Phys 362 2020

Lecture 21

Mon HW by 6pm

Tues: Read 4.8, 6.1

Canonical ensemble

The framework for the canonical ensemble is:

System is in contact with reservoir at temperature $T \Rightarrow$ system temperature $= T$

$\longrightarrow$ Describe states of the system ~ "s"

Microscopic physics gives energy E_s

Construct partition function

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

where $\beta = 1/kT$

$\longrightarrow$ Probability system is in state s

$$p_s = \frac{e^{-E_s \beta}}{Z}$$

Mean energy

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

$\longrightarrow$ Entropy

$$S = k \ln Z + \bar{E}/T$$

Helmholtz free energy

$$F = -kT \ln Z$$

THERMODYNAMICS!

We briefly consider the entropy and Helmholtz free energy statements.

Entropy and Helmholtz Free Energy

The entropy is

$$S = -k \sum p_s \ln[p_s]$$

$$= -k \sum \frac{e^{-E_s\beta}}{Z} \ln\left[\frac{e^{-E_s\beta}}{Z}\right]$$

$$= -k \sum \frac{e^{-E_s\beta}}{Z} \left\{\ln[e^{-E_s\beta}] - \ln Z\right\}$$

$$= -k \sum \frac{e^{-E_s\beta}}{Z} (-E_s\beta) + k \frac{\ln Z}{Z} \underbrace{\sum e^{-E_s\beta}}_{Z}$$

$$= k\beta \underbrace{\sum E_s \frac{e^{-E_s\beta}}{Z}}_{\bar{E}} + k \ln Z$$

$$= \frac{\cancel{k}}{\cancel{k}T} \bar{E} + k \ln Z$$

Thus

> If we identify the thermodynamic energy as $E = \bar{E}$ then
>
> $S = k \ln Z + E/T$

Separately $F = E - TS$ gives

> The Helmholtz free energy is
>
> $F = -kT \ln Z$

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3 **Mean value of energy for a single one-dimensional quantum oscillator**

A one dimensional quantum oscillator has energy states labeled by $n = 0, 1, 2, \ldots$ with energy $E_n = \hbar\omega\,(n + 1/2)$.

a) Determine the partition function for the oscillator.

b) Determine the mean value of the energy for the oscillator.

c) Determine the uncertainty in the oscillator energy.

d) Suppose the $\hbar\omega \gg kT$. Determine an expression for the mean value of the energy for the oscillator. What does this imply about the state of the oscillators in the ensemble?

e) Suppose the $\hbar\omega \ll kT$. Determine an expression for the mean value of the energy for the oscillator.

Answer a) List states and energies

label n	Energy E_n
0	$\hbar\omega/2$
1	$3\hbar\omega/2$
2	$5\hbar\omega/2$
n	$\hbar\omega(n+1/2)$
$\vdots$	

Then

$$Z = \sum_{n=0}^{\infty} e^{-E_n\beta}$$

$$= \sum_{n=0}^{\infty} e^{-\hbar\omega(n+1/2)\beta}$$

$$= e^{-\hbar\omega\beta/2} \sum_{n=0}^{\infty} e^{-\hbar\omega\beta n}$$

The latter is a geometric series with $x = e^{-\hbar\omega\beta}$

So $1 + x + x^2 + \cdots = \frac{1}{1-x}$ provided $x < 1$.

In this case $x = e^{-\hbar\omega\beta} < 1$ and thus

$$Z = \frac{e^{-\hbar\omega\beta/2}}{1 - e^{-\hbar\omega\beta}}$$

b) $$\bar{E} = -\frac{\partial}{\partial\beta} \ln Z = -\frac{\partial}{\partial\beta} \ln \left[\frac{e^{-\hbar\omega\beta/2}}{1-e^{-\hbar\omega\beta}} \right]$$

$$= -\frac{\partial}{\partial\beta} \left\{ \ln\left[e^{-\hbar\omega\beta/2}\right] - \ln\left[1-e^{-\hbar\omega\beta}\right] \right\}$$

$$= -\frac{\partial}{\partial\beta} \left\{ -\hbar\omega\beta/2 - \ln\left(1-e^{-\hbar\omega\beta}\right) \right\}.$$

$$= \frac{\hbar\omega}{2} + \frac{\partial}{\partial\beta} \ln\left(1-e^{-\hbar\omega\beta}\right)$$

$$= \frac{\hbar\omega}{2} + \frac{e^{-\hbar\omega\beta}}{1-e^{-\hbar\omega\beta}} \hbar\omega$$

$$\Rightarrow \bar{E} = \hbar\omega \left\{ \frac{1}{e^{\hbar\omega\beta}-1} + \frac{1}{2} \right\}$$

c) $$\sigma_E^2 = -\frac{\partial\bar{E}}{\partial\beta} = -\hbar\omega \frac{-\hbar\omega e^{\hbar\omega\beta}}{(e^{\hbar\omega\beta}-1)^2}$$

$$= (\hbar\omega)^2 \frac{e^{\hbar\omega\beta}}{(e^{\hbar\omega\beta}-1)^2}$$

$$\Rightarrow \sigma_E = \hbar\omega \frac{e^{\hbar\omega\beta/2}}{e^{\hbar\omega\beta}-1}$$

d) $\hbar\omega \gg kT \Rightarrow \frac{\hbar\omega}{kT} \gg 1 \Rightarrow \hbar\omega\beta \gg 1$

$\Rightarrow e^{\hbar\omega\beta} - 1 \approx e^{\hbar\omega\beta}$

Thus $\bar{E} \approx \hbar\omega\{\underbrace{e^{-\hbar\omega\beta}}_{\text{negligible}} + 1/2\} \Rightarrow \bar{E} \approx \hbar\omega/2$

The typical oscillator must be in the ground state

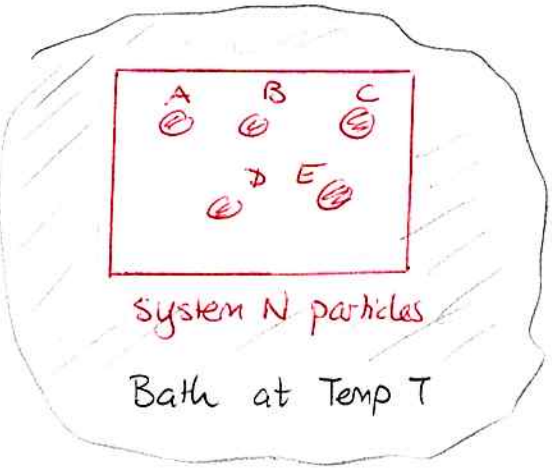
e) $\hbar\omega\beta \ll 1 \qquad e^{\hbar\omega\beta} \approx 1 + \hbar\omega\beta$

$\Rightarrow \bar{E} \approx \hbar\omega\left\{\frac{1}{\hbar\omega\beta} + \frac{1}{2}\right\}$

$\approx \frac{\hbar\omega}{\hbar\omega\beta} = kT \Rightarrow \bar{E} = kT$

Multiple particles

The canonical ensemble formalism applies equally well to systems that contain a single particle or many particles. In general thermodynamic ensembles consist of many particles, typically identical and often non-interacting. The thermodynamics can be generated by finding the partition function for the entire system.



Let

Z = partition function for entire system of all particles

We could separately consider a system consisting only of particle A and we could construct

Z_A = partition function for system only consisting of A

Z_B = " " " " " " " B

etc... Each of these would be easier to compute than Z. So we now consider the possibility:

Given partition functions $Z_A, Z_B, Z_C, \ldots$ $\longrightarrow$ Can one easily construct Z from $Z_A, Z_B \ldots$?

In general we require that A, B, C, D... be <u>distinguishable</u> (this only generally applies in classical physics.

Then

If systems $A, B, C, D, \ldots$ are distinguishable and non-interacting

$$Z = Z_A Z_B Z_C \ldots$$

where Z is the partition function for the collection $A, B, C, D \ldots$ and Z_A is the partition function for a system just consisting of A, etc…

Proof: Let

$\{s_A\}$ be the states for A $\quad$ s_A has energy E_{s_A}

$\{s_B\}$ " " " " B. $\quad$ s_B " " E_{s_B}

Then the states for the ensemble are collections:

$$(s_A, s_B, s_C, \ldots) \leadsto \text{energy } \underbrace{E_{s_A} + E_{s_B} + E_{s_C} + \cdots}_{\text{no interaction terms.}}$$

So

$$Z = \sum_{s_A, s_B, s_C} e^{-[E_{s_A} + E_{s_B} + E_{s_C} + \cdots]\beta}$$

$$= \sum_{s_A, s_B, s_C} e^{-E_{s_A}\beta} e^{-E_{s_B}\beta} \cdots$$

$$= \underbrace{\sum_{s_A} e^{-E_{s_A}\beta}}_{Z_A} \underbrace{\sum_{s_B} e^{-E_{s_B}\beta}}_{Z_B} \cdots$$

$$\Rightarrow Z = Z_A Z_B \ldots$$

2 Pair of distinguishable particles

Consider a system that consists of two identical distinguishable 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 two-particle system.

c) Consider just one of the particles as "the system." Determine the partition function for this single particle system.

d) Show that the partition function for the two particle system is the product of the partition functions for the single particle system.

Answer: a) Label the particles A and B. Then

State A	state B	energy
0	0	0
0	1	ϵ
0	2	2ϵ
1	0	ϵ
1	1	2ϵ
1	2	3ϵ
2	0	2ϵ
2	1	3ϵ
2	2	4ϵ

b) $$Z_{two} = \sum_s e^{-E_s\beta}$$

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

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

c) For a single particle

$$Z_{one} = \sum e^{-E_s\beta}$$

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

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

d) $$Z_{one} Z_{one} = \left(1+e^{-\epsilon\beta}+e^{-2\epsilon\beta}\right)\left(1+e^{-\epsilon\beta}+e^{-2\epsilon\beta}\right)$$

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

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

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

$$= Z_{two}$$

$$\Rightarrow \quad Z_{two} = Z_{one} Z_{one}$$

Energy for multiple non-interaction distinguishable particles

We can immediately reach conclusions about the energy for systems on non-interacting distinguishable particles.

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

$$= -\frac{\partial}{\partial \beta} \ln \left[Z_A Z_B Z_c \dots \right]$$

$$= -\frac{\partial}{\partial \beta} \left\{ \ln Z_A + \ln Z_B + \ln Z_C + \dots \right\}$$

$$= \underbrace{-\frac{\partial}{\partial \beta} \ln Z_A} \underbrace{- \frac{\partial}{\partial \beta} \ln Z_B} \underbrace{- \frac{\partial}{\partial \beta} \ln Z_C}$$

$$\Rightarrow \quad \bar{E} = \bar{E}_A + \bar{E}_B + \bar{E}_c$$

So the energy is additive. Then consider the uncertainty in the energy.

$$\sigma_E^2 = -\frac{\partial \bar{E}}{\partial \beta} = -\frac{\partial \bar{E}_A}{\partial \beta} - \frac{\partial \bar{E}_B}{\partial \beta} - \frac{\partial \bar{E}_C}{\partial \beta}$$

$$= \sigma_{E_A}^2 + \sigma_{E_B}^2 + \sigma_{E_C}^2$$

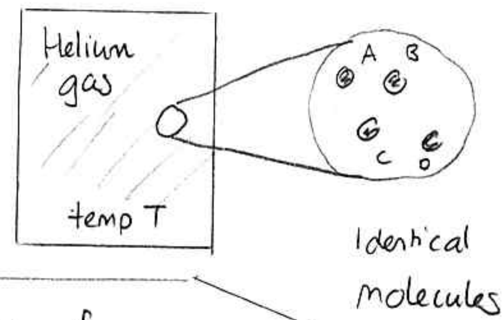
$$\Rightarrow \quad \sigma_E = \sqrt{\sigma_{EA}^2 + \sigma_{EB}^2 + \sigma_{Ec}^2 + \dots}$$

This is not additive because of the square root.

Thermodynamic ensembles

Generally thermodynamic ensembles consist of a large number of identical systems. Consider an ensemble consisting of N identical distinguishable, non-interacting systems.

Then the previous more general results immediately give:



The partition function for an ensemble of N identical, distinguishable, non-interacting systems is

$$Z_{ensemble} = \left(Z_{single\ particle}\right)^N$$

where

$$Z_{single\ particle} = \sum_{s} e^{-E_s \beta}$$

s ≡ single particle states

Then it immediately follows that

For an ensemble of N identical, distinguishable, non-interacting particles

$$\bar{E}_{ensemble} = N \bar{E}_{single\ particle}$$

and

$$\sigma_{E\ ensemble} = \sqrt{N}\ \sigma_{E\ single\ particle}$$

These can give statistical quantities such as

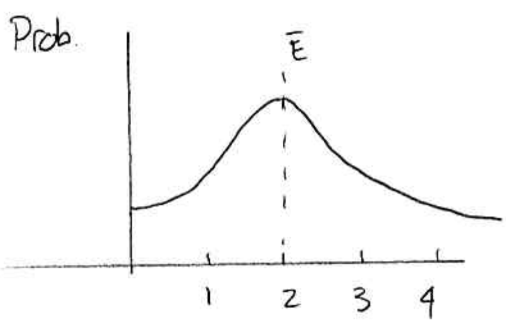
mean energy $\bar{E} = \bar{E}(N,T)$

mean entropy $\bar{S} = \bar{S}(N,T)$

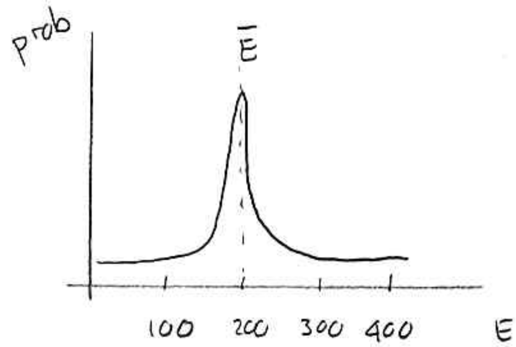
We make the identification

statistical physics $\rightsquigarrow \bar{E} = E$ for thermodynamics

Now statistical physics will give fluctuations in $\bar{E}$ and we do not want such fluctuations to affect E that is used in thermodynamics. We note though that as N increases the relative size of the fluctuations decreases. Roughly



one particle



100 particles

Generally as N increases the probability distribution (energy per particle) decreases and $\bar{E}$ becomes more representative of the energy. We can compare the typical size of the fluctuations to the typical energy.

$$\frac{\sigma_{E\,N\text{ particles}}}{\bar{E}_{N\text{ particles}}} = \frac{\sqrt{N}\,\sigma_{E\text{single}}}{N\,\bar{E}_{\text{single}}} = \frac{1}{\sqrt{N}}\,\frac{\sigma_{E\text{single}}}{\bar{E}_{\text{single}}} \to 0 \text{ as } N\to\infty$$

As $N \to \infty$ the distribution of possible energies is only appreciably non-zero over a relatively vanishing range of energies centered on $\bar{E}$. Thus $\bar{E}$ accurately represents the ensemble energy as $N \to \infty$