III.1.5 Canonical correlation function

Last we introduce Kubo's *canonical correlation function*, defined as [33]

$$K_{BA}(\tau) \equiv \frac{1}{\beta}\int_0^\beta \left\langle e^{\lambda \hat{H}_0} \hat{A}\, e^{-\lambda \hat{H}_0} \hat{B}_{\rm I}(\tau) \right\rangle_{\rm eq.} {\rm d}\lambda = \frac{1}{\beta}\int_0^\beta \left\langle \hat{A}_{\rm I}(-{\rm i}\hbar\lambda) \hat{B}_{\rm I}(\tau) \right\rangle_{\rm eq.} {\rm d}\lambda, \qquad \text{(III.21)}$$

for a system governed by the Hamilton operator $\hat{H}_0$, where β is the inverse temperature of the equilibrium state.

Using the explicit form of the equilibrium distribution $\hat{\rho}_{\text{eq.}}$—or equivalently, of the populations π_n of the energy eigenstates at canonical equilibrium—, one finds the Fourier transform

$$\tilde{K}_{BA}(\omega) \equiv \int_{-\infty}^{\infty} K_{BA}(\tau)\, \mathrm{e}^{\mathrm{i}\omega\tau}\, \mathrm{d}\tau = 2\pi \sum_{n,n'} \frac{\pi_n - \pi_{n'}}{\beta\hbar\omega_{n'n}} B_{nn'} A_{n'n}\, \delta(\omega - \omega_{n'n}). \tag{III.22}$$

Proof of the spectral decomposition (III.22):
The equilibrium expectation value in the integrand of definition (III.21) reads

$$\sum_{n,n'} \pi_{n'}\, \mathrm{e}^{\lambda E_{n'}} A_{n'n}\, \mathrm{e}^{-\lambda E_n} B_{nn'} \mathrm{e}^{\mathrm{i}\omega_{nn'}\tau} = \sum_{n,n'} \pi_{n'}\, \mathrm{e}^{\lambda\hbar\omega_{n'n}} B_{nn'} A_{n'n} \mathrm{e}^{-\mathrm{i}\omega_{n'n}\tau}.$$

The integration over λ is straightforward and gives

$$K_{BA}(\tau) = \frac{1}{\beta} \sum_{n,n'} \frac{\mathrm{e}^{\beta\hbar\omega_{n'n}} - 1}{\hbar\omega_{n'n}} \pi_{n'} B_{nn'} A_{n'n} \mathrm{e}^{-\mathrm{i}\omega_{n'n}\tau} = \sum_{n,n'} \frac{\pi_n - \pi_{n'}}{\beta\hbar\omega_{n'n}} B_{nn'} A_{n'n} \mathrm{e}^{-\mathrm{i}\omega_{n'n}\tau}, \tag{III.23}$$

where the second identity comes from $\mathrm{e}^{\beta\hbar\omega_{n'n}} = \pi_n/\pi_{n'}$, which follows from Eq. (III.2b). This alternative representation of the Kubo correlation function leads at once to the Fourier transform (III.22).

III.2.3 Relaxation

Let us now assume that the external "force" at equilibrium in the excitation (III.7) acting on the system of § III.1.1 is given by

$$f(t) = f\,\mathrm{e}^{\varepsilon t}\,\Theta(-t), \tag{III.32}$$

with a constant f, where at the end of calculations we shall take the limit $\varepsilon \to 0^+$. This force represents a perturbation turned on from $t = -\infty$ over the typical scale ε^{-1}, slowly driving the system out of its initial equilibrium state. At $t = 0$, the perturbation is turned off, and the system then relaxes to the original equilibrium state. We shall now compute the departure from equilibrium of the expectation value of an operator $\hat{B}$ due to this excitation.

Inserting Eq. (III.32) in the Kubo formula (III.8), one finds

$$\frac{1}{f}\Big[\big\langle \hat{B}_{\rm I}(t)\big\rangle_{\rm n.eq.} - \big\langle \hat{B}\,\big\rangle_{\rm eq.}\Big] = \int_{-\infty}^{\infty} \chi_{BA}(t-t')\,{\rm e}^{\varepsilon t'}\,\Theta(-t')\,{\rm d}t' \\ = \int_{-\infty}^{\infty} {\rm e}^{\varepsilon t'}\Theta(-t')\int_{-\infty}^{\infty}\tilde{\chi}_{BA}(\omega)\,{\rm e}^{-{\rm i}\omega(t-t')}\,\frac{{\rm d}\omega}{2\pi}\,{\rm d}t',$$

where we have introduced the generalized susceptibility. Exchanging the order of the integrals and performing that over t' give

$$\frac{1}{f}\Big[\big\langle \hat{B}_{\rm I}(t)\big\rangle_{\rm n.eq.} - \big\langle \hat{B}\,\big\rangle_{\rm eq.}\Big] = \int_{-\infty}^{\infty}\frac{\tilde{\chi}_{BA}(\omega)}{{\rm i}\omega+\varepsilon}\,{\rm e}^{-{\rm i}\omega t}\,\frac{{\rm d}\omega}{2\pi}.$$

That is, the linear response $\big\langle \hat{B}_{\rm I}(t)\big\rangle_{\rm n.eq.} - \big\langle \hat{B}\,\big\rangle_{\rm eq.}$ is proportional to the inverse Fourier transform of the ratio of the generalized susceptibility over ${\rm i}\omega+\varepsilon = {\rm i}(\omega - {\rm i}\varepsilon)$.

Expressing $\tilde{\chi}_{BA}(\omega)$ in terms of the spectral function with Eq. (III.29) and exchanging the order of the integrals, the above relation becomes

$$\frac{1}{f}\Big[\big\langle \hat{B}_{\rm I}(t)\big\rangle_{\rm n.eq.} - \big\langle \hat{B}\,\big\rangle_{\rm eq.}\Big] = \frac{1}{\pi}\lim_{\varepsilon'\to 0^+}\int_{-\infty}^{\infty}\tilde{\xi}_{BA}(\omega')\bigg[\int_{-\infty}^{\infty}\frac{{\rm e}^{-{\rm i}\omega t}}{(\omega-{\rm i}\varepsilon)(\omega'-\omega-{\rm i}\varepsilon')}\,\frac{{\rm d}\omega}{2\pi{\rm i}}\bigg]\,{\rm d}\omega'. \qquad \text{(III.33)}$$

The integration over ω is then straightforward with the theorem of residues, where the term ${\rm e}^{-{\rm i}\omega t}$ dictates whether the integration contour consisting of the real axis and a half-circle at infinity should be closed in the upper (for $t<0$) or in the lower (for $t>0$) complex half-plane of the variable ω.

- For $t<0$, one has to consider the only pole of the integrand in the upper half-plane, which lies at $\omega = {\rm i}\varepsilon$. The corresponding residue is ${\rm e}^{\varepsilon t}/(\omega' - {\rm i}\varepsilon - {\rm i}\varepsilon')$, which yields

$$\big\langle \hat{B}_{\rm I}(t)\big\rangle_{\rm n.eq.} - \big\langle \hat{B}\,\big\rangle_{\rm eq.} = \frac{f\,{\rm e}^{\varepsilon t}}{\pi}\lim_{\varepsilon'\to 0^+}\int_{-\infty}^{\infty}\frac{\tilde{\xi}_{BA}(\omega')}{\omega'-{\rm i}\varepsilon-{\rm i}\varepsilon'}\,{\rm d}\omega' = \frac{f(t)}{\pi}\int_{-\infty}^{\infty}\frac{\tilde{\xi}_{BA}(\omega')}{\omega'-{\rm i}\varepsilon}\,{\rm d}\omega'.$$

  Taking now the limit $\varepsilon\to 0^+$ and using relation (III.29) for $\omega=0$, one obtains

$$\big\langle \hat{B}_{\rm I}(t)\big\rangle_{\rm n.eq.} - \big\langle \hat{B}\,\big\rangle_{\rm eq.} = f(t)\,\tilde{\chi}_{BA}(0) \quad \text{for } t\leq 0. \qquad \text{(III.34)}$$

  This result is easily interpreted: the system is driven out of equilibrium so slowly that the departure of the expectation value of $\hat{B}_{\rm I}(t)$ from the equilibrium value can be computed with the help of the *static* susceptibility, i.e. $\tilde{\chi}_{BA}(0)$ at zero frequency.

- For $t>0$, the only pole in the lower half-plane of the integrand in Eq. (III.33) is at $\omega = \omega' - {\rm i}\varepsilon'$. This leads to

$$\frac{1}{f}\Big[\big\langle \hat{B}_{\rm I}(t)\big\rangle_{\rm n.eq.} - \big\langle \hat{B}\,\big\rangle_{\rm eq.}\Big] = \frac{1}{\pi}\lim_{\varepsilon'\to 0^+}\int_{-\infty}^{\infty}\frac{\tilde{\xi}_{BA}(\omega')}{\omega'-{\rm i}\varepsilon-{\rm i}\varepsilon'}\,{\rm e}^{-{\rm i}(\omega'-{\rm i}\varepsilon')t}\,{\rm d}\omega' \quad \text{for } t>0 \qquad \text{(III.35)} \\ = \frac{1}{\pi}\int_{-\infty}^{\infty}\frac{\tilde{\xi}_{BA}(\omega')}{\omega'-{\rm i}\varepsilon}\,{\rm e}^{-{\rm i}\omega' t}\,{\rm d}\omega'.$$

  Replacing the spectral density by its explicit expression (III.20) and exchanging the sum and the integral, one finds

$$\frac{1}{\pi}\int_{-\infty}^{\infty}\frac{\tilde{\xi}_{BA}(\omega')}{\omega'-{\rm i}\varepsilon}\,{\rm e}^{-{\rm i}\omega' t}\,{\rm d}\omega' = \frac{1}{\hbar}\sum_{n,n'}(\pi_n-\pi_{n'})B_{nn'}A_{n'n}\int_{-\infty}^{\infty}\frac{{\rm e}^{-{\rm i}\omega' t}}{\omega'-{\rm i}\varepsilon}\,\delta(\omega-\omega_{n'n})\,{\rm d}\omega' \\ = \frac{1}{\hbar}\sum_{n,n'}(\pi_n-\pi_{n'})B_{nn'}A_{n'n}\frac{{\rm e}^{-{\rm i}\omega_{n'n}t}}{\omega_{n'n}-{\rm i}\varepsilon}.$$

  In the limit $\varepsilon\to 0^+$, one recognizes on the right-hand side the spectral decomposition (III.23) of the canonical correlation function

$$\frac{1}{\pi}\lim_{\varepsilon\to 0^+}\int_{-\infty}^{\infty}\frac{\tilde{\xi}_{BA}(\omega)}{\omega-\mathrm{i}\varepsilon}\,\mathrm{e}^{-\mathrm{i}\omega t}\,\mathrm{d}\omega = \beta K_{BA}(t). \tag{III.36}$$

Inserting this identity in the above expression of the departure from equilibrium of the average value of $\hat{B}_{\rm I}(t)$ finally gives

$$\frac{1}{f}\Big[\big\langle \hat{B}_{\rm I}(t)\big\rangle_{\rm n.eq.} - \big\langle \hat{B}\,\big\rangle_{\rm eq.}\Big] = \beta K_{BA}(t) \quad \text{for } t>0. \tag{III.37}$$

That is, the Kubo correlation function describes the relaxation from an out-of-equilibrium state—which justifies why Kubo called it[(44)] "relaxation function" in his original paper [33].

Remark: Instead of letting ε' go to 0^+ in Eq. (III.35), one may as well take first the (trivial) limit $\varepsilon \to 0^+$. The remaining denominator of the integrand is exactly the factor multiplying t in the complex exponential. Differentiating both sides of the identity with respect to t and considering afterwards $\varepsilon' \to 0^+$ then gives

$$\frac{1}{f}\frac{\mathrm{d}}{\mathrm{d}t}\Big[\big\langle \hat{B}_{\rm I}(t)\big\rangle_{\rm n.eq.} - \big\langle \hat{B}\,\big\rangle_{\rm eq.}\Big] = -2\mathrm{i}\xi_{BA}(t).$$

Taking the initial condition at time $t=0$ from Eq. (III.34), one finally obtains

$$\frac{1}{f}\Big[\big\langle \hat{B}_{\rm I}(t)\big\rangle_{\rm n.eq.} - \big\langle \hat{B}\,\big\rangle_{\rm eq.}\Big] = \tilde{\chi}_{BA}(0) - 2\mathrm{i}\int_0^t \xi_{BA}(t')\,\mathrm{d}t' \quad \text{for } t>0. \tag{III.38}$$

Thus, the relaxation at $t>0$ involves the integral of the Fourier transform of the spectral function.

III.2.4 Fluctuations

Taking $\hat{B}=\hat{A}$ and setting $\tau=0$ in definitions (III.12) or (III.16), one finds

$$C_{AA}(\tau\!=\!0) = S_{AA}(\tau\!=\!0) = \big\langle \hat{A}^2\big\rangle_{\rm eq.}.$$

If $\hat{A}$ is centered, $\langle\hat{A}\rangle_{\rm eq.}=0$, then $\langle\hat{A}^2\rangle_{\rm eq.}$ is the variance of repeated measurements of the expectation value of $\hat{A}$, i.e. it is a measure of the *fluctuations* of the value taken by this observable.

When $\tau\neq 0$ or when $\hat{B}$ and $\hat{A}$ differ, $C_{BA}(\tau)$ and $S_{BA}(\tau)$ are no longer variances, but rather *covariances*—to be accurate, this holds if both $\hat{A}$ and $\hat{B}$ are centered—, which measure the degree of correlation between the two observables (see Appendix B.4.1).

(44) or rather, to be precise, the product $\beta K_{BA}(t)$, which he denotes by $\Phi_{BA}(t)$.