

7 Lesson 7

7.1 Fluctuation Theorems (Cont.)

7.1.1 Reminder

- We were talking about classical (non-quantum) description.
- We have described the Large Deviation Functions (LDFs).
- We have also stated the Gallavotti-Cohen relation between the values the LDF takes and the applied field. We have shown the response of the system, and saw that

$$\text{Prob}\left(\frac{x(t)}{t} = j \mid C \rightarrow C'\right) \sim e^{tG(j,E)} \quad (7.1)$$

where G is the LDF and E the applied field.

- We have shown the Detailed balance condition (in equilibrium):

$$M_x(C, C') P_{\text{eq}}(C') = M_{-x}(C', C) P_{\text{eq}}(C) \quad (7.2)$$

- We saw that one cannot break the detailed balance condition at will, but several constraints must be applied.

7.1.2 Out of Equilibrium

Out of equilibrium, $E \neq 0$ and Eq. (7.2) is changed into

$$\bar{M}_x(C, C') P_{\text{eq}}(C') = \bar{M}_{-x}(C', C) P_{\text{eq}}(C) \exp\left(\frac{E \cdot x}{k_B T}\right). \quad (7.3)$$

There exists a proof of (7.3) (not shown).

We therefore can calculate the outcome of the Detailed Balance probability:

$$\text{Prob}(C(t) \mid C \rightarrow C') = \text{Prob}(\Theta C(t) \mid C \rightarrow C') \frac{P_{\text{eq}}(C')}{P_{\text{eq}}(C)} \exp\left(\frac{E \cdot x(t)}{k_B T}\right) \quad (7.4)$$

where $x(t)$ is the total number of particles that has been exchanged after time t . Next, we sum over all the trajectories $C(t)$; a fixed $x(t)$ is transformed to

$$\text{Prob}(x(t) \mid C \rightarrow C') = \exp\left(\frac{E \cdot x(t)}{k_B T}\right) \text{Prob}(-x(t) \mid C' \rightarrow C) \frac{P_{\text{eq}}(C')}{P_{\text{eq}}(C)}. \quad (7.5)$$

We now apply the LDF assumption, $\frac{x(t)}{t} = j$, to obtain

$$\boxed{\frac{P\left(\frac{x}{t} = j\right)}{P\left(\frac{x}{t} = -j\right)} = \exp\left(\frac{tjE}{k_B T}\right)}. \quad (7.6)$$

Apply LDF's $P\left(\frac{x(t)}{t} = j\right) \sim e^{tG(j,E)}$ and get

$$tG(j, E) = tG(-j, E) + \frac{tjE}{k_B T}. \quad (7.7)$$

Hence, we have the Gallavotti-Cohen relations

$$\boxed{G(j, E) - G(-j, E) = \frac{jE}{k_B T}}. \quad (7.8)$$

The temperature T is the temperatures of the reservoirs (recall that it cannot be defined out of equilibrium).

7.1.3 Implications

The G&C relations implies the Fluctuation-Dissipation Theorem (FDT) and the Onsager relations.

Reminder: FDT states that for

$$\Delta = \left. \frac{\langle x^2(t) \rangle - \langle x(t) \rangle^2}{t} \right|_{E=0} \quad (7.9)$$

and a linear response of the applied field E

$$\sigma E = \frac{\langle x(t) \rangle}{t} \quad (7.10)$$

one has

$$\boxed{\Delta = 2k_B T \sigma.} \quad (7.11)$$

Another reminder: for two fields j_x and j_y one has the Onsager relations,

$$\boxed{\sigma_{xy} = \sigma_{yx}.} \quad (7.12)$$

To prove FDT, we expand G close to equilibrium has a up to second order,

$$G(j, E) = aj + BE + cj^2 + djE + eE + \dots \quad (7.13)$$

And since $G = 0$ for $j = \bar{j} = \sigma E$ one has

$$G(j, E) = -\frac{(j - \bar{j})^2}{2\Delta}. \quad (7.14)$$

From G&C we have

$$-\frac{(j - \sigma E)^2}{2\Delta} = -\frac{(j + \sigma E)^2}{2\Delta} + \frac{Ej}{k_B T} \quad (7.15)$$

hence

$$\Delta = 2k_B T \sigma. \quad (7.16)$$

To prove Onsager relations, we need at least two fields E_x, E_y to have

$$G(j_x, j_y, E_x, E_y) = G(-j_x, -j_y, E_x, E_y) + \frac{E_x j_x}{k_B T} + \frac{E_y j_y}{k_B T} \quad (7.17)$$

and after some algebra one has

$$\boxed{\sigma_{xy} = \sigma_{yx}.} \quad (7.18)$$

7.2 Quantum Statistical Mechanics

In this chapter we will try to describe the statistical mechanics of a pure quantum system.

7.2.1 KMS (Kubo-Martin-Schwinger) Condition

Let A be a quantum system. We define the thermal average of A by

$$\langle \hat{A} \rangle = \frac{\text{Tr}(\hat{A} e^{-\beta \hat{H}})}{\text{Tr}(e^{-\beta \hat{H}})} \quad (7.19)$$

and let us define the partition function

$$Z = \text{Tr}(e^{-\beta \hat{H}}). \quad (7.20)$$

We now would like to look on the correlation functions

$$C_{AB}(t) \equiv \langle \hat{A}(t) \hat{B}(0) \rangle = \frac{1}{Z} \text{Tr}(e^{\beta \hat{H}} \hat{A}(t) \hat{B}(0)), \quad (7.21)$$

where we used the Heisenberg evolution

$$\hat{A}(t) = e^{i\hat{H}t/\hbar} \hat{A}(0) e^{-i\hat{H}t/\hbar}. \quad (7.22)$$

Plug in and obtain

$$\begin{aligned} C_{AB}(t) &= \frac{1}{Z} \text{Tr}(e^{-\beta \hat{H}} e^{i\hat{H}t/\hbar} \hat{A}(0) e^{-i\hat{H}t/\hbar} \hat{B}(0)) \\ &= \frac{1}{Z} \text{Tr}(e^{i\hat{H}t/\hbar} e^{-\beta \hat{H}} \hat{A}(0) e^{-i\hat{H}t/\hbar} \hat{B}(0)) \\ &= \frac{1}{Z} \text{Tr}(e^{-\beta \hat{H}} \hat{A}(0) e^{-i\hat{H}t/\hbar} \hat{B}(0) e^{i\hat{H}t/\hbar}) \\ &= \langle \hat{A}(t) \hat{B}(-t) \rangle. \end{aligned} \quad (7.23)$$

where in the 3rd line we used the cyclicity of the trace. So far, nothing surprising. On the other hand,

$$\begin{aligned}
C_{AB}(t) &= \frac{1}{Z} \text{Tr} \left(e^{-i\hat{H}t/\hbar} \hat{B}(0) e^{i\hat{H}t/\hbar} e^{-\beta\hat{H}} \hat{A}(0) \right) \\
&= \frac{1}{Z} \text{Tr} \left(e^{-\beta\hat{H}} e^{+\beta\hat{H}} e^{-i\hat{H}t/\hbar} \hat{B}(0) e^{i\hat{H}t/\hbar} e^{-\beta\hat{H}} \hat{A}(0) \right) \\
&= \frac{1}{Z} \text{Tr} \left(e^{-\beta\hat{H}} e^{i\frac{\hat{H}}{\hbar}(-t-i\hbar\beta)} \hat{B}(0) e^{-i\frac{\hat{H}}{\hbar}(-t-i\hbar\beta)} \hat{A}(0) \right) \\
&= \left\langle \hat{B}(-t-i\hbar\beta) \hat{A}(0) \right\rangle.
\end{aligned} \tag{7.24}$$

We therefore have the KMS condition

$$\boxed{C_{AB}(t) = C_{BA}(-t-i\hbar\beta)}. \tag{7.25}$$

In other words, Quantum Mechanics is a game of imaginary time.

7.2.2 Remarks

In order to obtain the KMS results, we had to play with two operators. One is $e^{-\beta\hat{H}}$, which is a Trace Class (a trace of a given operator, $\text{Tr}(\hat{O}) < \infty$) and well defined. The other operator is $e^{+\beta\hat{H}}$, which is ill-defined.

If we go to the complex t plane, where $z = t + is$, we have

$$C_{AB}(z) = \frac{1}{Z} \text{Tr} \left(e^{-i\hat{H}z/\hbar} \hat{B}(0) e^{-i\frac{\hat{H}}{\hbar}(-z-i\hbar\beta)} \hat{A}(0) \right). \tag{7.26}$$

In order to this quantity to be defined, we must have two conditions,

$$\begin{cases} \Re(-iz) < 0 \\ \Re(-i(-z-i\hbar\beta)) < 0 \end{cases}, \tag{7.27}$$

or equivalently,

$$\boxed{-\hbar\beta < \Im(t) < 0}. \tag{7.28}$$

Similarly,

$$\tilde{C}_{AB} \equiv \left\langle \hat{B}(0) \hat{A}(t) \right\rangle$$

implies that

$$\boxed{0 < \Im(t) < \hbar\beta}. \tag{7.29}$$

7.2.3 The Opposite Direction

In other words, the KMS condition is very strong. It is a condition for a thermal equilibrium.

Now, let us assume the KMS and show thermal equilibrium. Let

$$\langle A \rangle = \text{Tr}(\rho A), \tag{7.30}$$

where $\text{Tr}(\rho) = 1$ and ρ is unknown. Some algebra gives

$$\begin{aligned}
\left\langle \hat{B}(0) \hat{A}(t+i\hbar\beta) \right\rangle &= \text{Tr} \left(\rho \hat{B}(0) \hat{A}(t+i\hbar\beta) \right) = \dots \\
&= \text{Tr} \left(e^{-\beta\hat{H}} \hat{A}(t) e^{\beta\hat{H}} \rho \hat{B}(0) \right) \\
&= \text{Tr} \left(\rho \hat{A}(t) \hat{B}(0) \right).
\end{aligned} \tag{7.31}$$

The last line is simply the KMS condition. Note that it is true for any t and any \hat{A} . It is possible only if $\rho e^{\beta\hat{H}} = N$ for N some number. Hence

$$\rho = N e^{-\beta\hat{H}} \tag{7.32}$$

7.2.4 Fourier Transforms

Let us define

$$\begin{cases} C_{AB}(t) = \left\langle \hat{A}(t) \hat{B}(0) \right\rangle = \frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega e^{i\omega t} \tilde{C}_{AB}(\omega) \\ C_{AB}(t) = \left\langle \hat{B}(t) \hat{A}(0) \right\rangle = \dots \end{cases} \tag{7.33}$$

KMS condition states that

$$\langle \hat{A}(t) \hat{B}(0) \rangle = \langle \hat{B}(-t - i\hbar\beta) \hat{A}(0) \rangle = \langle \hat{B}(0) \hat{A}(t + i\hbar\beta) \rangle, \quad (7.34)$$

hence

$$\boxed{\tilde{C}_{AB}(\omega) = \tilde{C}_{BA}(\omega) e^{\beta\hbar\omega}.} \quad (7.35)$$

This is the Detailed Balance condition. Recall that KMS has

$$C_{AB}(t) = C_{BA}(-t - i\hbar\beta). \quad (7.36)$$