

5.1. TIME-CORRELATION FUNCTIONS

Time-correlation functions are an effective and intuitive way of representing the dynamics of a system, and are one of the most common tools of time-dependent quantum mechanics. They provide a statistical description of the time-evolution of a variable for an ensemble at thermal equilibrium. They are generally applicable to any time-dependent process for an ensemble, but are commonly used to describe random or stochastic processes in condensed phases. We will use them in a description of spectroscopy and relaxation phenomena.

This work is motivated by finding a general tool that will help us deal with the inherent randomness of molecular systems at thermal equilibrium. The quantum equations of motion are deterministic, but this only applies when we can specify the positions and momenta of all the particles in our system. More generally, we observe a small subset of all degrees of freedom, and the time-dependent properties that we observe have random fluctuations and irreversible relaxation as a result of interactions with the surroundings. It is useful to treat the environment with the minimum number of variables and incorporate it into our problems in a statistical sense – for instance in terms of temperature. Time-correlation functions are generally applied to describe the time-dependent statistics of systems at thermal equilibrium, rather than pure states described by a single wavefunction.

Statistics

Commonly you would describe the statistics of a measurement on a variable A in terms of the moments of the distribution function, $P(A)$, which characterizes the probability of observing A between A and $A+dA$

$$\text{Average:} \quad \langle A \rangle = \int dA A P(A) \quad (5.1)$$

$$\text{Mean Square Value:} \quad \langle A^2 \rangle = \int dA A^2 P(A) . \quad (5.2)$$

Similarly, this can be written as a determination from a large number of measurements of the value of the variable A :

$$\langle A \rangle = \frac{1}{N} \sum_{i=1}^N A_i \quad (5.3)$$

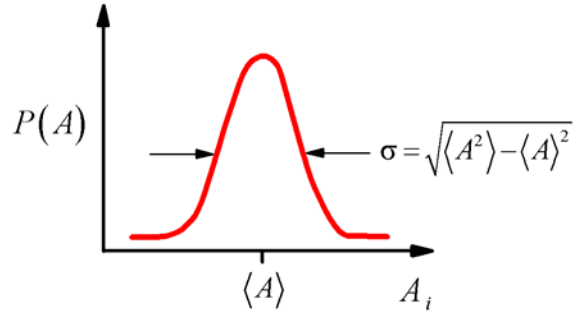
$$\langle A^2 \rangle = \frac{1}{N} \sum_{i=1}^N A_i A_i . \quad (5.4)$$

The ability to specify a value for A is captured in the variance of the distribution

$$\sigma^2 = \langle A^2 \rangle - \langle A \rangle^2 \quad (5.5)$$

The observation of an internal variable in a statistical sense is also intrinsic to quantum mechanics. A fundamental postulate is that the expectation value

of an operator $\hat{A} = \langle \psi | \hat{A} | \psi \rangle$ is the mean value of A obtained over many observations. The probability distribution function is associated with $|\psi|^2 dr$.



To take this a step further and characterize the statistical relationship between two variables, one can define a joint probability distribution, $P(A,B)$, which characterizes the probability of observing A between A and $A+dA$ and B between B and $B+dB$. The statistical relationship between the variables can also emerge from moments of $P(A,B)$. The most important measure is a correlation function

$$C_{AB} = \langle AB \rangle - \langle A \rangle \langle B \rangle \quad (5.6)$$

You can see that this is the covariance – the variance for a bivariate distribution. This is a measure of the correlation between the variables A and B , that is, if you choose a specific value of A , does that imply that the associated values of B have different statistics from those for all values. To interpret this it helps to define a correlation coefficient

$$\rho = \frac{C_{AB}}{\sigma_A \sigma_B} \quad (5.7)$$

ρ can take on values from +1 to -1. If $\rho = 1$ then there is perfect correlation between the two distributions. If the variables A and B depend the same way on a common internal variable, then they are correlated. If no statistical relationship exists between the two distributions, then they are uncorrelated, $\rho = 0$, and $\langle AB \rangle = \langle A \rangle \langle B \rangle$. It is also possible that the distributions depend in an equal and opposite manner on an internal variable, in which case we call them anti-correlated with $\rho = -1$.

Equation (5.6) can be applied to any two different continuous variables, but most commonly these are used to describe variables in time and space. For the case of time-correlation

functions that we will be investigating, rather than two different internal variables, we will be interested in the value of the same internal variable, although at different points in time.

Equilibrium systems

For the case of a system at thermal equilibrium, we describe the probability of observing a variable A through an equilibrium ensemble average $\langle A \rangle$. Classically this is

$$\langle A \rangle = \int d\mathbf{p} \int d\mathbf{q} A(\mathbf{p}, \mathbf{q}; t) f(\mathbf{p}, \mathbf{q}) \quad (5.8)$$

where f is the canonical probability distribution for an equilibrium system at temperature T

$$f = \frac{e^{-\beta H}}{Z} \quad (5.9)$$

Z is the partition function and $\beta = k_B T$. In the quantum mechanical case, we can write

$$\langle A \rangle = \sum_n p_n \langle n | A | n \rangle \quad (5.10)$$

where

$$p_n = e^{-\beta E_n} / Z \quad (5.11)$$

Equation (5.10) may not seem obvious, since it is different than our earlier expression $\langle A \rangle = \sum_{n,m} a_n^* a_m A_{mn} = \text{Tr}(\rho A)$. The difference is that in the present case, we are

dealing with a statistical mixture or mixed state, in which no coherences (phase relationships) are present in the sample. To look at it a bit more closely, the expectation value for a mixture

$$\langle A \rangle = \sum_k p_k \langle \psi_k | A | \psi_k \rangle \quad (5.12)$$

can be written somewhat differently as an explicit sum over N statistically independent molecules

$$\langle A \rangle = \frac{1}{N} \sum_{i=1}^N \sum_{n,m} (a_n^{(i)})^* a_m^{(i)} \langle n | A | m \rangle \quad (5.13)$$

Since the molecules are statistically independent, this sum over molecules is just the ensemble averaged value of the expansion coefficients

$$\langle A \rangle = \sum_{n,m} \langle a_n^* a_m \rangle \langle n | A | m \rangle \quad (5.14)$$

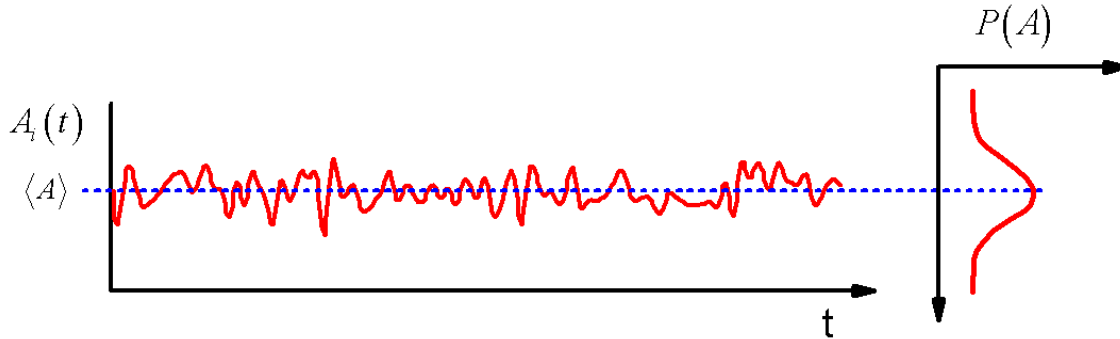
We can evaluate this average recognizing that these are complex numbers, and that the equilibrium ensemble average of the expansion coefficients is equivalent to phase averaging over the expansion coefficients. Since at equilibrium all phases are equally probable

$$\langle a_n^* a_m \rangle = \frac{1}{2\pi} \int_0^{2\pi} a_n^* a_m d\phi = \frac{1}{2\pi} |a_n| |a_m| \int_0^{2\pi} e^{-i\phi_{nm}} d\phi_{nm} \quad (5.15)$$

where $a_n = |a_n| e^{i\phi_n}$ and $\phi_{nm} = \phi_n - \phi_m$. The integral in (5.15) is quite clearly zero unless $\phi_n = \phi_m$, giving

$$\langle a_n^* a_m \rangle = p_n = \frac{e^{-\beta E_n}}{Z} \quad (5.16)$$

Of course, even at equilibrium the expectation value of A for a member of ensemble as a function of time $A_i(t)$. Although the behavior of $A_i(t)$ may be well-defined and periodic, for mixed states it generally is observed to fluctuate randomly:



The fluctuations are about a mean value $\langle A \rangle$. Given enough time, we expect that one molecule will be able to sample all of phase space, and therefore the sum over all instantaneous values of A for one molecule should represent the equilibrium probability distribution for that variable, $P(A)$. This is then related to the free energy projected onto A as

$$F(A) = -\beta \ln P(A) \quad (5.17)$$

If we look at this behavior there seems to be little information in the random fluctuations of A , but there are characteristic time scales and amplitudes to these changes. We can characterize these by comparing the value of A at time t with the value of A at time t' later. With

that in mind we define a time-correlation function (TCF) as a time-dependent quantity, $A(t)$, multiplied by that quantity at some later time, $A(t')$, and averaged over an equilibrium ensemble:

$$C_{AA}(t, t') \equiv \langle A(t) A(t') \rangle \quad (5.18)$$

Technically this is an auto-correlation function, which correlates the same variable at two points in time, whereas the correlation of two different variables in time is described through a cross-correlation function

$$C_{AB}(t, t') \equiv \langle A(t) B(t') \rangle \quad (5.19)$$

Following (5.8), the classical correlation function is

$$C_{AA}(t, t') = \int d\mathbf{p} \int d\mathbf{q} A(\mathbf{p}, \mathbf{q}; t) A(\mathbf{p}, \mathbf{q}; t') f(\mathbf{p}, \mathbf{q}) \quad (5.20)$$

while from (5.10) we can see that the quantum correlation function can be evaluated as

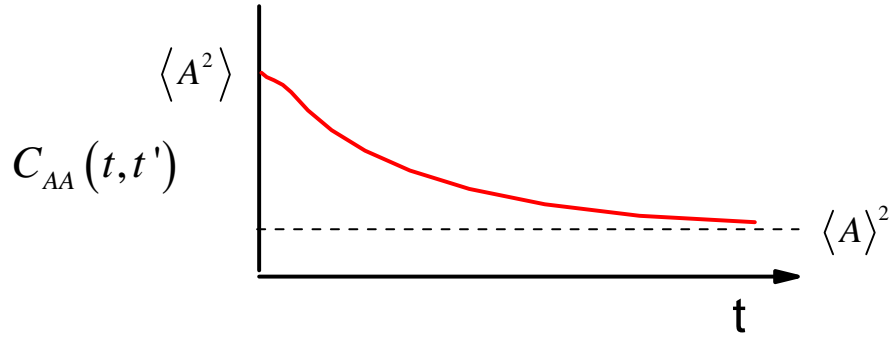
$$C_{AA}(t, t') = \sum_n p_n \langle n | A(t) A(t') | n \rangle. \quad (5.21)$$

So, what does a time-correlation function tell us? Qualitatively, a TCF describes how long a given property of a system persists until it is averaged out by microscopic motions of system. It describes how and when a statistical relationship has vanished. We can use correlation functions to describe various time-dependent chemical processes. We will use $\langle \mu(t) \mu(0) \rangle$ -the dynamics of the molecular dipole moment- to describe spectroscopy. We will also use it for relaxation processes induced by the interaction of a system and bath: $\langle H_{SB}(t) H_{SB}(0) \rangle$. Classically, you can use it to characterize transport processes. For instance a diffusion coefficient is related to the velocity correlation function:

$$D = \frac{1}{3} \int_0^\infty dt \langle v(t) v(0) \rangle$$

Properties of Correlation Functions

A typical correlation function for random fluctuations in the variable A might look like:



and is described by a number of properties:

1. When evaluated at $t = t'$, we obtain the maximum amplitude, the mean square value of A , which is positive for an autocorrelation function and independent of time.

$$C_{AA}(t, t) = \langle A(t) A(t) \rangle = \langle A^2 \rangle \geq 0 \quad (5.22)$$

2. For long time separations, the values of A become uncorrelated

$$\lim_{t \rightarrow \infty} C_{AA}(t, t') = \langle A(t) \rangle \langle A(t') \rangle = \langle A \rangle^2 \quad (5.23)$$

3. Since it's an equilibrium quantity, correlation functions are stationary. That means they do not depend on the absolute point of observation (t and t'), but rather the time-interval between observations. A stationary random process means that the reference point can be shifted by a value T

$$C_{AA}(t, t') = C_{AA}(t + T, t' + T). \quad (5.24)$$

So, choosing $T = -t'$, we see that only the time interval $t - t' \equiv \tau$ matters

$$C_{AA}(t, t') = C_{AA}(t - t', 0) = C_{AA}(\tau) \quad (5.25)$$

Implicit in this statement is an understanding that we take the time-average value of A to be equal to the equilibrium ensemble average value of A . This is the property of ergodic systems.

More on Stationary Processes¹

The ensemble average value of A can be expressed as a time-average or an ensemble average. For an equilibrium system, the time average is

$$\bar{A} = \lim_{T \rightarrow \infty} \frac{1}{2T} \int_{-T}^T dt A_i(t) \quad (5.26)$$

and the ensemble average is

$$\langle A \rangle = \sum_n \frac{e^{-\beta E_n}}{Z} \langle n | A | n \rangle. \quad (5.27)$$

These quantities are equal for an ergodic system $\langle A \rangle = \bar{A}$. We assume this property for our correlation functions. So, the correlation of fluctuations can be written

$$\overline{A(t)A(0)} = \lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T d\tau A_i(t+\tau) A_i(\tau) \quad (5.28)$$

or

$$\langle A(t)A(0) \rangle = \sum_n \frac{e^{-\beta E_n}}{Z} \langle n | A(t)A(0) | n \rangle \quad (5.29)$$

4. Classical correlation functions are real and even in time:

$$\begin{aligned} \langle A(t)A(t') \rangle &= \langle A(t')A(t) \rangle \\ C_{AA}(\tau) &= C_{AA}(-\tau) \end{aligned} \quad (5.30)$$

5. When we observe fluctuations about an average, we often redefine the correlation function in terms of the deviation from average

$$\delta A \equiv A - \langle A \rangle \quad (5.31)$$

$$C_{\delta A \delta A}(t) = \langle \delta A(t) \delta A(0) \rangle = C_{AA}(t) - \langle A \rangle^2 \quad (5.32)$$

Now we see that the long time limit when correlation is lost $\lim_{t \rightarrow \infty} C_{\delta A \delta A}(t) = 0$, and the zero time value is just the variance

$$C_{\delta A \delta A}(0) = \langle \delta A^2 \rangle = \langle A^2 \rangle - \langle A \rangle^2 \quad (5.33)$$

6. The characteristic time-scale of a random process is the correlation time, τ_c . This characterizes the time scale for TCF to decay to zero. We can obtain τ_c from

$$\tau_c = \frac{1}{\langle \delta A^2 \rangle} \int_0^\infty dt \langle \delta A(t) \delta A(0) \rangle \quad (5.34)$$

which should be apparent if you have an exponential form $C(t) = C(0) \exp(-t/\tau_c)$.

Examples of Time-Correlation Functions

EXAMPLE 1: Velocity autocorrelation function for gas.

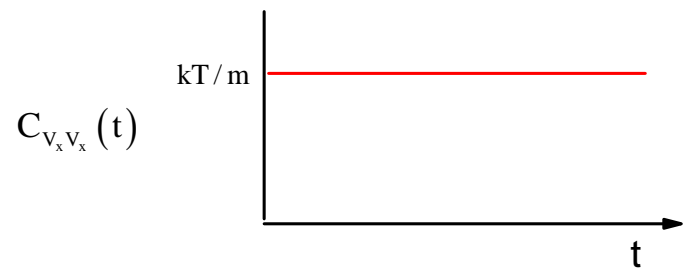
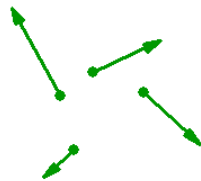
V_x : \hat{x} Component of molecular velocity $\langle V_x \rangle = 0$

$$C_{V_x V_x}(t) = \langle V_x(t) V_x(0) \rangle$$

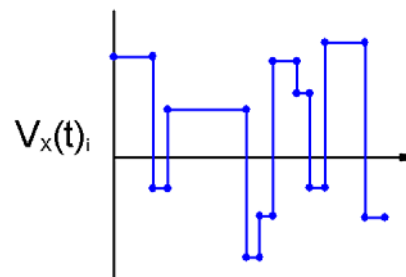
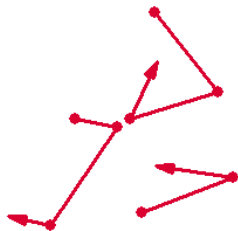
$$C_{V_x V_x}(0) = \langle V_x^2(0) \rangle = \frac{kT}{m}$$

Ideal gas:

- No collisions.
- Velocities are unchanged over t .



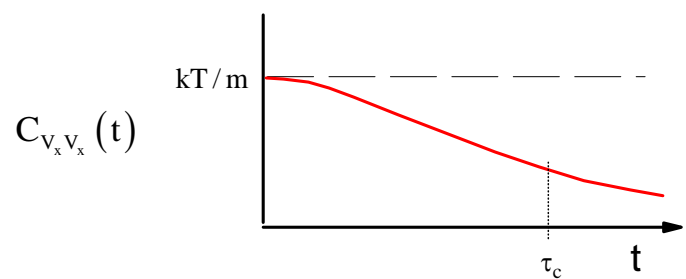
Dilute gas: Infrequent collisions



$$V_x(t) = V_x(0) \quad \text{for } t < \tau_c$$

$$V_x(t) = V_x(0) \pm \delta \quad \text{for } t \gtrsim \tau_c$$

τ_c is related to mean time between collisions. After collisions, correlation is lost.



EXAMPLE 2: Dipole moment for diatomic molecule in dilute gas: $\bar{\mu}_i$.

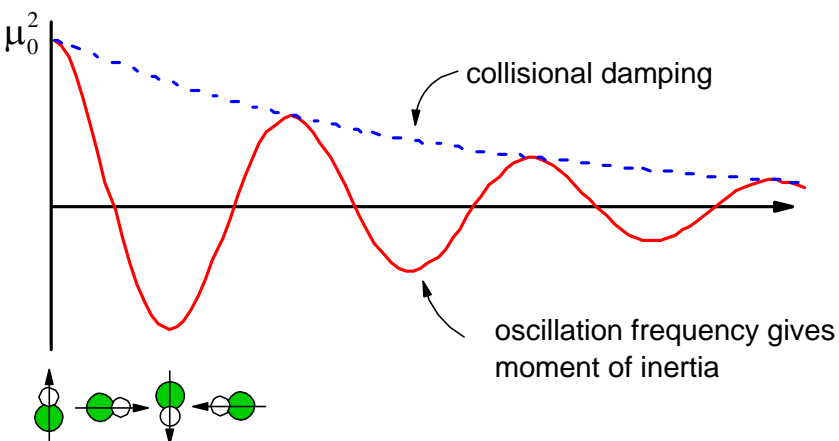
$$\langle \bar{\mu}_i \rangle = 0 \text{ (all angles are equally likely in an isotropic system)}$$

$$\bar{\mu}_i = \mu_0 \cdot \hat{u} \text{ (the dipole has a magnitude and direction)}$$

$$C_{\mu\mu}(t) = \langle \bar{\mu}(t) \bar{\mu}(0) \rangle$$

$$= \mu_0^2 \langle \hat{u}(t) \cdot \hat{u}(0) \rangle$$

The correlation function projects the time-dependent orientation onto the initial orientation



EXAMPLE 3: Displacement of harmonic oscillator.

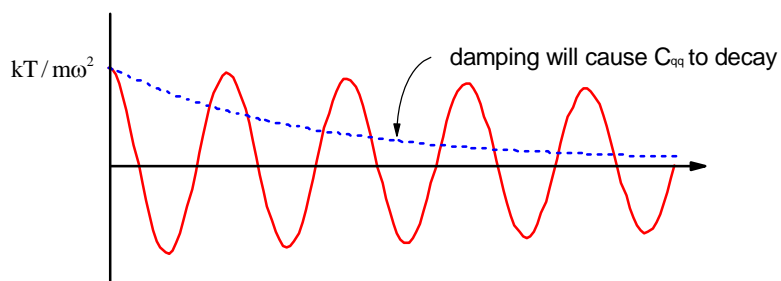
$$m\ddot{q} = -\kappa q \rightarrow \ddot{q} = -\omega^2 q$$

$$q(t) = q(0) \cos \omega t$$

$$\text{Since } \langle q^2(0) \rangle = \frac{kT}{m\omega^2}$$

$$C_{qq}(t) = \langle q(t) q(0) \rangle = \langle q^2(0) \rangle \cos \omega t$$

$$= \left(\frac{kT}{m\omega^2} \right) \cos \omega t$$



5.2. QUANTUM CORRELATION FUNCTIONS

Quantum correlation functions involve the equilibrium (thermal) average over a product of Hermetian operators evaluated two times. The thermal average is implicit in writing $C_{AA}(t, t') = \langle A(t) A(t') \rangle$. Naturally, this also invokes a Heisenberg representation of the operators, although in almost all cases, we will be writing correlation functions as interaction picture operators $A_I(t) = e^{+iH_0 t} A e^{-iH_0 t}$.

To emphasize the thermal average, the quantum correlation function can also be written as

$$C_{AA}(t, t') = \left\langle \frac{e^{-\beta H}}{Z} A(t) A(t') \right\rangle \quad (5.35)$$

If we evaluate this in a basis set $|n\rangle$, inserting a projection operator leads to our previous expression

$$C_{AA}(t, t') = \sum_n p_n \langle n | A(t) A(t') | n \rangle \quad (5.36)$$

with $p_n = e^{-\beta E_n} / Z$. Given the case of a time-independent Hamiltonian, we can also express this in the Schrödinger picture

$$\begin{aligned} C_{AA}(t, t') &= \sum_n p_n \left\langle n \left| \underline{U^\dagger(t) A U(t) U^\dagger(t') A U(t') A} \right| n \right\rangle \\ &= \sum_n p_n \langle n | A U(t - t') A | n \rangle e^{i\omega_n(t-t')} \\ &= \sum_{n,m} p_n \langle n | A | m \rangle \langle m | A | n \rangle e^{-i\omega_{mn}(t-t')} \\ &= \sum_{n,m} p_n |A_{mn}|^2 e^{-i\omega_{mn}(t-t')} \end{aligned} \quad (5.37)$$

Properties of Quantum Correlation Functions

There are a few properties of quantum correlation functions that can be obtained using the properties of the time-evolution operator. First, we can show the property of stationarity, which we have come to expect:

$$\begin{aligned}
\langle A(t)A(t') \rangle &= \langle U^\dagger(t)A(0)U(t)U^\dagger(t')A(0)U(t') \rangle \\
&= \langle U(t')U^\dagger(t)AU(t)U^\dagger(t')A \rangle \\
&= \langle U^\dagger(t-t')AU(t-t')A \rangle \\
&= \langle A(t-t')A(0) \rangle
\end{aligned} \tag{5.38}$$

Also, we can show that

$$\langle A(-t)A(0) \rangle = \langle A(t)A(0) \rangle^* = \langle A(0)A(t) \rangle \tag{5.39}$$

or

$$C_{AA}^*(t) = C_{AA}(-t) \tag{5.40}$$

This follows from

$$\begin{aligned}
\langle A(0)A(t) \rangle &= \langle A(0)U^\dagger AU \rangle = \langle UAU^\dagger A \rangle \\
&= \langle A(-t)A(0) \rangle
\end{aligned} \tag{5.41}$$

$$\begin{aligned}
\langle A(t)A(0) \rangle^* &= \langle U^\dagger AU A \rangle^* = \langle UAU^\dagger A \rangle \\
&= \langle A(0)A(t) \rangle
\end{aligned} \tag{5.42}$$

Note that the quantum $C_{AA}(t)$ is complex. You cannot directly measure a quantum correlation function, but observables are often related to the real or imaginary part of correlation functions, or other combinations of correlation functions.

$$C_{AA}(t) = C'_{AA}(t) + iC''_{AA}(t) \tag{5.43}$$

$$\begin{aligned}
C'_{AA}(t) &= \frac{1}{2} [C_{AA}(t) + C_{AA}^*(t)] = \frac{1}{2} [\langle A(t)A(0) \rangle + \langle A(0)A(t) \rangle] \\
&= \frac{1}{2} \langle [A(t), A(0)] \rangle_+
\end{aligned} \tag{5.44}$$

$$\begin{aligned}
C''_{AA}(t) &= \frac{1}{2i} [C_{AA}(t) - C_{AA}^*(t)] = \frac{1}{2i} [\langle A(t)A(0) \rangle - \langle A(0)A(t) \rangle] \\
&= \frac{1}{2i} \langle [A(t), A(0)] \rangle
\end{aligned} \tag{5.45}$$

We will see later in our discussion of linear response that C'_{AA} and C''_{AA} are directly proportional to the step response function S and the impulse response function R , respectively. R describes how a system is driven away from equilibrium by an external potential, whereas S describes the relaxation of the system to equilibrium when a force holding it away from equilibrium is released. The two are related by $R \propto \partial S / \partial t$.

We can also define a spectral or frequency-domain correlation function by Fourier transforming the TCF.

$$\tilde{C}_{AA}(\omega) = \tilde{\mathcal{F}}[C_{AA}(t)] = \int_{-\infty}^{+\infty} dt e^{i\omega t} C_{AA}(t) \quad (5.46)$$

For a time-independent Hamiltonian, as we might have in an interaction picture problem, the TCF in eq. (5.37) gives

$$\tilde{C}_{AA}(\omega) = \sum_{n,m} p_n |A_{mn}|^2 \delta(\omega - \omega_{mn}). \quad (5.47)$$

This expression looks very similar to the Golden rule transition rate from first order perturbation theory. In fact, the Fourier transform of time correlation functions evaluated at the energy gap gives the transition rate between states that we obtain from 1st order perturbation theory. Note that this expression is valid whether the initial states n are higher or lower in energy than final states m , and accounts for upward and downward transitions. If we compare the ratio of upward and downward transition rates between two states i and j , we have

$$\frac{\tilde{C}_{AA}(\omega_{ij})}{\tilde{C}_{AA}(\omega_{ji})} = \frac{p_j}{p_i} = e^{\beta E_{ij}}. \quad (5.48)$$

This is one way of showing the principle of detailed balance, which relates upward and downward transition rates at equilibrium to the difference in thermal occupation between states:

$$\tilde{C}_{AA}(\omega) = e^{\beta \hbar \omega} \tilde{C}_{AA}(-\omega). \quad (5.49)$$

5.3. RELAXATION RATES FROM CORRELATION FUNCTIONS

We have already seen that the rates obtained from first-order perturbation theory are related to the Fourier transform of the time-dependent external potential evaluated at the energy gap between the initial and final state. Here we will show that the rate of leaving an initially prepared state, typically expressed by Fermi's Golden Rule through a resonance condition in the frequency domain, can be expressed in the time-domain picture in terms of a time-correlation function for the interaction of the initial state with others.

The state-to-state form of Fermi's Golden Rule is

$$w_{k\ell} = \frac{2\pi}{\hbar} |V_{k\ell}|^2 \delta(E_k - E_\ell) \quad (5.50)$$

We will look specifically at the coupling of an initial state ℓ to all other states k . Time-correlation functions are expressions that apply to systems at thermal equilibrium, so we will thermally average this expression.

$$\bar{w}_{k\ell} = \frac{2\pi}{\hbar} \sum_{k,\ell} p_\ell |V_{k\ell}|^2 \delta(E_k - E_\ell) \quad (5.51)$$

where $p_\ell = e^{-\beta E_\ell} / Z$. The energy conservation statement expressed in terms of E or ω can be converted to the time-domain using the definition of the delta function

$$\delta(\omega) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} dt e^{i\omega t}, \quad (5.52)$$

giving

$$\bar{w}_{k\ell} = \frac{1}{\hbar^2} \sum_{k,\ell} p_\ell |V_{k\ell}|^2 \int_{-\infty}^{+\infty} dt e^{i(E_k - E_\ell)t/\hbar} \quad (5.53)$$

Writing the matrix elements explicitly and recognizing that $e^{iH_0 t} |\ell\rangle = e^{iE_\ell t} |\ell\rangle$, we have

$$\bar{w}_{mn} = \frac{1}{\hbar^2} \sum_{k,\ell} p_\ell \int_{-\infty}^{+\infty} dt e^{i(E_k - E_\ell)t/\hbar} \langle \ell | V | k \rangle \langle k | V | \ell \rangle \quad (5.54)$$

$$= \frac{1}{\hbar^2} \sum_{k,\ell} p_\ell \int_{-\infty}^{+\infty} dt \langle \ell | V | k \rangle \langle k | e^{iH_0 t} V e^{-iH_0 t} | \ell \rangle \quad (5.55)$$

Then, since $\sum_k |k\rangle \langle k| = 1$

$$\bar{w}_{mn} = \frac{1}{\hbar^2} \sum_{\ell=m,n} p_\ell \int_{-\infty}^{+\infty} dt \langle \ell | V_I(t) V_I(0) | \ell \rangle \quad (5.56)$$

$$\bar{w}_{mn} = \frac{1}{\hbar^2} \int_{-\infty}^{+\infty} dt \langle V_I(t) V_I(0) \rangle \quad (5.57)$$

As before $V_I(t) = e^{iH_0 t} V e^{-iH_0 t}$. The final expression indicates that integrating over a correlation function for the time-dependent interaction of the initial state with its surroundings gives the relaxation or transfer rate. Note that although eq. (5.54) expressed the transfer rate in terms of a Fourier transform evaluated at the energy gap $E_k - E_\ell$, eq. (5.57) is not a Fourier transform.