

9. Quantum Statistics, 1

lecture 31, November 10, 2017

housekeeping

Honors project

last night

tonight I need to know via email:

if you're doing the honors project

There's no term paper! Story there.

wanna hear the The Tom Story again?

Next week:

homework workshop will be Wednesday

homework will be due Friday

lectures will happen M,T,F

Exam 2

average was 31/50

you may redo any 2 problems

turn in at the beginning of class next Monday

return both your old exam and the redo...a black will be on the homework site



today

statistical physics - classically speaking





KINETIC THEORY

Remember for an ideal gas $\langle K \rangle = \frac{3}{2} kT$

Imagine now a continuum of velocities and energies

$n(v) dv$ = number of molecules per unit volume
with velocities between v and $v+dv$

↑
density

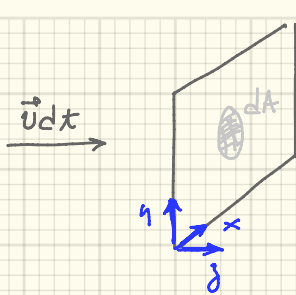
molecules per unit volume = $n = \int n(\vec{v}) d^3v$

or probabilities $f(\vec{v}) d^3v = n(\vec{v}) \frac{d^3v}{n}$

prob of finding
a molecule with
 \vec{v} to $\vec{v}+d\vec{v}$

$f(\vec{v}) d^3v = f(\vec{v}) dv_x dv_y dv_z$

↑
probability density function $f(\vec{v}) = \frac{n(\vec{v})}{n}$



a beautiful wall

each molecule:

contributes pressure on dA
during dt

by transferring momentum P_z during t

momentum transfer from molecules w/ \vec{v} between \vec{v} & $\vec{v} + d\vec{v}$:

$$= (2m v_z) [n(\vec{v}) d^3\vec{v}] dA v_z dt$$

$$= 2m dA dt v_z^2 n(\vec{v}) d^3\vec{v}$$

total momentum transferred

$$\Delta p = 2m dA dt \int_{\text{all } \vec{v}} v_z^2 n(\vec{v}) d^3\vec{v}$$

Pressure

$$P = \frac{\Delta p}{dt dA} = 2m \int v_z^2 n(\vec{v}) d^3\vec{v}$$

no direction is special:

$$n(\vec{v}) = n(v)$$

now $v = \text{speed}$.

$$v_z > 0 \Rightarrow \text{all speeds} \times \frac{1}{2}$$

$$P = \frac{2m}{3} \int_{\text{all } v} \left(\frac{v_z^2 + v_y^2 + v_x^2}{3} \right) n(v) d^3v$$

$$= \frac{m}{3} \int v^2 n(v) d^3v = n \frac{m}{3} \int \underbrace{v^2}_{\langle v^2 \rangle} f(v) d^3v$$

$$= \frac{2}{3} n \int d^3 \left(\frac{1}{2} m v^2 \right) f(v)$$

$$P = \frac{2}{3} n \langle K \rangle \neq n \langle K \rangle = \frac{3}{2} n k T = \frac{1}{2} n m \langle v^2 \rangle$$

↑
per unit
volume, remember

what's $f(v)$?

f depends on ... speed, only ... or its square

so probabilities are independent in different directions:

$$F(v_1, v_2, v_3) = f(v_1) f(v_2) f(v_3) = \phi(v_1^2 + v_2^2 + v_3^2) = \phi(v^2)$$

differentiate wrt v_1 :

$$\frac{df(v_1)}{dv_1} f(v_2) f(v_3) = \frac{d\phi(u)}{du} \frac{\partial u}{\partial v_1}$$

divide by ϕ :

$$\frac{\frac{df(v_1)}{dv_1} f(v_2) f(v_3)}{f(v_1) f(v_2) f(v_3)} = \frac{1}{\phi} \frac{d\phi(u)}{du} \frac{\partial u}{\partial v_1} = \frac{1}{\phi} \frac{d\phi(u)}{du} 2v_1$$

$$\frac{\frac{df(v_1)}{dv_1}}{f(v_1) 2v_1} = \frac{1}{\phi} \frac{d\phi(u)}{du} = \text{constant} = A$$

we can functionally integrate this

$$\frac{\frac{df(v_i)}{dv_i}}{f(v_i)} = Azv_i$$

$$\ln f(v_i) = Av_i^2 + D$$

so $f(v_i) = e^D e^{Av_i^2}$

useful to note: this is a probability and must converge, so the exponent needs to be negative

$$f(v_i) = C e^{-Bv_i^2}$$

normalize: $1 = \int C e^{-Bv_i^2} dv_i$

↑ a member of a class of integrals that will happen a lot

$$\int e^{-x^2} dx = \sqrt{\pi} \quad \text{change variables} \\ x = \sqrt{B} v_i$$

$$1 = C \sqrt{\frac{\pi}{B}} \Rightarrow C = \sqrt{\frac{B}{\pi}}$$

So: $f(v_1) = \sqrt{\frac{B}{\pi}} e^{-Bv_1^2}$ $\frac{1}{B}$
 $\frac{3}{2}$
 $-\frac{1}{2} B^2$

To find B, appeal to physics of ideal gas:

$$\langle v_1^2 \rangle = \sqrt{\frac{B}{\pi}} \int v_1^2 e^{-Bv_1^2} dv_1 \rightarrow \text{trick: } = -\sqrt{\frac{B}{\pi}} \frac{d}{dB} \left[\int e^{-Bv_1^2} dv_1 \right]$$

$$= -\sqrt{\frac{B}{\pi}} \frac{d}{dB} \left[\sqrt{\frac{\pi}{B}} \right]$$

$$= -\sqrt{\frac{B}{\pi}} \sqrt{\pi} \left(-\frac{1}{2} \sqrt{B} \right)$$

$$= \frac{\sqrt{B}}{2} \frac{1}{B^{3/2}} = \frac{\sqrt{B}}{2} \frac{1}{\sqrt{B}} \frac{1}{B}$$

$$\langle v_1^2 \rangle = \frac{1}{2B}$$

remember: $\langle K_1 \rangle = \frac{1}{2} m \langle v_1^2 \rangle = \frac{1}{2} kT$

so $\langle v_1^2 \rangle = \frac{kT}{m}$

$$\frac{kT}{m} = \frac{1}{2B} \Rightarrow B = \frac{m}{2kT}$$

(your book uses a standard notation $\beta = \frac{1}{kT}$)

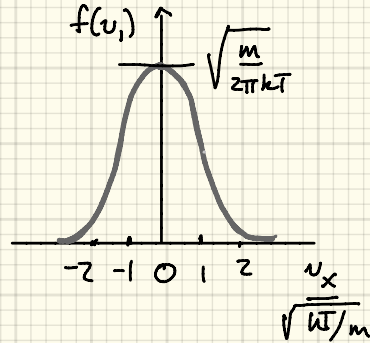
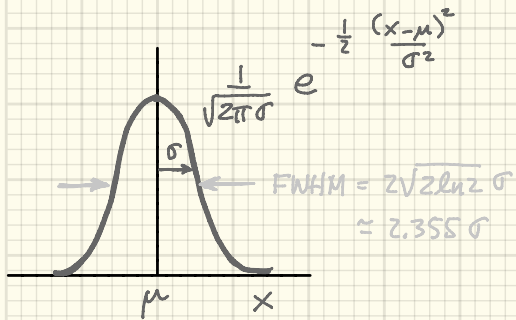
$$f(v_1) = \sqrt{\frac{m}{2\pi kT}} e^{-\frac{mv_1^2}{2kT}}$$

Maxwell Velocity Distribution

$$f(v_x) = \sqrt{\frac{m}{2\pi kT}} e^{-\frac{mv_x^2}{2kT}}$$

This is a Gaussian with mean = 0 & $\sigma = \frac{kT}{m}$

$$\sigma = \frac{kT}{m} \quad \mu = 0$$



remember:

$$f(\vec{v}) d^3v = n(\vec{v}) \frac{d^3v}{n} \quad \text{so,} \quad f(v_i) dv_i = n(v_i) \frac{dv_i}{n_i}$$

But the other directions have identical functional dependencies $f(v_2), f(v_3)$

$$n f(\vec{v}) d^3v = n(\vec{v}) d^3v$$

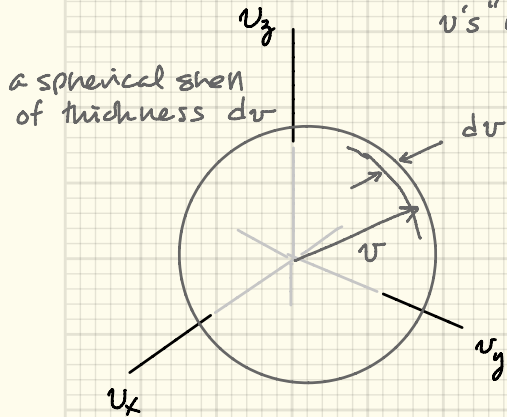
↓

$$\begin{aligned} n f(v_1) f(v_2) f(v_3) dv_1 dv_2 dv_3 &= n \sqrt{\frac{m}{2\pi\hbar T}} e^{-\frac{mv_1^2}{2\hbar T}} \sqrt{\frac{m}{2\pi\hbar T}} e^{-\frac{mv_2^2}{2\hbar T}} \sqrt{\frac{m}{2\pi\hbar T}} e^{-\frac{mv_3^2}{2\hbar T}} dv_1 dv_2 dv_3 \\ &= n \left(\frac{m}{2\pi\hbar T}\right)^{3/2} \exp\left[-\frac{m}{2\hbar T} \underbrace{(v_1^2 + v_2^2 + v_3^2)}_{v^2}\right] dv_1 dv_2 dv_3 \end{aligned}$$

$$n(\vec{v}) d^3\vec{v} = n \left(\frac{m}{2\pi\hbar T}\right)^{3/2} e^{-\frac{mv^2}{2\hbar T}} dv_1 dv_2 dv_3$$

want the number between v and $v+dv \dots$ over all directions

Count # molecules having
 v 's "inside" that shell



inside sphere of radius v
we have volume element $dv_1 dv_2 dv_3 \dots$
replace with volume element appropriate to
the shell

$$V_i = \frac{4}{3} \pi v^3$$

$$V_o = \frac{4}{3} \pi (v+dv)^3$$

$$V_{\text{shell}} = V_o - V_i = \lim \frac{4}{3} \pi [(v+dv)^3 - v^3]$$

$$\begin{aligned} \Rightarrow & (v^2 + dv^2 + 2v dv)(v+dv) - v^3 \\ & = \cancel{v^3} + \cancel{v dv^2} + \cancel{2v^2 dv} + v^2 dv \\ & \quad + \cancel{dv^3} + \cancel{2v dv^2} - \cancel{v^3} \\ & = 3v^2 dv \end{aligned}$$

$$V_{\text{shell}} = \frac{4}{3} \pi \cdot 3v^2 dv = 4\pi v^2 dv$$

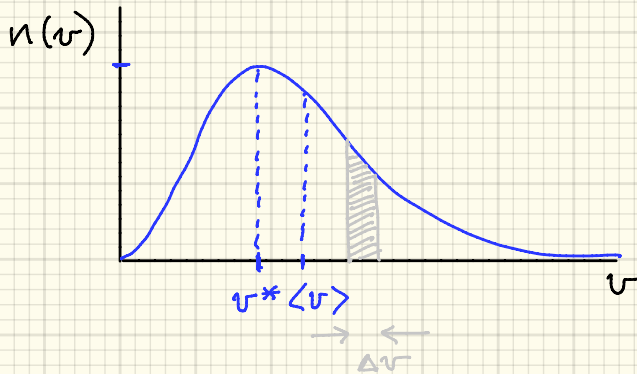
So $dv_1 dv_2 dv_3 = 4\pi v^2 dv$

$$n(\vec{v}) d^3\vec{v} = n \left(\frac{m}{2\pi kT} \right)^{3/2} e^{-\frac{mv^2}{2kT}} dv_1 dv_2 dv_3$$

$$n(v) dv = n \left(\frac{m}{2\pi kT} \right)^{3/2} 4\pi v^2 e^{-\frac{mv^2}{2kT}} dv$$



Maxwell Speed Distribution for Gas Molecules



molecules with speeds in range Δv is the area of that rectangle

The peak:

$$v^*: \quad \frac{dF(v)}{dv} = 0$$

$$4\pi \left(\frac{m}{2\pi\hbar T} \right)^{3/2} \left[2v e^{-mv^2/2\hbar T} - v^2 \frac{1}{2} \frac{m}{\hbar T} 2v e^{-mv^2/2\hbar T} \right] = 0$$

$$2v - v^2 \frac{m^3}{\hbar T} = 0 \Rightarrow v=0 \quad \& \quad v^2 = \frac{2\hbar T}{m}$$

$$\text{so } v^* = \sqrt{\frac{2\hbar T}{m}} \quad \text{or} \quad \hbar T = \frac{1}{2} m v^{*2}$$

$$\langle v \rangle: \quad \int v F(v) dv = 4\pi \left(\frac{m}{2\pi\hbar T} \right)^{3/2} \int_0^{\infty} v^3 e^{-mv^2/2\hbar T} dv$$

$$\int_0^{\infty} x^n e^{-ax^2} dx = \frac{[(n-1)/2]!}{2a^{(n+1)/2}} \quad n \text{ odd}$$

$$= \frac{1 \cdot 3 \cdot 5 \cdots (n-1)}{2^{(n/2)+1} a^{n/2}} \sqrt{\frac{\pi}{a}} \quad n \text{ even}$$

a class of integrals

← that happen a lot

$$\langle v \rangle = \frac{4}{\sqrt{2\pi}} \sqrt{\frac{kT}{m}} > x^* \Rightarrow \frac{\langle v \rangle}{v^*} \approx 1.13$$

Confirmed by Stern ~ 1920

rule of thumb: $kT \sim \frac{1}{40} \text{ eV}$

example - why no hydrogen?

Escape velocity $v_{\text{esc}} \approx 11 \times 10^3 \text{ m/s} \Rightarrow \rho \approx 4 \times 10^{-5}$

notice that $\langle v \rangle \propto \frac{1}{\sqrt{m}} \Rightarrow$ lighter go faster

$$\langle v \rangle = \frac{4}{\sqrt{2\pi}} \sqrt{\frac{kT c^2}{m c^2}} = \frac{4}{\sqrt{2\pi}} c \sqrt{\left(\frac{1}{40} \text{ eV}\right) \frac{1}{938 \times 10^6 \text{ eV}}}$$

$$\langle v \rangle \approx 8.2 \times 10^{-6} c = 2.5 \times 10^3 \text{ m/s}$$

so, $\sim \frac{1}{4}$ of v_{esc} .

water has atomic hydrogen $1 \text{ g/mole} = 0.001 \text{ kg/mole}$

but $\sim 0.01\%$ would have $v > v_{\text{esc}}$ -- that's enough.

5.2×10^{-6}
 $8.2 \times 10^{-6} c$
 2.5×10^3

a game



the energy box

9 units of energy, 0-8

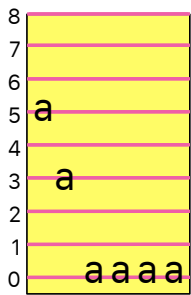
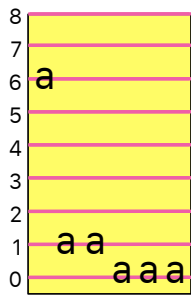
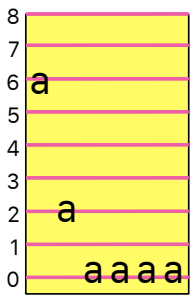
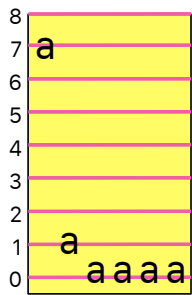
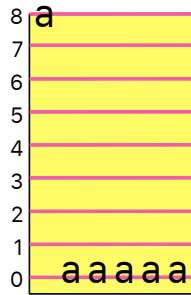
6 molecules

named "a"

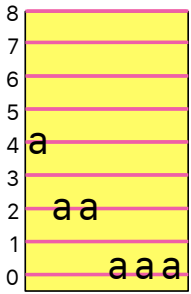
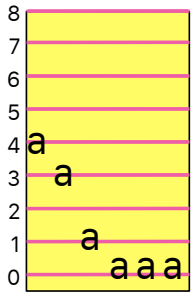
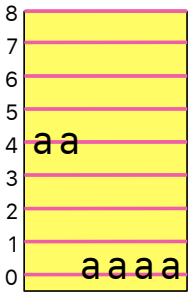
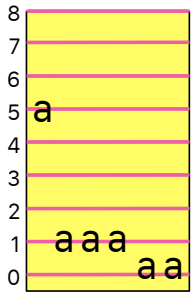
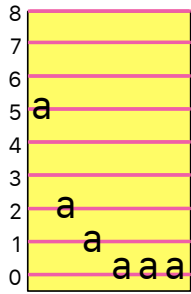
How many ways to make the energy = 8?

when you've seen one "a" you've seen them all
indistinguishable

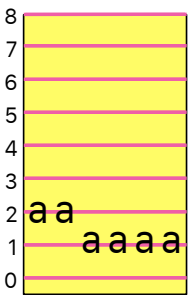
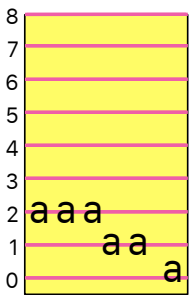
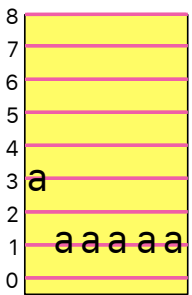
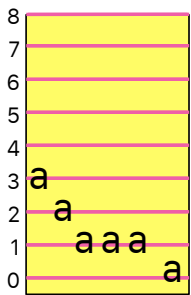
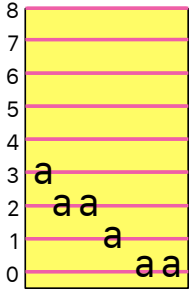
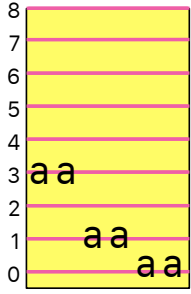
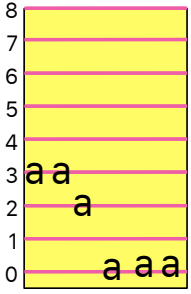
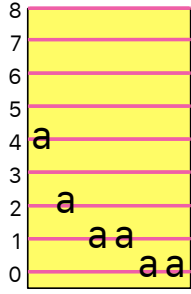




20 arrangements



each is a:
"Macrostate"



alphabet soup



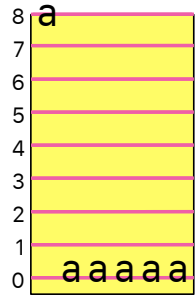
Label each of the individual molecules

name them

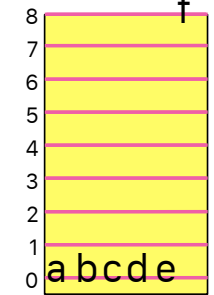
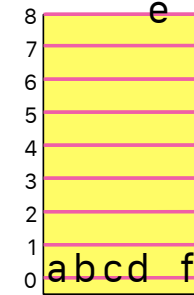
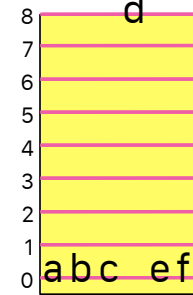
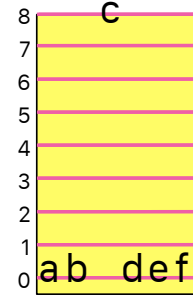
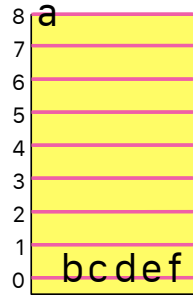
they're then *distinguishable*

If the molecules are distinguishable:

macrostate



microstates



label the energies:

$(n_0, n_1, n_2, n_3, n_4, n_5, n_6, n_7, n_8, n_9)$

macrostate:

$(5, 0, 0, 0, 0, 0, 0, 0, 1)$

is realized as 6 different microstates

a distinguished microstate



be careful

For the $(5,0,0,0,0,0,0,0,1)$

once one is raised to the energy 8 slot, the others could be be rearranged in the energy 0 slot

don't want to double count, so divide them out:

$$\# \text{ microstates in } (5, 0, 0, 0, 0, 0, 0, 0, 1) = \frac{6!}{5!} = 6$$

Fundamental assumption of Statistical Mechanics:

ALL MICROSTATES ARE EQUALLY PROBABLE.

count 'em up...distinguished

	energy slot value										
Mac(i)	0	1	2	3	4	5	6	7	8		# micro
1	5	0	0	0	0	0	0	0	1		6
2	4	1	0	0	0	0	0	1	0		30
3	4	0	1	0	0	0	1	0	0		30
4	4	0	0	1	0	1	0	0	0		30
5	4	0	0	0	2	0	0	0	0		15
6	3	2	0	0	0	0	1	0	0		60
7	3	0	2	0	1	0	0	0	0		60
8	3	0	1	2	0	0	0	0	0		60
9	3	1	1	0	0	1	0	0	0		120
10	3	1	0	1	1	0	0	0	0		120
11	2	0	4	0	0	0	0	0	0		15
12	2	2	0	2	0	0	0	0	0		90
13	2	1	2	1	0	0	0	0	0		180
14	2	2	1	0	1	0	0	0	0		60
15	2	3	0	0	0	1	0	0	0		30
16	1	4	0	0	1	0	0	0	0		120
17	1	3	1	1	0	0	0	0	0		60
18	1	2	3	0	0	0	0	0	0		60
19	0	4	2	0	0	0	0	0	0		15
20	0	5	0	1	0	0	0	0	0		6
$n(E)$											1287

ALL MICROSTATES ARE EQUALLY PROBABLE.

How many microstates contribute to each E?

Take $E=0$:

likelihood to be in Mac(1) and be $E=0$ is $6/1287$

there are 5 microstates that make an $E=0$ macrostate

$$P_1(E=0) = 5 \left(\frac{6}{1287} \right) = 0.023$$

$$P_2(E=0) =$$

count 'em up:

	energy slot value										
Mac(i)	0	1	2	3	4	5	6	7	8		# micro
1	5	0	0	0	0	0	0	0	1		6
2	4	1	0	0	0	0	0	1	0		30
3	4	0	1	0	0	0	1	0	0		30
4	4	0	0	1	0	1	0	0	0		30
5	4	0	0	0	2	0	0	0	0		15
6	3	2	0	0	0	0	1	0	0		60
7	3	0	2	0	1	0	0	0	0		60
8	3	0	1	2	0	0	0	0	0		60
9	3	1	1	0	0	1	0	0	0		120
10	3	1	0	1	1	0	0	0	0		120
11	2	0	4	0	0	0	0	0	0		15
12	2	2	0	2	0	0	0	0	0		90
13	2	1	2	1	0	0	0	0	0		180
14	2	2	1	0	1	0	0	0	0		60
15	2	3	0	0	0	1	0	0	0		30
16	1	4	0	0	1	0	0	0	0		120
17	1	3	1	1	0	0	0	0	0		60
18	1	2	3	0	0	0	0	0	0		60
19	0	4	2	0	0	0	0	0	0		15
20	0	5	0	1	0	0	0	0	0		6
$n(E)$	2.31										1287

ALL MICROSTATES ARE EQUALLY PROBABLE.

How many microstates contribute to each E?

Take $E=0$:

likelihood to be in Mac(1) and be $E=0$ is $6/1287$

there are 5 microstates that make an $E=0$ macrostate

$$P_1(E=0) = 5 \left(\frac{6}{1287} \right) = 0.023$$

$$P_2(E=0) = 4 \left(\frac{30}{1287} \right) = 0.093$$

⋮

$$\sum_{i=1}^{20} P_i(E=0) = 2.31$$

count 'em up:

Mac(i)	energy slot value									# micro
	0	1	2	3	4	5	6	7	8	
1	5	0	0	0	0	0	0	0	1	6
2	4	1	0	0	0	0	0	1	0	30
3	4	0	1	0	0	0	1	0	0	30
4	4	0	0	1	0	1	0	0	0	30
5	4	0	0	0	2	0	0	0	0	15
6	3	2	0	0	0	0	1	0	0	60
7	3	0	2	0	1	0	0	0	0	60
8	3	0	1	2	0	0	0	0	0	60
9	3	1	1	0	0	1	0	0	0	120
10	3	1	0	1	1	0	0	0	0	120
11	2	0	4	0	0	0	0	0	0	15
12	2	2	0	2	0	0	0	0	0	90
13	2	1	2	1	0	0	0	0	0	180
14	2	2	1	0	1	0	0	0	0	60
15	2	3	0	0	0	1	0	0	0	30
16	1	4	0	0	1	0	0	0	0	120
17	1	3	1	1	0	0	0	0	0	60
18	1	2	3	0	0	0	0	0	0	60
19	0	4	2	0	0	0	0	0	0	15
20	0	5	0	1	0	0	0	0	0	6
$n(E)$	2.31	1.54	0.98	0.59	0.33	0.16	0.07	0.02	0.005	1287

ALL MICROSTATES ARE EQUALLY PROBABLE.

How many microstates contribute to each E?

Take $E=0$:

likelihood to be in Mac(1) and be $E=0$ is $6/1287$

there are 5 microstates that make an $E=0$ macrostate

$$P_1(E=0) = 5 \left(\frac{6}{1287} \right) = 0.023$$

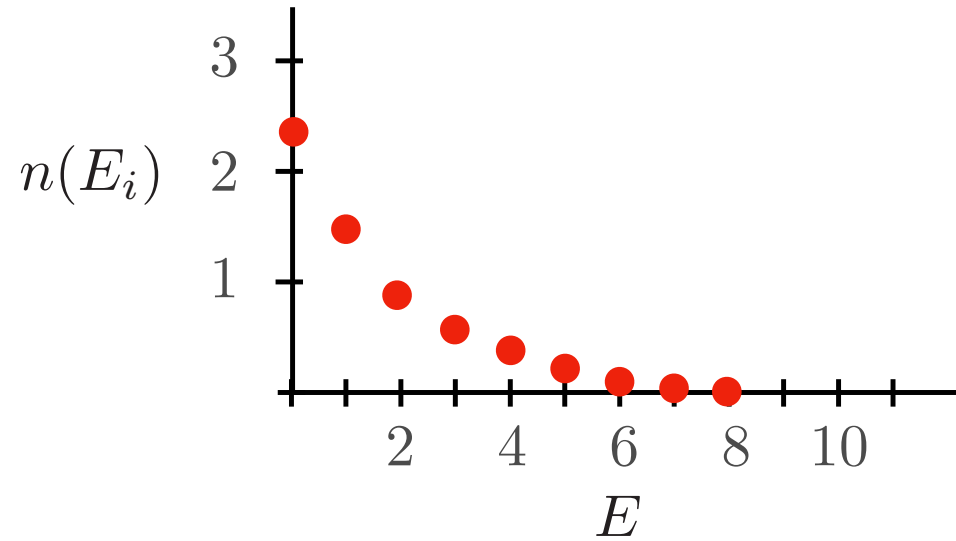
$$P_2(E=0) = 4 \left(\frac{30}{1287} \right) = 0.093$$

•
•
•

$$\sum_{i=1}^{20} P_i(E=0) = 2.31$$

plot them...

energy slot value										
Mac(i)	0	1	2	3	4	5	6	7	8	# micro
1	5	0	0	0	0	0	0	0	1	6
2	4	1	0	0	0	0	0	1	0	30
3	4	0	1	0	0	0	1	0	0	30
4	4	0	0	1	0	1	0	0	0	30
5	4	0	0	0	2	0	0	0	0	15
6	3	2	0	0	0	0	1	0	0	60
7	3	0	2	0	1	0	0	0	0	60
8	3	0	1	2	0	0	0	0	0	60
9	3	1	1	0	0	1	0	0	0	120
10	3	1	0	1	1	0	0	0	0	120
11	2	0	4	0	0	0	0	0	0	15
12	2	2	0	2	0	0	0	0	0	90
13	2	1	2	1	0	0	0	0	0	180
14	2	2	1	0	1	0	0	0	0	60
15	2	3	0	0	0	1	0	0	0	30
16	1	4	0	0	1	0	0	0	0	120
17	1	3	1	1	0	0	0	0	0	60
18	1	2	3	0	0	0	0	0	0	60
19	0	4	2	0	0	0	0	0	0	15
20	0	5	0	1	0	0	0	0	0	6
$n(E)$	2.31	1.54	0.98	0.59	0.33	0.16	0.07	0.02	0.005	1287



What's that look like?

back

Classical Distributions have the following properties:

1. Particles are identical in terms of physics properties but distinguishable in terms of position. So energies are identical.
2. The equilibrium distribution is the most probable way subject to constraints on the number of particles and the total energy.
3. There is no limit on the fraction of the total number of particles in a given energy state.



Energy ... sneak up on something general.

Our gas model:

$$E = \frac{1}{2} m v^2$$

$$dE = m v dv$$

$$dv = \frac{dE}{m v} = \frac{dE}{\sqrt{2mE}}$$

$$\text{So } n(v) dv = n \left(\frac{m}{2\pi kT} \right)^{3/2} 4\pi v^2 e^{-mv^2/2kT} dv$$

$$n(E) dE = n \left(\frac{m}{2\pi kT} \right)^{3/2} 4\pi \frac{2E}{m} e^{-E/kT} \frac{dE}{\sqrt{2mE}}$$

$$n(E) dE = n \frac{2}{\sqrt{\pi}} \frac{1}{(kT)^{3/2}} E^{1/2} e^{-E/kT} dE$$

normalization:
gas model

from $dE \neq dv_1 dv_2 dv_3$ volumes

completely general

$$n(E) dE = A e^{-E/kT} dE$$

$$n(E)dE = A e^{-E/kT} dE$$

Maxwell-Boltzmann Distribution Function

$$F_{MB} = A e^{-E/kT}$$

$e^{-E/kT}$: "Boltzmann Factor"

$n(E)$ is the distribution of the number of states with energies between E and $E + dE$

Write generally: $n(E) = g(E)F_{MB}(E)$

$g(E)$ is the number of states per unit energy range

→ the number of ways a system can achieve an energy E

Density of States

$$n(E) = g(E) F_{MB}(E)$$

Continuous

But also can be discrete

$$n_i(E) = g_i F_{MB}(E)$$

↑

still # states that can achieve E

now: degeneracy.