Tutorial sheet 13

Discussion topic: Green-Kubo formula

30. Non-uniform linear response

In the lecture on linear response and in particular on the retarded propagator, we only considered uniform systems, perturbed by position-independent excitations. The formalism is readily extended to non-uniform phenomena, as sketched in this exercise.

Consider a system with volume $\mathcal{V}$, governed by the Hamiltonian $\hat{H}_0$, in canonical equilibrium. This system is subject to a mechanical perturbation, which gives rise to an extra term in the Hamiltonian given by

$$\hat{W}(t) = -\int f(t,\vec{r})\,\hat{A}(\vec{r})\,\mathrm{d}^3\vec{r}, \tag{1}$$

with f a classical function and $\hat{A}$ an operator acting on the Hilbert space of the system.

i. Linear response function

As in the uniform case, the retarded propagator χ_{BA} quantifies the departure from equilibrium of the expectation value of the operator $\hat{B}$ in response to the above perturbation:

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

Convince yourself that the response function is given by

$$\chi_{BA}(t,\vec{r},t',\vec{r}\,') = \frac{\mathrm{i}}{\hbar}\left\langle \big[\hat{B}_{\mathrm{I}}(t,\vec{r}),\hat{A}_{\mathrm{I}}(t',\vec{r}\,')\big]\right\rangle_{\text{eq.}} \Theta(t-t') = \frac{\mathrm{i}}{\hbar}\left\langle \big[\hat{B}_{\mathrm{I}}(t-t',\vec{r}),\hat{A}_{\mathrm{I}}(0,\vec{r}\,')\big]\right\rangle_{\text{eq.}} \Theta(t-t').$$

Assuming that the system is invariant under spatial translation, which we do from now on, one finds that χ_{BA} actually only depends on the separation $\vec{r}-\vec{r}\,'$. This suggests the introduction of spatial Fourier transforms

$$\tilde{X}(t,\vec{q}) \equiv \int_{\mathbb{R}^3} X(t,\vec{r})\,\mathrm{e}^{-\mathrm{i}\vec{q}\cdot\vec{r}}\,\mathrm{d}^3\vec{r}$$

(note the minus sign in the exponential!) for a quantity $X(t,\vec{r})$.

Fourier transforming with respect to both time and space, one defines the

ii. Generalized susceptibility

$$\tilde{\chi}_{BA}(\omega,\vec{q}) \equiv \int_{\mathbb{R}^3}\left[\lim_{\varepsilon\to 0^+}\int_{-\infty}^{\infty}\chi_{BA}(t,\vec{r})\,\mathrm{e}^{\mathrm{i}\omega t}\,\mathrm{e}^{-\varepsilon t}\,\mathrm{d}t\right]\mathrm{e}^{-\mathrm{i}\vec{q}\cdot\vec{r}}\,\mathrm{d}^3\vec{r}.$$

Assuming $\langle\hat{B}\rangle_{\text{eq.}} = 0$, check that the Kubo formula (2) leads to the identity

$$\big\langle \tilde{\hat{B}}(\omega,\vec{q})\big\rangle_{\text{n.eq.}} = \tilde{\chi}_{BA}(\omega,\vec{q})\,\tilde{f}(\omega,\vec{q}). \tag{3}$$

In analogy to the uniform case the

iii. Non-symmetrized correlation function is defined as $C_{BA}(t,\vec{r}) \equiv \big\langle \hat{B}(t,\vec{r})\,\hat{A}(0,\vec{0})\big\rangle_{\text{eq.}}$.

Show that its spatial Fourier transform is given by

$$\int_{\mathbb{R}^3} C_{BA}(t,\vec{r})\,\mathrm{e}^{-\mathrm{i}\vec{q}\cdot\vec{r}}\,\mathrm{d}^3\vec{r} = \frac{1}{\mathcal{V}}\Big\langle \tilde{\hat{B}}_{\mathrm{I}}(t,\vec{q})\,\tilde{\hat{A}}_{\mathrm{I}}(0,-\vec{q})\Big\rangle_{\text{eq.}}.$$

Let then $\tilde{C}_{BA}(\omega,\vec{q}) \equiv \dfrac{1}{\mathcal{V}}\displaystyle\int_{-\infty}^{\infty}\Big\langle \tilde{\hat{B}}_{\mathrm{I}}(t,\vec{q})\,\tilde{\hat{A}}_{\mathrm{I}}(0,-\vec{q})\Big\rangle_{\text{eq.}}\,\mathrm{e}^{\mathrm{i}\omega t}\,\mathrm{d}t$ be the double Fourier transform of $C_{BA}(t,\vec{r})$.

iv. Focusing now on the case $\hat{B} = \hat{A}$, show the identities

- $\langle \tilde{\hat{A}}_{\rm I}(t,\vec{q})\, \tilde{\hat{A}}_{\rm I}(0,-\vec{q})\rangle_{\rm eq.} = \langle \tilde{\hat{A}}_{\rm I}(0,\vec{q})\, \tilde{\hat{A}}_{\rm I}(-t,-\vec{q})\rangle_{\rm eq.}$,
- $\langle \tilde{\hat{A}}_{\rm I}(t,\vec{q})\, \tilde{\hat{A}}_{\rm I}(0,-\vec{q})\rangle^*_{\rm eq.} = \langle \tilde{\hat{A}}_{\rm I}(0,\vec{q})\, \tilde{\hat{A}}_{\rm I}(t,-\vec{q})\rangle_{\rm eq.}$, and
- $\langle \tilde{\hat{A}}_{\rm I}(t,\vec{q})\, \tilde{\hat{A}}_{\rm I}(0,-\vec{q})\rangle^*_{\rm eq.} = \langle \tilde{\hat{A}}_{\rm I}(t-{\rm i}\hbar\beta,-\vec{q})\, \tilde{\hat{A}}_{\rm I}(0,\vec{q})\rangle_{\rm eq.}$.

The latter is known as *Kubo–Martin–Schwinger condition*.

Deduce from these results that $\tilde{C}_{AA}(\omega,\vec{q})$ is real-valued and that it obeys the *detailed balance condition* $\tilde{C}_{AA}(-\omega,-\vec{q}) = \tilde{C}_{AA}(\omega,\vec{q})\,{\rm e}^{-\beta\hbar\omega}$.

v. Let $\hat{A}(t,\vec{r})$ now be the particle-density operator $\hat{n}(\vec{r})$.[1] $\tilde{C}_{nn}(\omega,\vec{q}) \equiv \tilde{S}(\omega,\vec{q})$ is then referred to as *dynamic structure factor*.

a) The spectral function of the system is given by (can you justify this formula?)

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

Show that it is related to the dynamic structure factor according to

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

What do you recognize in the second identity?

b) In the specific case $\hat{A} = \hat{n}$, the perturbation (1) in the Hamiltonian is generally written

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

with $V_{\rm ext.}$ an external potential, which given the definition of $\hat{n}$ makes sense. Let $\chi \equiv \chi_{nn}$ denote the corresponding response function, as defined by Eq. (2) with $\hat{B} = \hat{n}$. Show that ${\rm Im}\,\tilde{\chi}(\omega,\vec{q}) = -\tilde{\xi}(\omega,\vec{q})$.

[1] Denoting by $\hat{\vec{r}}_j$ the position operator for the system particle j, one has $\hat{n}(\vec{r}) \equiv \sum_j \delta^{(3)}(\vec{r}-\hat{\vec{r}}_j)$.