

Example : N distinguishable atoms, each of which

has energy of either 0 or ϵ



discrete but classical
system



two-level system

integral \rightarrow sum

If we define $n_i \in \{0, 1\}$, then $E = \sum_i n_i \epsilon = N_{ex} \epsilon$

\nearrow
sum overall
particles

For fixed N and ϵ , how many states are consistent
w/ N and ϵ ?

$$T(E, N) = \frac{N!}{N_{ex}! (N - N_{ex})!}$$

$$\Rightarrow S = k \log T = k \log \frac{N!}{N_{ex}! (N - N_{ex})!}$$

Stirling approximation:

Stirling approx.

$$\log N! \approx N \log N - N$$

$$\Rightarrow S \approx k \left[N \log N - N_{ex} \log N_{ex} - (N - N_{ex}) \log (N - N_{ex}) - N + (N - N_{ex}) + N_{ex} \right]$$

$$\text{So: } S \approx k \left[N \log N - N_{\text{ex}} \log N_{\text{ex}} - (N-N_{\text{ex}}) \log (N-N_{\text{ex}}) \right]$$

collect terms

$$\cancel{N_{\text{ex}} \log N} + (N-N_{\text{ex}}) \log N \quad (\text{the two } N_{\text{ex}} \text{ terms cancel})$$

$$= -k \left[N_{\text{ex}} \log \left(\frac{N_{\text{ex}}}{N} \right) + (N-N_{\text{ex}}) \log \left(\frac{N-N_{\text{ex}}}{N} \right) \right]$$

$$\begin{aligned} E &= N_{\text{ex}} \varepsilon \\ N_{\text{ex}} &= \frac{E}{\varepsilon} \end{aligned}$$

$$\rightarrow = -k \left[\frac{E}{\varepsilon} \log \left(\frac{E}{\varepsilon N} \right) + \left(N - \frac{E}{\varepsilon} \right) \log \left(1 - \frac{E}{\varepsilon N} \right) \right]$$

$$S(E, N) = -k \left[\frac{E}{\varepsilon N} \log \left(\frac{E}{\varepsilon N} \right) + \left(1 - \frac{E}{\varepsilon N} \right) \log \left(1 - \frac{E}{\varepsilon N} \right) \right]$$

↑
 entropy for two-level
 system w/ E, N, V
 (calculated in microcanonical
 ensemble)

Let's use our definition: $\frac{1}{T} = \left(\frac{\partial S}{\partial E} \right)_{N,V}$

we can evaluate this
 easily since we have
 S as a fct. of E

$$\Rightarrow \frac{1}{T} = -Nk \left[\frac{1}{EN} \log\left(\frac{\bar{E}}{EN}\right) - \frac{1}{EN} \log\left(1 - \frac{\bar{E}}{EN}\right) + \underbrace{\frac{\bar{E}}{EN} \frac{1}{E}}_{\frac{1}{EN}} - \underbrace{(1 - \frac{\bar{E}}{EN}) \left(\frac{1}{-E+EN}\right)}_{\frac{1}{EN}} \right]$$

evaluating
the derivative

Simplifying →

$$= -Nk \frac{1}{EN} \log\left(\frac{\frac{\bar{E}}{EN}}{\frac{EN-E}{EN}}\right)$$

$$= -\frac{k}{E} \log\left(\frac{E}{EN-E}\right) = \frac{k}{E} \log\left(\frac{EN-E}{E}\right) = \frac{k}{E} \log\left(\frac{EN}{E}-1\right)$$

$$\boxed{\frac{1}{T} = \frac{k}{E} \log\left(\frac{N-N_{ex}}{N_{ex}}\right)}$$

using
 $E = EN_{ex}$

inverse temperature
of two-level system

(note: the temperature is calculated by treating the full N -particle system)

It follows:
(straightforward rearranging)

$$\frac{E}{kT} = \log\left(\frac{N-N_{ex}}{N_{ex}}\right)$$

$$\Rightarrow 1 + e^{\frac{E}{kT}} = \frac{N}{N_{ex}}$$

$$\boxed{E = N \frac{1}{1 + e^{\frac{E}{kT}}}}$$

total energy of
two-level system
(E is macro variable)

Let's look at total energy for limiting cases:

$$T \rightarrow 0 \Rightarrow E \rightarrow 0 \rightarrow \text{all particles in lowest energy state}$$

$$T \rightarrow \infty \Rightarrow E = \frac{\varepsilon N}{2}$$

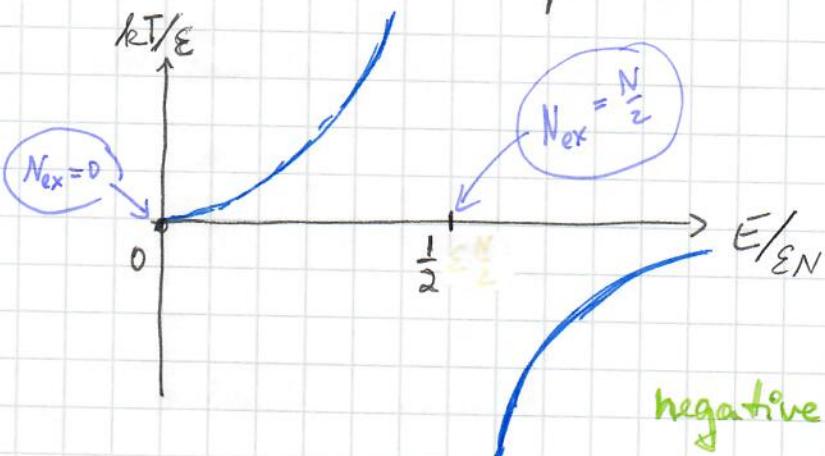
→ all states are equally likely

Equivalently, we can say (use $\frac{\varepsilon}{kT} = \log(N_{ex} - 1)$):

$$\text{For } N_{ex} \rightarrow 0 \Rightarrow \frac{\log(\infty)}{T} \rightarrow \infty \text{ or } T \rightarrow 0$$

$$\text{For } N_{ex} \rightarrow \frac{N}{2} \Rightarrow \frac{1}{T} \rightarrow 0 \text{ or } T \rightarrow \infty$$

Summarize in a plot:



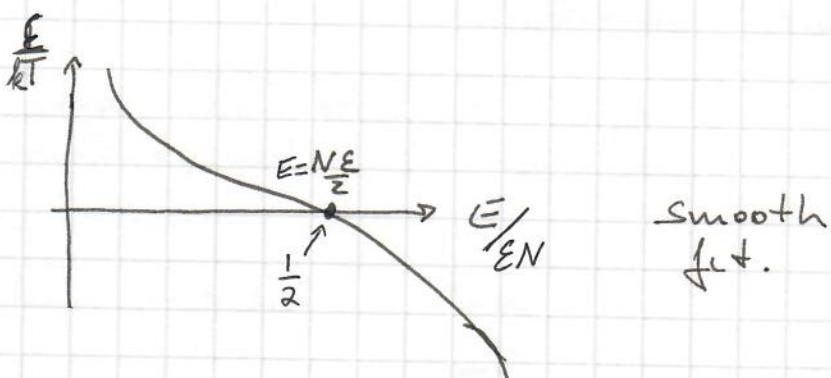
negative temperature!

Weird? → no!

As E exceeds $\frac{NE}{2}$ there are fewer ways to arrange the system  as E increases.

It might be more natural to think about

$\frac{1}{T}$:



$$\begin{aligned}\frac{1}{T} &= \left(\frac{\partial S}{\partial E}\right)_{N,V} = \left(\frac{\partial}{\partial E} (k \log T)\right)_{N,V} \\ &= k \left(\frac{\partial \ln}{\partial E}\right)_{N,V} \hat{=} k \frac{\Delta \ln}{\Delta E} \frac{1}{\Delta E}\end{aligned}$$

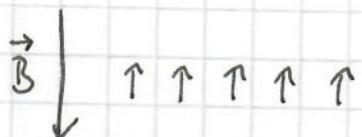
Where do we encounter negative temperature?

↳ direct consequence of boundedness of energy levels

(i) nuclear spins in magnetic field



Suddenly switch \vec{B} :



switch is too fast for nuclear
spins to follow

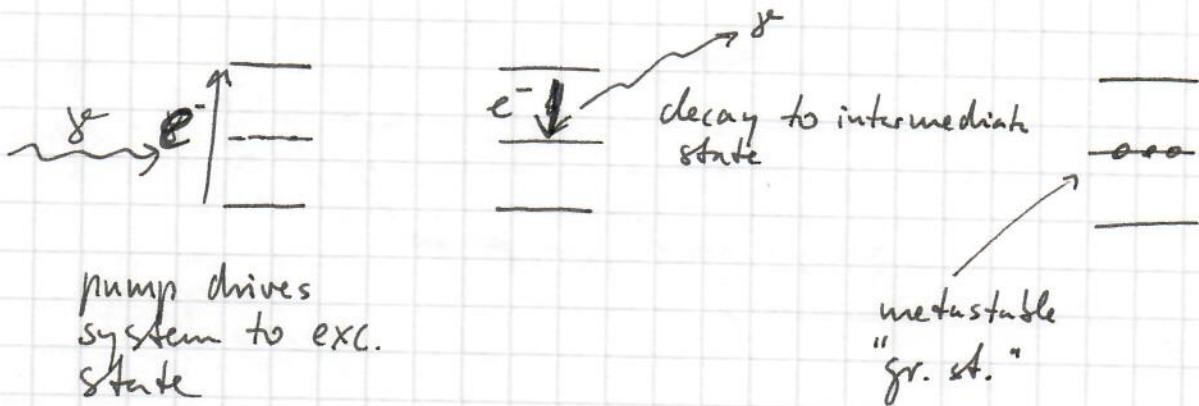
→ internal equilibrium
is reached within 10^{-5} - 10^{-6} sec

(spin-spin interaction
energy \ll Zeeman
energy)

time scale for spin relaxation $\sim 1-10$ min

The state with negative temperature can be maintained for minutes

(ii) population inversion in laser



population inversion

\Rightarrow negative temperature

Additional plots:

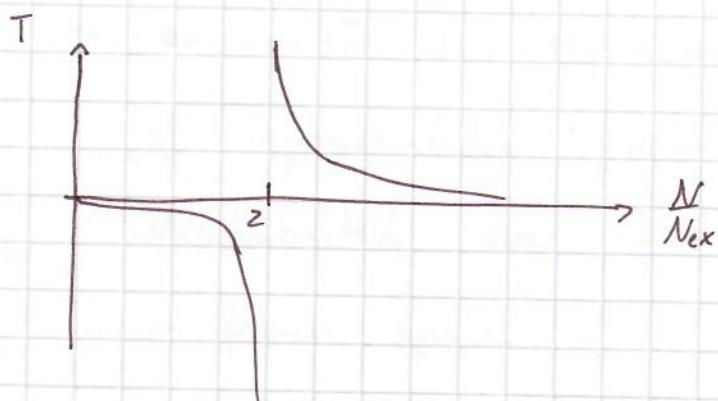
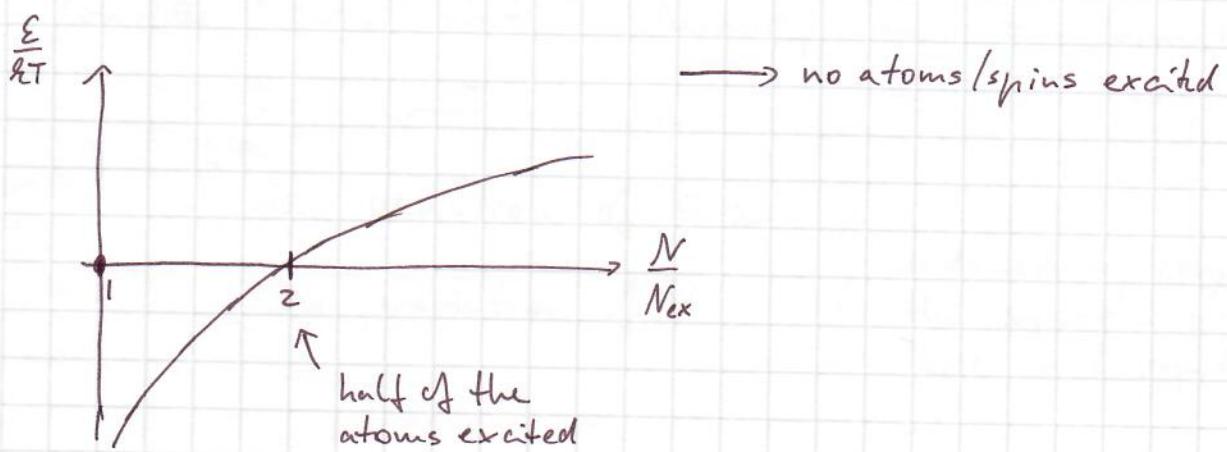
$$\frac{E}{kT} = \log \left(\frac{N}{N_{ex}} - 1 \right)$$

inverse temperature
for two-level system
(from page 26)

$$\frac{N}{N_{ex}} \in [1, \infty]$$

all spins/
atoms excited

no spins/atoms excited



energy increases

6.3 Derivation of thermodynamics

We defined entropy S so that it is consistent w/ 2nd law of thermodynamics : $S = S(E, V)$

\Rightarrow complete thermodynamics of system
can be obtained

Consider "quasi-static" thermodynamic transformation

slow variation of E & }
 slow variation of V } induced by coupling
 the system to
 "external agent"

→ ensemble is represented by a collection of representative points that are uniformly distributed over a slowly varying region in phase space

Mathematically:

$$dS(E, V) = \left(\frac{\partial S}{\partial E}\right)_V dE + \left(\frac{\partial S}{\partial V}\right)_E dV$$

$\underbrace{}$

by def. $\frac{1}{T}$

$\underbrace{}$

now define

$$\frac{P}{T} = \left(\frac{\partial S}{\partial V}\right)_E$$

P: pressure

Thus: $\boxed{dS = \frac{1}{T} (dE + P dV)}$

first law of thermodynamics

Third law of thermodynamics (q.m. in nature):

The entropy of a system at absolute zero is a universal constant, which may be taken to zero.

$\underbrace{}$
cannot be derived at this point since we are dealing with classical statistical mechanics

How to obtain thermodynamic function of isolated system w/ Hamiltonian \mathcal{H} , which occupies volume V and has an energy E (known up to small uncertainty ΔE)?

Recipe:

(a) Calculate $w(E)$ \rightsquigarrow can be done since we know \mathcal{H}

(b) Calculate $S(E, V) = k \log w(E)$

\nearrow

we can get S up to some constant that we don't care about

(c) Solve for E in terms of S and V :

$$E = E(S, V) = \underline{h}(S, V)$$

(d) Calculate other thermodynamic functions:

$$\bar{T} = \left(\frac{\partial h}{\partial S} \right)_V$$

\nearrow

absolute temperature

(e) $P = T \left(\frac{\partial S}{\partial V} \right)_E$

↑
from our old.
(page 31)

$$= \left(\frac{\partial U}{\partial S} \right)_V \left(\frac{\partial S}{\partial V} \right)_E$$

$$\Rightarrow P = \left(\frac{\partial U}{\partial V} \right)_S$$

↑
pressure

(f) Helmholtz free energy $A = U - TS$

(g) Gibbs potential $G = U + PV - TS$

(h) heat capacity at constant volume $C_V = \left(\frac{\partial U}{\partial T} \right)_V$

6.4 Equipartition theorem

→ we will come across virial theorem (again, if you took S153)

→ we will find an explicit expression for C_V

Let's calculate ensemble average of

$$x_i \frac{\partial \mathcal{H}}{\partial x_j}$$

$$x_i = p_i \text{ or } q_i$$

Do it:

$$\langle x_i \frac{\partial \mathcal{H}}{\partial x_j} \rangle = \frac{\int_{E < \mathcal{H} < E + \Delta E} x_i \frac{\partial \mathcal{H}}{\partial x_j} d^{3N} p d^{3N} q}{\int_{E < \mathcal{H} < E + \Delta E} d^{3N} p d^{3N} q}$$

$P(E)$ by def.

$$\int_{E < \mathcal{H} < E + \Delta E} \dots = \underbrace{\int_{\mathcal{H} < E + \Delta E} \dots}_{f(E+\Delta E)} - \underbrace{\int_{\mathcal{H} < E} \dots}_{f(E)}$$

$$= f(E) + \Delta E \frac{\partial f}{\partial E} \Big|_E + \dots - f(E) \approx \Delta E \frac{\partial f}{\partial E} \Big|_E$$

$$\Rightarrow \langle x_i \frac{\partial \mathcal{H}}{\partial x_j} \rangle = \frac{1}{P(E)} \Delta E \frac{\partial}{\partial E} \int_{\mathcal{H} < E} x_i \frac{\partial \mathcal{H}}{\partial x_j} d^{3N} p d^{3N} q$$

Work on integrand:

$$x_i \frac{\partial \mathcal{H}}{\partial x_j} = x_i \frac{\partial}{\partial x_j} (\mathcal{H} - E)$$

$E = \text{const}$

$$\frac{\partial E}{\partial x_j} = 0$$

$$= \frac{\partial}{\partial x_j} \left[x_i (\mathcal{H} - E) \right] - \frac{\partial x_i}{\partial x_j} (\mathcal{H} - E)$$

\uparrow
 δ_{ij}

$$\Rightarrow \langle x_i \frac{\partial \mathcal{H}}{\partial x_j} \rangle = \frac{\Delta E}{P(E)} \frac{\partial}{\partial E} \int_{\mathcal{H} < E} \frac{\partial}{\partial x_j} \left[x_i (\mathcal{H} - E) \right] d^{3N} p d^{3N} q$$

$$- \frac{\Delta E}{P(E)} \underbrace{\int_{\mathcal{H} < E} \frac{\partial}{\partial E} (\mathcal{H} - E) d^{3N} p d^{3N} q}_{-\sum (E)}$$

First integral goes to zero
(see page 35a for details).

Using $\frac{\Delta E}{P(E)} = \frac{1}{w(E)}$: continued on page 36 ...

Math
details

Why does the first integral go to zero?

L35a

Consider $\int_{\mathcal{H} \subset E} \frac{\partial}{\partial x_j} [x_i (\mathcal{H} - E)] d^{3N} p d^{3N} \xi$

recall $x_j = p_1 \text{ or } p_2 \text{ or... } q_1 \text{ or } q_2 \text{ or...}$

So we can convert the $6N$ -dimensional integral to a $(5N-1)$ -dimensional integral by performing the integration over x_j .

The limits of x_j are "constrained" by the condition that $\mathcal{H} \subset E$. We can write x_j as $x_j(E, (\vec{p}, \vec{\xi})')$, where $(\vec{p}, \vec{\xi})'$ denotes the $6N-1$ coordinates (all coordinates but x_j).

But on the surface, we require $\mathcal{H} = E$

\Rightarrow ~~the boundary is empty~~

When we insert the limits, we get 0.

As a result, the entire integral vanishes.

$$\Rightarrow \langle x_i \frac{\partial \mathcal{H}}{\partial x_j} \rangle = \frac{1}{\omega(E)} \delta_{ij} \sum(E)$$

$$= \delta_{ij} \frac{\sum(E)}{\frac{\partial}{\partial E} (\sum(E))}$$

$$= \delta_{ij} \left(\underbrace{\frac{\partial}{\partial E} \log(\sum(E))}_{\frac{S}{k} \text{ by def.}} \right)^{-1}$$

$$\text{So } \langle x_i \frac{\partial \mathcal{H}}{\partial x_j} \rangle = \delta_{ij} \frac{k}{\frac{\partial S}{\partial E}} = \delta_{ij} k T$$

Finally : $\boxed{\langle x_i \frac{\partial \mathcal{H}}{\partial x_j} \rangle = \delta_{ij} k T}$

generalized equipartition theorem

$$\text{Let } i=j \text{ and } x_i = p_i : \langle p_i \frac{\partial \mathcal{H}}{\partial p_i} \rangle = k T$$

$$\text{Let } i=j \text{ and } x_i = q_i : \langle q_i \frac{\partial \mathcal{H}}{\partial q_i} \rangle = k T$$

$$\text{But } \frac{\partial \mathcal{H}}{\partial q_i} = -\dot{p}_i \Rightarrow \langle q_i \dot{p}_i \rangle = -k T$$

Summing over all $3N$ d.o.f.s

$$\boxed{\langle \sum_{i=1}^{3N} q_i \dot{p}_i \rangle = -3NkT}$$

virial theorem

(amazingly, independent
of \mathcal{H} ; applicable to
any Hamiltonian)

$$\sum_{i=1}^{3N} q_i \dot{p}_i \rightsquigarrow \begin{array}{l} i^{\text{th}} \text{ coordinate times} \\ i^{\text{th}} \text{ component of generalized force} \end{array}$$

$\hat{=}$ "virial" in classical mechanics

Assume: $\mathcal{H} = \sum_{i=1}^{3N} A_i \dot{P}_i^2 + \sum_i B_i \dot{Q}_i^2$



P_i and Q_i are canonically conjugate variables

we learned in S153 that
many Hamiltonian can
be written in this way

simple algebra $\Rightarrow \sum_{i=1}^{3N} \left(P_i \frac{\partial \mathcal{H}}{\partial P_i} + Q_i \frac{\partial \mathcal{H}}{\partial Q_i} \right) = 2\mathcal{H}$

let's take ensemble average:

$$\frac{1}{Z} \left\langle \sum_{i=1}^{3N} \left(P_i \frac{\partial \mathcal{H}}{\partial P_i} + Q_i \frac{\partial \mathcal{H}}{\partial Q_i} \right) \right\rangle = \langle \mathcal{H} \rangle$$

each term
gives kT

$$\Rightarrow \langle \mathcal{H} \rangle = \frac{1}{2} f k T$$

$f = \# \text{ of degrees}$
 of freedom
($f = 6N$)

theorem of equipartition
of energy

Example:

$$\text{Since } \langle \mathcal{H} \rangle = U \Rightarrow C_V = \frac{1}{2} f k$$

$$\begin{aligned} C_V &= \left(\frac{\partial U}{\partial T} \right)_V \\ &= \left(\frac{1}{2} f \left(\frac{1}{2} f k T \right) \right)_V \end{aligned}$$

$$\text{or } \frac{C_V}{k} = \frac{1}{2} f$$

heat capacity is directly related
to # of d.o.f

Recall: we are doing class. stat. mech. \rightarrow all d.o.f
are active

(in q.m., d.o.f can be "frozen out")

Let's look at another example (1st example was two-level system).

6.5 Classical ideal gas

$$\mathcal{H} = \sum_{i=1}^N \frac{\vec{p}_i^2}{2m}$$

Goal: Calculate S and from S ; C_V and P . calculate

Let's start: $\Sigma(E) = \frac{1}{h^{3N}} \int_{\mathcal{E} < E} d^3 p_1 d^3 p_2 \dots d^3 p_N d^3 q_1 d^3 q_2 \dots d^3 q_N$

this factor is new: some constant w/ units momentum \times distance
(introduced to make $\Sigma(E)$ dimensionless)

it's easier to work with mathematically than $T(E)$

The integration limits, as written, are not overly convenient ...

Introduce Heavyside step function:

$$\Theta(E - E') = \begin{cases} 1 & \text{for } E - E' \geq 0 \\ 0 & \text{for } E - E' < 0 \end{cases}$$

$$\Theta(E - E') = \begin{cases} 1 & \text{for } E \geq E' \\ 0 & \text{for } E < E' \end{cases}$$

$$\Rightarrow \Sigma(E) = \frac{1}{h^{3N}} \iint_{\substack{\text{all} \\ \text{space}}} \Theta(E - \vec{p}^2) d^{3N}p d^{3N}\vec{q}$$

~~~~~

$$\Theta(E - \sum_{i=1}^N \frac{\vec{p}_i^2}{2m})$$

$\rightsquigarrow$  integrand is independent  
of  $\vec{q}_1, \vec{q}_2, \dots, \vec{q}_N$

$\Rightarrow$  the integration over  $d^{3N}\vec{q}$  can be  
done straightforwardly

$$\therefore \Sigma(E) = \left(\frac{V}{h^3}\right)^N \int_{\text{all space}} \Theta(E - \sum_{i=1}^N \frac{\vec{p}_i^2}{2m}) d^3p_1 d^3p_2 \dots d^3p_N$$

$\left( \begin{array}{c} V: \text{volume} \end{array} \right)$

To do the integration, we introduce new coordinates:

$$\vec{p}_i = \sqrt{2m} \vec{u}_i$$

$$\Rightarrow d^3p_i = (2m)^{3/2} d^3u_i$$

note:  $\vec{u}_i$  have units of  $\sqrt{\text{energy}}$

Using the new coordinates, we have:

$$\Sigma(E) = \left( \frac{(\alpha_m)^{3/2} V}{h^3} \right)^N \int_{\text{all space}} \theta(E - \sum_{i=1}^N \vec{u}_i^2) d^3 u$$

$$\text{let } R_E = \sqrt{\sum_{i=1}^N \vec{u}_i^2}$$

our integral is the volume of a  $3N$ -dimensional sphere of radius  $R_E$

$R_E$  has units of  $\sqrt{\text{energy}}$

To evaluate the integral, we look at an - at first side - unrelated integral. The connection will become clear in a little bit.

will  $\rightarrow$  Auxiliary integral:  
be done

on p.45

$$\int \dots \int e^{-(\vec{u}_1^2 + \dots + \vec{u}_N^2)/\varepsilon} d^3 u_1 \dots d^3 u_N$$

$\varepsilon$  is some constant with units of energy

$$= \left( \int \int \int e^{-\vec{u}^2/\varepsilon} d^3 u \right)^N$$

$$= \left( \int_{-\infty}^{\infty} e^{-x^2/\varepsilon} dx \right)^{3N}$$

$$\text{set } x' = \frac{x}{\sqrt{\varepsilon}}$$

$$\Rightarrow dx' = \frac{dx}{\sqrt{\varepsilon}}$$

$$dx = \sqrt{\varepsilon} dx'$$

$$= \underbrace{\left( \sqrt{\varepsilon} \int_{-\infty}^{\infty} e^{-x'^2} dx' \right)^{3N}}_{\sqrt{\pi}}$$

$$= (\varepsilon \pi)^{3N/2} \quad \rightsquigarrow \text{we will use this on page 45}$$

Alternatively, we can rewrite the integral in a different way:

$$\int \dots \int e^{-(\sum_i u_i^2)/\varepsilon} d^{3N} u$$

$$= \int \dots \int e^{-R_E^2/\varepsilon} d^{3N} u$$

$R_E$  is the length of the vector  $(\vec{u}_1, \dots, \vec{u}_N) \rightsquigarrow$  if we have a

length, we can also define

$3N-1$  angles that define the

direction of the vector  $(\vec{u}_1, \dots, \vec{u}_N)$ :

I will write  $\hat{R}_E = (\vec{u}_1, \dots, \vec{u}_N)$  with  
direction  $\hat{R}_E$  and length  $R_E$

As a consequence, the integration  
over  $d^{3N}u$  can be rewritten in terms  
of an integration of  $dR_E$  and an  
integration over the  $3N-1$  angles:

we can denote this by  $d\Omega(\hat{R}_E) R_E^{3N-1}$

↗  
this term  
is needed to  
get the units  
right

in 2D:  $d\phi$   $p dp$

in 3D:  $\sin\theta d\theta$   $d\phi$   $r^2 dr$   
 $d\Omega$

With this:

$$\int \dots \int e^{-R_E^2/\varepsilon} d^{3N}n$$

$$= \int_0^\infty \int_{\text{3N-1 angles}} d\Omega(\vec{R}_E) R_E^{3N-1} e^{-R_E^2/\varepsilon} dR_E$$

I will call this

$3N C_{3N}$ , with  $C_{3N}$

being (for the moment)

unknown. Important:  $C_{3N}$  is

independent of  $R_E$

If we can do the integral over  $dR_E$ , then we can find an expression for  $C_{3N}$  by using our result from page 42.

Let's concentrate on  $dR_E$  integration:

$$\int_0^\infty R_E^{3N-1} e^{-R_E^2/\varepsilon} dR_E$$

$$\text{let } t = \frac{R_E^2}{\varepsilon} \Rightarrow dt = 2R_E dR_E \frac{1}{\varepsilon}$$

$$\Rightarrow dR_E = \frac{\varepsilon}{2} \frac{1}{R_E} dt \xrightarrow{R_E = \sqrt{\varepsilon t}} \frac{1}{2} \sqrt{\varepsilon} t^{-1/2} dt$$

$$\text{also: } R_E^{3N-1} = (\varepsilon t)^{\frac{3N-1}{2}}$$

(45)

$$\int_0^\infty R_E^{3N-1} e^{-R_E^2/\varepsilon} dR_E$$

$$= \int_0^\infty (\varepsilon t)^{\frac{3N-1}{2}} e^{-t} \frac{1}{2} \sqrt{\varepsilon} t^{-\frac{1}{2}} dt$$

$$= \frac{1}{2} \varepsilon^{\frac{3N}{2}} \int_0^\infty e^{-t} t^{\frac{3N}{2}-1} dt$$

$$= \Gamma\left(\frac{3N}{2}\right) \quad (\text{this is one way of defining the } \Gamma \text{ function})$$

$$\text{where } \Gamma(x) = (x-1)!$$

$$\text{Thus: } \int \dots \int e^{-R_E^2/\varepsilon} d^{3N} n = \frac{3N}{2} C_{3N} \cdot \varepsilon^{\frac{3N}{2}} \cdot \Gamma\left(\frac{3N}{2}\right)$$

this is the calculation we just finished

$$= (\varepsilon \pi)^{\frac{3N}{2}}$$

from page 42

Solve for  $C_{3N}$ :

$$\left\{ C_{3N} = \frac{\pi^{\frac{3N}{2}}}{\frac{3N}{2} \Gamma\left(\frac{3N}{2}\right)} = \frac{\pi^{\frac{3N}{2}}}{\left(\frac{3N}{2}\right)!} \right\}$$

This is the end of our auxiliary calculation!

Let's go back to page 41 and use the auxiliary calculation to calculate  $\Sigma(E)$ .

We had:

$$\Sigma(E) = \left( \frac{(2m)^{3/2} V}{h^3} \right)^N \int_{\text{all space}} \Theta(E - R_E^2) d^{3N} n$$

only dep. on  $R_E$   
and not dependent  
on  $\hat{R}_E$

$$= \left( \frac{(2m)^{3/2} V}{h^3} \right)^N \underline{3N} C_{3N} \int_0^\infty \Theta(E - R_E^2) R_E^{3N-1} dR_E$$

$$\int_0^{\sqrt{E}} R_E^{3N-1} dR_E$$

$$= \frac{1}{3N} R_E^{3N} \Big|_0^{\sqrt{E}}$$

$$= \frac{1}{3N} E^{3N/2}$$

{ the underlined (green) pieces  
cancel (now you know  
why I introduced  $3N$   
when I wrote down the  
angular integral.) }

Putting in  $C_{3N}$

$$= \left( \frac{(2m)^{3/2} V}{h^3} \right)^N C_{3N} E^{3N/2}$$

$$\Sigma(E) = \left( \frac{(2mE)^{3/2} V}{h^3} \right)^N \frac{\pi^{3N/2}}{\left(\frac{3N}{2}\right)!}$$

We finally have

$\Sigma(E) !! !$   $\Sigma(E, V, N)$

Let's calculate  $S(E, V) = k \log(\Sigma(E))$ :

$$S(E, V) = k \left[ \log C_{3N} + N \log \left( \frac{V}{h^3} \right) + \frac{3N}{2} \log (2mE) \right]$$

using  $\Sigma(E)$   
from previous page

let's look at  $\log C_{3N}$ :

$$\log \left( \frac{\pi^{3N/2}}{\Gamma(\frac{3N}{2} + 1)} \right) \approx \frac{3N}{2} \log \pi - \frac{3N}{2} \log \left( \frac{3N}{2} \right) + \frac{3N}{2}$$

*Stirling's approximation*

Collecting terms  $\Rightarrow S(E, V) = \frac{3Nk}{2} + Nk \log \left( V \left( \frac{4\pi m E}{3h^2 N} \right)^{3/2} \right)$

We have  $S$ , finally...

Solve for  $E$ :

$$\frac{S - \frac{3Nk}{2}}{Nk} = \log \left( V \left( \frac{4\pi m E}{3h^2 N} \right)^{3/2} \right)$$

$$\Rightarrow \left[ \frac{1}{V} \exp \left( \frac{S}{Nk} - \frac{3}{2} \right) \right]^{2/3} = \frac{4\pi m E}{3h^2 N}$$

$$\text{So: } E = \frac{3h^2}{4\pi m} \frac{N}{V^{2/3}} \exp\left(\frac{2S}{3Nk} - 1\right)$$

Now, we are ready to calculate  $T, C_V, P, \dots$

$$T = \left(\frac{\partial E}{\partial S}\right)_V = \frac{2}{3} \frac{E}{Nk} \Rightarrow E = \frac{3N}{2} kT$$

looks familiar...

$$C_V = \left(\frac{\partial E}{\partial T}\right)_V = \left(\frac{\partial}{\partial T} \left(\frac{3N}{2} kT\right)\right)_V = \frac{3Nk}{2}$$

$$C_V = \frac{3Nk}{2}$$

$$P = -\left(\frac{\partial E}{\partial V}\right)_S = -\left(-\frac{2}{3}\right) \frac{E}{V} = \frac{2}{3} \frac{\frac{3N}{2} kT}{V} = N \frac{kT}{V}$$

$T, S, \dots$   
come out from  
microscopic picture

$$\text{use } E = \frac{3N}{2} kT$$

$$P = N \frac{kT}{V}$$

Positive: We were able to re-derive ideal gas results from microcanonical ensemble.

Negative: We worked hard!

→ and this is frequently the case...  
calculations are tedious