Lecture 1

In the 19^{th} century chemists had concluded that atoms and molecules were real, but this was not generally accepted throughout science. In the 1870's Boltzmann, starting with the assumption that matter consists of particles obeying Newtonian mechanics, attempted to deduce the probability distribution that governs snapshots at successive times of such a particle system. In 1866 Maxwell independently postulated a Gaussian distribution for snapshots of velocities. In 1878 J. W. Gibbs introduced the starting point for these lectures, which is called the "grand canonical ensemble." This is believed to describe the distribution of particles in a large region which is a subset of an even larger domain that confines the Newtonian particles — think of the confinement as analogous to the way billiards are confined by the table. The advantage of not considering the whole system is that the number of particles and their total energy can fluctuate in a region whereas for the whole system they are conserved. This freedom makes the grand canonical ensemble easier to work with. How to work with this ensemble is the main topic of this lecture.

Notation

For a set X,

$$X^n = \{(x_1, \dots, x_n) : x_1, \dots, x_n \in X\}$$

is the set of sequences in X with length n. By convention X^0 is a set with one element written $()$.

$$X^* = \bigcup_{n=0}^{\infty} X_n$$

is the set of all sequences of arbitrary finite length. If $x \in X^*$ we write

$$x = (x_1, \dots, x_{N(x)})$$

and we write $N = N(x)$.

If $X \subset \mathbb{R}^d$ then we tacitly assume X is Lebesgue measurable and write $|X|$ = Lebesgue measure of X.

If X is a finite set $|X|$ = # elements in X.

Functions on $\mathbb{R}^d$ are tacitly assumed to be Lebesgue measurable.

$$\mathbb{1}_{x \in X} = \begin{cases} 1 & \text{if } x \in X \\ 0 & \text{else} \end{cases}$$

Potential Energy

This is a function

$$V : (\mathbb{R}^d)^* \longrightarrow \mathbb{R} \cup \{+\infty\}$$

such that $V(()) = 0$ and there exists $c \geq 0$ s.t.

$$V \geq -c\, N \qquad \text{(stability)}$$

We define $e^{-\infty} = 0$, $0 \cdot \infty = 0$.

Example 1   For some bounded $\phi : \mathbb{R}^d \to \mathbb{R}$, called an external field,

$$V(x) = -\sum_{i=1}^{N(x)} \phi(x_i)$$

Example 2   For some $\upsilon : \mathbb{R}^d \times \mathbb{R}^d \to \mathbb{R} \cup \{\infty\}$, called a two-body potential

$$V(x) = \sum_{1 \leq i < j \leq N(x)} \upsilon(x_i, x_j)$$

The Grand Canonical Ensemble

<u>Defn 1</u> Let $\Lambda \subset \mathbb{R}^d$ with $|\Lambda| < \infty$. Let $z > 0$. The grand canonical ensemble is the probability distribution defined on subsets of Λ^* by

$$\mathbb{P}(E) = \frac{1}{Z} \sum_{n \geq 0} \frac{z^n}{n!} \int_{E \cap \Lambda^n} e^{-V} \, dx_1 \cdots dx_n$$

where Z is the normalisation. $Z = Z(\Lambda, V, z)$ is called the <u>partition</u> <u>function</u>

By (stability)

$$Z = \sum_{n \geq 0} \frac{z^n}{n!} \int_{\Lambda^n} e^{-V} \, dx_1 \cdots dx_n$$

$$\leq \cdots\cdots\cdots \, e^{cn} \cdots\cdots$$

$$= \sum_{n \geq 0} \frac{z^n}{n!} e^{cn} |\Lambda|^n$$

$$= \exp\left(z e^c |\Lambda|\right) < \infty$$

<u>Example 3</u> For $V = -\sum \phi(x_i)$, $Z = Z(\phi)$ is

$$Z(\phi) = \exp\left(z \int_\Lambda e^{\phi(x)} dx\right)$$

Notation

For $F : \Lambda^* \to \mathbb{R}$

$$\langle F \rangle = \mathbb{E} F = \int F \, d\mathbb{P}$$

$$= \frac{1}{Z} \sum \frac{z^n}{n!} \int_{\Lambda^n} e^{-V} F \, dx_1 \cdots dx_n$$

The typical example of a function F is $N(X) = N(X, x)$

$N(X,x) = \#$ particles in X, $\qquad X \subset \Lambda$

$$= \sum_{i=1}^{N(x)} \mathbb{1}_{x_i \in X}$$

Thus we are working with the probability space $(\Lambda^*, \mathbb{P})$ and the sigma algebra generated by $(N(X),\ X \subset \Lambda)$.

The case $V = 0$ or more generally $V = \sum \phi(x_i)$ is called the ideal gas. It is a useful starting point because

$$\mathbb{P}(E) = \frac{1}{Z} \int_E e^{-V} \, d\mathbb{P}_{V=0}$$

$$Z = \int e^{-V} \, d\mathbb{P}_{V=0}$$

Notice this Z is not equal to the previous Z's

Lemma 1 (Ideal Gas)

Let $V = 0$. Let $X_1, \dots, X_m$ be subsets of Λ, $|\Lambda| < \infty$.

(a) $N(X_i) \sim \text{Poisson}(z|X_i|)$

(b) If $|X_i \cap X_j| = 0$ for $i \neq j$ then $N(X_1), \dots, N(X_m)$ are independent.

If $V = -\sum \phi(x_i)$ then $N(X_i) \sim \text{Poisson}(z \int_{X_i} e^{\phi} dx)$ and (b) holds.

Proof of (a)

Since the Laplace transform characterises measure, check Laplace transforms:
A Poisson(r) random variable Y has

$$\mathbb{E}\, e^{tY} = \sum_{n \geq 0} e^{tn}\, \mathbb{P}_{\text{Poisson}}(Y=n)$$

$$= \sum_{n \geq 0} e^{tn} \frac{r^n}{n!} e^{-r}$$

$$= \exp\left(r(e^t - 1)\right) \qquad (*)$$

By Example 3

$$\int e^{tN_X}\, d\mathbb{P} = \frac{1}{Z} \sum \frac{z^n}{n!} \int_{\Lambda^n} e^{\sum \overbrace{t \mathbb{1}_{x_i \in X}}^{\phi(x_i)}}$$

$$= \frac{1}{(\phi=0)} \exp\left(z \int_{\Lambda} e^{\phi} dx\right)$$

$$= \exp\left(z \int_{\cancel{\Lambda}\, X} (e^{\phi} - 1)\, dx\right) = \exp\left(z(e^t - 1)|X|\right)$$

$$= (*) \text{ with } r = z|X| \checkmark$$

$\blacksquare$

Problems

1. An $n \times n$ matrix A is said to be positive-definite if for all non-zero $\lambda = (\lambda_1, \ldots, \lambda_n)$ in $\mathbb{C}^n$, $\sum \lambda_i A_{ij} \bar{\lambda}_j > 0$. A continuous function $f: \mathbb{R} \to \mathbb{R}$ is said to be positive-definite if for every $x \in (\mathbb{R})^n$, $f(x_i - x_j)$ is a positive-definite matrix. Prove that

   (a) If f is positive-definite then V with $V(x,y) = f(x-y)$ satisfies (stability)

   (b) If f is integrable so that the Fourier transform $\hat{f}(k) = \int f(x) e^{-ikx} dx$ exists, if $\hat{f} \geq 0$, then f is positive-definite.

This extends to $\mathbb{R}^d$. Conjecture Every $V(x,y) = f(x-y)$ that satisfies (stability) has the form positive + positive-definite.

2. Complete the proof of Lemma 1

3. Prove the Ideal Gas Law which says, for $V = 0$,

$$P|\Lambda| = T \langle N(\Lambda) \rangle$$

where, by definition, $\frac{P}{T} = \ln Z$. P is called the Pressure, T is called the temperature.

4. Prove that $\langle N(\Lambda) \rangle$ is monotone in z.