III.3.3 Properties and relations in frequency space

III.3.3 a Detailed balance relation and properties of the spectral density

Recalling the spectral decomposition (III.14) of the Fourier transform of the non-symmetrized correlation function:

$$\tilde{C}_{BA}(\omega) = 2\pi \sum_{n,n'} \pi_n \, B_{nn'} A_{n'n} \, \delta(\omega_{n'n} - \omega).$$

one sees that the exchange of the dummy indices n and n' and the relation $\pi_n/\pi_{n'} = \mathrm{e}^{-\beta\hbar\omega_{nn'}}$ yield, under consideration of the constraint imposed by the δ-term, the *detailed balance relation*

$$\boxed{\tilde{C}_{BA}(-\omega) = \tilde{C}_{AB}(\omega) \, \mathrm{e}^{-\beta\hbar\omega}.} \tag{III.53}$$

This relation is a generic property of systems at canonical equilibrium.

The two obvious limits of this relation can be readily discussed. For $\hbar\omega \ll k_BT$, i.e. in the "classical regime", one finds the symmetric (in particular when $\hat{B} = \hat{A}$) relation $\tilde{C}_{BA}(-\omega) \simeq \tilde{C}_{AB}(\omega)$. On the other hand, the asymmetry—which reflects the difference between the probabilities for the absorption or emission of energy by the system—becomes large in the "quantum limit" $\hbar\omega \gg k_BT$, and in particular for vanishingly small T, in which case $\tilde{C}_{BA}(-\omega) \simeq 0$ for negative frequencies.

Either by Fourier transforming the identities (III.46b) and (III.47a) or by invoking directly the definition (III.20), one finds that the spectral density obeys the properties

- $\tilde{\xi}_{BA}(\omega) = -\tilde{\xi}_{AB}(-\omega);$ (III.54a)
- $\tilde{\xi}_{BA}(\omega)^* = \tilde{\xi}_{A^\dagger B^\dagger}(\omega) = -\tilde{\xi}_{B^\dagger A^\dagger}(-\omega);$ (III.54b)
- if $\hat{A} = \hat{A}^\dagger$ and $\hat{B} = \hat{B}^\dagger$, $\tilde{\xi}_{BA}(\omega)^* = -\tilde{\xi}_{BA}(-\omega) = \tilde{\xi}_{AB}(\omega).$ (III.54c)

As we shall now see, the functions $\tilde{\chi}_{BA}(\omega)$, $\tilde{C}_{BA}(\omega)$, $\tilde{S}_{BA}(\omega)$ and $\tilde{K}_{BA}(\omega)$ can all be expressed in terms of the spectral density $\tilde{\xi}_{BA}(\omega)$. There follows relations similar to Eqs. (III.54) for the other spectral representations, which we shall not list.

III.3.3 b Relations between different correlation functions in frequency space

Relation between $\tilde{\chi}_{BA}(\omega)$ and $\tilde{\xi}_{BA}(\omega)$

Using the decomposition (III.20) of the spectral density, relation (III.41) can be rewritten as

$$\widehat{\chi}_{BA}(z) = \frac{1}{\pi}\int_{-\infty}^{\infty}\frac{\tilde{\xi}_{BA}(\omega)}{\omega - z}\,\mathrm{d}\omega. \tag{III.55}$$

This identity constitutes yet another spectral representation of $\widehat{\chi}_{BA}(z)$, valid in the whole complex plane.

Renaming the integration variable ω', setting $z = \omega + \mathrm{i}\varepsilon$ and taking the limit $\varepsilon \to 0^+$ under consideration of Eq. (III.40), one naturally recovers Eq. (III.29)

$$\tilde{\chi}_{BA}(\omega) = \frac{1}{\pi}\lim_{\varepsilon\to 0^+}\int_{-\infty}^{\infty}\frac{\tilde{\xi}_{BA}(\omega')}{\omega' - \omega - \mathrm{i}\varepsilon}\,\mathrm{d}\omega'. \tag{III.29}$$

Equation (III.55) can be further exploited to yield another relation between $\tilde{\chi}_{BA}(\omega)$ and $\tilde{\xi}_{BA}(\omega)$. Writing the principal value of $1/(\omega' - \omega)$ [cf. Eq. (A.2b)] in two different ways and subtracting them, one finds

$$\lim_{\varepsilon\to 0^+}\big[\widehat{\chi}_{BA}(\omega + \mathrm{i}\varepsilon) - \widehat{\chi}_{BA}(\omega - \mathrm{i}\varepsilon)\big] = 2\mathrm{i}\tilde{\xi}_{BA}(\omega), \tag{III.56}$$

i.e. the difference between the values of $\widehat{\chi}_{BA}(z)$ in the upper and lower complex half-planes on each side of the point $\omega \in \mathbb{R}$ is proportional to $\tilde{\xi}_{BA}(\omega)$. Along a portion of the real axis where $\tilde{\xi}_{BA}(\omega)$ is continuous—which might happen in a system in the thermodynamic limit, when the Bohr frequencies span a continuous spectrum—and non-vanishing, $\widehat{\chi}_{BA}(z)$ thus has a cut.

The first term in Eq. (III.56) is given by Eq. (III.40). For the value in the lower half-plane, using Eq. (III.41) gives

$$\widehat{\chi}_{BA}(\omega - \mathrm{i}\varepsilon) = \frac{1}{\hbar}\sum_{n,n'}(\pi_n - \pi_{n'})B_{nn'}A_{n'n}\,\frac{1}{\omega_{n'n} - \omega + \mathrm{i}\varepsilon} = \frac{1}{\hbar}\sum_{n,n'}\bigg[(\pi_n - \pi_{n'})B^*_{nn'}A^*_{n'n}\,\frac{1}{\omega_{n'n} - \omega - \mathrm{i}\varepsilon}\bigg]^*.$$

Recognizing in $A^*_{n'n}$, $B^*_{n'n}$ the matrix elements of $\hat{A}^\dagger$, $\hat{B}^\dagger$ in the basis $\{|\phi_n\rangle\}$, the rightmost term can be rewritten as $[\widehat{\chi}_{A^\dagger B^\dagger}(\omega + \mathrm{i}\varepsilon)]^*$. Invoking Eq. (III.40) again, one finds

$$\lim_{\varepsilon\to 0^+}\widehat{\chi}_{BA}(\omega - \mathrm{i}\varepsilon) = \lim_{\varepsilon\to 0^+}[\widehat{\chi}_{A^\dagger B^\dagger}(\omega + \mathrm{i}\varepsilon)]^* = \tilde{\chi}_{A^\dagger B^\dagger}(\omega)^*.$$

All in all, Eq. (III.56) thus becomes

$$\tilde{\xi}_{BA}(\omega) = \frac{1}{2\mathrm{i}}\big[\tilde{\chi}_{BA}(\omega) - \tilde{\chi}_{A^\dagger B^\dagger}(\omega)^*\big]. \tag{III.57}$$

Since the susceptibilities $\tilde{\chi}_{BA}(\omega)$ and $\tilde{\chi}_{A^\dagger B^\dagger}(\omega)$ are in general not equal, even if $\hat{A}$ and $\hat{B}$ are Hermitian, $\tilde{\xi}_{BA}(\omega)$ will differ from the imaginary part of $\tilde{\chi}_{BA}(\omega)$.

In the specific case $\hat{B} = \hat{A}^\dagger$, Eq. (III.57) shows that the spectral function is the imaginary part of the generalized susceptibility

$$\boxed{\tilde{\xi}_{A^\dagger A}(\omega) = \mathrm{Im}\,\tilde{\chi}_{A^\dagger A}(\omega).} \tag{III.58}$$

As we have seen in § III.2.2, the spectral density characterizes energy dissipation in the system. As a consequence, the imaginary part of the susceptibility $\tilde{\chi}_{BA}(\omega)$ is often referred to as "dissipative part", even if $\hat{B} \neq \hat{A}^\dagger$.[50]

[50] This denomination can actually be dangerous if $\hat{A}$ and $\hat{B}$ behave differently under time reversal, see the second remark at the end of § III.3.5.

Remark: The relation between $\operatorname{Im}\tilde{\chi}_{A^\dagger A}(\omega)$ and dissipation can be recovered by the following heuristic argument. Viewing $\hat{A}(t)$ as the "generalized displacement" conjugate to the force $f(t)$ in the Hamiltonian (in the Heisenberg picture with respect to $\hat{H}_0$), then the power dissipated by the system is the product of the force with the "velocity", namely

$$\frac{\mathrm{d}E_{\text{tot.}}}{\mathrm{d}t} = f(t)\left\langle\frac{\mathrm{d}\hat{A}(t)}{\mathrm{d}t}\right\rangle_{\text{n.eq.}}.$$

Assuming a harmonic force $f(t) = f_\omega\hat{A}\cos\omega t = f_\omega \operatorname{Re}\big(\hat{A}\mathrm{e}^{-\mathrm{i}\omega t}\big)$, the linear response of $\hat{A} = \hat{A}^\dagger$ is given by $\langle\hat{A}^\dagger\rangle_{\text{n.eq.}} = f_\omega\big[\operatorname{Re}\tilde{\chi}_{A^\dagger A}(\omega)\cos\omega t + \operatorname{Im}\tilde{\chi}_{A^\dagger A}(\omega)\sin\omega t\big]$. Differentiating with respect to t yields at once the instantaneous power, which after averaging over one period of the force yields for the mean rate of energy dissipation

$$\overline{\frac{\mathrm{d}E_{\text{tot.}}}{\mathrm{d}t}} = \frac{f_\omega^2}{2}\,\omega\operatorname{Im}\tilde{\chi}_{A^\dagger A}(\omega),$$

which is of course equivalent to Eq. (III.31).

Relation between $\tilde{C}_{BA}(\omega)$ and $\tilde{\xi}_{BA}(\omega)$

Comparing the spectral decomposition (III.14) of the Fourier transform of the non-symmetrized correlation function with the spectral density (III.20), one sees that the only change is the replacement of $2\pi_n$ by $(\pi_n - \pi_{n'})/\hbar$.

The specific form (III.2b) of the canonical equilibrium populations leads to the identity

$$\pi_n = (\pi_n - \pi_{n'})\frac{\pi_n}{\pi_n - \pi_{n'}} = (\pi_n - \pi_{n'})\frac{1}{1-\mathrm{e}^{-\beta(E_{n'}-E_n)}} = (\pi_n - \pi_{n'})\frac{1}{1-\mathrm{e}^{-\beta\hbar\omega_{n'n}}}.$$

As the term $\delta(\omega_{n'n}-\omega)$ in Eq. (III.14) or (III.20) imposes $\omega_{n'n} = \omega$ in the exponent, one finds

$$\boxed{\tilde{C}_{BA}(\omega) = \frac{2\hbar}{1-\mathrm{e}^{-\beta\hbar\omega}}\,\tilde{\xi}_{BA}(\omega).} \tag{III.59}$$

Relation between $\tilde{K}_{BA}(\omega)$ and $\tilde{\xi}_{BA}(\omega)$

Consider the spectral representation (III.22) of the Fourier transform of Kubo's canonical correlation function. The term $\delta(\omega-\omega_{n'n})$ allows us to replace the Bohr frequencies in the denominator by ω. Comparison with the decomposition (III.20) of the spectral density then yields at once the identity

$$\boxed{\tilde{K}_{BA}(\omega) = \frac{2}{\beta}\frac{\tilde{\xi}_{BA}(\omega)}{\omega}.} \tag{III.60}$$

Relation between $\tilde{S}_{BA}(\omega)$ and $\tilde{\xi}_{BA}(\omega)$

As was done above for $\tilde{C}_{BA}(\omega)$, one sees that the spectral decomposition of the Fourier transform of the symmetric correlation function and the spectral function (III.20) only differ in that the latter involves the difference $\pi_n - \pi_{n'}$ of the populations of different energy eigenstates, while the former involves their sum. Invoking again the form (III.2b) of the equilibrium populations, one obtains the identity

$$\pi_n + \pi_{n'} = (\pi_n - \pi_{n'})\frac{\pi_n + \pi_{n'}}{\pi_n - \pi_{n'}} = (\pi_n - \pi_{n'})\frac{1+\mathrm{e}^{-\beta\hbar\omega_{n'n}}}{1-\mathrm{e}^{-\beta\hbar\omega_{n'n}}} = (\pi_n - \pi_{n'})\coth\frac{\beta\hbar\omega_{n'n}}{2}.$$

As before, $\omega_{n'n}$ is set to ω by the term $\delta(\omega_{n'n}-\omega)$, so that the argument of the hyperbolic cotangent in the rightmost member is actually independent of n and n'. Equation (III.18) then yields

$$\boxed{\tilde{S}_{BA}(\omega) = \hbar\coth\frac{\beta\hbar\omega}{2}\,\tilde{\xi}_{BA}(\omega).} \tag{III.61}$$

For $|\beta\hbar\omega| \ll 1$, one has $\coth(\frac{1}{2}\beta\hbar\omega) \sim 2/\beta\hbar\omega$. One thus finds with the help of relation (III.60)

$$\tilde{S}_{BA}(\omega) \sim \frac{2}{\beta\omega}\,\tilde{\xi}_{BA}(\omega) = \tilde{K}_{BA}(\omega).$$

That is, $\tilde{S}_{BA}(\omega)$ and $\tilde{K}_{BA}(\omega)$ tend towards each other in the classical limit $\hbar \to 0$

III.3.3 c Recapitulation of the various correlation functions

Let us summarize the main results we have found above for the various correlation functions we have introduced, indicating the physical phenomenon in which they naturally appear, as well as various relations among them.

	t-space	ω-space
Spectral function (dissipation)	$\xi_{BA}(t) = \frac{1}{2\hbar}\left\langle\left[\hat{B}_{\rm I}(t),\hat{A}\right]\right\rangle_{\rm eq.} = \frac{\beta}{2{\rm i}}\,K_{B\dot{A}}(t)$	$\tilde{\xi}_{BA}(\omega) = \frac{\pi}{\hbar}\sum_{n,n'}(\pi_n - \pi_{n'}) \times \times B_{nn'}A_{n'n}\,\delta(\omega_{n'n}-\omega)$
Response function / susceptibility	$\chi_{BA}(t) = 2{\rm i}\Theta(t)\xi_{BA}(t) = \beta\Theta(t)K_{B\dot{A}}(t)$	$\tilde{\chi}_{BA}(\omega) = \frac{1}{\pi}\lim_{\varepsilon\to 0^+}\int_{-\infty}^{\infty}\frac{\tilde{\xi}_{BA}(\omega')}{\omega'-\omega-{\rm i}\varepsilon}\,{\rm d}\omega'$
Symmetric correlation function (fluctuations)	$S_{BA}(t) = \frac{1}{2}\left\langle\left\{\hat{B}_{\rm I}(t),\hat{A}\right\}_+\right\rangle_{\rm eq.}$	$\tilde{S}_{BA}(\omega) = \hbar\coth\frac{\beta\hbar\omega}{2}\,\tilde{\xi}_{BA}(\omega)$
Canonical correlation function (relaxation for $t \geq 0$)	$K_{BA}(t) = \frac{1}{\beta}\int_0^\beta\left\langle {\rm e}^{\lambda\hat{H}_0}\hat{A}\,{\rm e}^{-\lambda\hat{H}_0}\hat{B}_{\rm I}(t)\,{\rm d}\lambda\right\rangle_{\rm eq.}$	$\tilde{K}_{BA}(\omega) = \frac{2}{\beta\omega}\,\tilde{\xi}_{BA}(\omega)$

Table III.1 – Summary of the various correlation functions in linear response theory.

III.3.4 Fluctuation–dissipation theorem

Equations (III.59), (III.60), and (III.61) relate the Fourier transforms of the non-symmetrized, canonical and symmetric correlation functions to the spectral function $\tilde{\xi}_{BA}(\omega)$. We now discuss the physical content of these relations and present an example of application.

III.3.4 a First fluctuation–dissipation theorem

Consider first the special case $\hat{B} = \hat{A}$, with $\hat{A}$ an observable, thus Hermitian. Together with Eq. (III.58), one has the series of identities

$$\operatorname{Im}\tilde{\chi}_{AA}(\omega) = \tilde{\xi}_{AA}(\omega) = \frac{\beta\omega}{2}\tilde{K}_{AA}(\omega) = \frac{1-{\rm e}^{\beta\hbar\omega}}{2\hbar}\tilde{C}_{AA}(\omega) = \frac{\tanh\frac{\beta\hbar\omega}{2}}{\hbar}\tilde{S}_{AA}(\omega). \tag{III.62}$$

The two leftmost functions are associated with dissipation in the system when it is excited by a perturbation coupling to $\hat{A}$ (§ III.2.2). That is, they represent (part of) the dynamical response of the system when it is driven out of equilibrium by an external constraint. Meanwhile, the two rightmost functions encode the temporal (auto)correlation and spontaneous fluctuations of $\hat{A}$ in the system at thermodynamic equilibrium. These two pairs of correlation functions thus model a priori different physical phenomena: their interrelation expressed by Eq. (III.62) is thus non-trivial, and constitutes the so-called *fluctuation–dissipation theorem*.

Traditionally, the denomination *fluctuation–dissipation theorem* is rather attached to relations in which the Fourier transform of the correlation function which stands for fluctuations is explicitly written as a time integral; for instance,

$$\operatorname{Im}\tilde{\chi}_{AA}(\omega) = \frac{1}{2k_BT}\int_{-\infty}^{\infty} \omega K_{AA}(t)\,\mathrm{e}^{\mathrm{i}\omega t}\,\mathrm{d}t, \tag{III.63}$$

where β has been replaced by its expression in terms of the temperature, or

$$\operatorname{Im}\tilde{\chi}_{AA}(\omega) = \frac{\tanh\frac{\beta\hbar\omega}{2}}{\hbar}\int_{-\infty}^{\infty} S_{AA}(t)\,\mathrm{e}^{\mathrm{i}\omega t}\,\mathrm{d}t. \tag{III.64}$$

More generally, for an arbitrary pair of observables $\hat{A}$, $\hat{B}$ one can simply Fourier transform the Kubo formula [Eq. (III.51)]

$$\chi_{BA}(t) = \frac{1}{k_BT}\,\Theta(t)K_{B\dot{A}}(t),$$

which gives

$$\boxed{\tilde{\chi}_{BA}(\omega) = \frac{1}{k_BT}\int_0^{\infty} K_{B\dot{A}}(t)\,\mathrm{e}^{\mathrm{i}\omega t}\,\mathrm{d}t.} \tag{III.65}$$

Following Kubo [36], this identity is referred to as first fluctuation–dissipation theorem.(51)

Remarks:

∗ Kubo's canonical function can be associated with a mechanical reaction of the system when it is perturbed (§ III.2.3). Yet the third term of Eq. (III.62) also becomes identical to the two rightmost ones in the classical limit, in which case it is rather related to the equilibrium dynamics of the fluctuations of $\hat{A}$. Accordingly, in relation (III.65) the "fluctuation" part of the theorem is played by the canonical correlation function.

∗ As explained in the second remark at the end of § III.3.5, which part, real of imaginary, of the susceptibility is dissipative depends on the time-reversal signatures of the two observables $\hat{A}$ and $\hat{B}$. In practice, Eq. (III.65) is often considered with $\hat{B} = \hat{\dot{A}}$, time-reversal parity is opposite to that of $\hat{A}$. In that case the dissipative part of $\tilde{\chi}_{BA}(\omega)$ is the real part, as e.g. in the example of next paragraph.

∗ The "second" fluctuation–dissipation theorem will be discussed in Chap. IV on Brownian motion.

III.3.4 b Application: Johnson–Nyquist noise

Consider an arbitrary passive electric circuit,(52) which can either be closed on itself or submitted to a voltage $V_{\text{ext.}}(t)$, at thermodynamic equilibrium at temperature T. Let $I(t)$ denote the electric current through the circuit. In the absence of external voltage, $I(t)$ vanishes at equilibrium.

Assume first that the circuit is submitted to $V_{\text{ext.}}(t)$. The average electric current $\langle I(t)\rangle_{\text{n.eq.}}$ in the circuit can be computed within the (classical) theory of linear response, where the angular brackets denote the result of a "typical" measurement, as obtained by averaging over many repeated measurements so as to minimize the uncertainty of a single observation.

The external voltage $V_{\text{ext.}}(t)$ couples to the electric charge Q flowing in the circuit, which thus plays the role of the excited (classical) observable A. In turn, the responding observable B is here the electric current $I(t)$. Going to frequency space, the response of $\langle I(t)\rangle_{\text{n.eq.}}$ to the excitation $V_{\text{ext.}}(t)$ is governed by the generalized admittance $\tilde{\chi}_{IQ}(\omega)$, which is simply the inverse of the *electric impedance* $Z(\omega)$ of the circuit:

$$\big\langle I(t)\big\rangle_{\text{n.eq.}} = \tilde{\chi}_{IQ}(\omega)\tilde{V}_{\text{ext.}}(\omega) \quad \text{with} \quad \tilde{\chi}_{IQ}(\omega) = \frac{1}{Z(\omega)}.$$

(51)... or fluctuation–dissipation theorem of the first kind.
(52)... consisting of *linear* elements only: resistors, inductors, capacitors and memristors.

Consider now the case in which the circuit is closed on itself, i.e. $V_{\rm ext.} = 0$. The circuit is in an equilibrium state, and the electric current $I(t)$ fluctuates around its average value $\langle I(t)\rangle_{\rm eq.} = 0$.

The fluctuation–dissipation theorem (III.65) relates $\tilde{\chi}_{IQ}(\omega)$ to the fluctuations of the electric current. Since $\dot{Q} = I$, one thus has under consideration of the classical limit (III.107) of the canonical correlation function

$$\tilde{\chi}_{IQ}(\omega) = \frac{1}{k_BT}\int_0^\infty \big\langle I(t)I(0)\big\rangle_{\rm eq.}\,{\rm e}^{{\rm i}\omega t}\,{\rm d}t. \tag{III.66}$$

Since $\langle I(t)I(0)\rangle_{\rm eq.}$ is a real and even function of t, the complex conjugate of the right member can be expressed as the integral of the same integrand between $-\infty$ and 0. Taking half the sum of Eq. (III.66) and its complex conjugate thus yields

$${\rm Re}\,\frac{1}{Z(\omega)} = \frac{R(\omega)}{|Z(\omega)|^2} = \frac{1}{2k_BT}\int_{-\infty}^\infty \big\langle I(t)I(0)\big\rangle_{\rm eq.}\,{\rm e}^{{\rm i}\omega t}\,{\rm d}t, \tag{III.67}$$

with $R(\omega)$ the real part—the *resistive part*—of the impedance $Z(\omega)$. This is a relation between the resistance and impedance on the one hand and the fluctuations of the current in the electric circuit on the other side. Performing the inverse Fourier transform and setting $t = 0$, one finds

$$\big\langle I^2\big\rangle_{\rm eq.} = \frac{2k_BT}{\pi}\int_0^\infty \frac{R(\omega)}{|Z(\omega)|^2}\,{\rm d}\omega, \tag{III.68}$$

where the evenness of $R(\omega)/|Z(\omega)|^2$, which can be read directly off Eq. (III.67), has been used. These thermal fluctuations of the electric current were first measured by Johnson[(as)] [37] and computed by Nyquist[(at)] [38], and now referred to as *Johnson–Nyquist noise*.

Let $V(t)$ denote the fictitious fluctuating voltage which, if applied to the circuit, would give rise to the same fluctuating current $I(t)$. One can show that the Fourier transforms of their autocorrelation functions are related to each other through

$$\int_{-\infty}^\infty \big\langle I(t)I(0)\big\rangle_{\rm eq.}\,{\rm e}^{{\rm i}\omega t}\,{\rm d}t = \frac{1}{|Z(\omega)|^2}\int_{-\infty}^\infty \big\langle V(t)V(0)\big\rangle_{\rm eq.}\,{\rm e}^{{\rm i}\omega t}\,{\rm d}t. \tag{III.69}$$

Comparing this relation with Eq. (III.67), one finds

$$\frac{k_BT}{\pi}\,R(\omega) = \frac{1}{2\pi}\int_{-\infty}^\infty \big\langle V(t)V(0)\big\rangle_{\rm eq.}\,{\rm e}^{{\rm i}\omega t}\,{\rm d}t, \tag{III.70}$$

which constitutes the *Nyquist theorem* relating the resistive part of the circuit impedance to the Fourier transform of the time-autocorrelation function of the voltage fluctuations at thermodynamic equilibrium.

Proof of Eq. (III.69):
The operation leading from $V(t)$ to $I(t)$ is an instance of *linear filter*, i.e. an operation relating an "input" $y_{\rm in.}(t)$ and an "output" $y_{\rm out.}(t)$ such that a) the output depends linearly on the input; b) the filter properties are independent of time; and c) the output cannot predate the input (causality). $y_{\rm out.}(t)$ is then expressed in function of $y_{\rm in.}(t-t')$ by a convolution over time, as in relation (III.8), which in frequency space becomes a simple multiplication

$$\tilde{y}_{\rm out.}(\omega) = G(\omega)\tilde{y}_{\rm in.}(\omega),$$

with $G(\omega)$ the *transfer function* of the filter. Here, $G(\omega)$ is the admittance $1/Z(\omega)$.

If $y_{\rm in.}(t)$ and $y_{\rm out.}(t)$ are now fluctuating quantities that can be viewed as stationary stochastic processes, their spectral functions are respectively proportional to $|\tilde{y}_{\rm in.}(\omega)|^2$ and $|\tilde{y}_{\rm out.}(\omega)|^2$

$$S_{\rm out.}(\omega) = |G(\omega)|^2 S_{\rm in.}(\omega).$$

According to the Wiener[(au)]–Khinchin[(av)] theorem (C.46), these spectral functions are the

[(as)] J. B. Johnson, 1887–1970 [(at)] H. Nyquist, 1889–1976 [(au)] N. Wiener, 1894–1964 [(av)] A. Ya. Khinchin, 1894–1959

Fourier transforms of the respective autocorrelation functions, that is

$$\int_{-\infty}^{\infty} \big\langle y_{\rm out.}(t)\, y_{\rm out.}(0)\big\rangle_{\rm eq.}\, {\rm e}^{{\rm i}\omega t}\, {\rm d}t = |G(\omega)|^2 \int_{-\infty}^{\infty} \big\langle y_{\rm in.}(t)\, y_{\rm in.}(0)\big\rangle_{\rm eq.}\, {\rm e}^{{\rm i}\omega t}\, {\rm d}t,$$

which with $y_{\rm in.}(t) = V(t)$, $y_{\rm out.}(t) = I(t)$, $G(\omega) = 1/Z(\omega)$ proves Eq. (III.69). □

Remark: One may "guess" that k_BT in the numerator on the right-hand side of the Nyquist relation (III.70) is actually the classical limit $k_BT \gg \hbar\omega$ of $\frac{1}{2}\hbar\omega \coth(\hbar\omega/2k_BT)$, which appears for instance on the right-hand side of Eq. (III.61).[53] That is, relation (III.70) would be the high-temperature limit of

$$\frac{\hbar\omega}{2\pi} \coth\frac{\hbar\omega}{2k_BT}\, R(\omega) = \frac{1}{2\pi}\int_{-\infty}^{\infty} \big\langle V(t)V(0)\big\rangle_{\rm eq.}\, {\rm e}^{{\rm i}\omega t}\, {\rm d}t.$$

The inverse Fourier transform of this identity reads

$$\big\langle V(t)V(0)\big\rangle_{\rm eq.} = \int_{-\infty}^{\infty} \hbar\omega \coth\frac{\hbar\omega}{2k_BT}\, R(\omega)\, {\rm e}^{-{\rm i}\omega t}\, \frac{{\rm d}\omega}{2\pi} = \frac{1}{\pi}\int_{-\infty}^{\infty} \bigg(\frac{1}{{\rm e}^{\hbar\omega/k_BT}-1} + \frac{1}{2}\bigg)\hbar\omega R(\omega)\, {\rm e}^{-{\rm i}\omega t}\, {\rm d}\omega.$$

Setting $t = 0$, one recovers the "generalized Nyquist relation"

$$\big\langle V^2\big\rangle_{\rm eq.} = \frac{2}{\pi}\int_0^{\infty} \bigg(\frac{1}{{\rm e}^{\hbar\omega/k_BT}-1} + \frac{1}{2}\bigg)\hbar\omega R(\omega)\, {\rm d}\omega. \tag{III.71}$$

This was historically the first quantum-mechanical instance of fluctuation–dissipation relation, as derived by Callen and Welton[aw] [39].

[53] This educated guess is motivated by the fact that $\frac{1}{2}\hbar\omega \coth(\hbar\omega/2k_BT)$ is actually the average energy at temperature T of the harmonic oscillator with frequency ω.

[aw] T. A. Welton, 1918–2010

III.3.6 Sum rules

Consider definition (III.19) with $\tau = t - t'$. Rewriting the right-hand side with the help of the stationarity property and expressing $\xi_{BA}(\tau)$ as inverse Fourier transform of the spectral density, one obtains

$$\int_{-\infty}^{\infty} \tilde{\xi}_{BA}(\omega)\, \mathrm{e}^{-\mathrm{i}\omega(t-t')}\, \frac{\mathrm{d}\omega}{2\pi} = \frac{1}{2\hbar}\Big\langle \big[\hat{B}_{\mathrm{I}}(t), \hat{A}_{\mathrm{I}}(t')\big]\Big\rangle_{\mathrm{eq.}}. \tag{III.80}$$

Let us differentiate this identity k times with respect to t and l times with respect to t':

$$(-\mathrm{i})^{k-l}\int_{-\infty}^{\infty} \omega^{k+l}\, \tilde{\xi}_{BA}(\omega)\, \mathrm{e}^{-\mathrm{i}\omega(t-t')}\, \frac{\mathrm{d}\omega}{2\pi} = \frac{1}{2\hbar}\left\langle \left[\frac{\mathrm{d}^k \hat{B}_{\mathrm{I}}(t)}{\mathrm{d}t^k}, \frac{\mathrm{d}^l \hat{A}_{\mathrm{I}}(t')}{\mathrm{d}t'^{\,l}}\right]\right\rangle_{\mathrm{eq.}}.$$

Given Eq. (III.3), each successive differentiation on the right-hand side gives rise to a commutator (with $\hat{H}_0$) divided by $\mathrm{i}\hbar$. This leads to k nested commutators in the left member of the commutator, and l nested commutators in its right member. Setting then $t' = t = 0$, one finds

$$\frac{(-1)^l}{\pi}\int_{-\infty}^{\infty} \omega^{k+l}\, \tilde{\xi}_{BA}(\omega)\, \mathrm{d}\omega = \frac{1}{\hbar^{l+k+1}}\left\langle \Big[\underbrace{\Big[\cdots\Big[[\hat{B}, \hat{H}_0], \hat{H}_0\Big]\cdots\Big]}_{k \text{ commutators}}, \underbrace{\Big[\cdots\Big[[\hat{A}, \hat{H}_0], \hat{H}_0\Big]\cdots\Big]}_{l \text{ commutators}}\Big]\right\rangle_{\mathrm{eq.}}. \tag{III.81}$$

The term on the left-hand side of this identity is, up to the prefactor, the moment of order $k+l$ of the spectral function $\tilde{\xi}_{BA}(\omega)$. The larger $k+l$ is, the more sensitive the moment becomes to large values of ω, that is, to the short-time behavior of the inverse Fourier transform $\xi_{BA}(t)$.

The *sum rules* (III.81) for the various values of k, l express the moments of the spectral function in terms of equilibrium expectation values of commutators. If the latter can be computed, using commutation relations, then the sum rules represent conditions that theoretical models for the spectral function $\tilde{\xi}_{BA}(\omega)$ should satisfy.

According to Eq. (III.50), the right-hand side of Eq. (III.80) also equals $\beta K_{B\dot{A}}(t-t')/2\mathrm{i}$:

$$\frac{1}{2\hbar}\Big\langle \big[\hat{B}_{\mathrm{I}}(t), \hat{A}(t')\big]\Big\rangle_{\mathrm{eq.}} = \frac{1}{2\mathrm{i}}\int_0^{\beta}\Big\langle \hat{\dot{A}}(t' - \mathrm{i}\hbar\lambda)\, \hat{B}_{\mathrm{I}}(t)\Big\rangle_{\mathrm{eq.}}\, \mathrm{d}\lambda.$$

Differentiating as above k times with respect to t and l times with respect to t', and setting $t' = t$, one obtains the alternative sum rules

$$\frac{-1}{(\mathrm{i}\hbar)^{l+k+1}}\left\langle \Big[\underbrace{\Big[\cdots\Big[[\hat{B}, \hat{H}_0], \hat{H}_0\Big]\cdots\Big]}_{k \text{ commutators}}, \underbrace{\Big[\cdots\Big[[\hat{A}, \hat{H}_0], \hat{H}_0\Big]\cdots\Big]}_{l \text{ commutators}}\Big]\right\rangle_{\mathrm{eq.}} = \int_0^{\beta}\left\langle \frac{\mathrm{d}^{l+1}\hat{A}_{\mathrm{I}}(-\mathrm{i}\hbar\lambda)}{\mathrm{d}t^{l+1}}\, \frac{\mathrm{d}^k \hat{B}_{\mathrm{I}}(0)}{\mathrm{d}t^k}\right\rangle_{\mathrm{eq.}} \mathrm{d}\lambda. \tag{III.82}$$

Up to a factor β^{-1}, the right-hand side of this identity is the canonical correlation function of the $(l+1)$-th time derivative of $\hat{A}$ and the k-th derivative of $\hat{B}$, taken at $t = 0$.

Examples of applications of these sum rules will be given in § IV.4.1 b.