

9 Lesson 9

9.1 Quantum Statistical Mechanics

9.1.1 Reminder

We defined the retarded Green's function,

$$\tilde{\chi}_{AB}(t-t') \equiv \frac{i}{\hbar} \langle [A(t), B(t')] \rangle_{\text{eq}} \Theta(t-t'), \quad (9.1)$$

and showed that its analytic continuation,

$$\hat{\chi}_{AB}(z) = \int_{-\infty}^{\infty} d\tau e^{iz\tau} \tilde{\chi}_{AB}(\tau), \quad (9.2)$$

is analytic for $\Im m(z) > 0$. We then showed that the limit

$$\chi_{AB}(\omega) = \frac{1}{\pi} \lim_{\varepsilon \rightarrow 0^+} \hat{\chi}_{AB}(z = \omega + i\varepsilon) \quad (9.3)$$

is well defined.

We finished with the spectral function

$$\xi_{AB}(\omega) \equiv \frac{\pi}{\hbar} \frac{1}{\hbar} \sum_{n,q} (\Pi_n - \Pi_q) A_{nq} B_{qn} \delta(\omega_{qn} - \omega), \quad (9.4)$$

and showed that's its time-space counterpart is

$$\tilde{\xi}_{AB}(t) = \frac{1}{2\hbar} \langle [A(t), B(0)] \rangle. \quad (9.5)$$

Therefore,

$$\tilde{\chi}_{AB}(t-t') = 2i\Theta(t-t') \xi_{AB}(t-t'). \quad (9.6)$$

We will inspect the function

$$\xi_{AA^\dagger}(\omega) = \Im m \chi_{AA^\dagger}(\omega) \equiv \chi''_{AA^\dagger}(\omega) \quad (9.7)$$

9.1.2 What we will do today

We will show that this spectral function is related to the dissipation in the system. We will also show that these results can be elementary derived from the KMS condition. We will finally show that these results are not unique to Bosons. We will see how is related to the Kramers-Krönig relations.

9.1.3 Physical meaning of $\xi_{AA^\dagger}(\omega)$ — Dissipation

Reminder: we are looking on a perturbation $V \cos \omega t$. Let's recall Fermi Golden Rule: the probability per unit time to have a transition between a state $|\phi_i\rangle$ and a group of final states $|\phi_f\rangle$ is

$$\sum_f \frac{\pi}{2\hbar^2} |\langle \phi_f | V | \phi_i \rangle|^2 [\delta(\omega_{fi} - \omega) + \delta(\omega_{if} - \omega)]. \quad (9.8)$$

If $E_f > E_i$, this is energy absorption; if $E_f < E_i$ this is emission.

Let us define $a(t) = a \cos \omega t$. Then, the total energy *absorbed* per unit time is

$$\frac{dW_{\text{abs}}}{dt} = \frac{\pi a^2}{2\hbar^2} \sum_{nq} \Pi_n \hbar \omega |A_{nq}|^2 \delta(\omega_{qn} - \omega), \quad (9.9)$$

and the total energy *emitted* per unit time is

$$\frac{dW_{\text{ems}}}{dt} = \frac{\pi a^2}{2\hbar^2} \sum_{nq} \Pi_n \hbar \omega |A_{nq}|^2 \delta(\omega_{nq} - \omega) = \frac{\pi a^2}{2\hbar^2} \sum_{nq} \Pi_q \hbar \omega |A_{nq}|^2 \delta(\omega_{qn} - \omega). \quad (9.10)$$

At thermal equilibrium the lowest levels are more populated, or $\Pi_n > \Pi_q$. Therefore, combining these last two equations we obtain

$$\boxed{\frac{dW}{dt} = \frac{\pi a^2}{2\hbar^2} \sum_{nq} (\Pi_n - \Pi_q) \hbar \omega |A_{nq}|^2 \delta(\omega_{qn} - \omega)} = \frac{a^2}{2} \xi_{AA^\dagger}(\omega). \quad (9.11)$$

9.1.4 Symmetrized version of FDT

Let's inspect again the correlation

$$\tilde{C}_{AB}(t) = \langle A(t) B(0) \rangle, \quad (9.12)$$

that define the statistical fluctuations in a quantum way. It is not real, since

$$\langle A(t) B(0) \rangle^* = \langle B(0) A(t) \rangle. \quad (9.13)$$

In order to symmetrize, we define

$$\begin{aligned} \tilde{S}_{AB}(t) &\equiv \frac{1}{2} \langle A(t) B(0) + B(0) A(t) \rangle \\ &= \frac{1}{2} \langle \{A(t) B(0)\}_+ \rangle. \end{aligned} \quad (9.14)$$

Taking its Fourier transform we have

$$S_{AB}(\omega) = \pi \sum_{nq} (\Pi_n + \Pi_q) A_{nq} B_{qn} \delta(\omega_{qn} - \omega). \quad (9.15)$$

Let's massage it a bit:

$$\begin{aligned} \Pi_n + \Pi_q &= (\Pi_n - \Pi_q) \frac{\Pi_n + \Pi_q}{\Pi_n - \Pi_q} \\ &= (\Pi_n - \Pi_q) \frac{1 + e^{-\beta(E_q - E_n)}}{1 - e^{-\beta(E_q - E_n)}} \\ &= (\Pi_n - \Pi_q) \frac{1 + e^{-\beta\hbar\omega}}{1 - e^{-\beta\hbar\omega}}, \end{aligned} \quad (9.16)$$

where we used the direct Gibbs factors of $\Pi_{n,q}$. Therefore,

$$S_{AB}(\omega) = \hbar \frac{1 + e^{-\beta\hbar\omega}}{1 - e^{-\beta\hbar\omega}} \xi_{AB}(\omega), \quad (9.17)$$

or,

$$\boxed{S_{AB}(\omega) = \hbar \coth\left(\frac{\beta\hbar\omega}{2}\right) \xi_{AB}(\omega).} \quad (9.18)$$

This is the symmetrized FDT.

Exercise: Show that for $\hbar \rightarrow 0$ we get the classical version.

9.1.5 Einstein's relations

Let's return to the correlations.

$$C_{AB}(\omega) = \frac{2\hbar}{1 - e^{-\beta\hbar\omega}} \xi_{AB}(\omega) = 2\hbar(1 + n_B(\omega)) \xi_{AB}(\omega), \quad (9.19)$$

where

$$n_B(\omega) = \frac{1}{e^{\beta\hbar\omega} - 1}. \quad (9.20)$$

People like to say: "Oh, look! We have the Bose-Einstein factor. Therefore it proves the Bosonic nature of the photons". However, our derivation had nothing to do with Bosons! Therefore, it has no relation with the Bose-Einstein statistics.

9.1.6 Another derivation based on KMS

Let's inspect

$$\tilde{\xi}_{AB} = \frac{1}{2\hbar} \langle [A(t), B(0)] \rangle = \frac{1}{2\hbar} (\tilde{C}_{AB}(t) - \tilde{C}_{BA}(-t)). \quad (9.21)$$

From KMS we have

$$\tilde{C}_{AB}(t) = \tilde{C}_{BA}(-t - i\hbar\beta). \quad (9.22)$$

It implies that

$$\tilde{C}_{BA}(-t) = \tilde{C}_{AB}(t - i\hbar\beta). \quad (9.23)$$

It implies, in turn, that its Fourier transform reads

$$\begin{aligned} \int dt e^{i\omega t} \tilde{C}_{AB}(t - i\hbar\beta) &= \int dt e^{i\omega(t+i\hbar\beta)} \tilde{C}_{AB} \\ &= e^{-\beta\hbar\omega} \int dt e^{i\omega t} \tilde{C}_{AB}. \end{aligned} \quad (9.24)$$

Therefore,

$$\xi_{AB}(\omega) = \frac{1}{2\hbar} (C_{AB}(\omega) - e^{-\beta\hbar\omega} C_{AB}(\omega)) \quad (9.25)$$

or,

$$\boxed{C_{AB}(\omega) = 2\hbar(1 + n_B(\omega)) \xi_{AB}(\omega)}. \quad (9.26)$$

QED. □

Remark. In order to prove the quantum nature of photons (meaning, the radiation is quantized), one does not need the black body radiation. In fact, all one needs is the FDT. Einstein, in his 1905 proof, used thermodynamic arguments to show that light has to be quantized. However, the first real need of the quantum nature was Haroche's demonstration of single photons, on which he got the Nobel prize.

9.1.7 Another look on causality – Kramers-Krönig relations

Here the causality is manifested in $\Theta(\tau)$. We need a small set of assumptions:

1. $\tilde{\chi}_{AB}(\tau)$ is real (response function);
2. $|\chi_{AB}(\tau)|$ is bound ($< M$); and
3. $\chi_{AB}(\tau)$ is causal (meaning, it is 0 for $\tau < 0$).

Assumptions (2) and (3) imply that $\chi_{AB}(\omega)$ is well defined and does not have poles for $\Im m(z) > 0$ ($z = x + iy$). Therefore,

$$\chi_{AB}(x + iy) = \int_{-\infty}^{\infty} dz \tilde{\chi}_{AB}(\tau) e^{ix\tau} e^{-y\tau} < \frac{M}{y}. \quad (9.27)$$

Remark. Physical system has poles only in the lower half of the complex plane. For example, for the Harmonic oscillator

$$m\ddot{z} + m\gamma\dot{z} + m\omega_0^2 z = F(t), \quad (9.28)$$

we have solutions of the form

$$z(t) = - \int_{-\infty}^t dt' \underbrace{G(t-t')}_{\text{retarded Green's function}} f(t'), \quad (9.29)$$

where $f(t) = F(t)/m$. In other words,

$$\ddot{G}(\tau) + \gamma\dot{G}(\tau) + \omega_0^2 G(\tau) = -\delta(\tau), \quad (9.30)$$

such that

$$G(\tau) = \frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega g(\omega) e^{-i\omega\tau}, \quad (9.31)$$

where

$$g(\omega) = \frac{1}{\omega^2 + i\gamma\omega - \omega_0^2}. \quad (9.32)$$

We have poles at $\pm\omega_1 - \frac{i\gamma}{2}$, where $\omega_1 = \left(\omega_0^2 - \frac{\gamma^2}{4}\right)^{1/2}$.

Now, we want to calculate this retarded Green's function.

- For $\tau < 0$, $G(\tau) = 0$. Hence, $\omega = \alpha + i\beta$, $\beta > 0$ and $e^{-i\omega\tau} = e^{\beta\tau} e^{-i\alpha\tau}$.
- For $\tau > 0$, $\omega = \alpha - i\beta$, $\beta > 0$ and

$$G(\tau) = -2i\pi \sum_{\text{resid.}} \frac{1}{2\pi} \frac{e^{-i\omega\tau}}{(\omega - \omega_1 + i\frac{\gamma}{2})(\omega + \omega_1 + i\frac{\gamma}{2})} = -e^{-\gamma\tau/2} \frac{\sin\omega_1\tau}{\omega_1} \quad (9.33)$$

Note that in the Harmonic oscillator example we needed the γ in order to get poles in the lower half of the plane. However, we already showed in this course that this γ always exists in fluctuating systems. Equivalently, we could say that a response to a Harmonic perturbation cannot be infinite in time. [remark end]

Example. Let's inspect

$$\chi(\omega) \equiv \sum_n \frac{1}{\omega^2 - n^2\omega_0^2}, \quad (9.34)$$

has poles on the real axis, $\omega \equiv \omega_1 + i\varepsilon$. Then,

$$\chi(\omega_1 + i\varepsilon) = \frac{\pi}{\omega\omega_0} \left(1 + 2e^{-\frac{2\pi\varepsilon}{\omega_0}} e^{2i\pi\frac{\omega_1}{\omega_0}}\right). \quad (9.35)$$

These poles blur and become a line dividing the upper and lower planes.

The Kramers-Krönig relations imply that

$$\chi_{AB}(\omega) = \chi'(\omega) + i\chi''(\omega). \quad (9.36)$$

Let $\omega_0 \in \mathbb{R}$. Let's look on a half-circle contour Γ with $i\varepsilon$ distance above the real axis. Its integral reads

$$\oint_{\Gamma} \frac{\chi(\omega)}{\omega - \omega_0} d\omega = 0. \quad (9.37)$$

Let us define another contour Γ' , which is half-circle around ω_0 with radius $\delta \gg \varepsilon$. Then, its integral reads

$$\oint_{\Gamma'} \frac{\chi(\omega)}{\omega - \omega_0} d\omega = 0 = \int_{-\infty}^{\omega_0 - \delta} \dots + \int_{\omega_0 + \delta}^{\infty} \dots - \frac{1}{2} 2i\pi \chi(\omega_0). \quad (9.38)$$

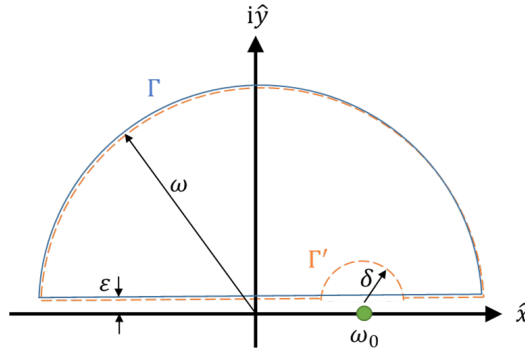


Figure 9.1: Integration contours of the Kramers-Krönig relations.

Let's look on the principal value,

$$\mathcal{P} \int_{-\infty}^{\infty} \frac{\chi(\omega)}{\omega - \omega_0} d\omega = \int_{-\infty}^{\omega_0 - \delta} \dots + \int_{\omega_0 + \delta}^{\infty} \dots \quad (9.39)$$

Hence,

$$\chi(\omega_0) = \frac{1}{\pi} \mathcal{P} \int_{-\infty}^{\infty} \frac{\chi(\omega)}{\omega - \omega_0} d\omega. \quad (9.40)$$

Therefore we obtain the Kramers-Krönig relations,

$$\begin{cases} \chi'(\omega_0) = +\frac{1}{\pi} \mathcal{P} \int_{-\infty}^{\infty} \frac{\chi''(\omega)}{\omega - \omega_0} d\omega, \\ \chi''(\omega_0) = -\frac{1}{\pi} \mathcal{P} \int_{-\infty}^{\infty} \frac{\chi'(\omega)}{\omega - \omega_0} d\omega. \end{cases} \quad (9.41)$$

These Kramers-Krönig relations are a result of the causality.

Recall that we had

$$\chi_{AB} = \lim_{\varepsilon \rightarrow 0^+} \int_{-\infty}^{\infty} \frac{\xi_{AB}(\omega')}{\omega' - \omega - i\varepsilon} d\omega'. \quad (9.42)$$