5 The Reservoir Correlation Function

5.1 General Properties of $C_{uv}(t)$

we discuss general properties of the correlation function as well as of its Fourier transform

$$C_{uv}(\omega) = \int dt \; e^{i\omega t} C_{uv}(t)$$

if the Φ_u are Hermitian we have $C_{uv}^*(t) = C_{vu}(-t)$;
it follows immediately that

$$C_{vu}(-\omega) = \int dt \; e^{i\omega t} C_{uv}^*(t)$$

and

$$C_{uv}^*(\omega) = C_{vu}(\omega)$$

it is convenient to introduce symmetric and antisymmetric correlation functions

$$C_{uv}^{(+)}(t) = C_{uv}(t) + C_{uv}^*(t) \qquad C_{uv}^{(-)}(t) = C_{uv}(t) - C_{uv}^*(t)$$

note, that $C_{uv}^{(+)}(t)$ is a real function while $C_{uv}^{(-)}(t)$ is imaginary; moreover, $C_{uv}^{(+)}(-t) = C_{vu}^{(+)}(t)$ as well as $C_{uv}^{(-)}(-t) = -C_{vu}^{(-)}(t)$ hold if $C_{uv}^*(t) = C_{vu}(-t)$ is valid;

another fundamental property of $C_{uv}(\omega)$ can be derived if one starts from the definition and introduces eigenstates $|\alpha\rangle$ and eigenvalues E_α of the reservoir Hamiltonian

$$C_{uv}(\omega) = \frac{1}{\hbar^2} \int dt\ e^{i\omega t} \sum_{\alpha,\beta} \langle\alpha|\hat{R}_{\text{eq}} e^{iH_{\text{R}}t/\hbar}\Delta\Phi_u e^{-iH_{\text{R}}t/\hbar}|\beta\rangle\langle\beta|\Delta\Phi_v|\alpha\rangle$$

$$= \frac{1}{\hbar^2} \sum_{\alpha,\beta} \int dt\ e^{i(\omega-\omega_{\beta\alpha})t} f_\alpha \langle\alpha|\Delta\Phi_u|\beta\rangle\langle\beta|\Delta\Phi_v|\alpha\rangle$$

here $\omega_{\beta\alpha} = (E_\beta - E_\alpha)/\hbar$ are the transition frequencies between the reservoir energy levels and

$$f_\alpha \equiv \langle\alpha|\hat{R}_{\text{eq}}|\alpha\rangle = \exp(-E_\alpha/k_{\text{B}}T)/\sum_\beta \exp(-E_\beta/k_{\text{B}}T)$$

denotes the thermal distribution function with respect to the reservoir states;
the time integration of the exponential function produces the delta function and we get

$$C_{uv}(\omega) = \frac{2\pi}{\hbar^2} \sum_{\alpha,\beta} f_\alpha \langle\alpha|\Delta\Phi_u|\beta\rangle\langle\beta|\Delta\Phi_v|\alpha\rangle\delta(\omega - \omega_{\beta\alpha})$$

now we consider the Fourier transform of the correlation function where the indices u and v are interchanged; interchanging also α and β gives

$$C_{vu}(\omega) = \frac{2\pi}{\hbar^2} \sum_{\alpha,\beta} f_\beta \langle\alpha|\Delta\Phi_u|\beta\rangle\langle\beta|\Delta\Phi_v|\alpha\rangle\delta(\omega - \omega_{\alpha\beta})$$

according to the identity

$$\exp\left\{-\frac{E_\beta}{k_\mathrm{B}T}\right\}\delta(\omega-\omega_{\alpha\beta}) = \exp\left\{-\frac{E_\alpha-\hbar\omega}{k_\mathrm{B}T}\right\}\delta(\omega+\omega_{\beta\alpha})$$

we arrive at the important result

$$C_{uv}(\omega) = \exp\left\{\frac{\hbar\omega}{k_\mathrm{B}T}\right\}C_{vu}(-\omega)$$

it builds upon the definition of $C_{uv}(\omega)$ with respect to the thermal equilibrium of the reservoir; again, if $C_{uv}^*(t) = C_{vu}(-t)$ is valid the Fourier transform of the symmetric and antisymmetric part of the correlation function can be written as

$$C_{uv}^{(\pm)}(\omega) = C_{uv}(\omega) \pm C_{vu}(-\omega)$$

it follows that

$$C_{uv}(\omega) = \frac{C_{uv}^{(\pm)}(\omega)}{1 \pm \exp\{-\hbar\omega/k_\mathrm{B}T\}} \equiv (1+n(\omega))\,C_{uv}^{(-)}(\omega)\ .$$

we introduced the Bose–Einstein distribution function

$$n(\omega) = \frac{1}{\exp\{\hbar\omega/k_\mathrm{B}T\}-1}$$

we get a relation between the Fourier transforms of the symmetric and antisymmetric parts of the correlation function

$$C_{uv}^{(+)}(\omega) = \coth\left(\frac{\hbar\omega}{2k_\mathrm{B}T}\right)C_{uv}^{(-)}(\omega)$$

since a relation between the correlation function and its antisymmetric part $C_{uv}^{(-)}(\omega)$ has been established it is easy to express $C_{uv}(t)$ by $C_{uv}^{(-)}(\omega)$;

the inverse Fourier transform can then be written in terms of the half–sided Fourier integral

$$C_{uv}(t) = \int\limits_{-\infty}^{\infty} \frac{d\omega}{2\pi}\, e^{-i\omega t}[1 + n(\omega)]C_{uv}^{(-)}(\omega) = \int\limits_{0}^{\infty} \frac{d\omega}{2\pi}\, \left(e^{-i\omega t}[1 + n(\omega)]C_{uv}^{(-)}(\omega) + e^{i\omega t}n(\omega)C_{vu}^{(-)}(\omega) \right)$$

5.2 Harmonic Oscillator Reservoir

we set

$$\Phi = \hbar \sum_\xi \omega_\xi g_\xi Q_\xi$$

and get the correlation function

$$C(t) = \sum_{\xi,\xi'} \omega_\xi g_\xi \, \omega_{\xi'} g_{\xi'} \mathrm{tr}_\mathrm{R} \{ \hat{R}_\mathrm{eq} Q_\xi(t) Q_{\xi'} \}$$

the trace is specified as the summation with respect to the product of normal–mode harmonic oscillator states weighted by the respective thermal distributions

$$f_{N_\xi} = \frac{1}{\mathcal{Z}} \times \exp(-N_\xi \hbar \omega_\xi / k_\mathrm{B} T)$$

since only operators are concerned with mode index ξ and ξ' the trace reduces to

$$\mathrm{tr}_\mathrm{R}\{\hat{R}_\mathrm{eq} Q_\xi(t) Q_{\xi'}\} = \sum_{N_\xi} \sum_{N_{\xi'}} f_{N_\xi} f_{N_{\xi'}} \langle N_\xi | \langle N_{\xi'} | Q_\xi(t) Q_{\xi'} | N_\xi \rangle | N_{\xi'} \rangle$$

the remaining parts of $\sum_{\{N_\zeta\}}$ always give 1;
we note that, for example, $\langle N_{\xi'} | Q_{\xi'} | N_{\xi'} \rangle = 0$ and see that only the case $\xi = \xi'$ contributes;

the correlation function reads

$$C(t) = \sum_\xi \omega_\xi^2 g_\xi^2 \sum_{N_\xi} f_{N_\xi} \langle N_\xi | [C_\xi e^{-i\omega_\xi t} + C_\xi^+ e^{i\omega_\xi t}][C_\xi + C_\xi^+] | N_\xi \rangle = \sum_\xi \omega_\xi^2 g_\xi^2 \sum_{N_\xi} f_{N_\xi} \left([1 + N_\xi] e^{-i\omega_\xi t} + e^{i\omega_\xi t} N_\xi \right)$$

in the second part of this expression it has been used that only the operator combinations $C_\xi^+ C_\xi$ and $C_\xi C_\xi^+$ contribute;

finally, they have been replaced by the respective occupation number N_ξ;

the summations with respect to the oscillator quantum numbers can be removed by introducing the mean occupation number of a harmonic oscillator mode (Bose–Einstein distribution)

$$\sum_{N_\xi} N_\xi f_{N_\xi} = n(\omega_\xi)$$

we obtain

$$C(t) = \sum_\xi (\omega_\xi g_\xi)^2 \left([1 + n(\omega_\xi)] e^{-i\omega_\xi t} + n(\omega_\xi) e^{i\omega_\xi t}\right]$$

the Fourier transformed version follows as

$$C(\omega) = \sum_\xi (\omega_\xi g_\xi)^2 \left([1 + n(\omega_\xi)]\delta(\omega - \omega_\xi) + n(\omega_\xi)\delta(\omega + \omega_\xi)\right)$$

to have a compact notation at hand we introduce the new quantity $J(\omega)$ called spectral density

$$J(\omega) = \sum_\xi g_\xi^2 \delta(\omega - \omega_\xi)$$

with the help of this relation the correlation function can be written as

$$C(\omega) = 2\pi \, \omega^2 [1 + n(\omega)] \big(J(\omega) - J(-\omega) \big)$$

the spectral density contains the specific information about the reservoir and its interaction with the relevant system;
although the spectral density is defined in terms of a sum of delta functions any macroscopic system will in practice have a continuous spectral density;
there exist different models for $J(\omega)$ which are adapted to particular system–environment situations; they are often characterized by a frequency dependence showing a power law rise for small frequencies which turns, after reaching a cut–off frequency ω_c, into an exponential decay for large frequencies:

$$\omega^2 J(\omega) = \theta(\omega) \, j_0 \, \omega^p \, e^{-\omega/\omega_\mathrm{c}}$$

a different frequency dependence is given by the so–called Debye spectral density

$$\omega^2 J(\omega) = \theta(\omega) \, \frac{j_0 \omega}{\omega^2 + \omega_\mathrm{D}^2}$$

if there exists an unambiguous relation between the mode index ξ and the mode frequency ω_ξ the quantity g_ξ can be defined as a frequency–dependent function;
using the abbreviation $\kappa(\omega_\xi) = g_\xi^2$ it is then possible to rewrite the spectral density by introducing the density of states (DOS) of the reservoir oscillators

$$\mathcal{N}_{\mathrm{R}}(\omega) = \sum_\xi \delta(\omega - \omega_\xi)$$

it gives the number of oscillators in the reservoir one may find in the frequency interval $\Delta\omega$; it follows the relation

$$J(\omega) = \kappa(\omega)\mathcal{N}_{\mathrm{R}}(\omega)$$

which highlights that the spectral density can be viewed as the reservoir oscillator DOS which is weighted by the coupling strength between system and reservoir coordinates.

5.2.1 An Example

once $J(\omega)$ is fixed the time–dependent correlation function $C(t)$ can be calculated; in order to do this we separate it into a real and imaginary part

$$C(t) = \int_0^\infty d\omega \left(\cos(\omega t) \coth \frac{\hbar\omega}{2k_{\mathrm{B}}T} - i \sin(\omega t) \right) \omega^2 J(\omega) \; .$$

for the subsequent computations we use the Debye spectral density; it is easy to calculate $C(t)$ in the high–temperature limit $k_{\mathrm{B}}T \gg \hbar\omega_{\mathrm{D}}$ where one can take the following approximation

$$\coth(\hbar\omega/2k_{\mathrm{B}}T) \approx 2k_{\mathrm{B}}T/\hbar\omega$$

if one inserts this approximation into $C(t)$ and replaces $\omega\sin(\omega t)$ by the time derivative of $\cos(\omega t)$ one obtains

$$C(t) = \frac{j_0}{\hbar} \left(2k_{\mathrm{B}}T + i\hbar\frac{\partial}{\partial t} \right) \int_0^\infty d\omega \, \frac{\cos(\omega t)}{\omega^2 + \omega_{\mathrm{D}}^2}$$

since the integrand is an even function of ω we can extend the frequency integral up to $-\infty$ and calculate it using the residue theorem

$$\int d\omega \, \frac{\cos(\omega t)}{\omega^2 + \omega_{\mathrm{D}}^2} =$$

$$\frac{i}{4\omega_{\mathrm{D}}} \left(\int_{\mathcal{C}_1} d\omega \, e^{i\omega t} \left(\frac{1}{\omega + i\omega_{\mathrm{D}}} - \frac{1}{\omega - i\omega_{\mathrm{D}}} \right) - \int_{\mathcal{C}_2} d\omega \, e^{-i\omega t} \left(\frac{1}{\omega + i\omega_{\mathrm{D}}} - \frac{1}{\omega - i\omega_{\mathrm{D}}} \right) \right) = \frac{\pi}{\omega_{\mathrm{D}}} \, e^{-\omega_{\mathrm{D}}|t|}$$

$\mathcal{C}_1$ and $\mathcal{C}_2$ are closed integration contours (with mathematically positive orientation) in the upper or lower half of the complex frequency plane, respectively;

for $t > 0$, $\mathcal{C}_1$ is closed in the upper plane and $\mathcal{C}_2$ in the lower plane; the situation is reverse for $t < 0$;

we obtain for the correlation function

$$C(t) = \frac{\pi j_0}{2\hbar\omega_{\mathrm{D}}} \left(2k_{\mathrm{B}}T - i\mathrm{sgn}(t)\hbar\omega_{\mathrm{D}} \right) e^{-\omega_{\mathrm{D}}|t|}$$

it decays with a time constant τ_{c} determined by the inverse of ω_{D}; if the Debye frequency is assumed to be large, the correlation time goes to zero, i.e. $C(t) \approx \delta(t)$; this is the Markovian limit;