

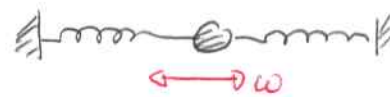
Fri: HW due

Tues 6.3, 6.4, 6.5.

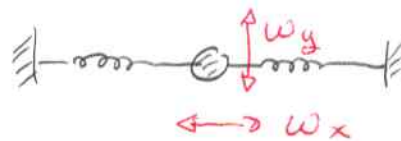
## Classical Oscillators

We can apply the canonical ensemble formalism to a collection of classical oscillators. Such oscillators can model the nuclei in crystalline solids. These lattice vibrations can eventually describe the thermal properties of such solids. There are many possibilities.

1) one dimensional oscillator



2) two or three dimensional oscillator



We will assume that the oscillators are distinguishable and use the usual canonical ensemble formalism to first determine a single system partition function and then extend this to a system of  $N$  oscillators.

## 1 Thermodynamics of a one dimensional classical harmonic oscillator

The energy of a single oscillator in one dimension is

$$E = \frac{p^2}{2m} + \frac{1}{2}kx^2$$

where  $x$  is the position coordinate,  $p$  is the momentum and  $k$  is the spring constant.

- Using  $\omega = \sqrt{k/m}$ , rewrite the energy in terms of  $\omega$  rather than  $k$ .
- Determine the mean energy of the system.
- Determine the heat capacity of the system.

Answer: a)  $E = \frac{p^2}{2m} + \frac{1}{2}kx^2$   $\omega^2 = \frac{k}{m}$

$\Rightarrow E = \frac{p^2}{2m} + \frac{1}{2}m\omega^2 x^2$   $\Rightarrow k = \frac{1}{2}m\omega^2$

- b) We need to describe the states and calculate the partition function  $Z$  so that we can determine

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

The states are described by a single position variable and a single momentum variable. Then

$$\begin{aligned} \text{Prob} \left( \begin{array}{l} x \rightarrow x+dx \\ p \rightarrow p+dp \end{array} \right) &= A e^{-E\beta} dx dp \\ &= A e^{-p^2\beta/2m} e^{-x^2 m\omega^2\beta/2} dx dp \end{aligned}$$

The partition function is

$$Z = \sum_{\text{states}} \text{prob} = A \int_{-\infty}^{\infty} dp \int_{-\infty}^{\infty} dx e^{-p^2\beta/2m} e^{-x^2 m\omega^2\beta/2}$$

Thus

$$Z = A \int_{-\infty}^{\infty} e^{-p^2 \beta / 2m} dp \int_{-\infty}^{\infty} e^{-x^2 m \omega^2 \beta / 2} dx$$

Then  $\int_{-\infty}^{\infty} e^{-\alpha u^2} du = \sqrt{\frac{\pi}{\alpha}}$  gives

$$Z = A \sqrt{\frac{2\pi m}{\beta}} \sqrt{\frac{2\pi}{m\omega^2 \beta}}$$

$$\Rightarrow Z = A \frac{2\pi}{\omega \beta}$$

Now  $\bar{E} = -\frac{\partial}{\partial \beta} \ln Z = -\frac{\partial}{\partial \beta} \ln \left[ A \frac{2\pi}{\omega \beta} \right]$

$$\Rightarrow \bar{E} = -\frac{\partial}{\partial \beta} \left\{ \ln \left[ \frac{A 2\pi}{\omega} \right] - \ln \beta \right\} = \frac{1}{\beta}$$

$$\Rightarrow \bar{E} = kT$$

c)  $C = \frac{\partial \bar{E}}{\partial T} \Rightarrow C = k \quad \square$

Thus the heat capacity of a classical oscillator system is independent of the oscillator mass or frequency.

The crucial mathematical ingredient in such calculations is an integral of the form  $\int_{-\infty}^{\infty} e^{-u^2 \alpha} du$ . As long as the energy is quadratic with respect to the variables used to describe the system states, the partition function can be evaluated

Each factor of

$$\int e^{-u^2 \beta \alpha} du$$

gives  $\sqrt{\frac{\pi}{\alpha \beta}} = \text{const} \times \beta^{-1/2}$ . If there are  $n$  such factors then

$$Z = \text{const} \beta^{-n/2}$$

and  $\ln Z = -n/2 \ln \beta + \text{const}$

$$\Rightarrow \bar{E} = -\frac{\partial}{\partial \beta} \ln Z = \frac{n}{2} \frac{1}{\beta} \Rightarrow \bar{E} = \frac{n}{2} kT$$

This is the basis of a general rule:

Energy of system depends on  $n$  variables  $u_1, \dots, u_n$  and is quadratic

$$E_{\text{state}} = \alpha_1 u_1^2 + \dots + \alpha_n u_n^2$$

Partition function

$$Z = \text{const} \times \beta^{-n/2}$$

↓

$$\bar{E} = \frac{n}{2} kT$$

↳ Heat capacity  $C = \frac{n}{2} k$

This gives the equipartition theorem

If a classical system has an energy that is quadratic in  $n$  independent variables and is in equilibrium with a bath of temp  $T$  then

$$\bar{E} = \frac{n}{2} kT$$

For a collection of  $N$  classical three-dimensional oscillators there are  $3N \times 2 = 6N$  position and momentum variables. Thus

$$\bar{E} = 3NkT$$

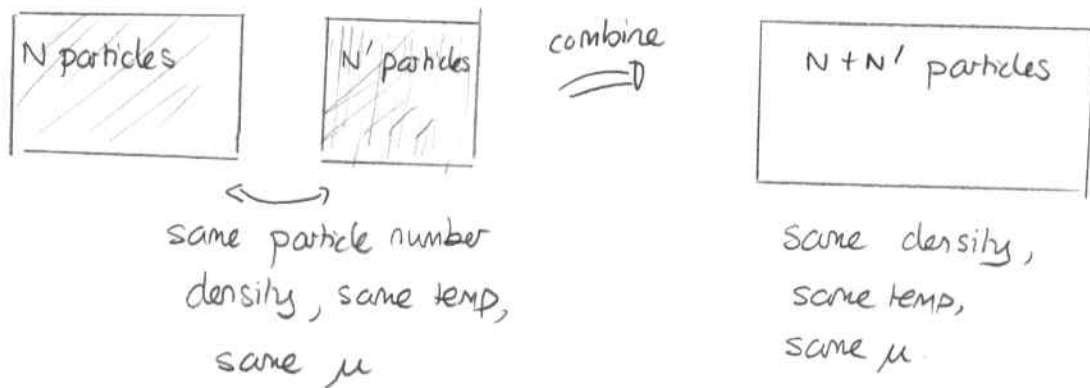
⇒

$$C = 3Nk$$

Dulong + Petit law.

## Entropy and systems of distinguishable particles

Suppose that we have a system of  $N$  particles. The canonical ensemble formalism allows us to determine the entropy of this system. These calculations can be tractable when the particles are distinguishable. We can check whether the resulting entropy is extensive, which describes how the entropy should change as the system size changes. Consider two copies of the similar systems:



Then we expect that:

- \* the volumes add  $V(N+N') = V(N) + V(N')$
- \* the energies add  $E(N+N') = E(N) + E(N')$
- \* the entropies add  $S(N+N') = S(N) + S(N')$

These must be true for all  $N, N'$  and the only way that this can be true is if:

- \*  $V(\lambda N) = \lambda V(N)$
  - \*  $E(\lambda N) = \lambda E(N)$
  - \*  $S(\lambda N) = \lambda S(N)$
- } such variables,  $V, E, S$  are called extensive.

By definition, clearly  $V = \rho N / \rho$  satisfies this.

↳ particle number density:

Now for a collection of  $N$  distinguishable semi-classical particles in an infinite well the partition function is

$$Z = \left( \frac{m}{2\pi\hbar^2} \right)^{3N/2} V^N \beta^{-3N/2}$$

Then

$$\bar{E} = -\frac{\partial}{\partial \beta} \ln Z \quad \Rightarrow \quad \bar{E} = \frac{3}{2} NkT.$$

This is clearly extensive: temp stays same and  $N \rightarrow \lambda N \Rightarrow \bar{E} \rightarrow \lambda \bar{E}$ .

Now entropy is calculated via

$$\begin{aligned} S &= -\frac{\partial F}{\partial T} \Rightarrow S = -\frac{\partial}{\partial T} [-kT \ln Z] \\ \Rightarrow S &= k \ln Z + kT \frac{\partial \beta}{\partial T} \underbrace{\frac{\partial}{\partial \beta} \ln Z}_{-\bar{E}} \\ &= k \ln Z + kT \left( -\frac{1}{kT^2} \right) (-\bar{E}) \\ &= k \ln Z + \frac{1}{T} \frac{3}{2} NkT \\ \Rightarrow S &= k \ln \left[ \left( \frac{m}{2\pi\hbar^2} \right)^{3N/2} V^N \beta^{-3N/2} \right] + \frac{3}{2} Nk \\ &= Nk \left\{ \ln \left[ \left( \frac{m}{2\pi\hbar^2} \right)^{3/2} \right] + \ln[V] - \frac{3}{2} \ln \beta \right\} + \frac{3}{2} Nk. \end{aligned}$$

Suppose  $V \rightarrow \lambda V$  and  $N \rightarrow \lambda N$ . Then

$$\begin{aligned} S &\rightarrow \lambda Nk \left\{ \ln [(\dots)^{3/2}] + \ln[\lambda V] - \frac{3}{2} \ln \beta \right\} + \frac{3}{2} \lambda Nk \\ &= \lambda \left[ \underbrace{Nk \left\{ \ln [(\dots)^{3/2}] + \ln V - \frac{3}{2} \ln \beta \right\} + \frac{3}{2} Nk}_S \right] + \lambda Nk \ln[\lambda] \end{aligned}$$

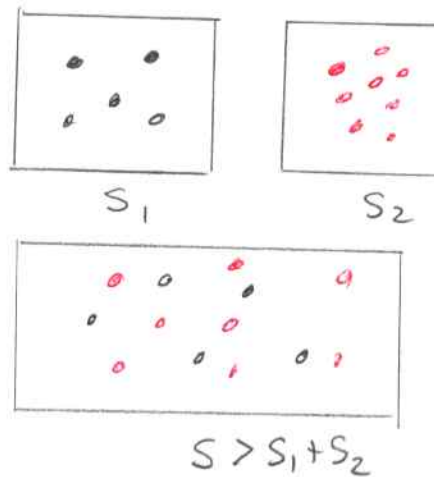
Thus we have

$$S \rightarrow \lambda S + \lambda N k \ln[\lambda] \neq \lambda S$$

So we have

Assume an ensemble of distinguishable particles, the canonical ensemble formalism provides an energy that is extensive but an entropy that is not extensive.

The reason for this is that if the particles were distinguishable then when two gasses of the same  $T, p, \mu$  are combined the particles that were previously separated are now mixed. They will not just spontaneously separate and the entropy of the combination must be greater than the two parts.



Thus we need to consider systems where the particles are indistinguishable. The canonical ensemble formalism can assess these but the crucial difficulty is that

$$Z_{N \text{ particles}} \neq (Z_{\text{single}})^N$$

## 2.1 Multiple indistinguishable particles

Consider an ensemble of indistinguishable particles. Each can be in one of two states, whose energies are 0 and  $\epsilon$ .

- Determine the partition function if the system consists of a single particle. Denote this  $Z_{\text{single}}$
- Determine the partition function if the system consists of two particles. Check if  $Z = (Z_{\text{single}})^2$ .
- Determine the partition function if the system consists of three particles. Check if  $Z = (Z_{\text{single}})^3$ .

Answer: a) 
$$Z_{\text{single}} = e^{-0\beta} + e^{-\epsilon\beta}$$

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

- b) List the states with number of particles  $n$  low,  $n_1$ , and number in high,  $n_2$

state		energy
$n_1$	$n_2$	$E$
2	0	0
1	1	$\epsilon$
0	2	$2\epsilon$

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

$$\Rightarrow Z = 1 + e^{-\epsilon\beta} + e^{-2\epsilon\beta}$$

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

c)

state		energy
$n_1$	$n_2$	
3	0	0
2	1	$\epsilon$
1	2	$2\epsilon$
0	3	$3\epsilon$

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

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

$$\neq (1 + e^{-\epsilon\beta})^3$$

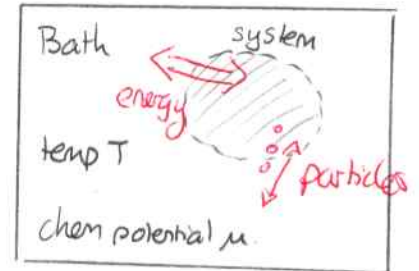


# Grand Canonical Ensemble

The canonical ensemble approach can be generalized to one where the system can exchange both energy and particles with its environment. This will simplify many statistical physics calculations.

We consider a system in equilibrium with a bath with temperature  $T$  and chemical potential  $\mu$

Then:



List all states of system - "s"

- energy  $E_s$

- particle number  $N_s$

↓

Probability that particle is in state "s"

$$P_s = \frac{1}{Z_G} e^{-(E_s - \mu N_s) \beta}$$

where the grand partition function is

$$Z_G = \sum_s e^{-(E_s - \mu N_s) \beta}$$

Mean particle number

$$\bar{N} = \frac{1}{\beta} \frac{\partial}{\partial \mu} \ln[Z_G]$$

Mean energy

$$\bar{E} = -\frac{\partial}{\partial \beta} \ln(Z_G) + \bar{N} \mu$$

We would then connect this to thermodynamics via:

system particle number  $N \equiv \bar{N}$  (mean particle number)

system energy  $E \equiv \bar{E}$  (mean energy)

Again one can show that as  $\bar{N} \rightarrow \infty$  the fluctuations in  $\bar{N}$  and  $\bar{E}$  become negligible, i.e.

$$\frac{\sigma_N}{\bar{N}} \rightarrow 0 \quad \frac{\sigma_E}{\bar{E}} \rightarrow 0$$

## Grand Canonical Ensemble: Indistinguishable Particles

To illustrate the grand canonical ensemble consider the situation where

- 1) each particle can be in one of two states - these have energies  $0, \epsilon$ .
- 2) there are many particles possibly available.

We can represent this via:

<u>Single particle state label</u>	<u>energy</u>		
$k=1$ (lower energy)	$\epsilon_1 \equiv 0$	$k=2$ —————	$\epsilon_2 = \epsilon$
$k=2$ (higher energy)	$\epsilon_2 \equiv \epsilon$	$k=1$ —————	$\epsilon_1 = 0$

Then with multiple particles possible we define the occupation number for each state as:

$$n_k = \text{number of particles in state } k$$

The state of the ensemble is then described by:

$$S = (n_1, n_2, n_3, \dots)$$

and we then need to sum over all such states. In this case

$$N_S = n_1 + n_2 + \dots = \sum n_k \Rightarrow$$

$$N_S = \sum_{\text{all single particle states } k} n_k$$

$$E_S = n_1 \epsilon_1 + n_2 \epsilon_2 + \dots = \sum \epsilon_k n_k \Rightarrow$$

$$E_S = \sum_{\text{all single particle states } k} \epsilon_k n_k$$

### 3 Indistinguishable spin-1/2 particles

Consider an ensemble of indistinguishable spin-1/2 particles. Any single particle can be in one of two states: "spin up" with energy  $E_+$  and "spin down" with energy  $E_-$ .

- a) Initially consider an ensemble of three indistinguishable spin-1/2 particles. Using a system of occupation numbers,  $\{n_k\}$ , list all states of the ensemble, their energies and particle numbers. *Note: This will ignore certain constraints that quantum physics imposes. We will consider these later.*
- b) Determine an expression for the grand partition function of this ensemble, assuming unlimited numbers of particles.

Answer a) Single particle states:

state	k	energy
up	1	$E_1 = E_+$
down	2	$E_2 = E_-$

For three particles list  $\{n_1, n_2\}$  s.t.  $n_1 + n_2 = 3$

$n_1$	$n_2$	$E_s$	$N_s$
3	0	$3E_+$	3
2	1	$2E_+ + E_-$	3
1	2	$E_+ + 2E_-$	3
0	3	$3E_-$	3

$$b) Z_G = \sum_s e^{-(E_s - \mu N_s)\beta}$$

$$\text{Then } E_s = \sum_{k=1}^2 n_k \epsilon_k = n_1 \epsilon_1 + n_2 \epsilon_2 \quad N_s = \sum_{k=1}^2 n_k = n_1 + n_2$$

So

$$Z_G = \sum_{n_1, n_2=0}^{\infty} e^{-(n_1 \epsilon_1 + n_2 \epsilon_2 - \mu n_1 - \mu n_2)\beta}$$

$$= \sum_{n_1=0}^{\infty} e^{-n_1(\epsilon_1 - \mu)\beta} \sum_{n_2=0}^{\infty} e^{-n_2(\epsilon_2 - \mu)\beta}$$

Assuming unlimited  $n_1, n_2$  the two sums are geometric and can be evaluated when  $(\epsilon_i - \mu)\beta > 0$ . In these cases

$$Z_G = \frac{1}{1 - e^{-(\epsilon_1 - \mu)\beta}} \frac{1}{1 - e^{-(\epsilon_2 - \mu)\beta}}$$

and we could now determine mean particle numbers....