

6.6 Gibbs Paradox

[49]

Entropy for ideal gas:

$$S = \frac{3N\epsilon}{2} + N\epsilon \log \left[V \left(\frac{4\pi m E}{3h^2 N} \right)^{3/2} \right]$$

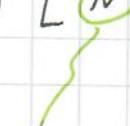
It turns out: For a gas of identical particles,
we counted the # of states incorrectly.

We should have ~~been~~ multiplied by $\frac{1}{N!}$.

\Rightarrow Subtract ~~$k \log N!$~~ $\approx \epsilon N \log N - k N$
from S

"Ad hoc fix" gives:

$$S(E, V) = Nk \log \left[\frac{V}{N} \left(\frac{4\pi m E}{3h^2 N} \right)^{3/2} \right] + \left(\frac{5}{2} \right) k N$$




from $-2N \log N$ $\frac{3}{2}$ from before
and 1 from
 $-(-\epsilon N)$
 $\left[\frac{5}{2} = \frac{3}{2} + 1 \right]$

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In general: We need to introduce $\frac{1}{N!}$ factor when counting states but, besides this, we keep ignoring that we're dealing with indistinguishable particles.

Not satisfactory! But we know that classical statistical mechanics is not what we should be starting with - we should use Q.M., and there we know that distinguishable/non-distinguishable particles have different conditions on wave functions.

How do we know about $\frac{1}{N!}$ factor?

If we don't introduce it, we get "crazy results" for mixing entropy.

hence the name...

Note: Subtracted term is independent of T and V

→ all thermodynamic functions are unchanged

"Final" definition:

$$\Sigma(E) = \frac{1}{N! h^{3N}} \int_{\mathcal{H} \leq E} d^{3N} p d^{3N} q$$

h^{3N} is needed to get units right!

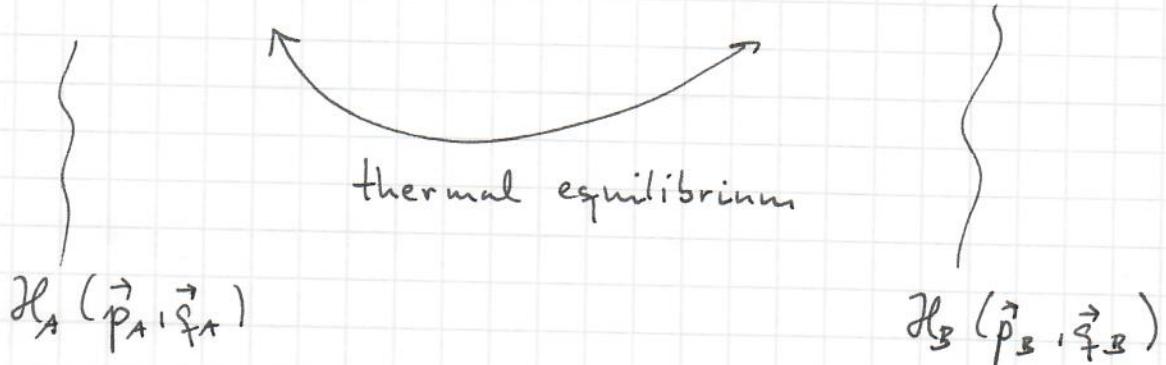
If (!) particles are locked in space (e.g., fixed at lattice site), then we do not need the factor of $(N!)^{-1}$.

If the integral is turned into a sum, then the factor of $(h)^{-3N}$ is not needed.

Chapter 7: Canonical and grand canonical ensemble

7.1 Canonical ensemble

System A in thermal contact w/ system B.



We are interested in system A: $N_A \ll N_B$

but N_A and N_B macroscopically large

Treat systems A and B as composite system.

→ we know how to do this:

microcanonical ensemble w/ total energy

between E and $E + 2\Delta$

We also know: E_A and E_B can take a range of values

$$E < E_A + E_B < E + 2\Delta$$

Let $T_B(E_B)$ be the phase space volume occupied by system B.

Let's ask: What is the probability to find system A within $d\vec{p}_A d\vec{q}_A$, regardless of the state of system B?

Answer: $\propto d\vec{p}_A d\vec{q}_A T_B(E_B)$

$$\begin{array}{c} | \\ E_B = E - E_A \end{array}$$

$$\Rightarrow \rho(\vec{p}_A, \vec{q}_A) \propto T_B(E - E_A)$$

$\underbrace{\quad}_{\text{density in phase}} \text{space for system A}$

Let's find expression for $T_B(E - E_A)$:

$$k \log(T_B(E - E_A)) \underset{\text{def.}}{\rightarrow} S_B(E - E_A)$$

def.

$$\approx S_B(E) + \left. \frac{\partial S_B(E_B)}{\partial E_B} \right|_{E_B=E} (E_B - E) \underbrace{\frac{1}{T_B}}_{-E_A}$$

$\overbrace{\quad}^{\text{Taylor expanding around}}$
 $E_B = E$ (first order in E_A)
 (recall: $N_B \gg N_A \Rightarrow E_B \gg E_A$)

Aside / more detail:

$$\text{Taylor expansion: } f(x) = f(x_0) + \frac{\partial f(x)}{\partial x} \Big|_{x=x_0} (x - x_0)$$

$$\text{here: } x_0 = E_{\text{tot}} = E$$

$$x = E_B$$

$$\Rightarrow S_B(E_B) \approx S_B(E_{\text{tot}}) + \left. \frac{\partial S_B(E_B)}{\partial E_B} \right|_{E_B=E_{\text{tot}}} (E_B - E_{\text{tot}})$$

$$= S_B(E) - \frac{E_A}{T_B}$$

$$\Rightarrow \vec{P}_B(E-E_A) = \underbrace{\exp\left(\frac{S_B(E)}{k}\right)}_{\text{independent of System A (just a constant as far as system A is concerned)}} \exp\left(-\frac{E_A}{kT_B}\right)$$

independent of
System A (just a
constant as far as system
A is concerned)

$$\Rightarrow p(\vec{p}_A, \vec{q}_A) \propto \vec{P}_B(E-E_A) \propto e^{-E_A/kT_B}$$

We now write:

$$p(\vec{p}_A, \vec{q}_A) = \exp\left(-\frac{\mathcal{H}_A(\vec{p}_A, \vec{q}_A)}{kT_B}\right)$$

ensemble density

the only info about
system B is its tem-
perature

larger system acts as a heat
reservoir in thermodynamics

From now on, we drop subscript B and subscript A.

Canonical ensemble is defined through

$$g(\vec{p}, \vec{q}) = \exp\left(-\frac{\mathcal{H}(\vec{p}, \vec{q})}{kT}\right)$$

Partition function $Q_N(V, T)$:

$$Q_N(V, T) = \frac{1}{N! h^{3N}} \int \exp(-\beta \mathcal{H}(\vec{p}, \vec{q})) d^{3N} p d^{3N} q$$

phase space
volume occu-
pied by cano-
nical ensemble

factor of $\frac{1}{N!}$ is
there to ensure
"correct Boltzmann
counting"

h : as before,
constant with
dimension "momentum
length"

$$\beta = \frac{1}{kT}$$

integral extends
over all space \rightarrow

this is inconsistent
w/ the fact that
 $g(\vec{p}_A, \vec{q}_A)$ should vanish
when $E_A > E$

The justification (more in
Sec. 7.2') is that the
integrand is vanishingly
small when $E_A > E$

\rightarrow we can extend
the limits w/o any
consequences

So, we have defined canonical ensemble...

How do we get thermodynamics from it?

$$\Omega_N(V, T) = \exp(-\beta A(V, T))$$

"we identify"

$A(V, T)$: Helmholtz free energy

If this identification is to make sense, we need:

(a) A is an extensive quantity.

(b) A is related to the internal energy U

(or S) and entropy by the thermodynamic relation $A = U - TS$.

$$U = \langle \mathcal{H} \rangle \quad -\left(\frac{\partial A}{\partial T}\right)_V$$

Essentially, once we have the partition function, we can calculate essentially all thermodynamic quantities.

Let's show (a):

$$\text{Recall: } Q_N(V, T) = \exp(-\beta A(V, T))$$

If we have a system that is made up of two subsystems (assume interactions between the two can be neglected), then Q_N is a product of two factors: $e^{-\beta A} = e^{-\beta A_1} \cdot e^{-\beta A_2} = e^{-\beta(A_1 + A_2)}$

✓ done

Let's show (b): $A = U - TS$

$$= \langle \mathcal{H} \rangle + T \left(\frac{\partial A}{\partial T} \right)_V$$

$$\Rightarrow \langle \mathcal{H} \rangle = A - T \left(\frac{\partial A}{\partial T} \right)_V$$

$\underbrace{}$
diff. eq. for A

We want to proof the last line
(this will be a bit longer...)

↑
will be done on
page 58

Proof of $\langle \mathcal{H} \rangle = A - T \left(\frac{\partial A}{\partial T} \right)_V$:

We will start w/:

$$\exp(-\beta A(V, T)) = \frac{1}{N! h^{3N}} \int e^{-\beta \mathcal{H}(\vec{p}, \vec{q})} d^{3N}p d^{3N}q$$

by def. of Q_N

Rearranging, we have:

$$\frac{1}{N! h^{3N}} \int e^{\beta A(V, T)} e^{-\beta \mathcal{H}(\vec{p}, \vec{q})} d^{3N} p d^{3N} q = 1 \quad (\star)$$

Apply $\frac{\partial}{\partial \beta}$ to both sides:

$$\frac{1}{N! h^{3N}} \left[A(V, T) + \left(\frac{\partial A(V, T)}{\partial \beta} \right)_V \beta \right] \int \dots d^{3N} p d^{3N} q$$

same integrand as before

indep. of \vec{p} and \vec{q} $- \frac{1}{N! h^{3N}} \int e^{\beta A} \mathcal{H}(\vec{p}, \vec{q}) e^{-\beta \mathcal{H}(\vec{p}, \vec{q})} d^{3N} p d^{3N} q = 0$
 Q_N^{-1}

the terms enclosed in green give 1
(according to (\star))

Thus:

$$A(V, T) + \left(\frac{\partial A(V, T)}{\partial \beta} \right)_V \beta - Q_N^{-1} \frac{1}{N! h^{3N}} \int \mathcal{H}(\vec{p}, \vec{q}) e^{-\beta \mathcal{H}(\vec{p}, \vec{q})} d^{3N} p d^{3N} q$$

$$\frac{\partial A}{\partial \beta} = \underbrace{\frac{\partial A}{\partial T} \frac{\partial T}{\partial \beta}}$$

$$\frac{\partial \left(\frac{1}{\beta h} \right)}{\partial \beta} = \frac{-1}{\beta^2 h^2}$$

$$\Rightarrow \beta \frac{\partial A}{\partial \beta} = - \frac{1}{\beta h} \frac{\partial A}{\partial T}$$

$$p = \frac{1}{h T} = -T \frac{\partial A}{\partial T}$$

$$\frac{\frac{1}{N! h^{3N}} \int \mathcal{H}(\vec{p}, \vec{q}) e^{-\beta \mathcal{H}(\vec{p}, \vec{q})} d^{3N} p d^{3N} q}{\frac{1}{N! h^{3N}} \int e^{-\beta \mathcal{H}(\vec{p}, \vec{q})} d^{3N} p d^{3N} q} = 0$$

plugging in Q_N^{-1}

$$= \langle \mathcal{H} \rangle = U$$

average energy!

Collecting pieces:

$$A(V,T) - T \left(\frac{\partial A}{\partial T} \right)_V - U = 0$$

and this is what we wanted to show

Recall: Since we were able to show
 this, we now know ^{that} the "identi-
 fication" $Q_N(V,T) = \exp(-\beta A(V,T))$
 leads us to

$$A = U - TS$$

↗
Helmholtz free energy

7.2 Energy fluctuations in canonical ensemble

Canonical ensemble contains all energies

\Rightarrow there exist energy fluctuations

In contrast:

Microcanonical ensemble: energy fixed (Δ can be made small - at the end, all physical quantities are independent of Δ)

If almost all systems in the canonical ensemble have the same energy, then the energy fluctuations should become vanishingly small and then there is "hope" that the canonical and microcanonical ensemble yield the same physical results.

Let's calculate energy fluctuations in canonical ensemble.

will be
done on
page 62

Start with:

$$U = \langle \mathcal{H} \rangle = \frac{\int \mathcal{H} e^{-\beta \mathcal{H}} d^{3N}p d^{3N}q}{\int e^{-\beta \mathcal{H}} d^{3N}p d^{3N}q}$$

Rearrange:

$$\int U e^{-\beta \mathcal{H}} d^{3N} p d^{3N} q - \int \mathcal{H} e^{-\beta \mathcal{H}} d^{3N} p d^{3N} q = 0$$

Multiply by $e^{\beta A}$:

$$\int (U - \mathcal{H}) e^{\beta(A - \mathcal{H})} d^{3N} p d^{3N} q = 0$$

Apply $\frac{\partial}{\partial \beta}$:

$$\frac{\partial U}{\partial \beta} \int e^{\beta(A - \mathcal{H})} d^{3N} p d^{3N} q$$

$$+ \int e^{\beta(A - \mathcal{H})} (U - \mathcal{H}) \left(A + \beta \frac{\partial A}{\partial \beta} - \mathcal{H} \right) d^{3N} p d^{3N} q$$

$= 0$

$\underbrace{(U - \mathcal{H})^2}_{\text{U according to page 56}}$

Look at integral in first term: $\int e^{\beta(A - \mathcal{H})} d^{3N} p d^{3N} q = e^{\beta A} \int e^{-\beta \mathcal{H}} d^{3N} p d^{3N} q$

$= N! h^{3N} Q_N^{-1} \quad N! h^{3N} Q_N$

Putting it all together:

$$\frac{\partial U}{\partial \beta} + \frac{1}{N! h^{3N}} e^{\beta \mathcal{H}} \underbrace{\int e^{-\beta \mathcal{H}} (U - \mathcal{H})^2 d^{3N} p d^{3N} q}_{Q_N^{-1}} = 0$$

$$\underbrace{\left(\int e^{-\beta \mathcal{H}} d^{3N} p d^{3N} q \right)^{-1}}_{\langle (U - \mathcal{H})^2 \rangle}$$

So: $\frac{\partial U}{\partial \beta} + \underbrace{\langle (U - \mathcal{H})^2 \rangle}_{U^2 - 2U \langle \mathcal{H} \rangle + \langle \mathcal{H}^2 \rangle} = 0$

$$\Rightarrow \underbrace{\frac{\partial U}{\partial \beta}}_{-kT^2 \frac{\partial U}{\partial T}} - \langle \mathcal{H} \rangle^2 + \langle \mathcal{H}^2 \rangle = 0$$

$$-kT^2 \frac{\partial U}{\partial T}$$

$$= -kT^2 C_V$$

So: $\underbrace{\langle \mathcal{H}^2 \rangle - \langle \mathcal{H} \rangle^2}_{\langle (\Delta E)^2 \rangle} = kT^2 C_V$

For a "typical" macroscopic system, $C_V \sim N$

Fluctuations scale as N .

Want to look at

$$\frac{\sqrt{\langle (\Delta E)^2 \rangle}}{\langle \delta E \rangle} \sim \frac{1}{\sqrt{N}} \xrightarrow{N \rightarrow \infty} 0$$

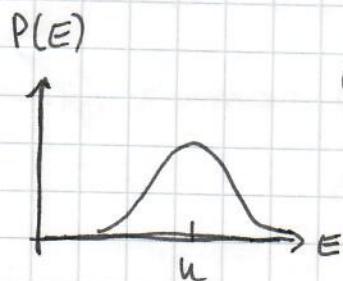


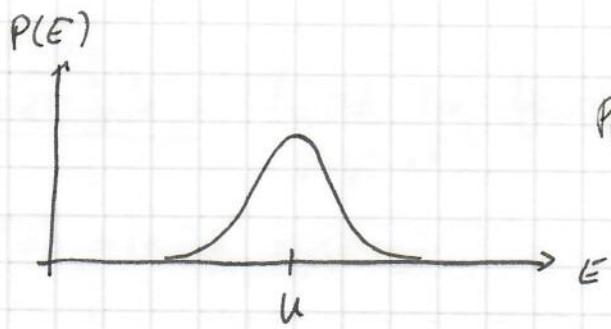
energy scales
as N

We conclude: energy uncertainty is typically small

\Rightarrow nearly all systems in the ensemble have the energy $\underline{\langle \delta E \rangle}$
internal energy

One can show: in the canonical ensemble, the distribution in energy is a Gaussian distribution centered at U





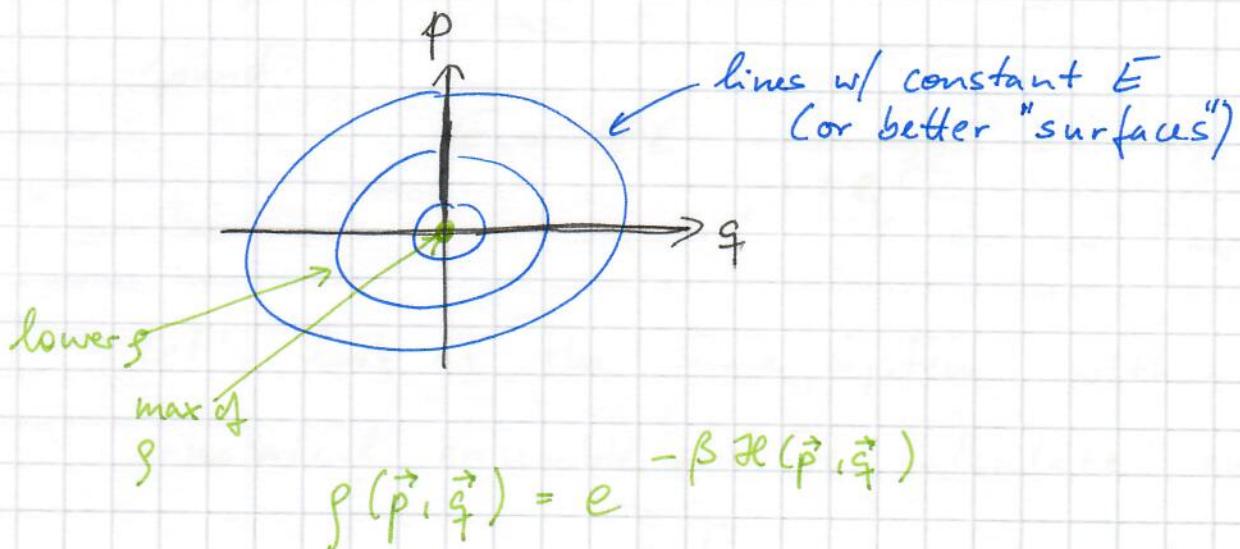
$$P(E) \propto \exp\left(-\frac{(E-U)^2}{2kT^2C_V}\right)$$

$$= \exp\left(-\frac{(E-U)^2}{2(\Delta E)^2}\right)$$

as $N \rightarrow \infty$, Gaussian

goes to delta-function

Simple physical picture:



lowest $E \rightarrow$ highest g

Rule of thumb: density of states $\sim e^E$

$$E \sim N$$

$$N \rightarrow \infty$$

} this is why
statistical
mechanics
works

Example: (will be finished w/ example at end of page 68)

Two-level system:

$$\underline{\epsilon}$$

$$\underline{0}$$

N distinguishable non-interacting atoms/spins

single-particle energy levels

Using the microcanonical ensemble, we had found:

$$\left\{ E = N\epsilon \frac{1}{1 + e^{\beta\epsilon}} \right\} \quad \beta = \frac{1}{kT}$$

Let's look at the same system within canonical ensemble and "re-calculate" energy.

this will be internal energy

→ Premise: we should find the same "thermodynamics"

Let ν denote an allowed state:

$$\nu = (n_1^{(\nu)}, n_2^{(\nu)}, \dots, n_N^{(\nu)})$$

↑ ↑ R
atom 1 atom 2 atom N

$n_i^{(\nu)} = 0 \text{ or } 1$

The energy E_v of state v is

$$E_v = \sum_{i=1}^N \epsilon_i n_i^{(v)}$$

We want to calculate the partition fct. Q_N :

$$Q_N = e^{-\beta A} \quad A: \text{Helmholtz free energy}$$

$$\Rightarrow -\beta A = \log Q_N = \log \sum_v e^{-\beta E_v}$$

our final goal is to get A

$$\text{we know: } U = \langle H \rangle = A - T \left(\frac{\partial A}{\partial T} \right)_V$$

So: if we can get A , we can
get U

we can get A from Q_N

$$\text{Evaluate } Q_N = \sum_v e^{-\beta E_v}$$

↗
sum over all
states

Plugging in
 E_v

$$Q_N = \sum_v e^{-\beta \sum_{i=1}^N \varepsilon n_i^{(v)}} \quad (**)$$

$$\underbrace{\prod_{i=1}^N e^{-\beta \varepsilon n_i^{(v)}}}$$

for the i^{th} particle, we have $n_i^{(v)} = 0, 1$
 for state v

$$= \prod_{i=1}^N \sum_{n_i^{(v)}=0,1} e^{-\beta \varepsilon n_i^{(v)}}$$

$$= \prod_{i=1}^N (1 + e^{-\beta \varepsilon})$$

$$= (1 + e^{-\beta \varepsilon})^N \quad (*)$$

let's look at $N=3$ as an example:

What are the states v ?

$N=3$ illustration

$$v = (0, 0, 0) \rightsquigarrow E=0$$

$$(1, 0, 0)$$

$$(0, 1, 0)$$

$$(0, 0, 1) \quad \left. \begin{array}{l} \\ \\ \end{array} \right\} E=\varepsilon$$

$$(1, 1, 0)$$

$$(1, 0, 1) \quad \left. \begin{array}{l} \\ \\ \end{array} \right\} E=2\varepsilon$$

$$(0, 1, 1)$$

$$(1, 1, 1) \rightsquigarrow E=3\varepsilon$$

Let's look at $\textcircled{*}$ for $N=3$:

$$(1 + e^{-\beta \varepsilon})^N =$$

$$(1 + e^{-\beta \varepsilon})(1 + e^{-\beta \varepsilon})(1 + e^{-\beta \varepsilon})$$

$$= \underbrace{1 \cdot 1 \cdot 1}_{E=0 \\ (0,0,0)} + \underbrace{1 \cdot 1 \cdot e^{-\beta \varepsilon}}_{E=\varepsilon \\ (0,0,1)} + \underbrace{1 \cdot e^{-\beta \varepsilon} \cdot 1}_{E=\varepsilon \\ (0,1,0)} + \dots$$

...

$N=3$ illustration

So: We see that the microcanonical states contribute w/ different "weights"

$$E=0 \rightarrow N_{ex} = 0 \rightarrow \frac{N!}{N_{ex}! N_{gr}!} = 1$$

$$E=\varepsilon \rightarrow N_{ex} = 1 \rightarrow \dots = 3$$

$$E=2\varepsilon \rightarrow N_{ex} = 2 \rightarrow \dots = 3$$

$$E=3\varepsilon \rightarrow N_{ex} = 3 \rightarrow \dots = 1$$

Back to page 66, Eq. (**):

$$Q_N = (1 + e^{-\beta \epsilon})^N$$

$$\text{From } -\beta A = \log Q_N$$

$$= N \log (1 + e^{-\beta \epsilon})$$

$$\Rightarrow A = -kT N \log (1 + e^{-\epsilon/kT})$$

As alluded to on p. 65, let's now use

$$U = A - T \left(\frac{\partial A}{\partial T} \right)_V$$

$$\Rightarrow U = -kT N \log (1 + e^{-\epsilon/kT})$$

$$+ T k N \log (1 + e^{-\epsilon/kT})$$

$$+ T k T N (1 + e^{-\epsilon/kT})^{-1} \frac{\epsilon}{k T^2} e^{-\epsilon/kT}$$

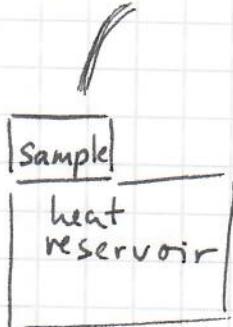
So: $U = \epsilon N (1 + e^{-\epsilon/kT})^{-1}$

Same as in
micro canonical
ensemble!!!

7.3 Grand canonical ensemble

micro canonical ensemble: E, V, N fixed

canonical ensemble: T, V, N fixed



whether we fix E or T matters little

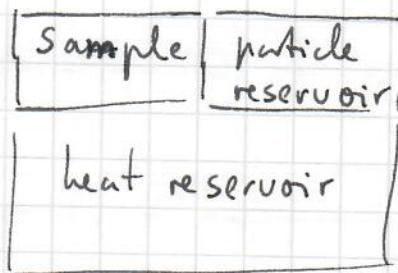
→ one fixes the other

(e.g., temperature of reservoir
that the sample or system
is in contact with sets
the value of the average or
internal energy)



yes, there are fluctuations but
they are small

grand canonical ensemble: both E and N are allowed to fluctuate



in practice, we may not
know exactly how many
particles we have...

Phase space for the ^{grand} canonical ensemble is spanned by all canonical momenta and canonical coordinates of systems with $0, 1, \dots, N-1, N, N+1, \dots$ particles

We define grand partition function $\Omega(\mu, V, T)$:

$$\Omega(\mu, V, T) = \sum_{N=0}^{\infty} z^N Q_N(V, T)$$

Where $z = e^{\beta\mu}$

↑
fugacity

This definition implies

$$PV = kT \log \Omega \quad (*)$$

Average number of particles \bar{N} :

$$\bar{N} = \langle N \rangle = \frac{\sum_{N=0}^{\infty} N z^N Q_N(V, T)}{\sum_{N=0}^{\infty} z^N Q_N(V, T)} = z \frac{\partial}{\partial z} \log \Omega(\mu, V, T)$$

(**)

We can use $\textcircled{*}$ and $\textcircled{**}$ from previous page to eliminate μ (or the fugacity) and to get expressions in terms of the average number \bar{N} of particles \Rightarrow pressure as fct. of $\langle N \rangle, V, T$

If we know \mathcal{H} (note, \mathcal{H} depends on $N!!!$), we can calculate Q_N for all N . If we know $Q_0, Q_1, Q_2, \dots, Q_N, Q_{N+1}, \dots$, then we can calculate \mathcal{Q} .

\rightsquigarrow this is true at least in principle (in practice, things may be complicated)

Internal energy U :

$$\begin{aligned} U &= - \frac{\partial}{\partial \beta} \log \mathcal{Q}(z, V, T) \\ &= - \frac{\frac{\partial}{\partial \beta} \mathcal{Q}(z, V, T)}{\mathcal{Q}(z, V, T)} \\ &= - \frac{\frac{\partial}{\partial \beta} \sum_{N=0}^{\infty} z^N Q_N(V, T)}{\mathcal{Q}(z, V, T)} \end{aligned}$$

z and β are considered independent variables!

\rightsquigarrow see also next page...

Using the \bar{N} equation, we can rewrite $U(z, V, T)$ as $U(\bar{N}, V, T)$.

Once we have $U = U(\bar{N}, V, T)$, we can get

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V$$

$$S = \int_0^T \frac{C_V}{T} dT$$

$$A = U - TS$$

Look at $U = -\frac{\partial}{\partial \beta} \log Q$ again:

$$\bar{E} = \frac{1}{Q} \sum_N \sum_j \bar{E}_{N,j}(V) e^{-\beta \bar{E}_{N,j}(V)} z^N$$

$$-\frac{\partial}{\partial \beta} e^{-\beta \bar{E}_{N,j}(V)}$$

$$= \frac{1}{Q} \sum_N \left(-\frac{\partial}{\partial \beta} \sum_j e^{-\beta \bar{E}_{N,j}(V)} \right) z^N$$

$$= \frac{1}{Q} \sum_N \left(-\frac{\partial}{\partial \beta} Q_N \right) z^N$$

Example : ideal gas (will be done w/ this on p. 79)

We want to calculate \mathcal{Q} .

Need Q_N !

$$Q_N = \frac{1}{N! h^{3N}} \int e^{-\beta \sum_i \vec{p}_i^2 / 2m} d^{3N} p d^{3N} q$$

\uparrow
 q is indep. of p

$$= \frac{V^N}{N! h^{3N}} \underbrace{\int e^{-\beta \sum_i \vec{p}_i^2 / 2m} d^{3N} p}_{\left(\frac{2m\pi}{\beta}\right)^{\frac{3N}{2}}}$$

Define : $\lambda = \frac{h}{\sqrt{2\pi m kT}}$

thermal or
de Broglie wave
length

$$\Rightarrow Q_N = \frac{1}{N!} \left(\frac{V}{\lambda^3} \right)^N$$

$$\lambda = \frac{h}{p} \sim \frac{h}{\sqrt{2mE}}$$

$$E \sim \frac{1}{2} kT \quad \sim \frac{h}{\sqrt{mkT}}$$

$$\frac{p^2}{2m} = E$$

gives correct scaling

Now:

$$\Omega = \sum_N z^N Q_N$$

$$= \sum_N \frac{1}{N!} e^{\beta \mu N} \left(\frac{V}{\lambda^3}\right)^N$$

$$= \sum_{N=0}^{\infty} \frac{1}{N!} \left(e^{\beta \mu} \frac{V}{\lambda^3}\right)^N$$

$$= \exp\left(e^{\beta \mu} \frac{V}{\lambda^3}\right)$$

$$\left\{ e^x = \sum_{N=0}^{\infty} \frac{1}{N!} x^N \right.$$

recognize
this as Taylor
expansion of
exponential

$$= e^{\frac{zV}{\lambda^3}}$$

$$\text{So: } \left\{ \Omega = e^{\frac{zV}{\lambda^3}} \right. \quad (*)$$

Next:

$$PV = kT \log \Omega$$

from our def.

inserting (*)

$$= kT \frac{zV}{\lambda^3}$$

see next
page

$$\bar{N} = kT \left(\frac{\partial \log \Omega}{\partial \mu} \right)_{V,T} \stackrel{(*)}{=} kT \left(\frac{\partial \left(\frac{zV}{\lambda^3} \right)}{\partial \mu} \right)_V$$

$$z = e^{\beta \mu} \rightarrow = \beta kT \frac{zV}{\lambda^3} = \frac{zV}{\lambda^3}$$

Aside: on page 70, we found:

$$\bar{N} = z \frac{\partial}{\partial z} \log Q$$

this explains
the \bar{N} eq.
from previous
page

let's rewrite this:

$$z \frac{\partial \log Q}{\partial z} = z \frac{\partial \log Q}{\partial n} \frac{\partial n}{\partial z}$$

Alternatively:

$$PV = \gamma T \log Q$$

$$d(PV) = SdT + \bar{N}dn + PdV$$

$$\frac{\partial(PV)}{\partial n}$$

$$= \gamma T \frac{\partial \log Q}{\partial n}$$

$$z = e^{\beta n} \Rightarrow \frac{\partial z}{\partial n} = \beta z$$

$$\Rightarrow z \left(\frac{\partial n}{\partial z} \right) = z \left(\frac{\partial z}{\partial n} \right)^{-1} = z \frac{1}{\beta z}$$

$$= \frac{1}{\beta} = \gamma T$$

$$\Rightarrow z \frac{\partial \log Q}{\partial z} = \gamma T \frac{\partial \log Q}{\partial n}$$

So: $PV = \gamma T \frac{zV}{\lambda^3}$ & $\bar{N} = \frac{zV}{\lambda^3}$ results from
previous page

combine

$$\Rightarrow \underbrace{PV = \gamma T \bar{N}}$$

thermal eq. of state of the
ideal gas

From $\bar{N} = \frac{zV}{\lambda^3}$ and $z = e^{\beta\mu}$, we find

$$\mu = \frac{1}{\beta} \log z = \frac{1}{\beta} \log \left(\frac{\lambda^3 \bar{N}}{V} \right)$$

$$\bar{N} = \frac{PV}{kT} \quad \Rightarrow \quad \mu = \frac{1}{\beta} \log \left(\frac{\lambda^3 P}{kT} \right)$$

$$\boxed{\mu = kT \log P - kT \log \left(\frac{kT}{\lambda^3} \right)}$$

$$S = \frac{\partial(PV)}{\partial T}$$

$$\text{recall } d(PV) = SdT + \bar{N}d\mu + PdV$$

$$S = \frac{\partial(PV)}{\partial T}$$

$$\Rightarrow S = \frac{\partial}{\partial T} \left(kT \frac{zV}{\lambda^3} \right) = k \frac{zV}{\lambda^3} + \frac{3}{2} kT z V \left(\frac{h}{2\pi mk} \right)^3 \frac{(+1)}{T^{5/2}}$$

$$+ kT \frac{V}{\lambda^3} \underbrace{\frac{d\mu}{kT}}_{(-\frac{1}{T}z)} \geq$$

$$S = \frac{5}{2} k z \frac{V}{\lambda^3} - k z \frac{V}{\lambda^3} \underbrace{\frac{d\mu}{kT}}_{\log z} = k \bar{N} \left(\frac{5}{2} - \log \frac{V/\bar{N}}{\lambda^3} \right)$$

$$\log z = \log \frac{\lambda^3 \bar{N}}{V}$$

$$\text{So: } S = k \bar{N} \left(\frac{5}{2} + \log(\bar{n} \lambda^3) \right)$$

where $\bar{n} = \frac{\bar{N}}{V}$
 ↑
 average density

Last: $U = -PV + TS + \mu \bar{N}$

$$= -kT \bar{N} + T \left(k \bar{N} \frac{5}{2} + k \bar{N} \log(\bar{n} \lambda^3) \right)$$

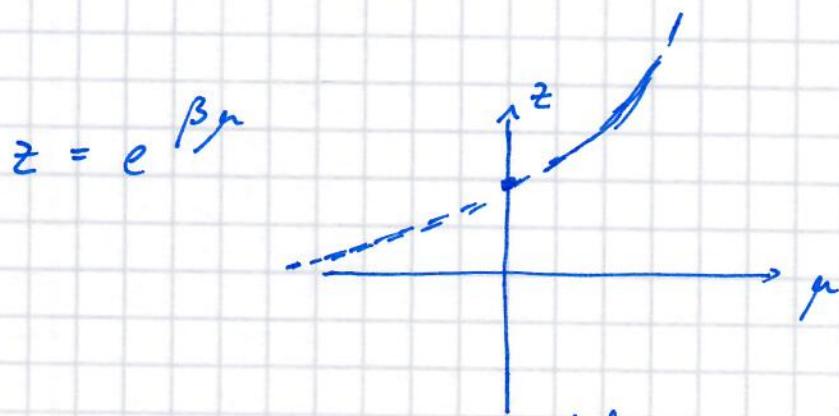
we did not derive this

$$+ \mu \bar{N}$$

see 2nd line of p. 76

$$kT \log z = kT \log(\bar{n} \lambda^3)$$

$$\Rightarrow U = \frac{3}{2} kT \bar{N}$$



$$z = e^{\beta \mu}$$

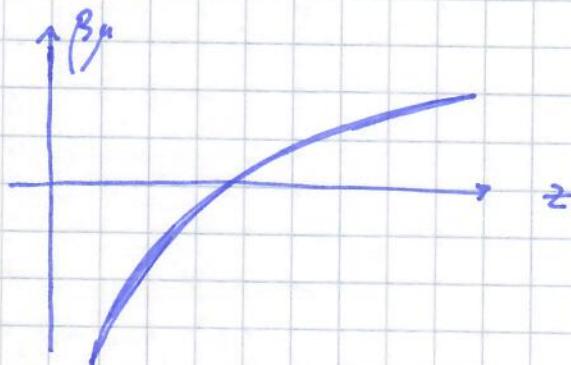
We found: $\log z = \log \bar{n} \lambda^3 \Rightarrow z = \bar{n} \lambda^3$

$$\bar{n} = \frac{1}{\langle r \rangle^3}$$

$\langle r \rangle$: average particle spacing

in the classical regime, $\bar{n} \lambda^3 = \frac{\lambda^3}{\langle r \rangle^3} \ll 1$

Plot $\beta \mu = \log z$



\leftarrow
T increases

\bar{n} decreases

\leftarrow classical regime quantum regime \rightarrow

So: μ is negative!

\uparrow
change in energy if one adds a particle
to the system at constant volume and
constant entropy

$$\mu = \left(\frac{\partial U}{\partial N} \right)_{S,V}$$

if a particle is added, the entropy goes up. To "compensate", the energy has to go down.

→ negative chemical potential

(system is "happy" to accept new particle)