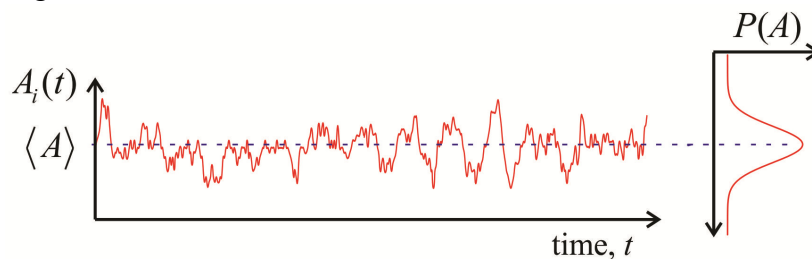


## 9. TIME-CORRELATION FUNCTIONS

### 9.1. Definitions, Properties, and Examples

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 an internal variable or expectation value for an ensemble at thermal equilibrium. They are generally applicable to any time-dependent process, but are commonly used to describe random (or stochastic) and irreversible processes in condensed phases. We will use them extensively in the description of spectroscopy and relaxation phenomena. Although they can be used to describe the oscillatory behavior of ensembles of pure quantum states, our work is motivated by finding a general tool that will help us deal with the inherent randomness of molecular systems at thermal equilibrium. They will be effective at characterizing irreversible relaxation processes and the loss of memory of an initial state in a fluctuating environment.



Returning to the microscopic fluctuations of a molecular variable  $A$ , there seems to be little information in observing the trajectory for a variable characterizing the time-dependent behavior of an individual molecule. However, this dynamics is not entirely random, since they are a consequence of time-dependent interactions with the environment. We can provide a statistical description of the characteristic time scales and amplitudes to these changes 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:

$$C_{AA}(t, t') \equiv \langle A(t) A(t') \rangle_{eq} \quad (9.1)$$

The classical form of the correlation function is evaluated as

$$C_{AA}(t, t') = \int d\mathbf{p} \int d\mathbf{q} A(\mathbf{p}, \mathbf{q}; t) A(\mathbf{p}, \mathbf{q}; t') \rho_{eq}(\mathbf{p}, \mathbf{q}) \quad (9.2)$$

whereas the quantum correlation function can be evaluated as

$$\begin{aligned}
 C_{AA}(t, t') &= \text{Tr}[\rho_{eq} A(t) A(t')] \\
 &= \sum_n p_n \langle n | A(t) A(t') | n \rangle
 \end{aligned}
 \tag{9.3}$$

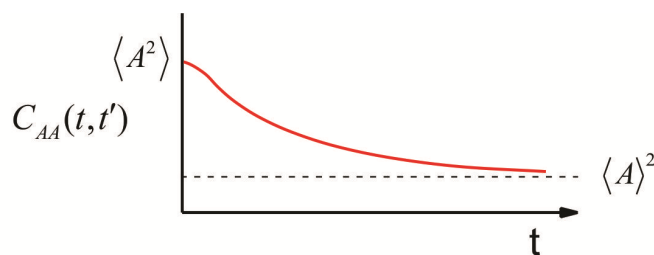
where  $p_n = e^{-\beta E_n} / Z$ . These are auto-correlation functions, which correlates the same variable at two points in time, but one can also define a cross-correlation function that describes the correlation of two different variables in time

$$C_{AB}(t, t') \equiv \langle A(t) B(t') \rangle \tag{9.4}$$

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 and interactions with its surroundings. It describes how and when a statistical relationship has vanished. We can use correlation functions to describe various time-dependent chemical processes. For instance, we will use  $\langle \mu(t) \mu(0) \rangle$  –the dynamics of the molecular dipole moment– to describe absorption spectroscopy. We will also use them for relaxation processes induced by the interaction of a system and bath:  $\langle H_{SB}(t) H_{SB}(0) \rangle$ . Classically, you can use TCFs 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 at thermal equilibrium in the variable  $A$  might look like



It 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.

$$C_{AA}(t, t) = \langle A(t) A(t) \rangle = \langle A^2 \rangle \geq 0 \tag{9.5}$$

2. For long time separations, as thermal fluctuations act to randomize the system, the values of  $A$  become uncorrelated

$$\lim_{t \rightarrow \infty} C_{AA}(t, t') = \langle A(t) \rangle \langle A(t') \rangle = \langle A \rangle^2 \tag{9.6}$$

3. Since it is 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 an arbitrary value  $T$

$$C_{AA}(t, t') = C_{AA}(t+T, t'+T) \quad (9.7)$$

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

$$C_{AA}(t, t') = C_{AA}(t - t', 0) = C_{AA}(\tau) \quad (9.8)$$

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  $A$ , i.e., the system is ergodic. So, the correlation of fluctuations can be expressed as either a time-average over a trajectory of one molecule

$$\overline{A(t)A(0)} = \lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T d\tau A_i(t+\tau)A_i(\tau) \quad (9.9)$$

or an equilibrium ensemble average

$$\langle A(t)A(0) \rangle = \sum_n \frac{e^{-\beta E_n}}{Z} \langle n | A(t)A(0) | n \rangle \quad (9.10)$$

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

$$\begin{aligned} \langle A(t)A(t') \rangle &= \langle A(t')A(t) \rangle \\ C_{AA}(\tau) &= C_{AA}(-\tau) \end{aligned} \quad (9.11)$$

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

$$\delta A \equiv A - \langle A \rangle \quad (9.12)$$

$$C_{\delta A \delta A}(t) = \langle \delta A(t) \delta A(0) \rangle = C_{AA}(t) - \langle A \rangle^2 \quad (9.13)$$

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

$$C_{\delta A \delta A}(0) = \langle \delta A^2 \rangle = \langle A^2 \rangle - \langle A \rangle^2 \quad (9.14)$$

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

$$\tau_c = \frac{1}{\langle \delta A^2 \rangle_0} \int_0^\infty dt \langle \delta A(t) \delta A(0) \rangle \quad (9.15)$$

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

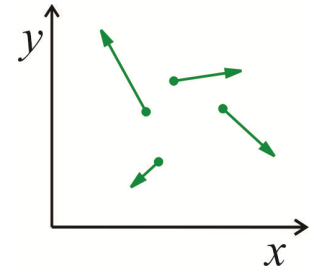
Let's analyze a dilute gas of molecules which have a Maxwell-Boltzmann distribution of velocities. We focus on the component of the molecular velocity along the  $\hat{x}$  direction,  $v_x$ . We know that the average velocity is  $\langle v_x \rangle = 0$ . The velocity correlation function is

$$C_{v_x v_x}(\tau) = \langle v_x(\tau) v_x(0) \rangle$$

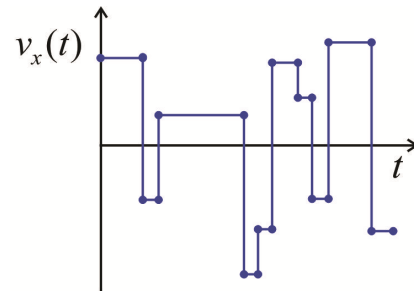
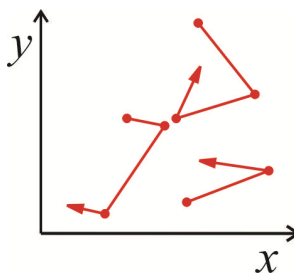
From the equipartition principle the average translational energy is  $\frac{1}{2} m \langle v_x^2 \rangle = k_B T / 2$ , so

$$C_{v_x v_x}(0) = \langle v_x^2(0) \rangle = \frac{k_B T}{m}$$

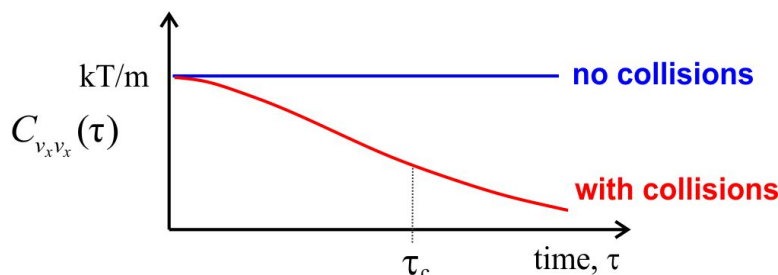
For time scales short compared to collisions between molecules, the velocity of any given molecule remains constant and unchanged, so the correlation function for the velocity is also unchanged at  $k_B T / m$ . This non-interacting regime corresponds to the behavior of an ideal gas.



For any real gas, there will be collisions that randomize the direction and speed of the molecules, so that any molecule over a long enough time will sample the various velocities within the Maxwell-Boltzmann distribution. From the trajectory of x-velocities for a given molecule we can calculate  $C_{v_x v_x}(\tau)$  using time-averaging. The correlation function will drop on with a correlation time  $\tau_c$ , which is related to mean time between collisions. After enough collisions, the correlation with the initial velocity is lost and



$C_{v_x v_x}(\tau)$  approaches  $\langle v_x^2 \rangle = 0$ . Finally, we can determine the diffusion constant for the gas, which relates the time and mean square displacement of the molecules:  $\langle x^2(t) \rangle = 2D_x t$ . From  $D_x = \int_0^\infty dt \langle v_x(t) v_x(0) \rangle$  we have  $D_x = k_B T \tau_c / m$ . In viscous fluids  $\tau_c / m$  is called the mobility,  $\mu$ .

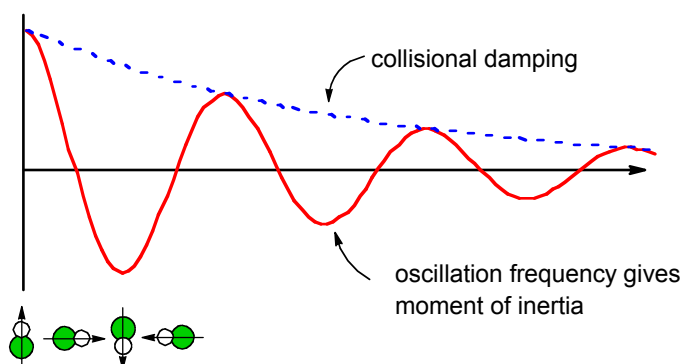


### Example 2: Dipole moment correlation function

Now consider the correlation function for the dipole moment of a polar diatomic molecule in a dilute gas,  $\bar{\mu}$ . For a rigid rotating object, we can decompose the dipole into a magnitude and a direction unit vector:  $\bar{\mu}_i = \mu_0 \cdot \hat{u}$ . We know that  $\langle \hat{u} \rangle = 0$  since all orientations of the gas phase molecules are equally probable. The correlation function is

$$\begin{aligned} C_{\mu\mu}(t) &= \langle \bar{\mu}(t) \bar{\mu}(0) \rangle \\ &= \langle \mu_0^2 \rangle \langle \hat{u}(t) \cdot \hat{u}(0) \rangle \end{aligned}$$

This correlation function projects the time-dependent orientation of the molecule onto the initial orientation. Free inertial rotational motion will lead to oscillations in the correlation function as the dipole spins. The oscillations in this correlation function can be related to the speed of rotation and thereby the molecule's moment of inertia (discussed below). Any apparent damping in this correlation function would reflect the thermal distribution of angular velocities. In practice a real gas would also have the collisional damping effects described in Example 1 superimposed on this relaxation process.



### Example 3: Harmonic oscillator correlation function

The time-dependent motion of a harmonic vibrational mode is given by Newton's law in terms of the acceleration and restoring force as  $m\ddot{q} = -\kappa q$  or  $\ddot{q} = -\omega^2 q$  where the force constant is  $\kappa = m\omega^2$ . We can write a common solution to this equation as  $q(t) = q(0) \cos \omega t$ . Furthermore, the equipartition theorem says that the equilibrium thermal energy in a harmonic vibrational mode is

$$\frac{1}{2} \kappa \langle q^2 \rangle = \frac{k_B T}{2}$$

We therefore can write the correlation function for the harmonic vibrational coordinate as

$$\begin{aligned} C_{qq}(t) &= \langle q(t)q(0) \rangle = \langle q^2 \rangle \cos \omega t \\ &= \frac{k_B T}{\kappa} \cos \omega t \end{aligned}$$

## 9.2. Correlation Function from a Discrete Trajectory

In practice classical correlation functions in molecular dynamics simulations or single molecule experiments are determined from a time-average over a long trajectory at discretely sampled data points. Let's evaluate eq. (9.9) for a discrete and finite trajectory in which we are given a series of  $N$  observations of the dynamical variable  $A$  at equally separated time points  $t_i$ . The separation between time points is  $t_{i+1}-t_i=\Delta t$ , and the length of the trajectory is  $T=N\Delta t$ . Then we have

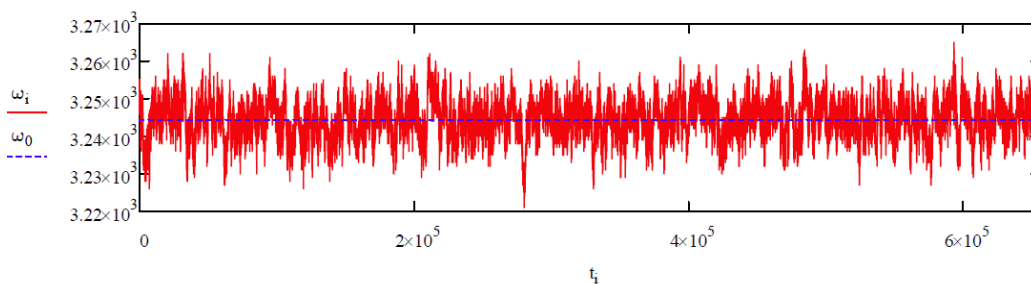
$$C_{AA} = \frac{1}{T} \sum_{i,j=1}^N \Delta t A(t_i)A(t_j) = \frac{1}{N} \sum_{i,j=1}^N A_i A_j \quad (9.16)$$

where  $A_i = A(t_i)$ . To make this more useful we want to express it as the time interval between points  $\tau = t_j - t_i = (j - i)\Delta t$ , and average over all possible pairwise products of  $A$  separated by  $\tau$ . Defining a new count integer  $n = j - i$ , we can express the delay as  $\tau = n\Delta t$ . For a finite data set there are a different number of observations to average over at each time interval ( $n$ ). We have the most pairwise products— $N$  to be precise—when the time points are equal ( $t_i=t_j$ ). We only have one data pair for the maximum delay  $\tau = T$ . Therefore, the number of pairwise products for a given delay  $\tau$  is  $N-n$ . So we can write eq. (9.16) as

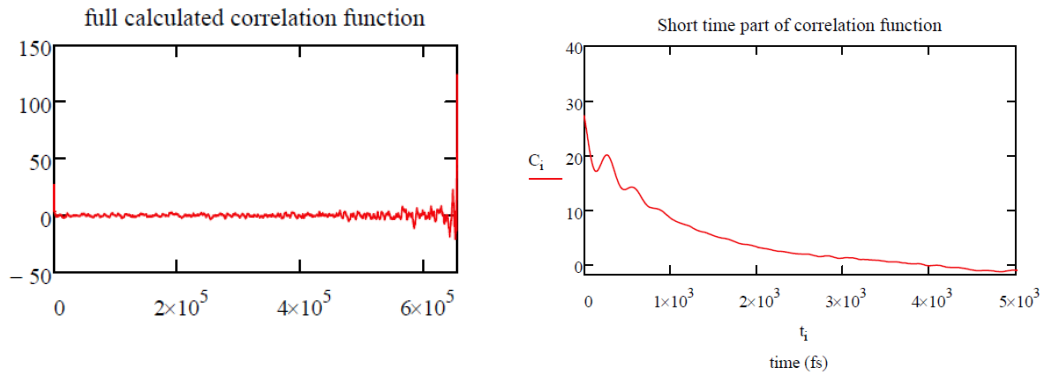
$$C_{AA}(\tau) = C(n) = \frac{1}{N-n} \sum_{i=1}^{N-n} A_{i+n} A_i \quad (9.17)$$

Note that this expression will only be calculated for positive values of  $n$ , for which  $t_j \geq t_i$ .

As an example consider the following calculation for fluctuations in a vibrational frequency  $\omega(t)$ , which consists of 32000 consecutive frequencies in units of  $\text{cm}^{-1}$  for points separated by 10 femtoseconds, and has a mean value of  $\omega_0 = 3244 \text{ cm}^{-1}$ . This trajectory illustrates that there are fast fluctuations on femtosecond time scales, but the behavior is seemingly random on 100 picosecond time scales



After determining the variation from the mean  $\delta\omega(t_i) = \omega(t_i) - \omega_0$ , the frequency correlation function is determined from eq. (9.17), with the substitution  $\delta\omega(t_i) \rightarrow A_i$ .



We can see that the correlation function reveals no frequency correlation on the time scale of  $10^4$ – $10^5$  fs, however a decay of the correlation function is observed for short delays signifying the loss of memory in the fluctuating frequency on the  $10^3$  fs time scale. From eq. (9.15) we find that the correlation time is  $\tau_c = 785$  fs.



### 9.3. Quantum Time-Correlation Functions

Quantum correlation functions involve the equilibrium (thermal) average over a product of Hermitian operators evaluated two times. The thermal average is implicit in writing  $C_{AA}(\tau) = \langle A(\tau)A(0) \rangle$ . 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

$$C_{AA}(\tau) = \left\langle \frac{e^{-\beta H}}{Z} A(\tau) A(0) \right\rangle \quad (9.18)$$

with  $\beta = (k_B T)^{-1}$ . If we evaluate this for a time-independent Hamiltonian in a basis of states  $|n\rangle$ , inserting a projection operator leads to our previous expression

$$C_{AA}(\tau) = \sum_n p_n \langle n | A(\tau) A(0) | n \rangle \quad (9.19)$$

with  $p_n = e^{-\beta E_n} / Z$ . Given the case of a time-independent Hamiltonian for which we have knowledge of the eigenstates, we can also express the correlation function in the Schrödinger picture as

$$\begin{aligned} C_{AA}(\tau) &= \sum_n p_n \langle n | U^\dagger(\tau) A U(\tau) A | n \rangle \\ &= \sum_{n,m} p_n \langle n | A | m \rangle \langle m | A | n \rangle e^{-i\omega_{mn}\tau} \\ C_{AA}(\tau) &= \sum_{n,m} p_n |A_{mn}|^2 e^{-i\omega_{mn}\tau} \end{aligned} \quad (9.20)$$

#### Properties of Quantum Correlation Functions

There are a few properties of quantum correlation functions for Hermitian operators that can be obtained using the properties of the time-evolution operator. First, we can show that correlation functions are stationary:

$$\begin{aligned} \langle A(t) A(t') \rangle &= \langle U^\dagger(t) A(0) U(t) U^\dagger(t') A(0) U(t') \rangle \\ &= \langle U(t') U^\dagger(t) A U(t) U^\dagger(t') A \rangle \\ &= \langle U^\dagger(t-t') A U(t-t') A \rangle \\ &= \langle A(t-t') A(0) \rangle \end{aligned} \quad (9.21)$$

$$\text{Similarly, we can show} \quad \langle A(-t) A(0) \rangle = \langle A(t) A(0) \rangle^* = \langle A(0) A(t) \rangle \quad (9.22)$$

or in short

$$C_{AA}^*(t) = C_{AA}(-t). \quad (9.23)$$

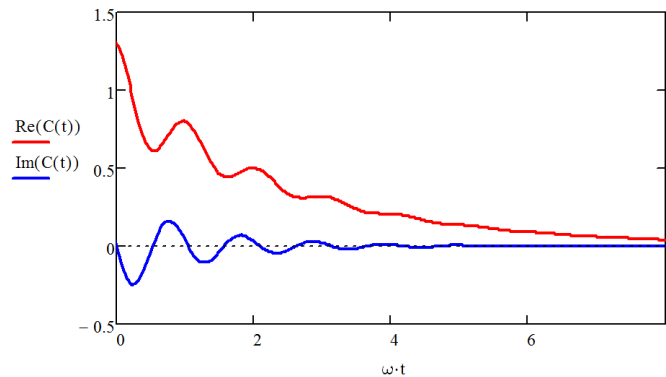
Note that the quantum  $C_{AA}(t)$  is complex. You cannot directly measure a quantum correlation function, but observables are often related to the real or imaginary part of correlation functions. The real and imaginary parts of  $C_{AA}(t)$  can be separated as

$$C_{AA}(t) = C'_{AA}(t) + iC''_{AA}(t) \quad (9.24)$$

$$\begin{aligned} C'_{AA}(t) &= \frac{1}{2} [C_{AA}(t) + C_{AA}^*(t)] = \frac{1}{2} [\langle A(t)A(0) \rangle + \langle A(0)A(t) \rangle] \\ &= \frac{1}{2} \langle [A(t), A(0)]_+ \rangle \end{aligned} \quad (9.25)$$

$$\begin{aligned} C''_{AA}(t) &= \frac{1}{2} [C_{AA}(t) - C_{AA}^*(t)] = \frac{1}{2} [\langle A(t)A(0) \rangle - \langle A(0)A(t) \rangle] \\ &= \frac{1}{2} \langle [A(t), A(0)] \rangle \end{aligned} \quad (9.26)$$

Above  $[A, B]_+ \equiv AB + BA$  is the anticommutator. As illustrated below, the real part is even in time, and can be expanded as Fourier series in cosines, whereas the imaginary part is odd, and can be expanded in sines. We will see later that the magnitude of the real part grows with temperature, but the imaginary does not. At 0 K, the real and imaginary components have equal amplitudes, but as one approaches the high temperature or classical limit, the real part dominates the imaginary.



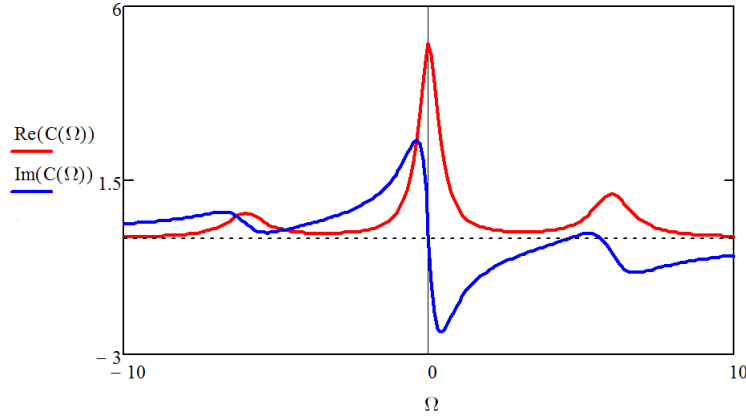
We will also see in our discussion of linear response that  $C'_{AA}$  and  $C''_{AA}$  are directly proportional to the step response function  $S$  and the impulse response function  $R$ , respectively.  $R$  describes how a system is driven away from equilibrium by an external potential, whereas 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

Since time and frequency are conjugate variables, we can also define a spectral or frequency-domain correlation function by the Fourier transformation of the TCF. The Fourier transform and its inverse are defined as

$$\tilde{C}_{AA}(\omega) = \tilde{\mathcal{F}}[C_{AA}(t)] = \int_{-\infty}^{+\infty} dt e^{i\omega t} C_{AA}(t) \quad (9.27)$$

$$C_{AA}(t) = \tilde{\mathcal{F}}^{-1}[\tilde{C}_{AA}(\omega)] = \frac{1}{2\pi} \int_{-\infty}^{+\infty} d\omega e^{-i\omega t} \tilde{C}_{AA}(\omega) \quad (9.28)$$

Examples of the frequency-domain correlation functions are shown below.



For a time-independent Hamiltonian, as we might have in an interaction picture problem, the Fourier transform of the TCF in eq. (9.20) gives

$$\tilde{C}_{AA}(\omega) = \sum_{n,m} p_n |A_{mn}|^2 \delta(\omega - \omega_{mn}) \quad (9.29)$$

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 first-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

$$\frac{\tilde{C}_{AA}(\omega_{ij})}{\tilde{C}_{AA}(\omega_{ji})} = \frac{p_j}{p_i} = e^{\beta E_{ij}} \quad (9.30)$$

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:

$$\tilde{C}_{AA}(\omega) = e^{\beta \hbar \omega} \tilde{C}_{AA}(-\omega) \quad (9.31)$$

This relationship together with a Fourier transform of eq. (9.23) allows us to obtain the real and imaginary components using

$$\tilde{C}_{AA}(\omega) \pm \tilde{C}_{AA}(-\omega) = (1 \pm e^{-\beta h \omega}) \tilde{C}_{AA}(\omega) \quad (9.32)$$

$$\tilde{C}'_{AA}(\omega) = \tilde{C}_{AA}(\omega)(1 + e^{-\beta h \omega}) \quad (9.33)$$

$$\tilde{C}''_{AA}(\omega) = \tilde{C}_{AA}(\omega)(1 - e^{-\beta h \omega}) \quad (9.34)$$

## 9.4. Transition 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

$$w_{k\ell} = \frac{2\pi}{\hbar} |V_{k\ell}|^2 \delta(E_k - E_\ell) \quad (9.35)$$

We will look specifically at the case of a system at thermal equilibrium in which the initially populated states  $\ell$  are coupled to all states  $k$ . Time-correlation functions are expressions that apply to systems at thermal equilibrium, so we will thermally average this expression.

$$\bar{w}_{k\ell} = \frac{2\pi}{\hbar} \sum_{k,\ell} p_\ell |V_{k\ell}|^2 \delta(E_k - E_\ell) \quad (9.36)$$

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

$$\delta(\omega) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} dt e^{i\omega t} \quad (9.37)$$

giving

$$\bar{w}_{k\ell} = \frac{1}{\hbar^2} \sum_{k,\ell} p_\ell |V_{k\ell}|^2 \int_{-\infty}^{+\infty} dt e^{i(E_k - E_\ell)t/\hbar} \quad (9.38)$$

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

$$\bar{w}_{k\ell} = \frac{1}{\hbar^2} \sum_{k,\ell} p_\ell \int_{-\infty}^{+\infty} dt e^{i(E_k - E_\ell)t/\hbar} \langle \ell | V | k \rangle \langle k | V | \ell \rangle \quad (9.39)$$

$$= \frac{1}{\hbar^2} \sum_{k,\ell} p_\ell \int_{-\infty}^{+\infty} dt \langle \ell | V | k \rangle \langle k | e^{iH_0 t/\hbar} V e^{-iH_0 t/\hbar} | \ell \rangle \quad (9.40)$$

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

$$\bar{w}_{mn} = \frac{1}{\hbar^2} \sum_{\ell=m,n} p_\ell \int_{-\infty}^{+\infty} dt \langle \ell | V_I(0) V_I(t) | \ell \rangle \quad (9.41)$$

$$\bar{w}_{mn} = \frac{1}{\hbar^2} \int_{-\infty}^{+\infty} dt \langle V_I(t) V_I(0) \rangle \quad (9.42)$$

As before  $V_I(t) = e^{iH_0 t/\hbar} V e^{-iH_0 t/\hbar}$ . 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. This is a general expression. Although the derivation emphasized specific eigenstates, eq. (9.42) shows that with a knowledge of a time-dependent interaction potential of any sort, we can calculate transition rates from the time-correlation function for that potential.

The same approach can be taken using the rates of transition in an equilibrium system induced by a harmonic perturbation

$$\bar{w}_{k\ell} = \frac{\pi}{2\hbar^2} \sum_{\ell,k} p_\ell |V_{k\ell}|^2 [\delta(\omega_{k\ell} - \omega) + \delta(\omega_{k\ell} + \omega)] \quad (9.43)$$

resulting in a similar expression for the transition rate in terms of a interaction potential time-correlation function

$$\begin{aligned} \bar{w}_{k\ell} &= \frac{1}{\hbar^2} \int_{-\infty}^{+\infty} dt e^{-i\omega t} \langle V_I(0) V_I(t) \rangle \\ &= \frac{1}{\hbar^2} \int_{-\infty}^{+\infty} dt e^{i\omega t} \langle V_I(t) V_I(0) \rangle \end{aligned} \quad (9.44)$$

We will look at this closer in the following section. Note that here the transfer rate is expressed in terms of a Fourier transform over a correlation function for the time-dependent interaction potential. Although eq. (9.42) is not written as a Fourier transform, it can in practice be evaluated by a Fourier transformation and evaluating its value at zero frequency.

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