

$$\begin{aligned}\frac{d\rho}{dt}+\vec{\nabla}\cdot(\rho\vec{v})&=0\\ m\frac{\partial\rho\vec{v}}{\partial t}+\vec{\nabla}\cdot(\rho m\vec{v}:\vec{v})+\vec{\nabla}P&=\vec{\nabla}\cdot\overrightarrow{\vec{\Pi}}\\ \frac{\partial \rho s}{\partial t}+\vec{\nabla}\cdot(\rho s\vec{v})-\lambda\vec{\nabla}\cdot\left(\frac{\vec{\nabla}T}{T}\right)&=0\end{aligned}$$

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.

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

$$\mathcal{L}(A)=\frac{\partial A}{\partial t} \tag{3.2.22}$$

For a time-independent quantity A_S,

$$\mathcal{L}\left(A_S\right)=\frac{\partial A_S}{\partial t}=0 \tag{3.2.23}$$

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

$$A=A_S+\delta A \tag{3.2.24}$$

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

$$\mathcal{L}(A)=\mathcal{L}\left(A_S+\delta A\right)=\mathcal{L}\left(A_S\right)+\mathcal{L}(\delta A)=\frac{\partial\delta A}{\partial t} \tag{3.2.25}$$

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

$$\rho_o,\overrightarrow{v_o}=0,S_o \tag{3.2.26}$$

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:

$$\begin{aligned} \rho &= \rho_o + \delta\rho \\ S &= S_o + \delta S \\ &\vec{v} \end{aligned}$$

We can also expand around a constant temperature and pressure:

$$\begin{aligned} T &= T_o + \delta T \\ P &= P_o + \delta P \end{aligned}$$

Start by substituting the density expansion into the density continuity equation

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

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.

$$\rho\frac{\partial\delta s}{\partial t} + s_o\frac{\partial\rho}{\partial t} + s_o\vec{\nabla}\cdot(\rho\vec{v}) + \rho\vec{\nabla}\cdot(\delta s\vec{v}) - \lambda\vec{\nabla}\cdot\left(\frac{\vec{\nabla}T}{T}\right) = 0 \tag{3.2.27}$$

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:

$$\rho_o\frac{\partial\delta s}{\partial t} - \frac{\lambda}{T_o}\nabla^2\delta T = 0 \tag{3.2.28}$$

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

$$m\rho_o\frac{\partial\vec{v}}{\partial t} + \vec{\nabla}\delta P = \left(\frac{1}{3}\eta + \eta_B\right)(\vec{\nabla}:\vec{\nabla})\cdot\vec{v} + \eta\nabla^2\vec{v} \tag{3.2.29}$$

In summary, the linearized hydrodynamic equations are given by

$$\begin{aligned} \frac{d\delta\rho}{dt} + \rho_o\vec{\nabla}\cdot\vec{v} &= 0 \\ m\rho_o\frac{\partial\vec{v}}{\partial t} + \nabla\delta P &= \left(\frac{1}{3}\eta + \eta_B\right)(\vec{\nabla}:\vec{\nabla})\cdot\vec{v} + \eta\nabla^2\vec{v} \\ \rho_o\frac{\partial\delta s}{\partial t} - \frac{\lambda}{T_o}\nabla^2\delta T &= 0 \end{aligned}$$

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

$$\vec{v}(r,t) = \frac{1}{(2\pi)^3}\int\vec{v}(k,t)e^{i\vec{k}\cdot\vec{r}}d\vec{k} \tag{3.2.30}$$

Through substitution, the momentum continuity equation becomes

$$m\rho_o\frac{\partial\overrightarrow{v_k}}{\partial t} + i\vec{k}P_k = \left(\frac{1}{3}\eta + \eta_B\right)(i\vec{k})\left(i\vec{k}\cdot\overrightarrow{v_k}\right) + \eta(\vec{k})^2\overrightarrow{v_k} \tag{3.2.31}$$

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

$$v(k,t) = v_{xk}(t)\hat{x} + v_{yk}(t)\hat{y} + v_{zk}(t)\hat{z} \tag{3.2.32}$$

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.

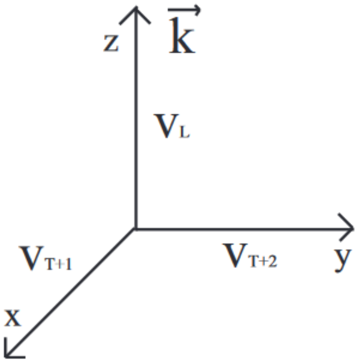

Figure 3.8: Velocity components in k-space

which is easy to solve, yielding the solution

$$v_{Tk}(t) = v_{Tk}(0)e^{-\gamma_T k^2 t} \tag{3.2.33}$$

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

This result looks like a diffusion equation

$$\frac{\partial P_k}{\partial t} = -Dk^2 P_k \tag{3.2.34}$$

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

Longitudinal Hydrodynamic modes

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

$$\vec{\rho}(r,t) = \frac{1}{(2\pi)^3}\int \vec{\rho}(k,t)e^{i\vec{k}\vec{r}}\,d\vec{k} \tag{3.2.35}$$

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.

$$\begin{aligned} \frac{d\rho_k}{dt} + ik\rho_o v_k &= 0 \\ m\rho_o\frac{\partial v_k}{\partial t} + ikP_k + \left(\frac{4}{3}\eta + \eta_B\right)k^2 v_k &= 0 \\ \rho_o\frac{\partial s_k}{\partial t} + \frac{\lambda}{T_o}k^2 T_k &= 0 \end{aligned}$$

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:

$$dF = -SdT + Pd\rho \tag{3.2.36}$$

This is a total differential of the form:

$$dz=\left(\frac{\partial z}{\partial x}\right)_y dx+\left(\frac{\partial z}{\partial y}\right)_x dy \tag{3.2.37}$$

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

$$\alpha=\left(\frac{\partial P}{\partial T}\right)_\rho=\frac{\partial}{\partial T}\left(\frac{\partial F}{\partial \rho}\right)_T=\frac{\partial}{\partial \rho}\left(\frac{\partial F}{\partial T}\right)_\rho=-\left(\frac{\partial S}{\partial \rho}\right)_T \tag{3.2.38}$$

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:

$$c_T=\sqrt{\frac{1}{m}\left(\frac{\partial P}{\partial \rho}\right)_T} \tag{3.2.39}$$

and the specific heat:

$$C_V=T\left(\frac{\partial S}{\partial T}\right)_\rho \tag{3.2.40}$$

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.

$$\begin{aligned}\frac{d\rho_k}{dt}+ik\rho_o v_k&=0\\ \dot{v}_k+\frac{ik}{m\rho_o}\left[C_T^2 m\rho_k+\alpha T_k\right]+bk^2 v_k&=0\\ \dot{T}_k+ik\left(\frac{T_o\alpha\rho_o}{C_V}\right)v_k+ak^2 T_k&=0\end{aligned}$$

where we have defined the constants a and b

$$a=\frac{\lambda}{\rho_o C_V}$$
$$b=\left(\eta_B+\frac{4}{3}\eta\right)\frac{1}{m\rho_o}$$

and $\rho_k=-ik\rho_o v_k$ is used to simplify the last equation.

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

$$
\begin{aligned}
&\hat{\rho}_k(z)=\int_0^\infty e^{-zt}\rho_k(t)dt \quad \text{and} \quad \rho_k(t)=\frac{1}{2\pi i}\int_{\delta-i\infty}^{\delta+i\infty} e^{zt}\hat{\rho}_k(z)dz\\
&\hat{v}_k(z)=\int_0^\infty e^{-zt}v_k(t)dt \quad \text{and} \quad v_k(t)=\frac{1}{2\pi i}\int_{\delta-i\infty}^{\delta+i\infty} e^{zt}\hat{v}_k(z)dz\\
&\hat{T}_k(z)=\int_0^\infty e^{-zt}T_k(t)dt \quad \text{and} \quad T_k(t)=\frac{1}{2\pi i}\int_{\delta-i\infty}^{\delta+i\infty} e^{zt}\hat{T}_k(z)dz
\end{aligned} \tag{3.2.41}
$$

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

$$
\begin{bmatrix} z & ik\rho_o & 0 \\ ik\frac{C_T^2}{\rho_o} & z+bk^2 & \frac{ik}{m\rho_o}\alpha \\ 0 & \frac{ik}{C_V}\alpha T_o\rho_o & z+ak^2 \end{bmatrix} = \begin{bmatrix} \hat{\rho}_k \\ \hat{v}_k \\ \hat{T}_k \end{bmatrix} = \begin{bmatrix} \rho_k(0) \\ v_k(0) \\ T_k(0) \end{bmatrix}. \tag{3.2.42}
$$

Thermodynamic Identities

Isothermal and Adiabatic Speed of Sound

The adiabatic c_s and isothermal c_T speeds of sound are given by:

$$
\begin{aligned}
c_S^2 &= \frac{1}{m}\left(\frac{\partial P}{\partial \rho}\right)_S\\
c_T^2 &= \frac{1}{m}\left(\frac{\partial P}{\partial \rho}\right)_T
\end{aligned}
$$

We can rewrite these quantities using:

$$
\left(\frac{\partial P}{\partial \rho}\right)_T = \frac{\left(\frac{\partial P}{\partial S}\right)_T}{\left(\frac{\partial \rho}{\partial S}\right)_T} = \frac{\left(\frac{\partial P}{\partial T}\right)_S\left(\frac{\partial T}{\partial S}\right)_P}{\left(\frac{\partial \rho}{\partial T}\right)_S\left(\frac{\partial T}{\partial S}\right)_\rho} = \frac{C_V}{C_P}\left(\frac{\partial P}{\partial \rho}\right)_S \tag{3.2.43}
$$

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

$$
\begin{aligned}
C_V &= T\left(\frac{\partial S}{\partial T}\right)_\rho\\
C_P &= T\left(\frac{\partial S}{\partial T}\right)_P
\end{aligned}
$$

and the identity for differentials:

$$
\left(\frac{\partial x}{\partial y}\right)_z = \left(\frac{\partial x}{\partial z}\right)_y\left(\frac{\partial z}{\partial y}\right)_x \tag{3.2.44}
$$

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

$$
\frac{c_T^2}{c_S^2} = \frac{\frac{1}{m}\frac{C_V}{C_P}\left(\frac{\partial P}{\partial \rho}\right)_S}{\frac{1}{m}\left(\frac{\partial P}{\partial \rho}\right)_S} = \frac{C_V}{C_P} = \frac{1}{\gamma} \tag{3.2.45}
$$

Thermodynamic identities can be used to rewrite the quantity

$$
mC_T^2\left(C_P - C_V\right) \tag{3.2.46}
$$

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

$$
mC_T^2\left(C_P - C_V\right) = T\left(\frac{\partial P}{\partial \rho}\right)_T\left[\left(\frac{\partial S}{\partial T}\right)_P - \left(\frac{\partial S}{\partial T}\right)_\rho\right] \tag{3.2.47}
$$

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

$$
\left(\frac{\partial x}{\partial y}\right)_z = \left(\frac{\partial x}{\partial y}\right)_w + \left(\frac{\partial x}{\partial w}\right)_y\left(\frac{\partial w}{\partial y}\right)_z \tag{3.2.48}
$$

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

$$\left(\frac{\partial S}{\partial T}\right)_P = \left(\frac{\partial S}{\partial T}\right)_\rho + \left(\frac{\partial S}{\partial \rho}\right)_T \left(\frac{\partial \rho}{\partial T}\right)_P = \left(\frac{\partial S}{\partial T}\right)_\rho - \left(\frac{\partial S}{\partial \rho}\right)_T \left(\frac{\partial \rho}{\partial P}\right)_T \left(\frac{\partial P}{\partial T}\right)_\rho \tag{3.2.49}$$

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

$$mC_T^2 \left(C_P - C_V\right) = -T_o \left(\frac{\partial S}{\partial \rho}\right)_T \left(\frac{\partial P}{\partial T}\right)_\rho \tag{3.2.50}$$

Adiabatic and Isothermal Compressibility

The adiabatic χ_S and isothermal χ_T compressibilities are given by:

$$\begin{aligned} \chi_S &= \frac{1}{\rho}\left(\frac{\partial \rho}{\partial P}\right)_S \\ \chi_T &= \frac{1}{\rho}\left(\frac{\partial \rho}{\partial P}\right)_T \end{aligned}$$

Therefore,

$$\gamma = \frac{C_P}{C_V} = \frac{\chi_T}{\chi_S} = \frac{c_S^2}{c_T^2} \tag{3.2.51}$$

Eigensolution

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

$$\hat{\rho}(z) = \frac{\operatorname{Det}' M(1 \mid 1)}{\operatorname{Det} M} = \left(M^{-1}\right)_{11} \rho(0) \tag{3.2.52}$$

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

$$\hat{F}(\vec{k}, z) = \left(M^{-1}\right)_{11} \left\langle \left|\rho_k\right|^2 \right\rangle \tag{3.2.53}$$

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

$$\begin{aligned} \operatorname{Det}' M(1 \mid 1) &= \left(z + ak^2\right)\left(z + bk^2\right) + \frac{k^2 T_o \alpha^2}{mC_V} \\ &= \left(z + ak^2\right)\left(z + bk^2\right) + k^2 C_T^2 (\gamma - 1) \end{aligned}$$

and

$$\operatorname{Det} M = z\left(z + ak^2\right)\left(z + bk^2\right) + zk^2 c_S^2 + zk^4 c_T^2 \tag{3.2.54}$$

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

The eigenfrequencies can be obtained from $\operatorname{Det} M(z) = 0$. The eigenvalues can be solved using perturbation $z = s_o + s_1 k + s_2 k + \ldots$. The solutions are

$$\begin{aligned} z_\pm &= -a \frac{c_T^2}{c_S^2} k^2 = -\frac{a}{T} k^2 \\ z_\pm &= \pm i c_S k - \Gamma k^2 \end{aligned}$$

where

$$\Gamma = \frac{1}{2}\left[(a + b) - \frac{a}{\gamma}\right] \tag{3.2.55}$$

To first order in k, we have

$$\left(M^{-1}\right)_{11}=\frac{\operatorname{Det}' M(1 \mid 1)}{\operatorname{Det} M} \approx \frac{z^{2}+\left(1-\frac{1}{\gamma}\right) c_{S}^{2} k^{2}}{z^{3}+z k^{2} c_{S}^{2}}=\left(1-\frac{1}{\gamma}\right) \frac{1}{z}+\frac{1}{\gamma} \frac{1}{z^{2}+k^{2} c_{S}^{2}} \tag{3.2.56}$$

Then, to second order in k, we have

$$\hat{\rho}_{k}(t)=\hat{\rho}_{k}(0)\left[\left(1-\frac{1}{\gamma}\right) e^{-\frac{a}{\gamma} k^{2} t}+\frac{1}{\gamma} \cos \left(c_{S} k t\right) e^{-\Gamma k^{2} t}\right] \tag{3.2.57}$$

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 $\frac{1}{\gamma}$.

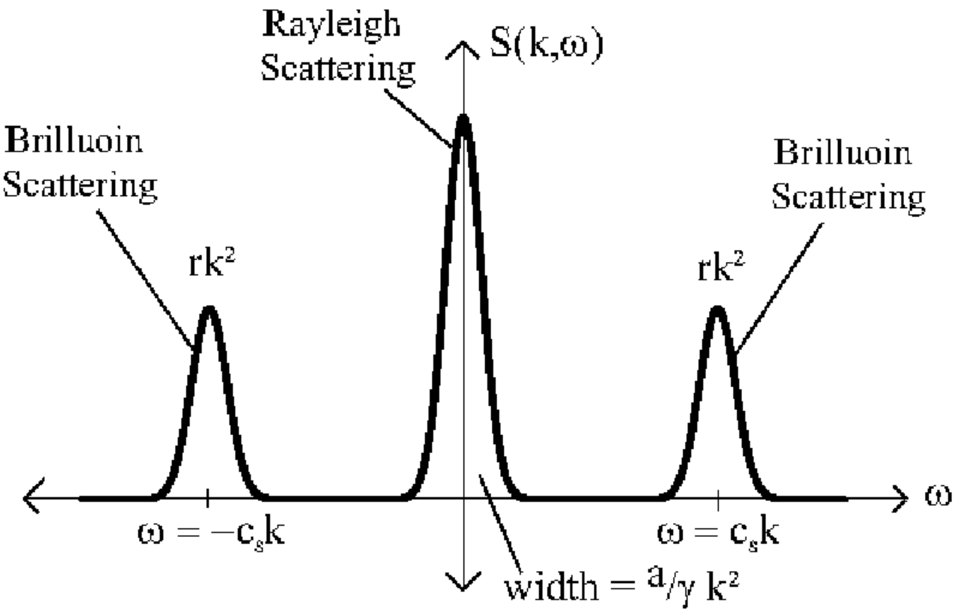

Figure 3.9: Light Scattering Spectrum

Light Scattering

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

$$\frac{I_{\text{thermal}}}{I_{\text{acoustic}}}=\frac{\left\langle(\delta \rho)^{2}\right\rangle_{\text{thermal}}}{\left\langle(\delta \rho)^{2}\right\rangle_{\text{mech}}}=\frac{\left(\frac{\partial \rho}{\partial S}\right)_{P}^{2}\left\langle\Delta S^{2}\right\rangle}{\left(\frac{\partial \rho}{\partial P}\right)_{S}^{2}\left\langle\Delta P^{2}\right\rangle}=\frac{C_{P}-C_{V}}{C_{V}}=\gamma-1 \tag{3.2.58}$$

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

$$S(\vec{k}, \omega)=\int_{\infty}^{\infty} F(\vec{k}, t) e^{-i \omega t} d t=2 \operatorname{Re} \hat{F}(z=-i \omega) \tag{3.2.59}$$

The initial value of this function is

$$F(k, 0)=\frac{1}{N}\left\langle\left|\delta \rho_{k}\right|^{2}\right\rangle=\rho_{o} h+1=\frac{\rho_{o} \chi_{T}}{\beta} \tag{3.2.60}$$

Acoustic Scattering

By ignoring the coupling to entropy flow, we have

$$dP = \left(\frac{\partial P}{\partial \rho}\right)_S d\rho \tag{3.2.61}$$

so that

$$\begin{gathered} \frac{d\delta\rho_k}{dt} + ik\rho_o v_k = 0 \\ \dot{v_k} + ic_S^2 k\rho_k + bk^2 v_k = 0 \end{gathered} \tag{3.2.62}$$

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

$$z = \pm ic_S k \tag{3.2.63}$$

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

$$z = \pm ic_S k - \frac{1}{2} bk^2 \tag{3.2.64}$$

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

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

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

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

Then solve for D

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

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

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

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

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

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

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

Therefore, the viscosity coefficient can be written as

$$\eta=\frac{\rho_o m^2\beta}{2}\lim_{\omega\to 0}\lim_{k\to 0}\frac{\omega^2}{k^2}C_t(\vec{k},\omega) \tag{3.3.28}$$

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

$$\eta=\frac{1}{Vk_BT}\int_{0}^{\infty}\sigma_{xz}(t)\sigma_{xz}(0)dt$$

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

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

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

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 :

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

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

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

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

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

By equating the k^2 terms, we find that

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

Therefore,

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

where

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

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: Univerity Science Books, 2000. MIT OpenCourseWare

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CHAPTER OVERVIEW

4: 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

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

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

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 $t \rightarrow 0$ 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 $\langle A^{(2n)}(0) \mid A(0)\rangle = -\langle A^{(n)}(0) \mid A^{(n)}(0)\rangle$, where the notation $\langle A \mid B\rangle = \langle AB^{+}\rangle = \operatorname{Tr} AB^{+}\rho_{eq}$

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

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

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

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 $\beta=(k_BT)^{-1}$. 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

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

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

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

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

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

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

$$\langle\nabla UA\rangle=\frac{1}{Q}\int d\mathbf{r}A\nabla Ue^{-\beta U}=k_BT\langle\nabla A\rangle \tag{4.1.22}$$

We have shown that the second term in the expansion of $C(t)$ is proportional to $\left\langle\frac{\partial_z^2U}{m}\right\rangle$, 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

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

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 $\omega_o = kv_o$, 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

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

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

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

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

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

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

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

Now, define the parameter l as

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

This term gives the average thermal velocity, $\sqrt{\frac{3k_B T}{m}}$, 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 :

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

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

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

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

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

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

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

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

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

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

The second and third term can be combined to give

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

And the fourth term gives

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

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

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

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

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

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.

Definitions

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

$$\mathcal{P}_A B=\frac{\langle B \mid A\rangle}{\langle A \mid A\rangle} A \tag{4.2.1}$$

By definition,

$$\mathcal{P}_A^2=\mathcal{P}_A \tag{4.2.2}$$

For an equilibrium system, the operator product is

$$\langle B \mid A\rangle=\operatorname{Tr} B A^{+} \rho_{eq} \tag{4.2.3}$$

or, in the phase space representation

$$\langle B \mid A\rangle=\int d \Gamma B(\Gamma) A^{+}(\Gamma) \rho_{eq} \tag{4.2.4}$$

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

$$\begin{gathered}\frac{1}{s-a-b}=\frac{1}{s-a}+\frac{1}{s-a-b} b \frac{1}{s+a} \\ e^{(a+b) t}=e^{a t}+\int_0^t e^{(a+b)(t-\tau)} b e^{a \tau} d \tau\end{gathered}$$

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

$$\frac{d A}{d t}=i \mathcal{L} A \tag{4.2.5}$$

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

$$i \mathcal{L} A \equiv \frac{1}{i \hbar}[A, \mathcal{H}] \tag{4.2.6}$$

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

$$i \mathcal{L} A \equiv i\{A, \mathcal{H}\} \tag{4.2.7}$$

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

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

The Generalized Langevin Equation

The Liouville equation

$$\frac{d}{d t} A(t)=i L A(t) \tag{4.2.8}$$

has the formal solution

$$A(t)=e^{i \mathcal{L} t} A(0) \tag{4.2.9}$$

From this equation it is clear that the function $e^{i L t}$ 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 $A(t)$

$$\frac{d A}{d t}=i \mathcal{L} e^{i \mathcal{L} t} A \tag{4.2.10}$$

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

$$\frac{d A}{d t}=e^{i \mathcal{L} t}(\mathcal{P}+\mathcal{Q}) i \mathcal{L} A=e^{i \mathcal{L} t} P i \mathcal{L} A+e^{i \mathcal{L} t} \mathcal{Q} i \mathcal{L} A \tag{4.2.11}$$

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}} \operatorname{Pi\mathcal} A=e^{i \mathcal{L} t} \frac{\langle i \mathcal{L} A \mid A\rangle}{\langle A \mid A\rangle} A \\ =i \frac{\langle\mathcal{L} A \mid A\rangle}{\langle A \mi
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where Ω is called the frequency matrix and is defined as

$$\Omega = \frac{\langle \mathcal{L}A \mid A\rangle}{\langle A \mid A\rangle} \tag{4.2.12}$$

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 $(a+b) = -i\mathcal{L}$

$$\begin{aligned} e^{i\mathcal{L}t} &= e^{i(\mathcal{P}+\mathcal{Q})\mathcal{L}t} \\ &= e^{i\mathcal{Q}Lt} + \int_0^t e^{i\mathcal{L}(t-\tau)}\, iP\mathcal{L}e^{i\mathcal{Q}Lt}\, d\tau \end{aligned}$$

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

$$e^{i\mathcal{L}t}\, i\mathcal{Q}\mathcal{L}A = e^{i\mathcal{Q}\mathcal{L}t}\, i\mathcal{Q}\mathcal{L}A + \int_0^t e^{i\mathcal{L}(t-\tau)}\, iP\mathcal{L}e^{i\mathcal{Q}\mathcal{L}t}\, (i\mathcal{Q}\mathcal{L}A) d\tau \tag{4.2.13}$$

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 $R(t)$

$$R(t) = e^{i\mathcal{Q}Lt}\, i\mathcal{Q}\mathcal{L}A \tag{4.2.14}$$

where $R(0) = i\mathcal{Q}\mathcal{L}A$ and $e^{i\mathcal{L}t}$ 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

$$\int_0^t e^{i\mathcal{L}(t-\tau)}\, iP\mathcal{L}e^{i\mathcal{Q}\mathcal{L}t}\, (i\mathcal{Q}\mathcal{L}A) d\tau = \int_0^t e^{i\mathcal{L}(t-\tau)}\, iP\mathcal{L}R(t) d\tau \tag{4.2.15}$$

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

$$\int_0^t e^{i\mathcal{L}(t-\tau)} \frac{\langle i\mathcal{L}R(t) \mid A\rangle}{\langle A \mid A\rangle} A d\tau \tag{4.2.16}$$

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 $\mathcal{P}, \mathcal{P}^2 = \mathcal{P}$)

$$\int_0^t e^{i\mathcal{L}(t-\tau)} \frac{\langle i\mathcal{L}\mathcal{Q}R(t) \mid A\rangle}{\langle A \mid A\rangle} A d\tau \tag{4.2.17}$$

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

$$-\int_0^t e^{i\mathcal{L}(t-\tau)} \frac{\langle R(t) \mid i\mathcal{Q}\mathcal{L}A\rangle}{\langle A \mid A\rangle} A d\tau \tag{4.2.18}$$

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

$$-\int_0^t \frac{\langle R(t) \mid R(0)\rangle}{\langle A \mid A\rangle} A(t-\tau) d\tau \tag{4.2.19}$$

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

$$\kappa(t) = \frac{\langle R(t) \mid R(0)\rangle}{\langle A \mid A\rangle} \tag{4.2.20}$$

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

$$-\int_0^t \kappa(t) A(t-\tau) d\tau \tag{4.2.21}$$

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

$$\frac{dA}{dt} = i\Omega A(t) - \int_0^t \kappa(t) A(t-\tau) d\tau + R(t) \tag{4.2.22}$$

where the frequency matrix is

$$\Omega = \frac{\langle \mathcal{L}A \mid A\rangle}{\langle A \mid A\rangle} \tag{4.2.23}$$

the random force is

$$R(t) = e^{i\mathcal{Q}\mathcal{L}t}\, i\mathcal{Q}\mathcal{L}A \tag{4.2.24}$$

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

$$\kappa(t) = \frac{\langle R(t) \mid R(0)\rangle}{\langle A \mid A\rangle} \tag{4.2.25}$$

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 $\left\langle \frac{dA}{dt} \mid A \right\rangle$, which is simply the derivative of the correlation function $C(t) = \langle A(t) \mid A(0)\rangle$, 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, $\langle R(t) \mid R(0)\rangle \langle A \mid A\rangle^{-1}$, 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.

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

$$\frac{dv}{dt} = -\int_0^t \gamma(t-\tau) v(\tau) d\tau + \frac{f(t)}{m} \tag{4.2.26}$$

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

$$\gamma(t) = \frac{\langle f(t) \mid f(0)\rangle}{m^2\langle v \mid v\rangle} \tag{4.2.27}$$

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

$$\gamma(t) = \frac{\beta}{m}\langle f(t) \mid f(0)\rangle \tag{4.2.28}$$

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

$$\xi(t) = \beta\langle f(t) \mid f(0)\rangle \tag{4.2.29}$$

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

$$s\hat{C}(s) + \hat{\gamma}(s)\hat{C}(s) = C(0) \tag{4.2.30}$$

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

$$C(\hat{s}) = \frac{v_0^2}{s+\hat{\gamma}(s)} \tag{4.2.31}$$

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

$$D = \int_0^\infty C(t)d\tau = \hat{C}(s=0) \tag{4.2.32}$$

Using the solution that we derived above

$$D = \frac{v_0^2}{\hat{\gamma}(0)} = \frac{k_BT}{m\hat{\gamma}(0)} \tag{4.2.33}$$

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

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

which has the formal solution (chapter 1)

$$v(t) = v(0)e^{-\gamma t} + \frac{1}{m}\int_0^t e^{-\gamma(t-\tau)}f(t)d\tau \tag{4.2.34}$$

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

$$D = \frac{k_BT}{m\hat{\gamma}(0)} = \frac{k_BT}{\xi} \tag{4.2.35}$$

3. 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

$$\gamma(t) = \gamma_o\alpha e^{-\alpha t} \tag{4.2.36}$$

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 $\gamma_o\delta\left(t^+\right)$.

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

$$\hat{\gamma}(t) = \frac{\gamma_o\alpha}{s+\alpha} \tag{4.2.37}$$

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

$$\gamma(0) = \frac{\langle iQ\mathcal{L}v \mid iQ\mathcal{L}v\rangle}{m^2\left\langle v^2\right\rangle} \tag{4.2.38}$$

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

$$\gamma(0) = \frac{\left\langle \partial_x^2 U\right\rangle}{m} \equiv \Omega_o^2 \tag{4.2.39}$$

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.

$$\hat{C}(0)=\frac{v_o^2}{s+\frac{\Omega_o^2}{s+\alpha}}=v_o^2\frac{s+\alpha}{s^2+s\alpha+\Omega_o^2} \tag{4.2.40}$$

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

$$\begin{aligned}\lambda_{\pm} &=-\frac{\alpha}{2}\pm\sqrt{\frac{\alpha-4\Omega_o^2}{4}}\\ C(t) &=v_o^2\frac{1}{\lambda_{+}+\lambda_{-}}\left(e^{-\lambda+t}-e^{-\lambda_{-}t}\right)\end{aligned}$$

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

$$C(t)=v_o^2\frac{1}{\lambda_{+}+\lambda_{-}}(\cos\Delta t) \tag{4.2.41}$$

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.

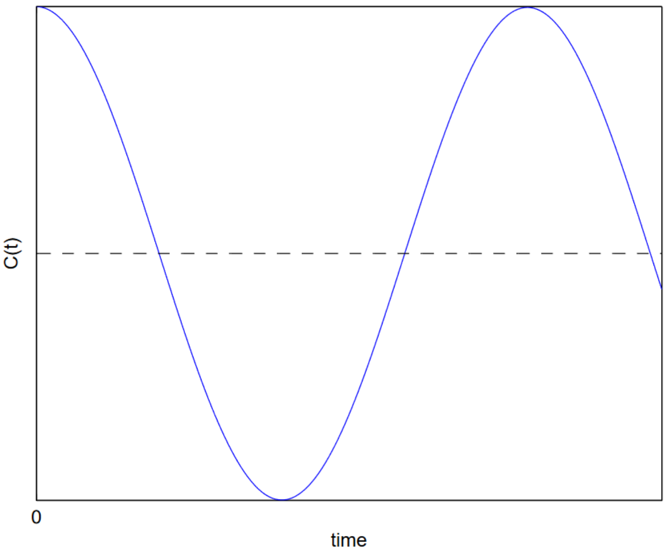

Figure 4.1: Velocity correlation function of a solid

3. 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.

4. 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.

4. 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

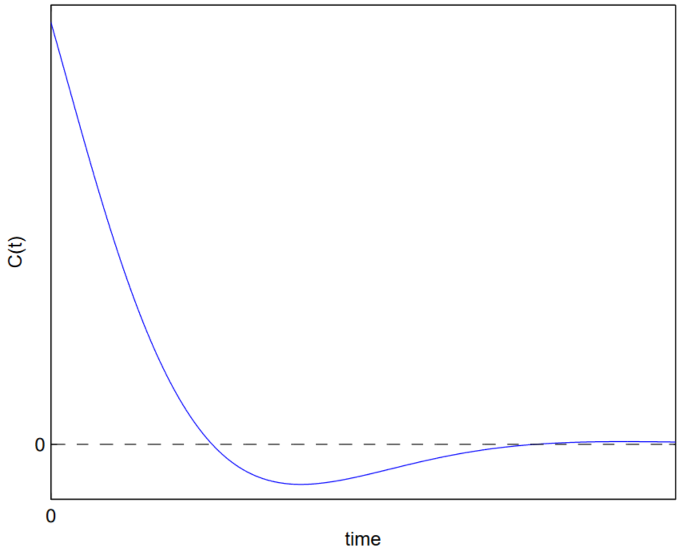

Figure 4.2: Velocity correlation function of a liquid

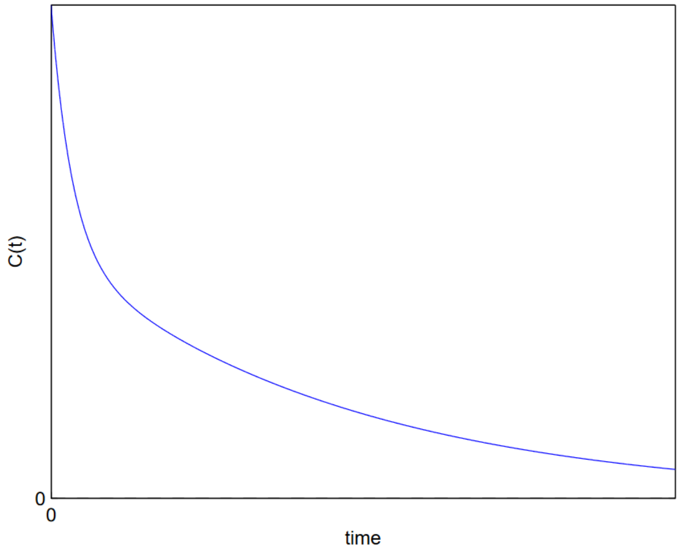

Figure 4.3: Velocity correlation function of a gas

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

$$\dot{F}(\vec{k},t)=-k^2\int_0^t D(\vec{k},\tau)F(\vec{k},t-\tau)d\tau \tag{4.2.42}$$

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

$$D=\int_0^\infty D(0,t)dt=\int_0^\infty C(t)dt \tag{4.2.43}$$

4.3: Viscoelastic Model

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 *[Math Processing Error]* and *[Math Processing Error]*. It uses the transport coefficients *[Math Processing Error]*, *[Math Processing Error]*, and *[Math Processing Error]* 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 *[Math Processing Error]* and *[Math Processing Error]*. 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.

Phenomenological Viscosity

Consider a constant shear force applied to a viscous liquid. At long times, the shear stress *[Math Processing Error]* in the liquid is related to the rate of strain *[Math Processing Error]* by

[Math Processing Error]

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

[Math Processing Error]

where *[Math Processing Error]* is the modulus of rigidity. When the liquid is behaving like a solid, it supports shear waves propagating at a speed of *[Math Processing Error]*.

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

[Math Processing Error]

This is the Maxwell relaxation time. For the timescales *[Math Processing Error]* when

[Math Processing Error]

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

[Math Processing Error]

the system behaves like a viscous liquid.

Viscoelastic Approximation

To interpolate between the two extremes, we can write

[Math Processing Error]

The Laplace transform of this equation yields

[Math Processing Error]

In the steady-state limit, as *[Math Processing Error]*

[Math Processing Error]

and in the high-frequency limit, as *[Math Processing Error]*

[Math Processing Error]

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

[Math Processing Error]

and the transverse current correlation function as

[Math Processing Error]

We have studied the transverse current in both the hydrodynamic limit *[Math Processing Error]* and the short-time expansion limit *[Math Processing Error]*. In chapter 3, we used the Navier Stokes equation to find an equation of motion for the transverse correlation function in the hydrodynamic limit

[Math Processing Error]

This has the solution

[Math Processing Error]

where *[Math Processing Error]* is the **shear viscosity**. Therefore, in the hydrodynamic limit, transverse current fluctuations decay exponentially with a rate determined by the shear viscosity *[Math Processing Error]*.

In section I of this chapter, we used the short-time expansion approximation to show that in the *[Math Processing Error]* limit, the transverse current correlation function can be written as

[Math Processing Error]

where the transverse frequency *[Math Processing Error]* is related to the transverse speed of sound *[Math Processing Error]* by

[Math Processing Error]

And the transverse speed of sound is given by

[Math Processing Error]

where *[Math Processing Error]* is the pairwise correlation function and *[Math Processing Error]* is the pairwise interaction potential. This frequency term can also be written as [3]

[Math Processing Error]

where *[Math Processing Error]* 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 *[Math Processing Error]*.

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

[Math Processing Error]

where *[Math Processing Error]* is the memory function and *[Math Processing Error]* is the noise term. Multiplying through by *[Math Processing Error]* and taking the average gives us the equation of motion for the transverse current correlation function

[Math Processing Error]

Take a closer look at the memory kernel

[Math Processing Error]

The normalization factor is simply *[Math Processing Error]*. By writing the projection operator *[Math Processing Error]* as *[Math Processing Error]* and eliminating terms, this can be written

[Math Processing Error]

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

[Math Processing Error]

where *[Math Processing Error]* is the zx-component of the microscopic stress tensor

[Math Processing Error]

Then the memory kernel becomes

[Math Processing Error]

where [Math Processing Error] is defined as

[Math Processing Error]

This demonstrates that the memory kernel is proportional to [Math Processing Error]. Then the transverse current correlation function can be written

[Math Processing Error]

The memory kernel is the key element that links the two limits. In general, the presence of the propagator [Math Processing Error] makes it very difficult to evaluate [Math Processing Error] explicitly. However, the presence of [Math Processing Error] indicates that we can separate out fast and slow motions and use this to construct a form for [Math Processing Error] 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:

[Math Processing Error]

where [Math Processing Error] is the **Maxwell relaxation time**, discussed above. Before using this function, it is necessary to specify the values of the two parameters, [Math Processing Error] and [Math Processing Error]. 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.

The Short Time Limit

The value of [Math Processing Error] at short times can be obtained by comparing the GLE at time [Math Processing Error] to the short time expansion of the transverse correlation function. To find the GLE at time [Math Processing Error], take its time derivative

[Math Processing Error]

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

[Math Processing Error]

The second derivative of this expansion gives

[Math Processing Error]

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

[Math Processing Error]

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

[Math Processing Error]

where [Math Processing Error] and the speed of the waves are [Math Processing Error].

The Hydrodynamic Limit

The value of [Math Processing Error] at long times can be obtained by comparing the hydrodynamic equation to the long time limit of the GLE for [Math Processing Error] :

[Math Processing Error]

To take the long time limit of this equation, note that the memory function will generally be characterized by some relaxation time [Math Processing Error]. When the time [Math Processing Error] is much greater than this relaxation time, the major contribution to the integral will come when [Math Processing Error]. Therefore, we can approximate [Math Processing Error]. With this approximation, the correlation function can be taken out of the integral in the GLE:

[Math Processing Error]

where the integration limit has been extended to [Math Processing Error] 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 *[Math Processing Error]* and comparing to the hydrodynamic result (Eq.(4.35)), we see that this only holds when:

[Math Processing Error]

The Viscoelastic Solution

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

[Math Processing Error]

From the short time limit, we found that *[Math Processing Error]*, which allows us to write

[Math Processing Error]

From the long time limit, we know that

[Math Processing Error]

Now, plug in the exponential memory kernel for *[Math Processing Error]*

[Math Processing Error]

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

[Math Processing Error]

Finally, evaluate the integral to find the Maxwell relaxation time at *[Math Processing Error]*. It is reasonable to assume that the Maxwell relaxation time remains constant over all *[Math Processing Error]* 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 *[Math Processing Error]*.

[Math Processing Error]

When *[Math Processing Error]* is small compared to the time *[Math Processing Error]*, the viscosity term dominates and the system will behave as a viscous liquid. However, when *[Math Processing Error]* is large compared to the time *[Math Processing Error]*, 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.

[Math Processing Error]

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

[Math Processing Error]

Now, solve this equation using the exponential memory kernel *[Math Processing Error]*. The Laplace transform of an exponential function is well defined

[Math Processing Error]

Therefore, the Laplace transform of the viscoelastic memory kernel is

[Math Processing Error]

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

[Math Processing Error]

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].

[Math Processing Error]

where the eigenvalues *[Math Processing Error]*are given by the solutions to the quadratic equation *[Math Processing Error]* :

[Math Processing Error]

Complex eigensolutions exist if

[Math Processing Error]

Recall that *[Math Processing Error]*. Then we can rewrite the above inequality in terms of the wavenumber

[Math Processing Error]

Define the critical wavenumber, *[Math Processing Error]*. 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

The Problem

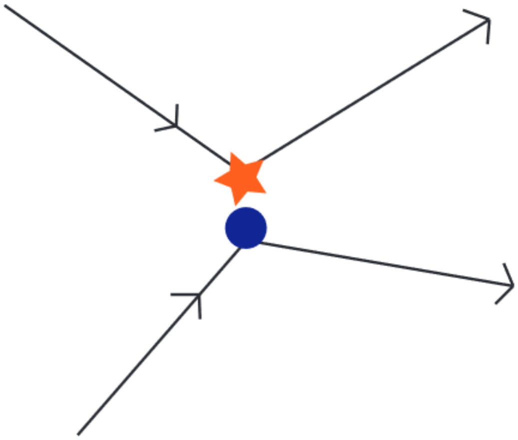

Figure 4.4: Uncorrelated collision of two particles in a fluid

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

[Math Processing Error]

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, *[Math Processing Error]* exhibits a power-law decay rather than an exponential decay. That is, *[Math Processing Error]* decays according to *[Math Processing Error]*

[Math Processing Error]

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

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 *[Math Processing Error]*, where *[Math Processing Error]* 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 *[Math Processing Error]* 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, *[Math Processing Error]*. 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 *[Math Processing Error]*, the particle has not had time to travel away from its initial position. Therefore, *[Math Processing Error]*. As *[Math Processing Error]* increases, the particle begins to diffuse away from its initial position. The radius of the sphere increases linearly

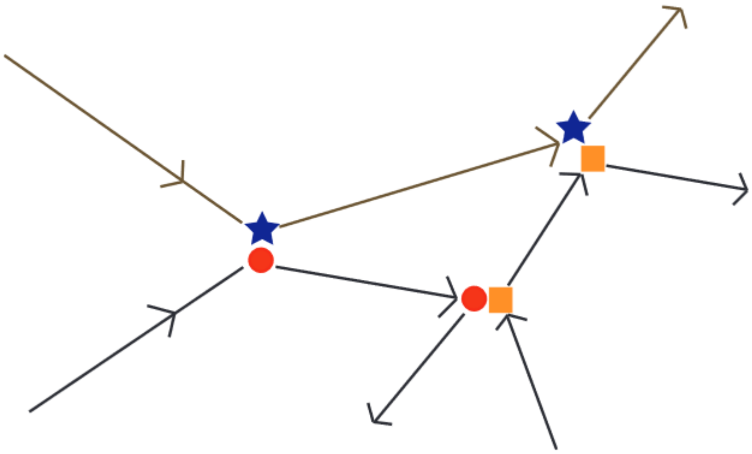

Figure 4.5: A test particle (blue star) collides with one particle (red circle), altering that particle's trajectory such that it collides with a third particle (yellow square). The subsequent collision of the third particle with the test particle is correlated with the initial collision.

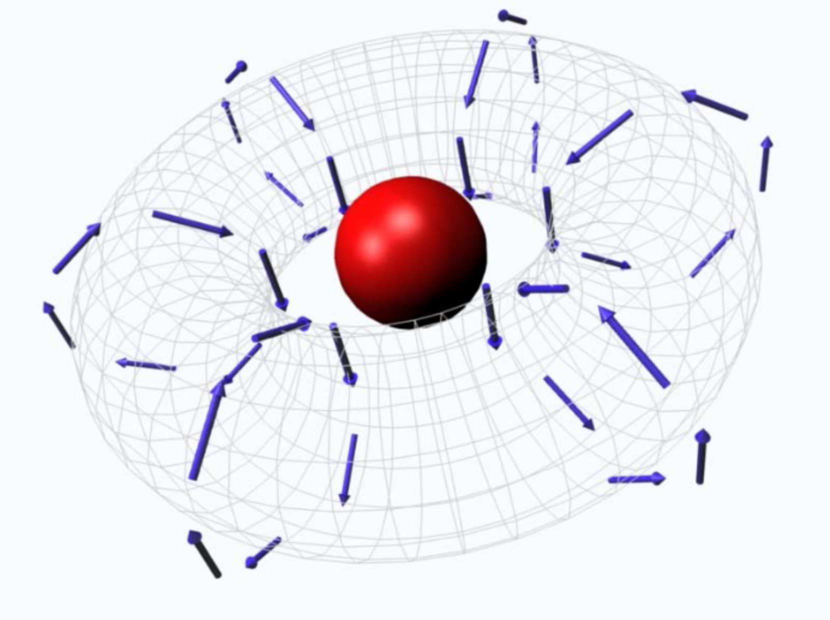

Figure 4.6: Vortex rings in the fluid around a hard sphere particle can contribute to the long-time tail of the velocity autocorrelation function [6]. with time according to *[Math Processing Error]*, where *[Math Processing Error]* is the diffusion constant.

To estimate *[Math Processing Error]* from probability sphere, note that the probability of finding the particle at any point in space must be unity:

[Math Processing Error]

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, *[Math Processing Error]*. Therefore, this integral simplifies to

[Math Processing Error]

The volume of the sphere goes as *[Math Processing Error]*, where *[Math Processing Error]* is the spatial dimension. Therefore, the probability goes as

[Math Processing Error]

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

[Math Processing Error]

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 *[Math Processing Error]* 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

[Math Processing Error]

where *[Math Processing Error]* is the diffusion constant, *[Math Processing Error]* is the shear viscosity, and *[Math Processing Error]*. The transverse current is written in *[Math Processing Error]*-space. By transforming this into real space, we obtain an expression for the dissipation of the velocity field over time and space

[Math Processing Error]

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 *[Math Processing Error]*.

Hydrodynamic Model

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

[Math Processing Error]

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

[Math Processing Error]

where *[Math Processing Error]* is the Boltzmann distribution and *[Math Processing Error]* is a non-equilibrium velocity field:

[Math Processing Error]

Here, *[Math Processing Error]* describes the tagged particle.

The non-equilibrium velocity field can be represented as a coupling of the linear modes *[Math Processing Error]* and *[Math Processing Error]*

[Math Processing Error]

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

[Math Processing Error]

For transverse modes,

[Math Processing Error]

Then, take the equilibrium average

[Math Processing Error]

Finally,

[Math Processing Error]

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, *[Math Processing Error]*. then

[Math Processing Error]

where *[Math Processing Error]* is the projection operator associated with *[Math Processing Error]*. By expanding the projection operator

[Math Processing Error]

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

[Math Processing Error]

Then

[Math Processing Error]

and

[Math Processing Error]

so that

[Math Processing Error]

Therefore,

[Math Processing Error]

Now,

[Math Processing Error]

and

[Math Processing Error]

Then

[Math Processing Error]

By incorporating the three-spatial components of *[Math Processing Error]* and *[Math Processing Error]*, we have

[Math Processing Error]

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