

## 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

$$\mathcal{P}_A B = \frac{\langle B | A \rangle}{\langle A | A \rangle} A \quad (4.2.1)$$

By definition,

$$\mathcal{P}_A^2 = \mathcal{P}_A \quad (4.2.2)$$

For an equilibrium system, the operator product is

$$\langle B | A \rangle = \text{Tr} B A^+ \rho_{eq} \quad (4.2.3)$$

or, in the phase space representation

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

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

## 2. Operator Identity

If  $a$  and  $b$  are operators, the following are identities

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

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

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  $\mathcal{L}$

$$\frac{dA}{dt} = i\mathcal{L}A \quad (4.2.5)$$

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

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

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

$$i\mathcal{L}A \equiv i\{A, \mathcal{H}\} \quad (4.2.7)$$

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

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

## The Generalized Langevin Equation

## The Liouville equation

$$\frac{d}{dt}A(t) = iLA(t) \quad (4.2.8)$$

has the formal solution

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

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

$$\frac{dA}{dt} = i\mathcal{L}e^{i\mathcal{L}t}A \quad (4.2.10)$$

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

$$\frac{dA}{dt} = e^{i\mathcal{L}t}(\mathcal{P} + \mathcal{Q})i\mathcal{L}A = e^{i\mathcal{L}t}P i\mathcal{L}A + e^{i\mathcal{L}t}Q i\mathcal{L}A \quad (4.2.11)$$

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

$$\begin{aligned} e^{\frac{i}{\hbar} \int_{\mathcal{L}} \mathcal{L}} \operatorname{Pi} A &= e^{\frac{i}{\hbar} \int_{\mathcal{L}} \mathcal{L}} \frac{\langle \mathcal{L} | A | \mathcal{L} \rangle}{\langle \mathcal{L} | A | \mathcal{L} \rangle} A = \frac{\langle \mathcal{L} | \mathcal{L} | \mathcal{L} \rangle}{\langle \mathcal{L} | \mathcal{L} | \mathcal{L} \rangle} A \end{aligned}$$

where  $\Omega$  is called the frequency matrix and is defined as

$$\Omega = \frac{\langle \mathcal{L}A | A \rangle}{\langle A | A \rangle} \quad (4.2.12)$$

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  $a = -i\mathcal{Q}\mathcal{L}$ ,  $b = -i\mathcal{P}\mathcal{L}$ , and  $(a+b) = -i\mathcal{L}$

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

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

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

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  $R(t)$

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

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

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

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

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

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

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

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

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

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

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

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

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

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

$$- \int_0^t \kappa(t) A(t-\tau) d\tau \quad (4.2.21)$$

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

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

where the frequency matrix is

$$\Omega = \frac{\langle \mathcal{L}A | A \rangle}{\langle A | A \rangle} \quad (4.2.23)$$

the random force is

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

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

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

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  $\langle \frac{dA}{dt} | A \rangle$ , which is simply the derivative of the correlation function  $C(t) = \langle A(t) | A(0) \rangle$ , evaluated at zero. Since all correlation functions are even in time, the derivative at zero must equal zero. This rule will apply to all of the problems that we address in this section.

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

## 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 velocity of the particle. For this system, the frequency matrix  $\Omega$  is zero, so the full GLE is given by

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

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

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

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

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

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

$$\xi(t) = \beta \langle f(t) | f(0) \rangle \quad (4.2.29)$$

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

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

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

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

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

$$D = \int_0^\infty C(t) dt = \hat{C}(s=0) \quad (4.2.32)$$

Using the solution that we derived above

$$D = \frac{v_o^2}{\hat{\gamma}(0)} = \frac{k_B T}{m\hat{\gamma}(0)} \quad (4.2.33)$$

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)

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

and the correlation function  $C(t) = C(0)e^{-\gamma_o t}$ . 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

$$D = \frac{k_B T}{m\hat{\gamma}(0)} = \frac{k_B T}{\xi} \quad (4.2.35)$$

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  $\gamma_o$  but varies with time. We can model this with the exponential decay memory kernel

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

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

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

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

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

$$\gamma(0) = \frac{\langle i\mathcal{Q}\mathcal{L}v | i\mathcal{Q}\mathcal{L}v \rangle}{m^2 \langle v^2 \rangle} \quad (4.2.38)$$

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

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

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.

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

This is relatively easy to solve because it is quadratic. To generate the solutions, find the eigenvalues by solving the quadratic equation  $s^2 + s\alpha + \Omega_o^2 = 0$ . This gives the results

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

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

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

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

We can examine these results for different relations between  $\alpha$  and  $\Omega_o$ .

1. Solids When  $\alpha \ll \Omega_o$ , the decay time is much longer than one oscillation period. The correlation function shows persistent 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.

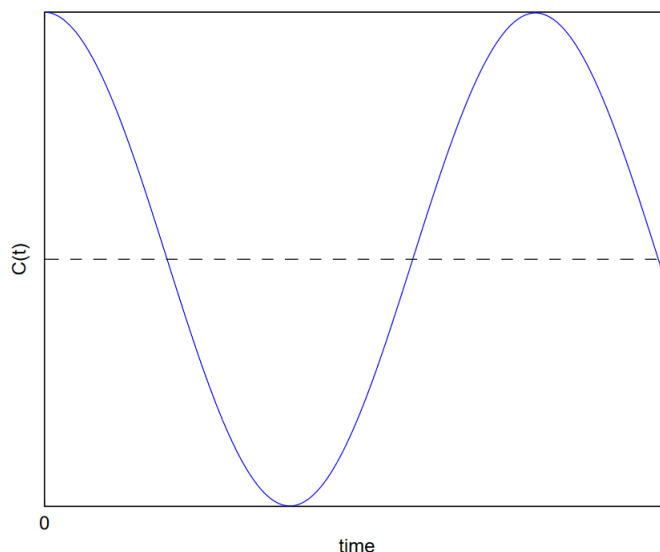


Figure 4.1: Velocity correlation function of a solid

3. Liquids When  $\alpha \approx \Omega_o$ , 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  $\alpha \gg \Omega_o$ , 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

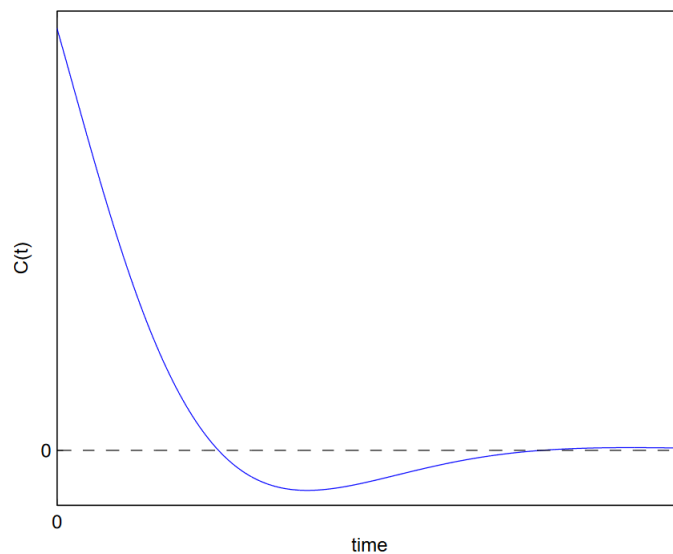


Figure 4.2: Velocity correlation function of a liquid

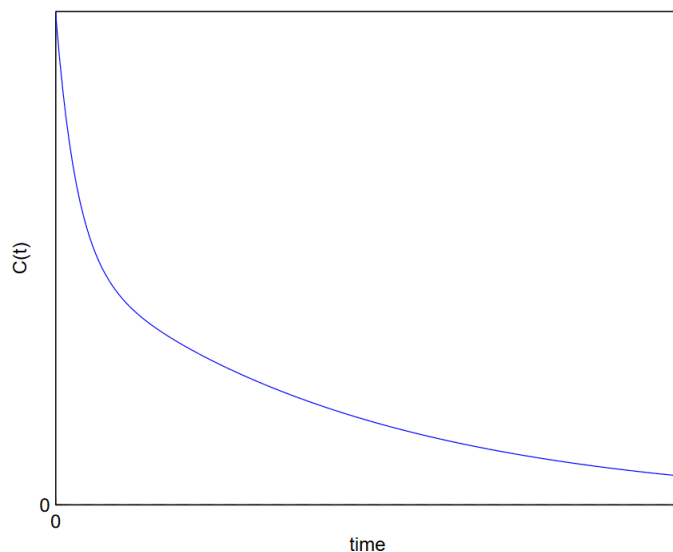


Figure 4.3: Velocity correlation function of a gas

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

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

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

$$D = \int_0^\infty D(0, t) dt = \int_0^\infty C(t) dt \quad (4.2.43)$$

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