

8 Lesson 8

8.1 Quantum Statistical Mechanics

8.1.1 Reminder

We saw the equilibrium condition for a quantum system (the KMS condition),

$$C_{AB}(t) = C_{BA}(t)(-t - i\hbar\beta). \quad (8.1)$$

for $-\hbar\beta < \Im(t) < \hbar\beta$. We then went to the Fourier space, where this equation reads,

$$\tilde{C}_{AB}(\omega) = \tilde{C}_{BA}(-\omega)e^{\beta\hbar\omega}. \quad (8.2)$$

This is the Detailed Balance Condition.

Remark. These results (previous and forthcoming) hold irrespective of the exact statistics (e.g., Fermi-Dirac or Bose-Einstein).

8.1.2 Quantum Version of the F-D Theorem¹

We have an Hamiltonian \mathcal{H} and a perturbation $f(t)\hat{B}(t)$. We are interested in the quantity

$$\langle \hat{A}(t) \rangle = \frac{1}{Z} \text{Tr} \left(e^{-\beta\mathcal{H}} \hat{U}_t(f) A(0) \hat{U}_t^{-1}(f) \right). \quad (8.3)$$

Note that unlike the classical case, we do not start at \mathcal{H} and stop at $t = 0$; nevertheless, the calculation will be the same.

The evolution operator $\hat{U}_t(f)$ holds

$$-i\hbar \frac{\partial}{\partial t} \hat{U}_t(f) = \left(\mathcal{H} + f(t)\hat{B}(t) \right) \hat{U}_t(f), \quad (8.4)$$

hence,

$$\begin{aligned} \hat{U}_t(f) &= U(t) + \frac{i}{\hbar} \int_0^t d\tau U(\tau) f(\tau) B(\tau) U(t-\tau) \\ &\quad - \frac{1}{\hbar^2} \int_0^t d\tau_1 \int_0^{\tau_1} d\tau_2 U(\tau_2) f(\tau_2) B(\tau_2) U(\tau_1 - \tau_2) f(\tau_1) B(\tau_1) U(t - \tau_1) + O(f^3). \end{aligned} \quad (8.5)$$

More compactly, we can write this equation with \mathcal{T} the time ordering operator:

$$\hat{U}_t(f) = \mathcal{T} \left[\exp \left(\frac{i}{\hbar} \int_0^t d\tau \left(\mathcal{H} + f(\tau)\hat{B}(\tau) \right) \right) \right]. \quad (8.6)$$

After we inserted this expression to $\langle \hat{A}(t) \rangle$ we obtain

$$\langle \hat{A}(t) \rangle = \langle \hat{A}(0) \rangle + \int_0^t d\tau R_{AB}(t-\tau) f(\tau) + O(f^2), \quad (8.7)$$

with

$$R_{AB}(t-\tau) = -\frac{i}{\hbar} \langle [A(t), B(\tau)] \rangle = -\frac{i}{\hbar} \frac{1}{Z} \text{Tr} \left(e^{-\beta\mathcal{H}} [A(t), B(\tau)] \right), \quad t > \tau. \quad (8.8)$$

8.1.3 A Massage and Games

We'd like to play with various functions. Let's begin with the correlation function

$$\begin{aligned} C_{[A,B]}(t) &\equiv \langle [A(t), B(0)] \rangle = \langle A(t)B(0) - B(0)A(t) \rangle \\ &= \langle A(t)B(0) - B(-t)A(0) \rangle. \end{aligned} \quad (8.9)$$

Now write the Fourier transform as

$$C_{[A,B]}(t) = \frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega e^{i\omega t} \tilde{C}_{[A,B]}(\omega), \quad (8.10)$$

to obtain

$$\tilde{C}_{[A,B]}(\omega) = \tilde{C}_{AB}(\omega) - \tilde{C}_{BA}(-\omega) = \tilde{C}_{AB}(\omega) (1 - e^{-\beta\hbar\omega}), \quad (8.11)$$

¹We will mostly follow the paper of Callen & Welton, PR., 1951

where in the last equation we used (8.2).

Now, let's inspect the correlation function of the anti-commutator

$$C_{\{A,B\}}(t) \equiv \langle \{A(t), B(0)\}_+ \rangle. \quad (8.12)$$

The same message gives

$$\tilde{C}_{\{A,B\}}(\omega) = \tilde{C}_{AB}(\omega) (1 - e^{-\beta\hbar\omega}). \quad (8.13)$$

This gives us a direct relation between the two:

$$\tilde{C}_{[A,B]}(\omega) = 2 \tanh\left(\frac{1}{2}\beta\hbar\omega\right) \tilde{C}_{\{A,B\}}(\omega). \quad (8.14)$$

We now can write (8.8) as

$$R_{AB}(t) = -\frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega e^{i\omega t} \frac{2}{\hbar} \tanh\left(\frac{1}{2}\beta\hbar\omega\right) \tilde{C}_{\{A,B\}}(\omega). \quad (8.15)$$

This is sometimes called the Quantum Fluctuation-Dissipation Theorem (QFDT).

8.1.4 Linear Response – Definitions and Properties

Let us write

$$R_{AB}(t - \tau) \equiv -\frac{i}{\hbar} \langle [A(t), B(\tau)] \rangle \Theta(t - \tau). \quad (8.16)$$

Usually in the literature we see the susceptibility

$$\tilde{\chi}_{AB}(t - t') \equiv \frac{i}{\hbar} \langle [A(t), B(t')] \rangle \Theta(t - t'). \quad (8.17)$$

This is sometimes called the Response function, Retarded Green function, Retarded propagator, etc.

Let us now write the properties of \mathcal{H} . We expand it in its eigenfunctions,

$$\mathcal{H}|\varphi_n\rangle = E_n|\varphi_n\rangle, \quad (8.18)$$

with the equilibrium population

$$\rho_{\text{eq}} = \frac{1}{Z} e^{-\beta\mathcal{H}}, \quad (8.19)$$

such that

$$\langle \varphi_n | \rho_{\text{eq}} | \varphi_n \rangle \equiv \Pi_n \delta_{nn'} = \frac{1}{Z} e^{-\beta E_n} \delta_{nn'}. \quad (8.20)$$

Therefore

$$\tilde{\chi}_{AB}(\tau) = \Theta(\tau) \frac{i}{\hbar} \sum_{n,q} (\Pi_n - \Pi_q) A_{nq} B_{qn} e^{i(E_n - E_q)\tau/\hbar}, \quad (8.21)$$

where $\Theta(\tau)$ ensures causality. We can now write its Fourier components,

$$\chi_{AB}(\omega) \equiv \int_0^{\infty} d\tau e^{i\omega\tau} \tilde{\chi}_{AB}(\tau). \quad (8.22)$$

Let us introduce a factor $e^{\varepsilon\tau/\hbar}$ with $\varepsilon \rightarrow 0^+$ to have

$$\chi_{AB}(\omega) = \frac{1}{\hbar} \sum_{n,q} (\Pi_n - \Pi_q) A_{nq} B_{qn} \lim_{\varepsilon \rightarrow 0^+} \frac{1}{\omega_{qn} - \omega - i\varepsilon}, \quad (8.23)$$

where $\hbar\omega_{qn} \equiv E_q - E_n$. This value $\chi_{AB}(\omega)$ is called the Susceptibility, Admittance, 1/Impedance.

Remark. Note that we used simple quantum mechanics, and not quantum statistics. Quantum statistics came after introducing QFT into quantum mechanics: when you need to quantize a field (scalar or spinor), you need to know whether it is a Fermion or a Boson. The statistics we used when calculating, for example, black body radiation were not quantized. The FD or BE distributions are simply a matter of choice. Therefore all this derivation is valid.

8.1.5 Extension of $\chi_{AB}(\omega)$ to the Complex Plane

This is related to the Kramers-Krönig relations.

Let us look on the complex plane $z = x + iy$,

$$\hat{\chi}_{AB}(z) = \int_{-\infty}^{\infty} d\tau e^{iz\tau} \tilde{\chi}_{AB}(\tau) = \int_{-\infty}^{\infty} d\tau e^{-y\tau} e^{ix\tau} \tilde{\chi}_{AB}(\tau), \quad (8.24)$$

on the upper half-plane $y = \Im(z) \geq 0$. Here the $\hat{\square}$ denotes a function on the complex plane. Note that $\hat{\chi}_{AB}(z)$ is well defined in the upper half-plane. It is analytic and given by $\chi_{AB}(\omega)$,

$$\chi_{AB}(\omega) = \lim_{\varepsilon \rightarrow 0^+} \hat{\chi}_{AB}(z = \omega + i\varepsilon). \quad (8.25)$$

Therefore,

$$\hat{\chi}_{AB}(z) = \frac{1}{\hbar} \sum_{n,q} (\Pi_n - \Pi_q) A_{nq} B_{qn} \frac{1}{\omega_{qn} - z}. \quad (8.26)$$

Therefore, all the singularities of $\hat{\chi}_{AB}(z)$ come from the poles of $\frac{1}{\omega_{qn} - z}$. Since ω_{qn} are real, all singularities of $\hat{\chi}_{AB}(z)$ are poles along the real axis.

There is a discrete energy spectrum for \mathcal{H} . In the $V \rightarrow \infty$ limit, we'll obtain a cut in the complex plane along the real axis (the poles become a line).

Corollary. *A single isolated atom does not dissipate energy. You need a continuum in order to dissipate.*

8.1.6 Spectral Function (Dissipation)

Let us define

$$\xi_{AB}(\omega) \equiv \frac{\pi}{\hbar} \frac{1}{\hbar} \sum_{n,q} (\Pi_n - \Pi_q) A_{nq} B_{qn} \delta(\omega_{qn} - \omega). \quad (8.27)$$

It is usually denoted by $\chi''_{AB}(\omega)$. Hence,

$$\hat{\chi}_{AB}(z) = \frac{1}{\pi} \int_{-\infty}^{\infty} d\omega \frac{\xi_{AB}(\omega)}{\omega - z}. \quad (8.28)$$

Therefore

$$\chi_{AB}(\omega) = \frac{1}{\pi} \lim_{\varepsilon \rightarrow 0^+} \int_{-\infty}^{\infty} d\omega' \frac{\xi_{AB}(\omega')}{\omega' - \omega - i\varepsilon}. \quad (8.29)$$

On the other hand,

$$\hat{\xi}_{AB}(t) = \frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega e^{-i\omega t} \xi_{AB}(\omega), \quad (8.30)$$

implies that

$$\hat{\xi}_{AB}(t) = \frac{1}{2\hbar} \langle [A(t), B(0)] \rangle. \quad (8.31)$$

Note that there is no Θ function; therefore $\hat{\xi}_{AB}(t)$ (the spectral / Green's function) does not preserve causality. The relation between the two reads

$$\tilde{\chi}_{AB}(t) = 2i\Theta(t) \xi_{AB}(t). \quad (8.32)$$

We can now write

$$\xi_{AB}(\omega) = \frac{1}{2i} \lim_{\varepsilon \rightarrow 0^+} [\hat{\chi}_{AB}(\omega + i\varepsilon) - \hat{\chi}_{AB}(\omega - i\varepsilon)], \quad (8.33)$$

where we used the Cauchy principal value relation,

$$\lim_{\varepsilon \rightarrow 0^+} \frac{1}{\omega' - \omega \mp i\varepsilon} = \mathcal{P} \left(\frac{1}{\omega' - \omega} \right) \pm i\pi\delta(\omega' - \omega). \quad (8.34)$$

Remark. The value $\hat{\chi}_{AB}(\omega - i\varepsilon)$ exists in the lower-half plane. Since $\chi_{AB}(\omega - i\varepsilon)$ was not shown to exist, it must preserve the hat $\hat{\chi}$. The hat on $\hat{\chi}_{AB}(\omega + i\varepsilon)$ is there for solidarity.

Let us continue. Causality

$$\begin{aligned} \hat{\chi}_{AB}(\omega - i\varepsilon) &= \frac{1}{\hbar} \sum_{n,q} (\Pi_n - \Pi_q) \frac{A_{nq} B_{qn}}{\omega_{qn} - \omega + i\varepsilon} \\ &= \frac{1}{\hbar} \sum_{n,q} (\Pi_n - \Pi_q) \left(\frac{A_{nq}^* B_{qn}^*}{\omega_{qn} - \omega - i\varepsilon} \right)^* \\ &= \frac{1}{\hbar} \sum_{n,q} (\Pi_n - \Pi_q) \left(\frac{B_{nq}^\dagger A_{qn}^\dagger}{\omega_{qn} - \omega - i\varepsilon} \right)^* \\ &= (\hat{\chi}_{B^\dagger A^\dagger}(\omega + i\varepsilon))^*, \end{aligned} \quad (8.35)$$

and therefore well defined. Hence

$$\xi_{AB}(\omega) = \frac{1}{2i} (\chi_{AB}(\omega) - \chi_{B^\dagger A^\dagger}^*(\omega)). \quad (8.36)$$

For $A^\dagger = B$ we have

$$\xi_{AA^\dagger}(\omega) = \Im(\chi_{AA^\dagger}(\omega)) \equiv \chi_{AA^\dagger}''(\omega) \quad (8.37)$$