Week 1

- More is different.

- Systems with small degrees of freedom
  - hydrogen atom
  - large scale structure of the solar system

  One may try to follow these time evolutions precisely.

- This approach is not practical when d.o.f. \( \gg 1 \).
  - gas molecules in this classroom
  - electrons in metal
  - stock market

\[ \Rightarrow \text{Statistical approach} \]
In this course, we will study **equilibrium statistical mechanics**. Namely, we will only consider static situations.

**Basic Assumption**

For a given quantum mechanical system, we consider a statistical ensemble consisting of all **allowed** quantum states.

Allowed by macroscopic parameters such as energy, # of particles, etc.

A closed system can be in any of these quantum states with equal probability.
Equal Probability Postulate

Most of what we will learn in this course will follow from this assumption.

So, what we need to do are tools to estimate the number of allowed quantum states so that we can compute the probability.

Note: The counting of the number of states is a quantum concept. The classical limit of this concept is the volume of the phase space.
About the course

- Textbook: “Thermal Physics” by Kittel & Kroemer. First 10 chapters

- Homework: handed out on Thursdays at the class, also posted on the course website. Due following Thursday.

- Mid-term/final exams:
  - Take home, partial open book
  - (You may use your own hand-written or hand-typed notes; Nothing else is allowed.)
I States of a model system

Examples:

- 1d harmonic oscillator

\[ H = \frac{1}{2} p^2 + \frac{1}{2} \omega^2 \hat{q}^2 \]
\[ E_n = (n + \frac{1}{2}) \hbar \omega \quad n = 0, 1, \ldots \]

\[ E \]
\[ \downarrow \]
\[ 0 \]

- 2d symmetric harmonic oscillator

\[ H = \frac{1}{2} \vec{p}^2 + \frac{1}{2} \omega^2 \vec{q}^2 \]
\[ \vec{p} = (p_1, p_2) \]
\[ \vec{q} = (q_1, q_2) \]
\[ E_{m_1, m_2} = (m_1 + m_2 + 1) \hbar \omega \]
\[ m_1, m_2 = 0, 1, 2, \ldots \]
In the latter case, the energy levels are \((N+1)\hbar \omega, \ N = 0, 1, \ldots\). The multiplicity of the \(N\)th level is \(N+1\).

i.e.,

\[
\dim \{ \psi \in \text{Hilbert space} : H\psi = (N+1)\hbar \omega \psi \} = N+1
\]
a single particle of mass \( M \) in a cube of side \( L \)

\[
E = \frac{\hbar^2}{2m} \left( \frac{n}{L} \right)^2 (m_x^2 + n_y^2 + n_z^2)
\]

\( m_x, n_y, n_z = 0, 1, 2, \ldots \)

(to be derived in Chapter 3)

e.g., \( m_x^2 + n_y^2 + n_z^2 = 18 \)

has 3 solutions: \((4,1,1)\), \((1,4,1)\), \((1,1,4)\)

Quantum states of a one-particle system are called orbitals.
So far we have looked at multiplicities of one-particle systems.

Let us look at \( N \)-particle systems.

**Binary Model Systems**

\[
\begin{array}{ccccccc}
\uparrow & \uparrow & \downarrow & \downarrow & \uparrow & \downarrow & \uparrow \\
1 & 2 & 3 & 4 & \ldots & \ldots & N \\
\end{array}
\]

\( N \) identical systems, each with 2 states.

Mathematically,

\[
\mathcal{H}^N = \mathcal{H} \otimes \mathcal{H} \otimes \ldots \otimes \mathcal{H}
\]

\( \mathcal{H} = \{ 1\uparrow, 1\downarrow \} \)

Each \( \mathcal{H} \) is called a site.
This can be a model of many different situations:

- $\uparrow \rightarrow$ spin up, $\downarrow \rightarrow$ spin down
- $\uparrow \rightarrow$ buy, $\downarrow \rightarrow$ sell
- $\uparrow \rightarrow$ parking space occupied
  $\downarrow \rightarrow$ empty

$\dim \mathcal{H} = 2$

$\dim \mathcal{H}^N = 2^N$

Shorthand notation

$\mathcal{H}^N \in \uparrow_1 \uparrow_2 \downarrow_3 \uparrow_4 \cdots \downarrow_N$
Suppose $\uparrow, \downarrow$ mean magnetic moment $m, -m$.

We can consider the total magnetic moment $M$

e.g. $N = 3$

$$M = 3m \quad \uparrow\uparrow\uparrow \quad 1$$

$$M = m \quad \uparrow\uparrow\downarrow, \quad \uparrow\downarrow\uparrow \quad 3$$

$$M = -m \quad \downarrow\downarrow\downarrow, \quad \downarrow\uparrow\downarrow \quad 3$$

$$M = -3 \quad \downarrow\downarrow\downarrow \quad 1$$

In general, there are $(N+1)$ different values of $M$,

$N m, (N-2) m, \ldots, -N m$

But $\dim H_N = 2^N$

For $N \gg 1$, $2^N \gg N+1$. 
total magnetic moment $(N-2k)m$

$k = 0, 1, \ldots, N$

$$(N-k) \text{ sites with } \uparrow$$

$k \text{ sites with } \downarrow$

$$(N-k)m + k(-m) = (N-2k)m.$$

# of states

$$= N \binom{N}{k} = \frac{N!}{(N-k)!k!}.$$

In the textbook, the authors set

$$k = \frac{1}{2} N - S \quad \text{so that}$$

$$N^\uparrow = N - k = \frac{1}{2} N + S$$

$$N^\downarrow = k = \frac{1}{2} N - S$$

$$M = (N-2k)m = 2S m$$
Total magnetic moment \( M = 2Sm \)

\[
g(N, s) = \frac{N!}{N_p! N_d!} = \frac{N!}{(\frac{1}{2}N+s)! (\frac{1}{2}N-s)!}
\]

Multiplicity function

Clearly \( \sum_s g(N, s) = \sum_k \frac{N!}{(N-k)! k!} \)

\[= 2^N \]

What happens when \( N \) is large?
large $N$ behavior of $g(N, s)$:

For a very large number, it is often useful to take a logarithm.

I will write $\log x = \log_e x = \ln x$.

(I will not use $\log_{10} x$ in this course.)

$$\log g(N, s) = \log N! - \log (\frac{1}{2}N + 5)!$$
$$\phantom{\log g(N, s)} - \log (\frac{1}{2}N - 5)!$$

So we want to evaluate

$N!$ for large $N$

--- Stirling's formula
\[ N! \sim (2\pi N)^{\frac{1}{2}} n^N e^{-N + O(\frac{1}{N})} \]

\[ \log N! \sim (N + \frac{1}{2}) \log N + \frac{1}{2} \log 2\pi - N + O\left(\frac{1}{N}\right) \]

**Proof**

Start with the Gamma function:

\[ \Gamma(N+1) = \int_0^\infty dx \ x^N \ e^{-x} \]

When \( N \) is a positive integer

\[ \Gamma(N+1) = N! \]

\[ \therefore \ \Gamma(N+1) = \int_0^\infty dx \ x^N \ (-\frac{d}{dx}) e^{-x} \]

\[ = N \int_0^\infty dx \ x^{N-1} e^{-x} \]

\[ \Gamma(1) = \int_0^\infty dx \ e^{-x} = 1 \]
We want to evaluate
\[ \int_0^\infty x^N e^{-x} \text{ when } N \gg 1. \]

Saddle point approximation

Consider \[ \int_0^\infty dx \ e^{-N f(x)} \]

When \( N \gg 1 \), look for \( x_0 \) s.t. \( f'(x_0) = 0 \)

There may be several of them.

Around each \( x_0 \),
\[ f(x) \sim f(x_0) + \frac{1}{2} f''(x_0) (x-x_0)^2 + \cdots \]

Define \( y = \sqrt{N} x \), \( y_0 = \sqrt{N} x_0 \)

\[ N f(x) \sim N f(x_0) + \frac{1}{2} f''(x_0) (y-y_0)^2 + O\left(\frac{1}{\sqrt{N}}\right) \]
If the contour $x : 0 \to \infty$ can be deformed so that it crosses $x_0$, this saddle pt contributes to the integral as
\[ \int dx \ e^{-N f(x_0) - \frac{N}{2} f''(x_0) (x-x_0)^2} \]
\[ \sim e^{-N f(x_0)} \sqrt{\frac{2\pi}{N f''(x_0)}} \]

I used the Gaussian integral
\[ \int_{-\infty}^{\infty} dx \ e^{-\frac{1}{2} \alpha x^2} = \sqrt{\frac{2\pi}{\alpha}} \]

\[ \therefore \quad (LHS)^2 = \int_0^\infty 2\pi r dr e^{-\frac{1}{2} \alpha r^2} \]
\[ = \int_0^\infty 2\pi dx e^{-\alpha \frac{x}{2}} (x = \frac{r^2}{2}) \]
\[ = \frac{2\pi}{a} \]
Coming back to our problem

\[ \Gamma(N+1) = \int_0^\infty dx \ x^N e^{-x} \]

\[ = \int_0^\infty dx \ \exp \left( N \log x - x \right) \]

\[ x = N \gamma \]

\[ = \int_0^\infty N \, d\gamma \ \exp \left( N \log N \gamma - N \gamma \right) \]

\[ = N^{N+1} \int_0^\infty d\gamma \ \exp \left( N \left( \log \gamma - \gamma \right) \right) \]

\[ \frac{d}{d\gamma} \left( \log \gamma - \gamma \right) = \frac{1}{\gamma} - 1 = 0 \text{ at } \gamma = 1 \]
\[(\log \gamma - c)' = -\frac{1}{\gamma^2}\]

\[\log \gamma - c = -1 - \frac{1}{2} (c - 1)^2 + \ldots\]

\[
\Gamma(N+1) = N^{N+1} \int_0^\infty d\gamma \, e^{N(\log \gamma - c)}
\]

\[
\sim N^{N+1} e^{-N} \int_0^\infty d\gamma \, e^{-\frac{N}{2} (c - 1)^2}
\]

\[
= (2\pi N)^{\frac{1}{2}} N^N e^{-N}
\]

Note that we could have derived

\[N! \sim N^N e^{-N}\]

by just estimating \[x^N e^{-x}\] at

the extremum.
See appendix A (p 441 ~) for
\[ N! \sim (2\pi N)^{\frac{1}{2}} N^N e^{-N + \frac{1}{12N} + o\left(\frac{1}{N^2}\right)} \]

Armed with this, let us estimate the large N behavior of
\[ g (N, s) = \frac{N!}{(\frac{1}{2}N+s)! (\frac{1}{2}N-s)!} \]

\[ \log N! \sim \frac{1}{2} \log 2\pi + (N + \frac{1}{2}) \log N - N \]

\[ \log g (N, s) \sim \frac{1}{2} \log 2\pi + (N + \frac{1}{2}) \log N - N \]
\[ - \frac{1}{2} \log 2\pi - (N_{\eta} + \frac{1}{2}) \log N_{\eta} + N_{\eta} \]
\[ - \frac{1}{2} \log 2\pi - (N_{\nu} + \frac{1}{2}) \log N_{\nu} + N_{\nu} \]
\[ = \frac{1}{2} \log \left(\frac{1}{2\pi N}\right) - (N_{\eta} + \frac{1}{2}) \log \frac{N_{\eta}}{N} \]
\[ - (N_{\nu} + \frac{1}{2}) \log \frac{N_{\nu}}{N} \]
\[
\log \frac{N^r}{N} = \log \left(1 + \frac{2s}{N}\right)
\]
\[
\sim - \log 2 + \frac{2s}{N} - \frac{2s^2}{N^2} + \cdots
\]
\[
\log \frac{N^r}{N} \sim - \log 2 - \frac{2s}{N} - \frac{2s^2}{N^2} + \cdots
\]

\[
\Rightarrow \quad \log \mathcal{L}(N, s) \sim \frac{1}{2} \log \left(\frac{1}{2\pi N}\right) + N \log 2
\]
\[
- \frac{2s^2}{N^2} + \cdots
\]

\[
\Rightarrow \quad \mathcal{L}(N, s) \sim \mathcal{L}(N, 0) \exp \left(-\frac{2s^2}{N}\right)
\]

\[
\mathcal{L}(N, 0) \sim \left(\frac{2}{\pi N}\right)^{\frac{1}{2}} 2^N
\]

(c.f. \(\mathcal{L}(N, 0) = \frac{N!}{(\frac{1}{2}N)!(\frac{1}{2}N)!}\))

\[
\mathcal{L}(N, s) \sim 2^N \cdot \left(\frac{2}{\pi N}\right)^{\frac{1}{2}} e^{-\frac{2s^2}{N}}
\]

\[
\left(\frac{2}{\pi N}\right)^{\frac{1}{2}} \int ds e^{-\frac{2s^2}{N}} = 1.
\]
When $S^2 = \frac{1}{2}N$, 

$$g(N, S) \sim g(N, 0) \times \frac{1}{\sqrt{e}}$$

For large $N$, e.g., $N \sim 10^{24}$

$$\sqrt{N} \sim 10^{12}$$

So, the fractional width is $\sim 10^{-12}$. 
Define

\[ g_0(N, s) = 2^N \left( \frac{2}{\pi N} \right)^{1/2} e^{-\frac{2s^2}{N}} \]

\[ \sum_s g(N, s) = 2^N \]

\[ \int ds \, g_0(N, s) = 2^N \]

Define \( P(s) = 2^{-N} g(N, s) \)

\[ P_0(s) = 2^{-N} g_0(N, s) \cdot \]

\[ \langle f(s) \rangle = \sum_s f(s) \, P(N, s) \]

\[ \langle f(s) \rangle_0 = \int ds \, f(s) \, P_0(N, s) \]

e.g. \( \langle s \rangle = 0, \quad \langle s \rangle_0 = 0 \)
\[
\langle S^2 \rangle_0 = \left(\frac{2}{\pi N}\right)^{\frac{1}{2}} \int ds \, s^2 \, e^{-\frac{2s^2}{N}}
\]

\[
\int dx \, e^{-\frac{a}{2} x^2} = \sqrt{\frac{2\pi}{a}}
\]

\[
\int dx \, x^2 \, e^{-\frac{a}{2} x^2} = -2 \frac{2}{a} \int dx \, e^{-\frac{a}{2} x^2}
= \sqrt{\frac{2\pi}{a^3}}
\]

= \frac{1}{4} N

In this case \( \frac{1}{2} \sqrt{N} \) is called the standard deviation, denoted by \( \sigma \).

\[
P(s) = \frac{1}{\sqrt{2\pi} \sigma} \, e^{-\frac{s^2}{2\sigma^2}}
\]

Normal distribution

(sometimes called Gaussian distribution)
This is an example of the central limit theorem.

\( P(X) \): arbitrary probability function for \( X \in S \)

\( S \): arbitrary set

\[
\left( \text{In our case, } S = \{ \uparrow, \downarrow \} \right) \\
\quad P(S) = \frac{1}{2}
\]

Assume \( P(X) \) has finite mean \( \mu \) and standard deviation \( \sigma \).

Consider \( N \) random variables \( X_1, X_2, \ldots, X_N \) obeying \( P(X) \) independently.
Set \[ x = \frac{x_1 + \ldots + x_N - N\mu}{\sigma \sqrt{N}} \]

Then, in the limit \( N \to \infty \),

\( x \) obeys the normal distribution

\[ \frac{1}{\sqrt{2\pi}} e^{-\frac{1}{2} x^2} \]

See:

http://en.wikipedia.org/wiki/Central_Limit_Theorem
We looked at the binary system \{ U, V \} and its N copies.

We can consider N copies of other systems.

- harmonic oscillator

  1 harmonic oscillator

  \[ \text{energy} = n \hbar \omega \quad (\text{subtract the zero point energy}) \]

  \[ m = 0, 1, \ldots \]

  Each level has multiplicity 1.

  \[ g \left( N=1, m \right) = 1 \]

N harmonic oscillators

\[ n \hbar \omega = \sum_{i=1}^{N} m_i \hbar \omega \]

What is \( g \left( N, m \right) \) in this case?
It is useful to consider the generating function:

\[ G_N(t) = \sum_{m=0}^{\infty} g(N, m) t^m \]

We know

\[ G_{N=1}(t) = \sum_{m=0}^{\infty} g(N=1, m) t^m = \sum_{n=0}^{\infty} t^n = \frac{1}{1-t} \]

Since

\[ g(N, m) = \sum_{m_1 + \ldots + m_N = m} g(1, m_1) \ldots g(1, m_N) \]

\[ G_N(t) = \sum_{m} \sum_{m_1 + \ldots + m_N = m} g(1, m_1) \ldots g(1, m_N) t^{m_1} \ldots t^{m_N} \]

\[ = (G_{1}(t))^N \]

\[ = \left( \frac{1}{1-t} \right)^N \]
Thus

\[ \sum_{m=0}^{\infty} g(N, m) t^m = \left( \frac{1}{1-t} \right)^N \]

\[ g(N, m) = \frac{1}{m!} \left( \frac{d}{dt} \right)^m \left( \frac{1}{1-t} \right)^N \bigg|_{t=0} \]

\[ = \frac{1}{m!} N(N+1) \cdots (N+m-1) \]

\[ = \frac{(N+m-1)!}{m!(N-1)!} \]