Thurs: Exam II

Covers Ch 3, 4,

Lectures 13 → 22 (part)

HW 13 – HW 16

Format: * Similar to first exam

- Review 2016, 2019 Exam II

* Take home due by ~~4pm~~ 5pm Thursday.

D2L ~~at~~ Exam Drop Box

Canonical ensemble

The canonical ensemble connects statistical phys to thermodynamics via the partition function

$$Z = \sum_{\text{all states}} e^{-E_s \beta}$$

and

$$\bar{E} = -\frac{\partial}{\partial \beta} \ln[Z]$$

For an ensemble consisting of N identical distinguishable particles the partition function is

$$Z_{\text{ensemble } N} = (Z_{\text{single}})^N$$

where Z_{single} is the partition function for a single particle.

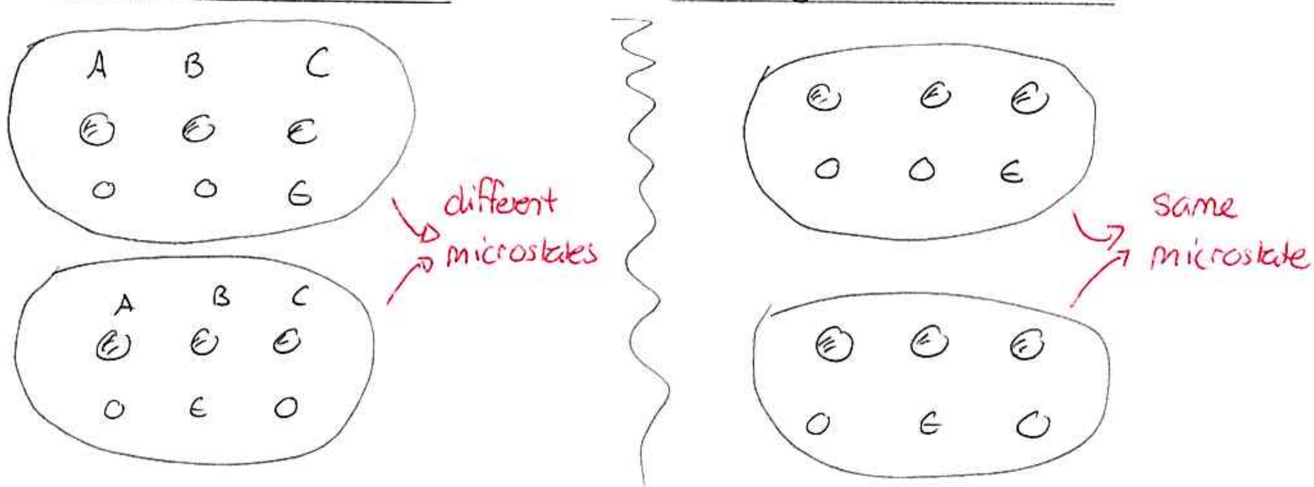
Indistinguishable particles

In the case where the particles are indistinguishable, the enumeration of distinct states for the ensemble changes and becomes more complicated. Consider a generic situation where the states of a single particle in the ensemble are:

state "s"	energy E_s
0	0
1	ϵ
2	2ϵ
3	3ϵ
⋮	

Then consider the following contrast:

Distinguishable particles | Indistinguishable particles



Count as two states in the partition function | only should be counted once in partition function

1 Pair of indistinguishable particles

Consider a system that consists of two identical indistinguishable particles. Each particle can be in one of three states, the energies for which are $0, \epsilon, 2\epsilon$.

a) Considering the pair of particles as "the system," list all possible states of the system and their energies.

b) Determine the partition function of the system.

c) Show that the state of the system can be described by listing the number of particles in each state available to an individual particle.

Answer: a)

Possibilities		ν_0	ν_1	ν_2
both have zero	0	2	0	0
one has one, other zero	ϵ	1	1	0
both have one	2ϵ	0	2	0
one has two, other zero	2ϵ	1	0	1
one has two, other one	3ϵ	0	1	1
both have two	4ϵ	0	0	2

b) $Z = \sum_{\text{all states "s"}} e^{-E_s\beta}$

$$Z = e^{-0\beta} + e^{-\epsilon\beta} + e^{-2\epsilon\beta} + e^{-2\epsilon\beta} + e^{-3\epsilon\beta} + e^{-4\epsilon\beta}$$

$$= 1 + e^{-\epsilon\beta} + 2e^{-2\epsilon\beta} + e^{-3\epsilon\beta} + e^{-4\epsilon\beta}$$

c) Let

$\nu_0 =$ number in state 0

$\nu_1 =$ " " " 1

$\nu_2 =$ " " " 2

Note $\nu_0 + \nu_1 + \nu_2 =$ number particles $= 2$.

We can describe all states by assigning all ν_0, ν_1, ν_2 that satisfy

We can then use the canonical ensemble via:

List all states of a single particle $\sim \{s\}$

e.g. oscillator

$n = 0, 1, 2, 3, \ldots$

Now ensemble of N indistinguishable particles

Let

$\nu_s =$ number in state s

e.g. $N = 17$

$\nu_0 = 10 \rightarrow 10$ in state "0"

$\nu_1 = 5 \rightarrow 5$ " "1"

$\nu_2 = 2$

rest zero

State of ensemble specified via list

$(\nu_0, \nu_1, \nu_2, \ldots)$

Constraint

$$\sum_{\text{all } s} \nu_s = N$$

The energy of the state is

$$E_{(\nu_0, \nu_1, \nu_2 \ldots} = \sum E_s \nu_s$$

$$E = 10 \times \frac{\hbar\omega}{2} + 5 \times \frac{3\hbar\omega}{2} + 2 \times \frac{5\hbar\omega}{2} = \frac{\hbar\omega}{2} 55$$

Canonical ensemble partition function is:

$$Z = \sum_{\text{all states}} e^{-E_s \beta} = \sum_{\substack{\text{all } \nu_0, \nu_1, \nu_2 \\ \text{s.t. } \nu_0 + \nu_1 + \nu_2 + \ldots = N}} e^{-\sum_s E_s \nu_s \beta}$$

This will always work in principle although in practice it can be complicated.

2 Indistinguishable particles with two various states

Consider a system of N indistinguishable particles, each of which can be in various states

a) Suppose that each particle can be in one of two states, with energies 0 and ε. Determine the partition function for a system of N such particles.

b) Suppose that each particle can be in one of three states, with energies $0, \varepsilon$ and 2ε. Determine the partition function for a system of N such particles.

Answer: a) List individual particle states

s	E_s
0	0
1	ϵ

Then the states of the system are described by

$\nu_0 =$ number in state 0 s.t $\nu_0 + \nu_1 = N$

$\nu_1 =$ " " " 1

So

$$Z = \sum_{\nu_0, \nu_1 \text{ s.t } \nu_0 + \nu_1 = N} e^{-(E_0 \nu_0 + E_1 \nu_1)\beta}$$

$$= \sum_{\nu_0, \nu_1} e^{-E_0 \nu_0 \beta} e^{-E_1 \nu_1 \beta}$$

But $\nu_1 = N - \nu_0$ implies that the sum can be reduced to

$$Z = \sum_{\nu_0} e^{-E_0 \nu_0 \beta} e^{-E_1 (N - \nu_0)\beta}$$

$$= e^{-E_1 N \beta} \underbrace{\sum_{\nu_0 = 0}^{N} e^{-(E_0 - E_1)\nu_0 \beta}}_{\text{geometric series}} \quad \text{ratio } e^{-\overbrace{(E_0 - E_1)}^{-\epsilon}\beta}$$

$$= e^{-\underbrace{E_1}_{\epsilon} N \beta} \frac{1 - e^{\epsilon\beta(N+1)}}{1 - e^{+\epsilon\beta}} = \frac{e^{-\epsilon N \beta} - e^{+\epsilon\beta}}{1 - e^{+\epsilon\beta}}$$

So

$$Z = \frac{e^{\epsilon\beta} - e^{-\epsilon N\beta}}{e^{\epsilon\beta} - 1}$$

b) Here we have . The states are described by ν_0, ν_1, ν_2 s.t.

S	Es
0	0
1	ϵ
2	2ϵ

$$\nu_0 + \nu_1 + \nu_2 = N$$

$$\Rightarrow \nu_2 = N - \nu_0 - \nu_1$$

We get

$$Z = \sum_{\substack{\nu_0, \nu_1, \nu_2 \\ \text{s.t. } \nu_0 + \nu_1 + \nu_2 = N}} e^{-[E_0\nu_0 + E_1\nu_1 + E_2\nu_2]\beta}$$

$$= \sum_{\nu_0, \nu_1 \leq N \text{ and such that } \nu_0 + \nu_1 \leq N} e^{-[E_0\nu_0 + E_1\nu_1 + E_2 N - E_2\nu_0 - E_2\nu_1]\beta}$$

$$= \sum_{\nu_0=0}^{N} e^{-(E_0 - E_2)\nu_0\beta} \sum_{\nu_1=0}^{N-\nu_0} e^{-(E_1 - E_2)\nu_1\beta} \, e^{-E_2 N\beta}$$

$$= e^{-E_2 N\beta} \sum_{\nu_0=0}^{N} e^{2\epsilon\nu_0\beta} \underbrace{\sum_{\nu_1=0}^{N-\nu_0} e^{\epsilon\nu_1\beta}}_{\frac{1 - e^{\epsilon\beta(N-\nu_0+1)}}{1 - e^{\epsilon\beta}}}$$

$$Z = e^{-2\epsilon N\beta} \sum_{\nu_0=0}^{N} e^{2\epsilon\nu_0\beta} \frac{1 - e^{\epsilon\beta(N-\nu_0+1)}}{1 - e^{\epsilon\beta}}$$

$$= \frac{e^{-2\epsilon N\beta}}{1 - e^{\epsilon\beta}} \underbrace{\sum_{\nu_0=0}^{N} e^{2\epsilon\nu_0\beta} \left[1 - e^{\epsilon\beta(N-\nu_0+1)}\right]}$$

can be evaluated, becomes increasingly complicated.

Note the sum becomes:

$$\underbrace{\sum_{\nu_0=0}^{N} e^{2\epsilon\nu_0\beta}} - \sum_{\nu_0=0}^{N} e^{\epsilon\beta(N+1)} e^{+\epsilon\beta\nu_0}$$

$$\frac{1-e^{2\epsilon\beta(N+1)}}{1-e^{2\epsilon\beta}} - e^{\epsilon\beta N} e^{\epsilon\beta} \frac{1-e^{+\epsilon\beta(N+1)}}{1-e^{+\epsilon\beta}}$$

$$= \frac{1-e^{2\epsilon_0\beta(N+1)}}{1-e^{2\epsilon\beta}} - \frac{e^{\epsilon\beta(N+1)} - e^{\epsilon\beta 2(N+1)}}{1-e^{\epsilon\beta}}$$

$$= \frac{1-e^{2\epsilon\beta(N+1)}}{\left(1-e^{\epsilon\beta}\right)\left(1+e^{\epsilon\beta}\right)} - \frac{e^{\epsilon\beta(N+1)} - e^{2\epsilon\beta(N+1)}}{1-e^{\epsilon\beta}}$$

$$= \frac{1}{(1-e^{\epsilon\beta})(1+\epsilon^{\epsilon\beta})}\left[1-e^{2\epsilon\beta(N+1)} - \left(1+e^{\epsilon\beta}\right)\left(e^{\epsilon\beta(N+1)} - e^{2\epsilon\beta(N+1)}\right)\right]$$

$$= \frac{1}{1-e^{2\epsilon\beta}}\left[1-2e^{2\epsilon\beta(N+1)} - e^{\epsilon\beta(N+1)} - e^{2\epsilon\beta N} e^{3\epsilon\beta}\right]$$

and this appears to evade further simplification.

Canonical ensemble: ideal gas

We now aim to apply the canonical ensemble formalism to determine the equations of state for an ideal gas. The general route will be:

Obtain Z

Energy $\bar{E} = -\frac{\partial}{\partial \beta} \ln Z$

Helmholtz free energy $\bar{F} = -kT \ln Z$

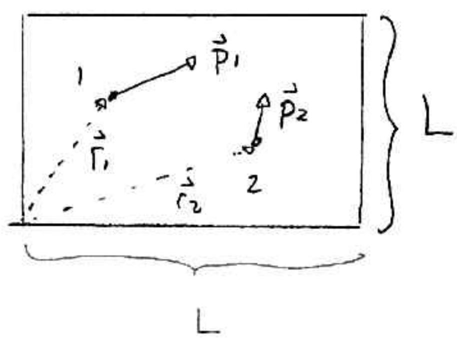
Entropy $S = (\bar{E} - \bar{F})/T$

We will consider two possible approaches

1) a purely classical approach
2) a semiclassical / quantum approach.

There are various possibilities:

Purely classical particles in a box



microstate for all particles:
specify $\vec{r}_1, \vec{r}_2, \ldots$
$\vec{p}_1, \vec{p}_2, \ldots$

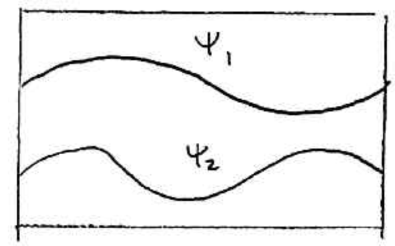
microstate for a single particle
specify $\vec{r}, \vec{p}$

energy for single particle

$$E = \frac{1}{2m} \vec{p}^{\,2}$$

issues * counting with continuous variables
* eventual issue with extensive nature of S
- if $V \to \lambda V$
$N \to \lambda N$
then $S \to \lambda S$
* chemical potential?

Semi-classical - quantum particles in a box



microstate for all particles
specify wavefunction for each.

$$\Psi_1 = \text{const} \sin\left(\frac{n_{1x}\pi x}{L}\right)\sin\left(\frac{n_{1y}\pi y}{L}\right)\sin(\ldots)$$

$\rightsquigarrow$ give n_{1x}, n_{1y}, n_{1z} particle 1
$\rightsquigarrow$ give n_{2x}, n_{2y}, n_{2z} particle 2

microstate for single particle
$\rightsquigarrow$ specify n_x, n_y, n_z
(possibilities are any integer 1, 2, ...)

energy for single particle

$$\rightsquigarrow E = \frac{h^2}{8mL^2}\left(n_x^2 + n_y^2 + n_z^2\right)$$

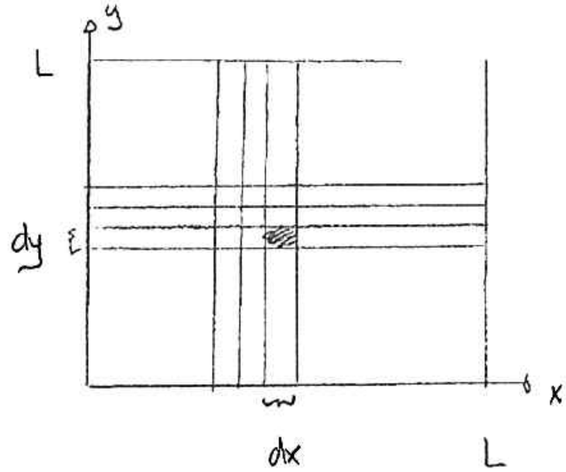
issues * counting n_x, n_y, n_z
* statistics of quantum particles
* need quantum to describe classical system?
* chemical potential?

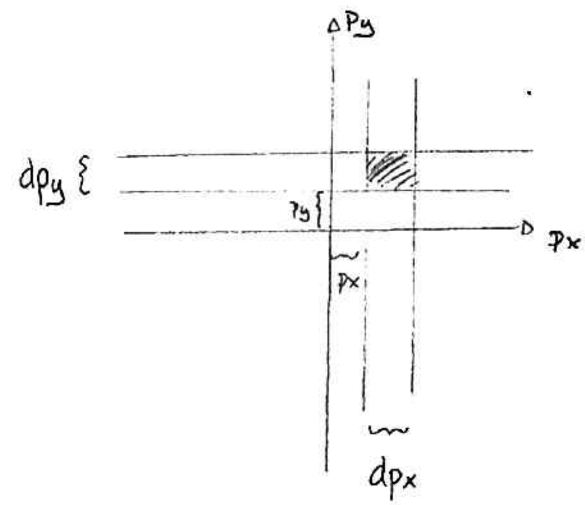
What we will eventually attain are:

1) energy equation of state
2) pressure equation of state
3) probability with which various states + velocities can occur.

<u>Classical description</u>

Consider a single classical particle in a box. We can specify the state in a countable fashion by discretizing the states





A state consists of

1) choosing $dx, dy, \ldots dp_x, dp_y$ to discretize the space of states
2) selecting one box in each realm

The illustrated state has energy

$$E = \frac{1}{2m}\left(p_x^2 + p_y^2 + p_z^2\right)$$

Then the canonical ensemble formalism gives:

1) the probability that the particle is in the illustrated state is

$$\frac{e^{-E\beta}}{Z_{single}} = \frac{e^{-(p_x^2+p_y^2+p_z^2)\beta/2m}}{Z_{single}}$$

2) the single particle partition function is

$$Z_{single} = \sum_{\substack{\text{states} \\ \text{in } \vec{r},\vec{p} \text{ space}}} e^{-(p_x^2+p_y^2+p_z^2)\beta/2m}$$

As the size of the discretization $\to 0$ the sum can be replaced by an integral but we need a scale factor α with units of $m^{-3}(kg\,m\,s^{-1})^{-3} = (kg\,m^{-2}s^{-1})^{-3}$ so that the partition function is unitless. We get

$$Z_{single} = \alpha \underbrace{\int dx \int dy \int dz \int dp_x \int dp_y \int dp_z}_{\substack{\text{all allowed values of} \\ x,y,z,p_x,p_y,p_z}} e^{-(p_x^2+p_y^2+p_z^2)\beta/2m}$$