

## 6 Lesson 6

We have talked about the fluctuation-dissipation relations, linear response, Kubo formula and Onsager reciprocal relations. All of these were done close to equilibrium. Today, we will talk about systems far from equilibrium.

### 6.1 Generalization of the F. D. Relations far from Equilibrium

#### 6.1.1 Synopsis

- Notion of Equilibrium: detailed balance.
- Generalization of the F. D. Relations: fluctuation theorems.<sup>1</sup>
- Large deviations.

#### 6.1.2 Thermal Equilibrium.

**Definition.** Thermal equilibrium is the  $\# \Omega$  of microscopic configurations  $C$  of energy  $E(C)$ . The probability is given by the Gibbs-Boltzmann distribution

$$P_{\text{eq}}(C) = \frac{1}{Z} e^{-E(C)/k_B T} \quad (6.1)$$

The entropy is given by

$$S = -k_B \sum_C P_{\text{eq}}(C) \ln P_{\text{eq}}(C) \quad (6.2)$$

#### 6.1.3 Markov process

Lets examine the process from configuration  $C_i$  to  $C_j$

$$C_i \xrightarrow[t]{t} C_j \xrightarrow[t+dt]{} \quad (6.3)$$

**The Markov Assumption:** Let  $M(C_j, C_i, t) dt$  the probability to have a transition  $C_i \rightarrow C_j$  at  $t$  during  $dt$ . And let's examine the network of transitions

$$\begin{array}{ccc} C_i & \longrightarrow & C_j & \longrightarrow \\ & & \uparrow & \\ C_l & \longrightarrow & C_k & \longrightarrow \end{array} \quad (6.4)$$

And let  $P_t(C)$  be the probability to be at configuration  $C$  at time  $t$ . We can write the master equation

$$\frac{d}{dt} P_t(C) = \sum_{C' \neq C} \underbrace{M(C, C') P_t(C')}_{\text{arrives to } C} - \underbrace{M(C', C) P_t(C)}_{\text{leaving } C} \quad (6.5)$$

A stationary state is

$$\frac{d}{dt} P_t(C) = 0 \quad (6.6)$$

and it gives conditions on  $\Omega$ .

#### Shorter Constraint (Onsager)

$$\forall C, C' \quad : \quad M(C, C') P_t(C') = M(C', C) P_t(C) \quad (6.7)$$

and we have  $\frac{1}{2}\Omega(\Omega - 1)$  constraints.

Eq. 6.7 is a necessary condition for equilibrium. A system that breaks Eq. 6.7 is necessarily out of equilibrium. This means, that in Detailed Balance we have absence of currents.

#### Time reversal

**Theorem.** The equilibrium state of a system, which satisfies Eq. 6.7 is necessarily invariant by time reversal,

$$P(C(t)) = P(\Theta C(t)) \quad (6.8)$$

where  $\Theta$  is the time reversal operator.

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<sup>1</sup>Gallavotti & Cohen, 1995

### 6.1.4 Physical Consequences of Detailed Balance

1. At equilibrium:

Let  $P(Q)$  is the probability that the system  $S$  gives heat  $Q$  to the reservoir  $R$ . Then,  $P(-Q)$  is the same:

$$\frac{P(Q)}{P(-Q)} = 1 \quad (6.9)$$

2. Out of Equilibrium (far from equilibrium):

Let us look on two reservoirs with temperatures  $T_H > T_C$



and the mean heat of flow is related to the system entropy

$$\frac{\langle Q \rangle}{T} = \langle S \rangle \quad (6.11)$$

Thermodynamics says nothing about fluctuations. We would like to know, what is the probability to observe a rare event, such that a heat flows to the other direction.

*Claim.* The probability distribution  $P(Q_\tau)$  of exchanging with the reservoir  $C$  the heat  $Q_\tau$  in a time  $\tau$  is related to that of exchanging  $-Q_\tau$ . In simple words,

$$\ln \left( \frac{P(Q_\tau)}{P(-Q_\tau)} \right) = \Delta\beta Q_\tau \quad (6.12)$$

where

$$\Delta\beta = \frac{1}{k_B} \left( \frac{1}{T_C} - \frac{1}{T_H} \right) \quad (6.13)$$

but

$$\Delta\beta Q_\tau = \underbrace{\sigma}_\text{rate of entropy change} \tau \quad (6.14)$$

hence

$$\frac{P(\sigma)}{P(-\sigma)} = e^{\sigma\tau} \quad (6.15)$$

This is the Large Deviation Function (LDF).

**Corollary.** *The fluctuations always dissipate heat.*

*Remark.* The heat and entropy are extensive properties. Therefore, in very large systems (e. g., human body),  $e^{\sigma\tau} \gg 1$ . Therefore,  $P(\sigma) \gg P(-\sigma)$ , and we don't see rare events. We need nanoscopic or mesoscopic systems to see such events.

### 6.1.5 Examples of Large Deviation Functions

**Example 1.** Consider a sum of independent random variables  $\varepsilon_1, \varepsilon_2, \dots, \varepsilon_N$ , where  $\varepsilon_i = \begin{cases} +1 & \text{probability } p \\ -1 & \text{probability } q \end{cases}$ . Then

1. Large Numbers Thm.: let  $S_N = \sum_{i=1}^N \varepsilon_i$ ; then  $\frac{S_N}{N} \xrightarrow{N \rightarrow \infty} \langle \varepsilon \rangle = p - q$ .

2. Central Limit Thm.:  $\frac{S_N - N(p-q)}{\sqrt{4pqN}}$  is the Gaussian

The behaviour of the probability  $P\left(\frac{S_N}{N} = r\right)$  for large  $N$  and  $r \in [-1, 1]$  is

$$\text{Prob} \left( \frac{S_N}{N} = r \right) \underset{N \rightarrow \infty}{\sim} e^{-N\phi(r)} \quad (6.16)$$

where

$$\phi(r) = \frac{1+r}{2} \ln \left( \frac{1+r}{2p} \right) + \frac{1-r}{2} \ln \left( \frac{1-r}{2q} \right) \quad (6.17)$$

and

$$\begin{cases} \phi(r = p - q) = 0 \\ \phi'(p - q) = 0 \end{cases} \quad (6.18)$$

The function  $\phi(r)$  is called the Large Deviation Function of this problem. It is a convex function with a minimum at  $p - q$ .

**Example 2.** Free Energy as an example of LDF. Consider  $N$  particles in a volume  $V$  with a density  $r = \frac{N}{V}$ . Let's look on some small volume  $v \ll V$  inside the large one with particles  $n$ . Therefore,

$$\text{Prob}\left(\frac{n}{v} = \rho\right) \sim e^{-va(\rho)} \quad (6.19)$$

for some density  $\rho$ .

The free energy  $f$  per unit volume is

$$f(\rho) = \lim_{V \rightarrow \infty} -k_B T \frac{\ln Z_V(\rho V)}{V} \quad (6.20)$$

with the partition function

$$Z = e^{-\beta V f\left(\frac{N}{V}\right)} \quad (6.21)$$

and the probability

$$P\left(\frac{n}{v} = \rho\right) = \frac{Z_V(n) Z_{V-v}(N-n)}{Z_V(N)} = e^{-va(\rho)} \quad (6.22)$$

and the LDF  $a(\rho)$ ,

$$va(\rho) = \frac{1}{k_B T} \left( v f(\rho) + (V-v) f\left(\frac{Vr-v\rho}{V-v}\right) - V f(r) \right) \underset{v \ll V}{\simeq} \frac{v}{k_B T} (f(\rho) - f(r) - (\rho-r) f'(r)). \quad (6.23)$$

*Remark.* We can consider the free energy  $f$  itself as a LDF.

*Remark.* From the LDF we can calculate all the former fluctuation theorems (Onsager relations, etc.).

## 6.2 Fluctuation Theorems (Gallavotti and Cohen Relations)

### 6.2.1 Introduction

Let's look on some system coupled to a reservoir



with  $E \equiv \Delta T, \Delta \rho, \Delta V, \dots$  and  $x(t)$  particles are transferred between  $S$  and  $R$ . Then the probability for some current  $j$  is

$$\text{Prob}\left(\frac{x(t)}{t} = j, C \rightarrow C'\right) \underset{t \rightarrow \infty}{\sim} e^{tG(j,E)}. \quad (6.25)$$

Note that in some cases this formula may not hold. The LDF  $G(j, E)$  is independent of  $C$  and  $C'$  (prefactors can). Also  $G(\bar{j}, E) = 0$  for the most probable current  $\bar{j}$ .

We will prove the Gallavotti and Cohen Relation:

$$G(j, E) - G(-j, E) = \frac{Ej}{k_B T} \quad (6.26)$$

and show that in order to break the detailed balance, we must follow a certain procedure. In other words, not every process can break DB.