Chapter I: Equilibrium statistical Physics

I Microcanonical ensemble

Complex system described by a set of configurations $\{\varphi\}$.

For instance, Hamiltonian system defined by $H(q_1,\dots,q_N,p_1,\dots,p_N)$ and the equations of motion

$$\dot{q}_i = \frac{\partial H(q_1,\dots,q_N,p_1,\dots,p_N)}{\partial p_i} \quad ; \quad \dot{p}_i = -\frac{\partial H}{\partial q_i}$$

Comment: H is a constant of motion $\frac{dH}{dt} = \sum_i \frac{\partial H}{\partial q_i}\dot{q}_i + \frac{\partial H}{\partial p_i}\dot{p}_i = 0$

Question: What is the probability of observing a configuration φ?

Microcanonical hypothesis: all configurations with the same energy have the same probability of occurence

$$P_E(\varphi) = \frac{1}{\Omega(E)}\,\delta_{E(\varphi)-E}$$ where $\Omega(E)$ is the number of configurations of energy E.

Comment: $\Omega(E)$ is simply a normalisation constant such that $\sum_\varphi P_E(\varphi) = 1$

Comment: the number of configurations of energy E depends on E; this is measured by the entropy

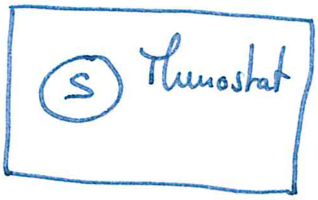
$$S_E = -k\sum_\varphi P_E(\varphi)\ln P_E(\varphi) = -\frac{k}{\Omega}\sum_{\varphi|E(\varphi)=E}\ln\frac{1}{\Omega} = k\ln\Omega$$

Temperature: the microcanonical temperature measures the variations of Ω with E

$$\frac{1}{T} \equiv \frac{\partial S}{\partial E}$$

In practice, almost no systems are isolated...

II The canonical ensemble



Idea: Système S + Thermostat are isolated

$\Rightarrow$ assumed to be in the canonical ensemble ; system an thermostat exchange energy but $E_{tot} = E_{th} + E(S)$ is fixed.

Let φ be a configuration of S. There are $\Omega_{th}(E_{tot} - E)$ configurations of the thermostat such that $E + E_{th} = E_{tot}$

$P(\varphi) = \sum_{\varphi_{tot}} P_{E_{tot}}(\varphi_{tot})$ where φ_{tot} is a configuration of the total system whose restriction to S is φ

$$= \Omega_{tot}^{-1}(E_{tot}) \sum_{\varphi_{th}} \delta_{E_{tot}-E-E_{th}} = \Omega_{tot}^{-1}(E_{tot})\, \Omega_{th}(E_{tot}-E) = \Omega_{tot}^{-1}(E_{tot})\, e^{k^{-1} S_{th}(E_{tot}-E)}$$

$$\underset{E \ll E_{tot}}{=} \Omega_{tot}^{-1}(E_{tot})\, e^{k^{-1} S_{th}(E_{tot}) - k^{-1} E\, S'_{th}(E_{tot})} = \frac{\Omega_{th}(E_{tot})}{\Omega_{tot}(E_{tot})}\, e^{-\beta E}$$

$\boxed{P(\varphi) = Z^{-1} \exp(-\beta E(\varphi))}$; Z normalisation constant $\boxed{Z = \sum_{\varphi} e^{-\beta E(\varphi)}}$

Comments:

- Z is the partition function of the system
- $F = -kT \ln Z$ is its free energy

Z and F contains all the information about the fluctuations of the energy:

$\langle E \rangle = -\partial_\beta \ln Z = -\partial_\beta (\beta F)$; $\langle E^2 \rangle_c = \partial_\beta^2 \ln Z = \partial_\beta^2 (\beta F)$

Successive derivative of / Z $\rightarrow$ moments of E

/ $\ln Z$ $\rightarrow$ cumulants of E

Computing Z & F is the holy grail of equilibrium statistical mechanics.

Comments: There are very few cases in which one can compute Z and F exactly

→ lots of 1D systems

→ some 2D systems (Ising, Vertex models, etc...)

→ numerical tools are very important. Computing Z by brute-force is hopeless when N is large → need to be smart (cf lectures by Viot & Krzakala)

Summary:

① Start from a complex system whose dynamics we cannot solve

② Microcanonical hypothesis

③ Compute all static properties using ad hoc probability measures

This remains tough but is conceptually much simpler

III Why does it work?

Not so clear and many ideas out there

① Chaos: H is a constant of motion but all other quantities are "stirred" by the dynamics so that energy shells are visited uniformly

② Maximum information: E is known, look for distribution $P(\ell)$ that maximise Shannon entropy given $\langle E\rangle$ ⇒ Boltzmann law

③ Landau's trick: $P_{1\cup 2} = P_1 \cdot P_2$ ⇒ $\log p$ additive, E only constant of mot° which is additive ⇒ $\log P \propto E$:-)

etc...

⇒ Still topic of research. Here we will see that equilibrium physics is contagious

Comment: Why is the steady probability distribution a constant of motion?

Let $\rho(q,p,t)$ be the probability density, i.e. $\rho(q,p,t)\,dq\,dp$ is the proba to find the system in $[q,q+dq]\times[p,p+dp]$ at time t.
The evolution of $\rho(q,p,t)$ is given by the Liouville equation

$$\partial_t \rho(q,p,t) = -\frac{\partial}{\partial q}\left(\frac{\partial H}{\partial p}\rho\right) + \frac{\partial}{\partial p}\left(\frac{\partial H}{\partial q}\rho\right)$$

Now consider the observable $\rho(q(t),p(t),t)$ of the trajectory $q(t),p(t)$.

$$\frac{d\rho(q(t),p(t),t)}{dt} = \partial_t \rho + \frac{\partial \rho}{\partial q}\dot{q} + \frac{\partial \rho}{\partial p}\dot{p} \quad \text{(chain rule)}$$

$$= -\frac{\partial}{\partial q}\left(\frac{\partial H}{\partial p}\rho\right) + \frac{\partial}{\partial p}\left(\frac{\partial H}{\partial q}\rho\right) + \frac{\partial \rho}{\partial q}\frac{\partial H}{\partial p} - \frac{\partial \rho}{\partial p}\frac{\partial H}{\partial q}$$

$$= \rho\left[-\frac{\partial^2 H}{\partial q\partial p} + \frac{\partial^2 H}{\partial p \partial q}\right] = 0 \quad \text{(Schwarz equality)}$$

$\Rightarrow \rho(q(t),p(t),t)$ is a constant of motion.

Some bibliography for Part III:

- J. R. Dorfman, "An introduction to chaos in Nonequilibrium Statistical mechanics", Cambridge University Press
- E.T. Jaynes, "Information Theory and Statistical Mechanics", Physical Review, 106, 620 (1957)
- L. Landau & E. Lifchitz, "Physique Statistique"