VI.B Classical linear response

The linear response formalism can also be applied to systems which are described classically, as e.g. fluids obeying hydrodynamical laws. Two parallel strategies can then be adopted: either to consider the classical limit of the quantum-mechanical results, or to tackle the problem in the classical framework from the beginning. In this section we give examples of both approaches, which quite naturally lead to the same results.

VI.B.1 Classical correlation functions

Let A, B be classical observables associated with quantum-mechanical counterparts $\hat{A}$, $\hat{B}$. Using (without proof) the correspondence between quantum-mechanical and classical statistical-mechanical expectation values, the non-symmetrized correlation function $C_{BA}(\tau)$, Eq. (VI.12), becomes in the classical limit

$$\text{classical limit of } C_{BA}(\tau) = \big\langle B(\tau)A(0)\big\rangle_{\text{eq.}} \equiv C^{\text{cl.}}_{BA}(\tau), \tag{VI.126}$$

where the expectation value is a Γ-space integral computed with the proper equilibrium phase-space distribution.

In the classical limit, operators become commuting numbers ("c-numbers"). Invoking the stationarity of the equilibrium state, one thus has

$$C^{\text{cl.}}_{BA}(\tau) = C^{\text{cl.}}_{AB}(-\tau), \tag{VI.127}$$

in contrast to the quantum-mechanical case where the identity is between $C_{BA}(\tau)$ and $C_{AB}(-\tau)^*$, see Eq. (VI.15). In the case of autocorrelations ($B = A$), the non-symmetrized correlation function (VI.126) is even.

Fourier transforming both sides of relation (VI.127), one finds at once

$$\tilde{C}^{\text{cl.}}_{BA}(\omega) = \tilde{C}^{\text{cl.}}_{AB}(-\omega), \tag{VI.128}$$

which is the classical limit $\hbar \to 0$ of the detailed balance relation, as was already discussed below Eq. (VI.53).

Thanks to the commutativity of the A and $B(\tau)$, the classical limit of $S_{BA}(\tau)$ is given by the same correlation function $\big\langle B(\tau)A(0)\big\rangle_{\text{eq.}}$

$$\text{classical limit of } S_{BA}(\tau) = \big\langle B(\tau)A(0)\big\rangle_{\text{eq.}} = C^{\text{cl.}}_{BA}(\tau). \tag{VI.129}$$

Similarly, the various operators in the defining integral for Kubo's canonical correlation functions commute with each other in the classical limit, and one obtains

$$\text{classical limit of } K_{BA}(\tau) = \big\langle B(\tau)A(0)\big\rangle_{\text{eq.}} \frac{1}{\beta}\int_0^\beta \mathrm{d}\lambda = \big\langle B(\tau)A(0)\big\rangle_{\text{eq.}} = C^{\text{cl.}}_{BA}(\tau). \tag{VI.130}$$

We thus recover the fact that S_{BA} and K_{BA} have the same classical limit, as mentioned for their Fourier transforms at the end of § VI.3.3 b.

Remark: More generally, even in the quantum-mechanical case if either $\hat{A}$ or $\hat{B}$ commutes with $\hat{H}_0$, then the non-symmetrized, symmetric and canonical correlation functions $C_{BA}(\tau)$, $S_{BA}(\tau)$, $K_{BA}(\tau)$ are equal.

In contrast, the linear response function $\chi_{BA}(\tau)$ and the Fourier transform $\xi_{BA}(\tau)$ of the spectral function are proportional to commutators divided by $\hbar$, see Eqs. (VI.26) and (VI.19). In the classical limit, these become proportional to some Poisson brackets, for instance [see also Eq. (VI.138b) hereafter]

$$\text{classical limit of } \xi_{BA}(\tau) = \frac{\mathrm{i}}{2}\big\langle\big\{B_N(\tau), A_N\big\}\big\rangle_{\text{eq.}} \equiv \xi^{\text{cl.}}_{BA}(\tau). \tag{VI.131}$$

VI.B.2 Classical Kubo formula

In this Subsection, we want to show how some results of linear response theory can be derived directly in classical mechanics, instead of taking the limit $\hbar \to 0$ in quantum-mechanical results.

For that purpose, we consider[92] a system of N pointlike particles with positions and conjugate momenta $\{q_i\}$, $\{p_i\}$ with $1 \leq i \leq 3N$. The Γ-space density and Hamilton function of this system are denoted by $\rho_N\big(t, \{q_i\}, \{p_i\}\big)$ and $H_N\big(t, \{q_i\}, \{p_i\}\big)$. The latter arises from slightly perturbing a time-independent Hamiltonian $H_N^{(0)}\big(\{q_i\}, \{p_i\}\big)$:

$$H_N\big(t, \{q_i\}, \{p_i\}\big) = H_N^{(0)}\big(\{q_i\}, \{p_i\}\big) - f(t) A_N\big(\{q_i\}, \{p_i\}\big), \tag{VI.132}$$

with $A_N\big(\{q_i\}, \{p_i\}\big)$ an observable of the system and $f(t)$ a time-dependent function which vanishes as $t \to -\infty$.

Let $\mathrm{i}\mathcal{L}_0$ be the Liouville operator (II.11) associated to $H_N^{(0)}$ and $\rho_{\text{eq.}}$ the N-particle phase-space density corresponding to the canonical equilibrium of the unperturbed system

$$\rho_{\text{eq.}}\big(\{q_i\}, \{p_i\}\big) = \frac{1}{Z_N(\beta)}\, \mathrm{e}^{-\beta H_N^{(0)}(\{q_i\},\{p_i\})} \quad \text{with} \quad Z_N(\beta) = \int \mathrm{e}^{-\beta H_N^{(0)}(\{q_i\},\{p_i\})}\, \mathrm{d}^{6N}\mathcal{V}, \tag{VI.133}$$

where the Γ-space infinitesimal volume element is given by Eq. (II.4a). Averages computed with $\rho_{\text{eq.}}$ will be denoted as $\langle\, \cdot \,\rangle_{\text{eq.}}$, those computed with ρ_N as $\langle\, \cdot \,\rangle_{\text{n.eq.}}$.

Let $B_N\big(\{q_i\}, \{p_i\}\big)$ denote another observable of the system. We wish to compute its out-of-equilibrium expectation value at time t, $\langle B_N(t, \{q_i\}, \{p_i\})\rangle_{\text{n.eq.}}$, and in particular its departure from the equilibrium expectation value $\langle B_N(\{q_i\}, \{p_i\})\rangle_{\text{eq.}}$. The latter is time-independent, as follows from Eqs. (II.18)–(II.19) and the time-independence of $\rho_{\text{eq.}}$.

For the sake of brevity we shall from now on drop the dependence of functions on the phase-space coordinates $\{q_i\}, \{p_i\}$.

In analogy to the quantum-mechanical case (Sec. VI.2.1), we start by calculating the phase-space density $\rho_N(t)$, or equivalently its deviation from the equilibrium density

$$\delta\rho_N(t) \equiv \rho_N(t) - \rho_{\text{eq.}}. \tag{VI.134}$$

Writing $\rho_N(t) = \rho_{\text{eq.}} + \delta\rho_N(t)$ and using the stationarity of $\rho_{\text{eq.}}$ the Liouville equation (II.10b) for the evolution of $\rho_N(t)$

$$\frac{\mathrm{d}\rho_N(t)}{\mathrm{d}t} + \big\{\rho_N(t), H_N(t)\big\} = 0$$

gives for $\delta\rho_N(t)$ to leading order in the perturbation

$$\begin{aligned}\frac{\mathrm{d}\delta\rho_N(t)}{\mathrm{d}t} &= \big\{H_N(t), \delta\rho_N(t)\big\} + \big\{-f(t)A_N, \rho_{\text{eq.}}\big\} + \mathcal{O}(f^2)\\ &= -\mathrm{i}\mathcal{L}_0\delta\rho_N(t) - f(t)\big\{A_N, \rho_{\text{eq.}}\big\} + \mathcal{O}(f^2).\end{aligned} \tag{VI.135}$$

In the second line, we took $f(t)$ outside of the Poisson brackets since it is independent of the phase-space coordinates.

This is an inhomogeneous first-order linear differential equation, whose solution reads

$$\delta\rho_N(t) = -\int_{-\infty}^{t} \mathrm{e}^{-\mathrm{i}(t-t')\mathcal{L}_0}\big\{A_N, \rho_{\text{eq.}}\big\} f(t')\, \mathrm{d}t' + \mathcal{O}(f^2),$$

where we used $f(-\infty) = 0$ which results in $\delta\rho_N(-\infty) = 0$. Again, the independence of $f(t')$ from the Γ-space coordinates allows one to move it to the left of the time-translation operator $\mathrm{e}^{-\mathrm{i}(t-t')\mathcal{L}_0}$. Adding $\rho_{\text{eq.}}$ to both sides then gives

$$\rho_N(t) = \rho_{\text{eq.}} - \int_{-\infty}^{t} f(t')\, \mathrm{e}^{-\mathrm{i}(t-t')\mathcal{L}_0}\big\{A_N, \rho_{\text{eq.}}\big\}\, \mathrm{d}t' + \mathcal{O}(f^2). \tag{VI.136}$$

[92] This is the generic setup of Sec. II.2.1.

Multiplying this identity left with B_N and integrating afterwards over phase space yields

$$\big\langle B_N(t)\big\rangle_{\text{n.eq.}} = \big\langle B_N\big\rangle_{\text{eq.}} - \int_{-\infty}^{t} f(t')\left[\int_\Gamma B_N\, \mathrm{e}^{-\mathrm{i}(t-t')\mathcal{L}_0}\big\{A_N,\rho_{\text{eq.}}\big\}\,\mathrm{d}^{6N}\mathcal{V}\right]\mathrm{d}t' + \mathcal{O}(f^2). \tag{VI.137}$$

Using the unitarity of $\mathrm{e}^{-\mathrm{i}(t-t')\mathcal{L}_0}$, Eq. (II.20), the phase-space integral on the right-hand side can be recast as

$$\int_\Gamma \left[\mathrm{e}^{\mathrm{i}(t-t')\mathcal{L}_0} B_N\right]\big\{A_N,\rho_{\text{eq.}}\big\}\,\mathrm{d}^{6N}\mathcal{V}.$$

Invoking Eq. (II.17), the term between square brackets is then $B_N(t-t')$ *as would follow from letting* B_N *evolve under the influence of* $H_N^{(0)}$ *only.*[(93)] Equation (VI.137) thus becomes

$$\big\langle B_N(t)\big\rangle_{\text{n.eq.}} = \big\langle B_N\big\rangle_{\text{eq.}} - \int_{-\infty}^{t} f(t')\left[\int_\Gamma B_N(t-t')\big\{A_N,\rho_{\text{eq.}}\big\}\,\mathrm{d}^{6N}\mathcal{V}\right]\mathrm{d}t' + \mathcal{O}(f^2).$$

By performing an integration by parts and using the fact that the phase-space distribution vanishes at infinity, one checks that the integral over phase space of $B_N(t-t')\big\{A_N,\rho_{\text{eq.}}\big\}$ equals that of $\rho_{\text{eq.}}\big\{B_N(t-t'),A_N\big\}$:

$$\big\langle B_N(t)\big\rangle_{\text{n.eq.}} = \big\langle B_N\big\rangle_{\text{eq.}} - \int_{-\infty}^{t} f(t')\left[\int_\Gamma \rho_{\text{eq.}}\big\{B_N(t-t'),A_N\big\}\,\mathrm{d}^{6N}\mathcal{V}\right]\mathrm{d}t' + \mathcal{O}(f^2).$$

The phase-space integral in this relation is now simply the equilibrium expectation value of the Poisson bracket $\big\{B_N(t-t'),A_N\big\}$. All in all, this gives

$$\begin{aligned}\big\langle B_N(t)\big\rangle_{\text{n.eq.}} &= \big\langle B_N\big\rangle_{\text{eq.}} - \int_{-\infty}^{t} f(t')\big\langle\big\{B_N(t-t'),A_N\big\}\big\rangle_{\text{eq.}}\,\mathrm{d}t' + \mathcal{O}(f^2)\\ &= \big\langle B_N\big\rangle_{\text{eq.}} + \int_{-\infty}^{\infty} f(t')\,\chi_{BA}^{\text{cl.}}(t-t')\,\mathrm{d}t' + \mathcal{O}(f^2),\end{aligned} \tag{VI.138a}$$

with

$$\chi_{BA}^{\text{cl.}}(\tau) \equiv -\big\langle\big\{B_N(\tau),A_N\big\}\big\rangle_{\text{eq.}}\,\Theta(\tau). \tag{VI.138b}$$

This result is—as it should be—what follows from the quantum-mechanical Kubo formula (VI.26) when making the substitution

$$\frac{1}{\mathrm{i}\hbar}[\,\cdot\,,\,\cdot\,] \to \{\,\cdot\,,\,\cdot\,\}.$$

[(93)] That is, corresponding to the interaction picture in the quantum mechanical case.