Math 254A Lecture 14 Notes

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1 Intro to Interacting Particles and Temperature

1.1 Properties of systems of non-interacting particles

Let's recap what we've proved so far about systems of n non-interacting particles. We have the phase space (M, λ), where $(M^n, \lambda^{\times n})$ describes the total state of all n particles. We have shown that

$$\lambda^{\times n}(\tfrac{1}{n}\Phi_n \in I) = \exp\left(n \cdot \sup_{x \in I} s(x) + o(n)\right),$$

where

$$s(x) = \inf_{\beta > 0}\{s^*(\beta) + \beta x\}$$

can be expressed in terms of its Fenchel-Legendre transform:

$$\begin{aligned} s^*(\beta) &= \underbrace{\log \int e^{-\beta \varphi}\, d\lambda}_{\log Z(\beta)} \\ &= \frac{1}{n} \log \int_{M^n} e^{-\beta \Phi_n}\, d\lambda^{\times n} \\ &= \frac{1}{n} \log Z_n(\beta). \end{aligned}$$

Here $Z_n(\beta)$ is called the **partition function**.

We have also proven some properties about $s : \mathbb{R} \to [-\infty, \infty)$ and s^* using their relationship to each other:

- $s \equiv -\infty$ on $(-\infty, 0)$.
- $$s(x) \to \begin{cases} \infty & x \to \infty \\ \text{const or } -\infty & x \downarrow 0. \end{cases}$$

- s is strictly concave (iff s^* is diferentiable) and differentiable (iff s^* is concave)
- $$s'(x) \to \begin{cases} 0 & x \to \infty \\ \infty & x \downarrow 0. \end{cases}$$

Define the **microcanonical ensemble**[1]

$$d\mu_{n,I}(p_1, \dots, p_n) = \frac{\mathbb{1}_{\{\frac{1}{n}\Phi_n \in I\}}(p_1, \dots, p_n)\, d\lambda(p_1) \cdots d\lambda(p_n)}{\lambda^{\times n}(\{\frac{1}{n}\Phi_n \in I\})}.$$

For $\beta > 0$,

$$d\mu_\beta(p) = \frac{1}{Z(\beta)} e^{-\beta\varphi(p)}\, d\lambda(p)$$

is the normalized **Gibbs measure**.

Then

$$\begin{aligned} d\mu_{n,\beta}(p_1, \dots, p_n) &= d\mu_\beta(p_1) \cdots d\mu_\beta(p_n) \\ &= \frac{1}{Z(\beta)^n} e^{-\beta\varphi(p_1)}\, d\lambda(p_1) \cdots e^{-\beta\varphi(p_n)}\, d\lambda(p_n) \\ &= \frac{e^{-\beta\Phi_n(p_1,\dots,p_n)}\, d\lambda^{\times n}(p_1, \dots, p_n)}{Z_n(\beta)} \end{aligned}$$

is the **canonical ensemble**, which applies to all the particles at once.

Last time, we said that

$$\mu_{n,I}(\{\tfrac{1}{n}\Psi_n \approx \langle \psi, \mu_\beta \rangle\}) \approx 1,$$

where $\Psi_n = \psi(p_1) + \cdots + \psi(p_n)$, I is a short interval around E, and β is chosen so that $\langle \varphi, \mu_\beta \rangle = E$. We have that

$$\mu_{n,I}(\{\tfrac{1}{n}\Psi_n \approx \tfrac{1}{n}\langle \Psi_n, \mu_{n,\beta} \rangle\}) \approx 1,$$

so there is an equivalence of the canonical ensemble and the microcanonical in the limit $n \to \infty$.

[1] The term "ensemble" goes back to Gibbs, who used it before measure theory and its terminology were around.

1.2 Wishlist for extending properties to interacting systems of particles

Suppose we have some sequence of σ-finite but not finite measure spaces (M_n, λ_n) with "total energy" functions $\Phi_n : M_n \to [0, \infty)$. Then we want

$$\lambda_n(\tfrac{1}{n}\Phi_n \in I) = \exp\left(n \cdot \sup_{x \in I} s(x) + o(n)\right),$$

where we can hopefully define s as usual and

$$s^*(\beta) = \lim_{n\to\infty} \frac{1}{n} \log \int_{M^n} e^{-\beta\Phi_n}\, d\lambda = \lim_{n\to\infty} \frac{1}{n} \log Z_n(\beta)$$

We will retain the following properties of s and s^*:

- $s \equiv -\infty$ on $(-\infty, 0)$.
- $$s(x) \to \begin{cases} \infty \text{ (sometimes)} & x \to \infty \\ \text{const or } -\infty & x \downarrow 0. \end{cases}$$
- s will not always be strictly concave but will usually be differentiable.
- $$s'(x) \to \begin{cases} 0 \text{ (not always)} & x \to \infty \\ \infty \text{ (usually)} & x \downarrow 0. \end{cases}$$

We can also define the canonical and microcanonical ensembles and hope for an equivalence of ensembles in the limit, as well.

1.3 Defining temperature

What is temperature? When two bodies of different temperature come into contact for a prolonged period of time, they will eventually both reach some equilibrium temperature. Temperature is a quantity that determines when bodies/systems are in thermal equilibrium. There is a canonical "thermodynamic temperature" (which can be measured, for example, by a mercury thermometer) which we want to be able to define.[2]

To interpret this, consider two systems $(M_n, \lambda_n), \Phi_n : M_n \to [0, \infty)$ and $(\widetilde{M}_n, \widetilde{\lambda}_n), \widetilde{\Phi}_n : \widetilde{M}_n \to [0, \infty)$. There is the combined system is $(M_n \times \widetilde{M}_n, \lambda_n \times \widetilde{\lambda}_n)$ with total energy $\Phi_n(p) + \widetilde{\Phi}_n(\widetilde{p})$. Note that once again we are assuming very weak interaction between the systems in terms of energy. If we condition on

$$\{(p, \widetilde{p}) \in M_n \times \widetilde{M}_n : \tfrac{1}{2n}(\Phi_n(p) + \widetilde{\Phi}_n(\widetilde{p})) \in I\},$$

[2] Historically, the mysterious quantity "entropy" was discovered first, and temperature was defined relative to it.

what is the typical split of total energy between Φ_n and $\widetilde{\Phi}_n$?

Suppose

$$\lambda_n(\{\tfrac{1}{n}\Phi_n \in I\}) = \exp\left(n \cdot \sup_I s + o(n)\right),$$

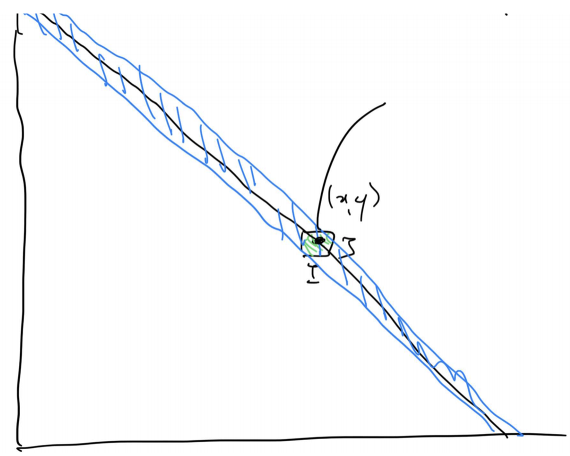
$$\widetilde{\lambda}_n(\{\tfrac{1}{n}\widetilde{\Phi}_n \in I\}) = \exp\left(n \cdot \sup_I \widetilde{s} + o(n)\right).$$

Then consider $(\Phi_n(p), \widetilde{\Phi}_n(\widetilde{p})) : M_n \times \widetilde{M_n} \to [0,\infty)^2$ with

$$\lambda_n \times \widetilde{\lambda}_n(\{(\tfrac{1}{n}\Phi_n, \tfrac{1}{n}\widetilde{\Phi}_n) \in I \times J\}) = \exp\left(n \cdot \sup_{x\in I, y\in J} (s(x) + \widetilde{s}(y)) + o(n)\right)$$

This is the same when $I \times J$ are replaced by general open, convex sets.

In the following picture of the microcanonical ensemble, conditioning on $\frac{1}{2n}(\Phi_n(p) + \widetilde{\Phi}_n(\widetilde{p})) \in \operatorname{int} K$ means conditioning on the blue strip:



The most likely energy split occurs where $s(x)+\widetilde{s}(y)$ is maximized on this strip. Suppose the strip is very thin around $\{x + y = E\}$. We want to maximize $s(x) + \widetilde{s}(E - x)$ as x varies in $[0, E]$. If $s, \widetilde{s}$ are differentiable, this requires

$$\frac{\partial}{\partial x}[s(x) + \widetilde{s}(E - x)] = 0,$$

i.e. $s'(x) = \widetilde{s}'(E-x)$. That is, systems are in thermal equilibrium at individual energies x and $y = E - x$ only if $\beta = s'(x) = \widetilde{s}'(y) = \widetilde{\beta}$. This is the unique maximizer, so this is "if and only if" in the case where $s, \widetilde{s}$ are strictly concave.

So we define the **thermodynamic temperature** of the system with entropy function s to be

$$T = \frac{1}{\beta} = \frac{1}{s'(x)}.$$

Here, β is known as the **inverse temperature**.