

Appendices to Chapter III

III.A Non-uniform phenomena

Until now in this chapter, we have implicitly considered only homogeneous systems, perturbed by uniform excitations. In this appendix, we generalize part of the formalism and results developed above to non-uniform systems. Much more can be found in the key article by L. Kadanoff^(az) and P. Martin^(ba) [46].

III.A.1 Space-time correlation functions

Consider a quantum-mechanical system at thermodynamic equilibrium. Under the influence of spontaneous fluctuations or of some localized external perturbation, its properties at a given instant and position, represented by some intensive variable, might depart from their equilibrium values. It then becomes interesting to quantify the correlation between such properties at different times and positions.

Associating space-dependent observables to intensive properties like the local density of particle number or of energy, we are thus led to consider averages of the type

$$\langle \hat{B}_I(t, \vec{r}) \hat{A}_I(t', \vec{r}') \rangle_{\text{eq.}}$$

As was done several times in this Chapter, we can invoke the stationarity of the equilibrium state to show that such an average only depends on the time difference $\tau = t - t'$. If in addition the equilibrated system is invariant under arbitrary spatial translations—as we shall assume from now on—, one also finds that the above expectation value depends only the separation $\vec{r} - \vec{r}'$, not on \vec{r} and \vec{r}' separately.

Remark: The assumed invariance under arbitrary spatial translations is less warranted as that under time translations. Strictly speaking, the assumption can only hold in fluids, since a crystalline solid is only invariant under some discrete translations. In addition, it can only hold if the system—in particular its volume \mathcal{V} , which explicitly appears in some of the formulae below—is infinitely large. In practice, these mathematical caveats are in many cases irrelevant.

Quite obviously, the various time-correlation functions introduced in Sec. III.1 can be generalized to functions of the spatial separation, which can all be expressed in terms of the non-symmetrized correlation function

$$C_{BA}(\tau, \vec{r}) \equiv \langle \hat{B}_I(\tau, \vec{r}) \hat{A}_I(0, \vec{0}) \rangle_{\text{eq.}} \quad (\text{III.94})$$

It will be fruitful to investigate these functions not only in “direct” space, but also in reciprocal space, i.e. after performing a spatial Fourier transform. For a generic function $X(t, \vec{r})$, this transform is defined as (note the minus sign!)

$$\tilde{X}_I(t, \vec{q}) \equiv \int_{\mathbb{R}^3} X_I(t, \vec{r}) e^{-i\vec{q}\cdot\vec{r}} d^3\vec{r}. \quad (\text{III.95})$$

Thus, rewriting Eq. (III.94) thanks to the assumed invariance under translations as

$$C_{BA}(\tau, \vec{r}) = \langle \hat{B}_I(\tau, \vec{r} + \vec{r}') \hat{A}_I(0, \vec{r}') \rangle_{\text{eq.}}$$

and multiplying both sides of the identity by $e^{-i\vec{q}\cdot\vec{r}} = e^{-i\vec{q}\cdot(\vec{r}+\vec{r}')} e^{i\vec{q}\cdot\vec{r}'}$, one finds after integrating

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over both $\vec{r} + \vec{r}'$ and \vec{r}'

$$\mathcal{V} \int C_{BA}(\tau, \vec{r}) e^{-i\vec{q}\cdot\vec{r}} d^3\vec{r} = \langle \tilde{B}(\tau, \vec{q}) \tilde{A}(0, -\vec{q}) \rangle_{\text{eq}},$$

with $\mathcal{V} = \int d^3\vec{r}'$. Dividing by \mathcal{V} and Fourier transforming with respect to τ , one defines

$$\tilde{C}_{BA}(\omega, \vec{q}) \equiv \int \left[\int_{-\infty}^{\infty} C_{BA}(\tau, \vec{r}) e^{i\omega\tau} d\tau \right] e^{-i\vec{q}\cdot\vec{r}} d^3\vec{r} = \frac{1}{\mathcal{V}} \int_{-\infty}^{\infty} \langle \tilde{B}(\tau, \vec{q}) \tilde{A}(0, -\vec{q}) \rangle_{\text{eq.}} e^{i\omega\tau} d\tau, \quad (\text{III.96})$$

where attention should be paid to the opposite arguments \vec{q} , $-\vec{q}$ of the observables.

III.A.2 Non-uniform linear response

Among the generalized correlation functions, the retarded propagator is the function that characterizes the local linear response to a non-uniform excitation by an inhomogeneous classical field $f(t, \vec{r})$, represented by an extra term in the Hamiltonian

$$\hat{W}(t) = - \int f(t, \vec{r}) \hat{A}(\vec{r}) d^3\vec{r}, \quad (\text{III.97})$$

which generalizes Eq. (III.7). Under the influence of this perturbation, the change of a local property with respect to its equilibrium value reads

$$\langle \hat{B}_I(t, \vec{r}) \rangle_{\text{n.eq.}} = \langle \hat{B}(\vec{r}) \rangle_{\text{eq.}} + \int_{\mathcal{V}} \left[\int_{-\infty}^{\infty} \chi_{BA}(t - t', \vec{r} - \vec{r}') f(t', \vec{r}') dt' \right] d^3\vec{r}' + \mathcal{O}(f^2), \quad (\text{III.98a})$$

which defines $\chi_{BA}(\tau, \vec{r})$. Repeating the derivation of § III.2.1, one easily finds that the latter is given by the Kubo formula

$$\chi_{BA}(\tau, \vec{r}) \equiv \frac{i}{\hbar} \langle [\hat{B}_I(\tau, \vec{r}), \hat{A}(0, \vec{0})] \rangle_{\text{eq.}} \Theta(\tau). \quad (\text{III.98b})$$

In Fourier space, the Kubo formula (III.98a) becomes (assuming that \hat{B} is centered at equilibrium)

$$\langle \tilde{B}(\omega, \vec{q}) \rangle_{\text{n.eq.}} = \tilde{\chi}_{BA}(\omega, \vec{q}) \tilde{f}(\omega, \vec{q}), \quad (\text{III.99a})$$

where the generalized susceptibility is given by

$$\tilde{\chi}_{BA}(\omega, \vec{q}) \equiv \int_{\mathbb{R}^3} \left[\lim_{\varepsilon \rightarrow 0^+} \int_{-\infty}^{\infty} \chi_{BA}(\tau, \vec{r}) e^{i\omega\tau} e^{-\varepsilon\tau} d\tau \right] e^{-i\vec{q}\cdot\vec{r}} d^3\vec{r}. \quad (\text{III.99b})$$

Dynamic structure factor

An important example of application is the coupling of a non-uniform external scalar potential $V_{\text{ext.}}(t, \vec{r})$ to a system of particles at thermal (and mechanical) equilibrium, and more precisely to their number density, $\hat{n}(\vec{r})$:

$$\hat{W} = \int \hat{n}(\vec{r}) V_{\text{ext.}}(t, \vec{r}) d^3\vec{r}.$$

The response of the number density itself is given by the *compressibility* of the system

$$\langle \hat{n}(t, \vec{r}) \rangle_{\text{n.eq.}} = \langle \hat{n}(\vec{r}) \rangle_{\text{eq.}} + \int \chi_{nn}(t - t', \vec{r} - \vec{r}') \hat{n}(t', \vec{r}') dt' d\vec{r}'.$$

In that case, the autocorrelation function $\tilde{C}_m(\omega, \vec{q})$ is usually denoted by $\tilde{S}(\omega, \vec{q})$ and called *dynamic structure factor*:⁽⁵⁶⁾

$$\tilde{S}(\omega, \vec{q}) \equiv \frac{1}{\mathcal{V}} \int_{-\infty}^{\infty} \langle \hat{n}(\tau, \vec{q}) \hat{n}(0, -\vec{q}) \rangle_{\text{eq.}} e^{i\omega\tau} d\tau = \frac{2\pi}{\mathcal{V}} \sum_{n, n'} \pi_n |(\pi_{\vec{q}})_{nn'}|^2 \delta(\omega_{n'n} - \omega), \quad (\text{III.100})$$

⁽⁵⁶⁾The factor $1/\mathcal{V}$ is sometimes omitted from the definition.

where we have introduced the Lehmann representation, involving the matrix elements $(n_{\vec{q}})_{nn'}$ of $\hat{n}(0, \vec{q})$, which obey the identity $(n_{\vec{q}})_{nn'} = (n_{-\vec{q}})_{n'n}^*$.

This dynamic structure function is directly measurable in a scattering experiment on the system. Assume that a beam of particles with momentum \vec{k} is sent onto the system. One can show that in the Born^(bb) approximation, the intensity scattered with some momentum \vec{k}' , amounting to a momentum transfer $\vec{q} \equiv \vec{k}' - \vec{k}$, is proportional to the product of $\tilde{S}(-\omega, -\vec{q})$ and the *form factor*. The latter characterizes the scattering probability on a single center, in particular it quantifies how much the scattering center differs from a point-like particle. In turn, the dynamic structure factor contains the information on the distribution and dynamics of the microscopic scattering centers in the system.⁽⁵⁷⁾

Introducing the spectral function of the system

$$\tilde{\xi}(\omega, \vec{q}) \equiv \frac{1}{2\hbar\mathcal{V}} \int_{-\infty}^{\infty} \langle [\hat{n}(\tau, \vec{q}), \hat{n}(0, -\vec{q})] \rangle_{\text{eq.}} e^{i\omega\tau} d\tau$$

one easily checks that it is related to the dynamic structure factor according to

$$\tilde{\xi}(\omega, \vec{q}) = \frac{1}{2\hbar} [\tilde{S}(\omega, \vec{q}) - \tilde{S}(-\omega, -\vec{q})] = \frac{1}{2\hbar} (1 - e^{-\beta\hbar\omega}) \tilde{S}(\omega, \vec{q}),$$

which expresses the fluctuation-dissipation theorem. Additionally, one finds the relation

$$\text{Im } \tilde{\chi}_{nn}(\omega, \vec{q}) = -\tilde{\xi}(\omega, \vec{q})$$

with the generalized susceptibility of the system.

III.A.3 Some properties of space-time autocorrelation functions

We now give a few relations obeyed by the non-symmetric correlation function, specializing to the case of identical observables $\hat{A} = \hat{B}$, that is of autocorrelation functions $C_{AA}(\tau, \vec{r})$. One can then check that the spatial Fourier transforms (we drop the factor $1/\mathcal{V}$) satisfy a few properties:

$$\bullet \langle \hat{A}(t, \vec{q}) \hat{A}(0, -\vec{q}) \rangle_{\text{eq.}} = \langle \hat{A}(0, \vec{q}) \hat{A}(-t, -\vec{q}) \rangle_{\text{eq.}}; \quad (\text{III.101a})$$

$$\bullet \langle \hat{A}(t, \vec{q}) \hat{A}(0, -\vec{q}) \rangle_{\text{eq.}}^* = \langle \hat{A}(0, \vec{q}) \hat{A}(t, -\vec{q}) \rangle_{\text{eq.}}; \quad (\text{III.101b})$$

$$\bullet \langle \hat{A}(t, \vec{q}) \hat{A}(0, -\vec{q}) \rangle_{\text{eq.}}^* = \langle \hat{A}(t - i\hbar\beta, -\vec{q}) \hat{A}(0, \vec{q}) \rangle_{\text{eq.}}. \quad (\text{III.101c})$$

The latter identity is known as the *Kubo–Martin–Schwinger*^(bc) condition for the observables of a system at canonical equilibrium.

From these identities follow a few properties of the double Fourier transform $\tilde{C}_{AA}(\omega, \vec{q})$:

$$\bullet \tilde{C}_{AA}(\omega, \vec{q}) \text{ is a real number}; \quad (\text{III.102a})$$

$$\bullet \text{detailed balance condition: } \tilde{C}_{AA}(\omega, \vec{q}) = \tilde{C}_{AA}(-\omega, -\vec{q}) e^{\beta\hbar\omega}, \quad (\text{III.102b})$$

where the latter generalizes Eq. (III.53).

III.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

⁽⁵⁷⁾For more details, see Van Hove's original article on the topic [47], which is easily readable.

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classical framework from the start. In this appendix we give examples of both approaches, which quite naturally lead to the same results.

III.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. (III.12), becomes in the classical limit

$$\text{classical limit of } C_{BA}(\tau) = \langle B(\tau)A(0) \rangle_{\text{eq.}} \equiv C_{BA}^{\text{cl.}}(\tau), \quad (\text{III.103})$$

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

$$C_{BA}^{\text{cl.}}(\tau) = C_{AB}^{\text{cl.}}(-\tau), \quad (\text{III.104})$$

in contrast to the quantum-mechanical case where the identity is between $C_{BA}(\tau)$ and $C_{AB}(-\tau)^*$, see Eq. (III.15). In the case of autocorrelations ($B = A$), the non-symmetrized correlation function (III.103) is even.

Fourier transforming both sides of relation (III.104), one finds at once

$$\tilde{C}_{BA}^{\text{cl.}}(\omega) = \tilde{C}_{AB}^{\text{cl.}}(-\omega), \quad (\text{III.105})$$

which is the classical limit $\hbar \rightarrow 0$ of the detailed balance relation, as was already discussed below Eq. (III.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 $\langle B(\tau)A(0) \rangle_{\text{eq.}}$

$$\text{classical limit of } S_{BA}(\tau) = \langle B(\tau)A(0) \rangle_{\text{eq.}} = C_{BA}^{\text{cl.}}(\tau). \quad (\text{III.106})$$

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

$$\text{classical limit of } K_{BA}(\tau) = \langle B(\tau)A(0) \rangle_{\text{eq.}} \frac{1}{\beta} \int_0^\beta d\lambda = \langle B(\tau)A(0) \rangle_{\text{eq.}} = C_{BA}^{\text{cl.}}(\tau). \quad (\text{III.107})$$

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 §III.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. (III.26) and (III.19). In the classical limit, these become proportional to some Poisson brackets, for instance [see also Eq. (III.115b) hereafter]

$$\text{classical limit of } \xi_{BA}(\tau) = \frac{i}{2} \langle \{B_N(\tau), A_N\} \rangle_{\text{eq.}} \equiv \xi_{BA}^{\text{cl.}}(\tau). \quad (\text{III.108})$$

III.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 $\hbar \rightarrow 0$ in quantum-mechanical results.

For that purpose, we consider⁽⁵⁸⁾ a system of N pointlike particles with positions and conjugate momenta $\{q^a\}, \{p_a\}$ with $1 \leq a \leq 3N$. The Γ -space probability density and Hamilton function of this system are denoted by $\rho_N(t, \{q^a\}, \{p_a\})$ and $H_N(t, \{q^a\}, \{p_a\})$. The latter arises from slightly perturbing a time-independent Hamiltonian $H_N^{(0)}(\{q^a\}, \{p_a\})$:

$$H_N(t, \{q^a\}, \{p_a\}) = H_N^{(0)}(\{q^a\}, \{p_a\}) - f(t)A_N(\{q^a\}, \{p_a\}), \quad (\text{III.109})$$

with $A_N(\{q^a\}, \{p_a\})$ an observable of the system and $f(t)$ a time-dependent function which vanishes as $t \rightarrow -\infty$.

Let $i\mathcal{L}_0$ 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

$$\rho_{\text{eq.}}(\{q^a\}, \{p_a\}) = \frac{1}{Z_N(\beta)} e^{-\beta H_N^{(0)}(\{q^a\}, \{p_a\})} \quad \text{with} \quad Z_N(\beta) = \int e^{-\beta H_N^{(0)}(\{q^a\}, \{p_a\})} d^{6N}\mathcal{V}, \quad (\text{III.110})$$

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 $B_N(\{q^a\}, \{p_a\})$ denote another observable of the system. We wish to compute its out-of-equilibrium expectation value at time t , $\langle B_N(t, \{q^a\}, \{p_a\}) \rangle_{\text{n.eq.}}$, and in particular its departure from the equilibrium expectation value $\langle B_N(\{q^a\}, \{p_a\}) \rangle_{\text{eq.}}$. 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 $\{q^a\}, \{p_a\}$.

In analogy to the quantum-mechanical case (§ III.2.1), we start by calculating the phase-space density $\rho_N(t)$, or equivalently its departure

$$\delta\rho_N(t) \equiv \rho_N(t) - \rho_{\text{eq.}} \quad (\text{III.111})$$

from the equilibrium density. 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 $\rho_N(t)$

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

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

$$\begin{aligned} \frac{d\delta\rho_N(t)}{dt} &= \{H_N(t), \delta\rho_N(t)\} + \{-f(t)A_N, \rho_{\text{eq.}}\} + \mathcal{O}(f^2) \\ &= -i\mathcal{L}_0\delta\rho_N(t) - f(t)\{A_N, \rho_{\text{eq.}}\} + \mathcal{O}(f^2). \end{aligned} \quad (\text{III.112})$$

In the second line, we pulled $f(t)$ outside of the Poisson brackets since it does not depend on the phase-space coordinates.

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

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

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 $e^{-i(t-t')\mathcal{L}_0}$. Adding $\rho_{\text{eq.}}$ to both sides then gives

$$\rho_N(t) = \rho_{\text{eq.}} - \int_{-\infty}^t f(t') e^{-i(t-t')\mathcal{L}_0} \{A_N, \rho_{\text{eq.}}\} dt' + \mathcal{O}(f^2). \quad (\text{III.113})$$

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

$$\langle B_N(t) \rangle_{\text{n.eq.}} = \langle B_N \rangle_{\text{eq.}} - \int_{-\infty}^t f(t') \left[\int_{\Gamma} B_N e^{-i(t-t')\mathcal{L}_0} \{A_N, \rho_{\text{eq.}}\} d^{6N}\mathcal{V} \right] dt' + \mathcal{O}(f^2). \quad (\text{III.114})$$

⁽⁵⁸⁾This is the generic setup of § II.2.1

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

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

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.⁽⁵⁹⁾ Equation (III.114) thus becomes

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

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 $B_N(t-t') \{A_N, \rho_{\text{eq.}}\}$ equals that of $\rho_{\text{eq.}} \{B_N(t-t'), A_N\}$:

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

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

$$\begin{aligned} \langle B_N(t) \rangle_{\text{n.eq.}} &= \langle B_N \rangle_{\text{eq.}} - \int_{-\infty}^t f(t') \langle \{B_N(t-t'), A_N\} \rangle_{\text{eq.}} dt' + \mathcal{O}(f^2) \\ &= \langle B_N \rangle_{\text{eq.}} + \int_{-\infty}^{\infty} f(t') \chi_{BA}^{\text{cl.}}(t-t') dt' + \mathcal{O}(f^2), \end{aligned} \quad (\text{III.115a})$$

with

$$\chi_{BA}^{\text{cl.}}(\tau) \equiv - \langle \{B_N(\tau), A_N\} \rangle_{\text{eq.}} \Theta(\tau). \quad (\text{III.115b})$$

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

$$\frac{1}{i\hbar} [\cdot, \cdot] \rightarrow \{ \cdot, \cdot \}$$

to derive the classical limit of a quantum-mechanical commutator.

⁽⁵⁹⁾That is, corresponding to the interaction picture in the quantum mechanical case.