Two key formulas from previous lecture and Schroeder Section 6.2

$$P_s = \frac{e^{-\beta E_s}}{Z} \qquad \beta = \frac{1}{kT}$$

$$\langle X \rangle = \sum_s P_s X_s = \frac{1}{Z}\sum_s e^{-\beta E_s} X_s$$

$$\langle E \rangle = \sum_s P_s E_s = -\frac{\partial \ln Z}{\partial \beta}$$

We applied these to paramagnet: $E_s = \mp \mu B$ 2 energy levels

Einstein solid: $E_s = n\epsilon$, $n = 0, 1, 2, \ldots$ ∞'ly many levels

Today's goals:

- discuss some elementary properties of Z and P_s, e.g. low- and high-T behavior, convergence of Z
- heat capacity $C(T)$ related to rotation of heteronuclear (non-symmetric) diatomic molecule like HCl
- applying Boltzmann factor to systems with continuously varying energy levels such as gas of atoms, $E_s = E_p = \frac{p^2}{2m}$

Derive equipartition theorem, Maxwell-Boltzmann speed distribution

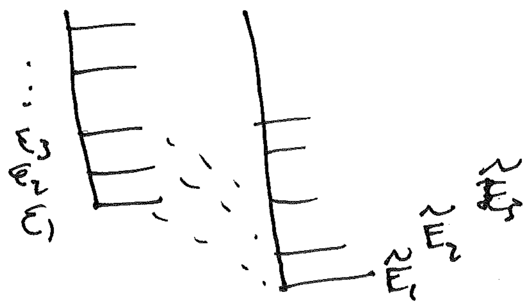
Properties of $e^{-\beta E_s}$, Z, P_s

<u>Observation:</u> Origin of energy scale used to measure energies E_s does not matter, get same P_s's, same averages $\langle X \rangle$ of any quantity X_s that varies with the state

Let's say small system has energy levels $\{E_s\}$, it is in thermodynamic equilibrium with large reservoir of temp T

Say someone else interested in this same system but uses different energy levels

$$\tilde{E}_s = E_s + E_0$$



all levels shifted by same constant amount E_0.

Then: $\tilde{Z}$ = partition f^n based on energies $\tilde{E}_s$

$$= \sum_s e^{-\beta \tilde{E}_s} = \sum_s e^{-\beta(E_s+E_0)} = \sum_s e^{-\beta E_s} e^{-\beta E_0}$$

$$= e^{-\beta E_0} \sum_s e^{-\beta E_s} = e^{-\beta E_0} Z$$

so $$\tilde{Z} = e^{-\beta E_0} Z$$

$$\tilde{P}_s = \frac{e^{-\beta \tilde{E}_s}}{\tilde{Z}} = \frac{e^{-\beta(E_s+E_0)}}{e^{-\beta E_0} Z} = \frac{e^{-\beta E_0}}{e^{-\beta E_0}} \frac{e^{-\beta E_s}}{Z} = P_s$$

So shifting energies $E_s \to \tilde{E}_s = E_s + E_0$

does not change probabilities: $\tilde{P}_s = P_s$

so averages don't change:

$$\widetilde{\langle X \rangle} = \sum_s \tilde{P}_s X_s = \sum_s P_s X_s = \langle X \rangle$$

<u>Deduction</u>: We can always choose the ground state E_1 to be zero by shifting all levels by $E_0 = -E_1$

$$E_s \to \hat{E}_s = E_s - E_1 \Rightarrow \hat{E}_1 = 0$$

$$E_1 = 0 \leqslant E_2 \leqslant E_3 \leqslant \cdots$$

$$Z = 1 + e^{-\beta E_2} + e^{-\beta E_3} + \cdots$$

<u>Deduction</u>: If we have arranged energies to have $E_1 = 0$

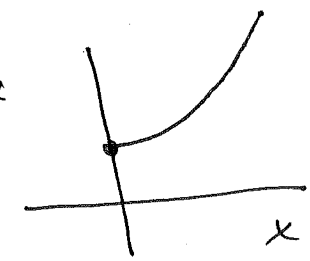
so $\quad E_1 = 0 \leqslant E_2 \leqslant \cdots$

then $\quad P_1 = \dfrac{e^{-\beta E_1}}{Z} = \dfrac{1}{Z}$ assuming $E_1 = 0$

so partition f^n has physical meaning that $\frac{1}{Z}$ = prob of being in $E_1 = 0$ ground state when reservoir has temp. T.

Properties of Z, P_s, $\langle X \rangle$ continued

Deduction: $1 \leq Z(T) \leq \infty$



Assume $E_1 = 0 \leq E_2 \leq \cdots$

$$Z = 1 + e^{-\beta E_2} + e^{-\beta E_3} + \cdots$$

But $e^x \geq 1$ if $x \geq 0$ so $\boxed{Z \geq 1}$

Small-T limit of Z and P_s:

For small temperatures T, $kT \ll E_2, E_3, \cdots$

$$\beta = \frac{1}{kT} \text{ is large}$$

$$e^{-\beta E_s} = e^{-\frac{E_s}{kT}} = \frac{1}{e^{E_s/(kT)}} \sim 0$$

so:

$$Z = 1 + e^{-\beta E_2} + e^{-\beta E_3} + \cdots$$

$$\simeq 1 + 0 + 0$$

$$\simeq 1$$

$$P_1 \simeq \frac{1}{Z} = 1 \qquad P_n \simeq \frac{e^{-\beta E_s}}{1} \simeq 0 \qquad \langle X \rangle = X_1$$

so one is certain to be in ground state for T small enough.

High-temperature limit: Z, P_s, $\langle X \rangle$

For T large, $\beta = \frac{1}{kT}$ is small, $e^{-\beta E_s} \to e^{0} \to 1$

$$Z = 1 + e^{-\beta E_2} + e^{-\beta E_3} + \cdots$$

$$\simeq 1 + 1 + 1 + \cdots$$

will discuss convergence problem in a moment

If there are finitely many energy levels N, $Z \to N$ as $T \to \infty$

$$P_s = \frac{e^{-E_s/(kT)}}{Z} \to \frac{1}{N} \quad \text{as } T \to \infty$$

all levels are equally likely at high-enough temperatures

$$\langle X \rangle = \sum_s P_s X_s = \sum_{s=1}^{N} \left(\frac{1}{N}\right) X_s = \frac{1}{N} \sum_{s=1}^{N} X_s$$

thermal average

$=$ direct average of ~~energy levels~~ X values: $\frac{X_1 + X_2 + \cdots + X_N}{N}$

arithmetic average

Another way to see this result that avoids possible divergence of Z: calculate relative probabilities of two different states

$$\frac{P_s}{P_{s'}} = \frac{e^{-\beta E_s}/Z}{e^{-\beta E_{s'}}/Z} = e^{-\beta(E_s - E_{s'})}$$

as $T \to \infty$, $\beta \to 0$, $\frac{P_s}{P_{s'}} \to e^{0} = 1$ for any two states

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Challenge (not a potential quiz or exam problem):

(a) For small temperature T, calculate the leading correction to the average of some quantity:

$$\langle X \rangle = X_1 + [\text{some small correction}] \overset{?}{=}$$

hint: T small implies $e^{-\beta E_s}$ small

(b) For large temperature T, calculate the leading correction to the average:

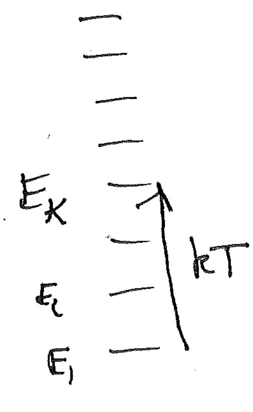
$$\langle X \rangle = \frac{X_1 + \cdots + X_N}{N} + [\text{some small correction}] \overset{?}{=}$$

hint: expand in β, small parameter

Deduction: physical meaning of partition function for some intermediate temperature T is number of energy states within range kT of ground state $E_1 = 0$

For $E_s \ll kT$, $e^{-\beta E_s} \simeq e^{-\frac{E_s}{kT}} \simeq 1$

$E_s \gg kT$, $e^{-\beta E_s} \simeq e^{-\frac{E_s}{kT}} \simeq 0$



$$Z = 1 + e^{-\beta E_i} + \cdots + e^{-\beta E_K} + \cdots + e^{-\beta E_s}$$

assume $kT \simeq E_K$ for some integer K

$$\simeq \underbrace{1 + 1 + \cdots + 1}_{K} + 0 + 0 + \cdots$$

$$\simeq K$$

Z generalizes multiplicity ~~of~~ Ω, gives all energy states within distance kT of E_1

Examples of Z, P_s

Problem 6.3, p. 225 Schroeder

system with two states $E_1 = 0$, $E_2 = 2\,eV$

$$1\,eV = 1.6 \cdot 10^{-19}\,J \simeq 2 \cdot 10^{-19}\,J$$

$kT = 1\,eV$ when $T \simeq 12{,}000\,K$ (hot!!)

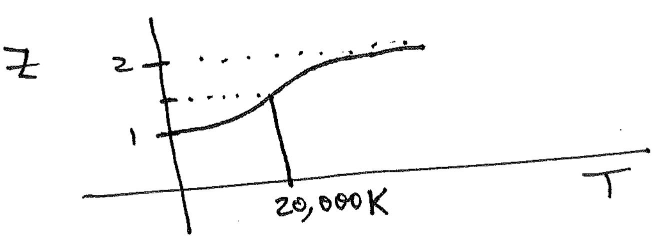
$T = 300\,K$ room temp corresponds to $E \simeq \frac{1}{40}\,eV$

$$k \simeq 9 \cdot 10^{-5}\,\frac{eV}{K}$$

For estimation: $e^3 \approx 20$ $\quad e^{23} \simeq 10^{10}$ $\quad 2^{10} \simeq 10^3$ (1024)

What is $Z(T)$?

$$Z = 1 + e^{-\frac{2eV}{kT}} = 1 + e^{-\frac{20{,}000}{T}} \qquad 1 \le Z \le 2$$



$T = 2000\,K \quad Z = 1 + e^{-10} \approx 1.0001$

$T = 20{,}000\,K \quad Z = 1 + e^{-1} \approx 1.4$

$e^3 \simeq 20 \Rightarrow$
$e^{10} \simeq e^9 \approx (e^3)^3 \approx 8 \cdot 10^3$
$\simeq 10^4$

For large T, $P_1 = P_2 = \frac{1}{2}$

$$\langle X \rangle = \frac{X_1 + X_2}{2}$$ high temp limit of thermal average

$$= X_1$$ low temp. limit $T \to 0$

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Partition Function for Hydrogen Atom

Astrophysics problem: Sun has surface temp of $T \simeq 6000\,K$, what is prob to observe H atom in 1st excited energy level?

E_2 — — — — ← degenerate level, 4 states have same energy

E_1 —

E_n notation, subscript n means <u>distinct</u> energy values

$$E_0 \leqslant E_{s_1} \leqslant E_{s_2} \leqslant \cdots E_s \qquad \text{states can be degenerate}$$

or

$$E_0 < E_1 < E_2 \cdots < E_n$$

$$E_n = -\frac{R}{n^2} \qquad R = \text{Rydberg} \simeq 13.6\,eV \qquad n = 1, 2, \ldots$$

shift all levels so $E_1 = 0$:

$$\boxed{E_n = R\left(1 - \frac{1}{n^2}\right)} \qquad n = 1, 2, \ldots$$

$$0 \leqslant E_n \leqslant R \qquad \text{infinitely many levels in finite } \text{~~area~~ range}$$

Z_H = partition f^n for hydrogen atom

$$= \sum_s e^{-\beta E_s} \qquad \text{sum over all states}$$

$$= \sum_n d_n e^{-\beta E_n} \qquad \text{sum over distinct energies}$$

d_n = degeneracy of n^{th} energy level $E_n = \Omega(E_n)$

$\boxed{d_n = n^2}$ for hydrogen atom (from QM solution)

So for H atom

$$Z_H = 1 + 4e^{-\beta E_2} + 9e^{-\beta E_3} + \cdots + n^2 e^{-\beta E_n} + \cdots$$

For $E_2 = 10.2\,eV$, $T_{sun} = 6000\,K \times \frac{1\,eV}{12000\,K} \simeq 0.5\,eV$

$$e^{-E_2/(kT)} \simeq e^{-\frac{10.2}{0.5}} \simeq e^{-20} \simeq 10^{-9} \quad \underline{\text{tiny}}$$

$$e^{20} = \frac{e^{23}}{e^3} \simeq \frac{10^{10}}{20} \simeq 10^9$$

$e^{-E_3/kT}$ even smaller

so surface of Sun is <u>cold</u> compared to energy scale of excited states

$T \simeq 0 \qquad Z \simeq 1$

$\text{prob}(E=E_2)$ = prob for H atom to be in any one of the 4 excited states with $E_s = E_2 = 10.2\,eV$

$$\cong \frac{4e^{-E_2/kT}}{Z} \simeq \boxed{4 \cdot 10^{-9}}$$

<u>so only about four H atoms in a billion are excited to 1st level!</u>

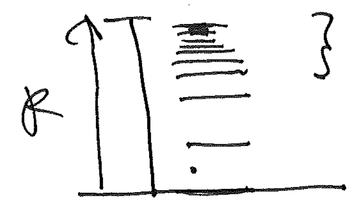
at room temperature, $T \simeq 300$, $p(E=E_2) \sim 4e^{\frac{-10.2}{(1/40)}} \simeq e^{-400} \simeq 10^{-100}$

utterly negligible since roomful of H has $\simeq 10^{28}$ atoms.

so $T=300$ is effectively absolute zero if you are an H atom

Seeming divergence of partition f^n for H

Look more carefully at Z_H, partition f^n for H atom



} levels get arbitrarily close as $n \to \infty$

$$E_n = R\left(1 - \frac{1}{n^2}\right)$$

$$Z_H = \sum_{n=1}^{\infty} n^2 e^{-\beta E_n}$$

For $T = 6000\,K$, we argued $e^{-\beta E_n}$ is tiny for $n \geq 2$ and we approximated $Z \simeq 1$. But there are infinitely many terms in Z, can they accumulate to something substantial, cause error?

Note:

$$E_1 < E_2 < \cdots < E_\infty$$

$$\Rightarrow \quad -\beta E_1 > -\beta E_2 > \cdots > -\beta E_\infty$$

$$\Rightarrow \quad e^{-\beta E_1} > e^{-\beta E_2} > \cdots > e^{-\beta E_\infty}$$

since $x > y \Rightarrow e^x > e^y$

e^x is monotonic increasing f^n

So:

$$Z = \sum_{n=1}^{\infty} n^2 e^{-\beta E_n} > \sum_{n=1}^{\infty} n^2 e^{-\beta E_\infty}$$

$$= e^{-\beta R} \underbrace{\sum_{n=1}^{\infty} n^2}_{\text{diverges}}$$

In fact:

$$\sum_{n=1}^{k} n^2 = \frac{k(k+1)(2k+1)}{6} = \frac{k^3}{3} + \frac{k^2}{2} + \frac{k}{6} \simeq \frac{k^3}{6} \quad k \gg 1$$

so looks like serious trouble here, Z diverges to ∞ for H atom

But we need to think physically, not just mathematically: what is happening to H atom has it enters higher and higher excited states? It is growing rapidly in size!

$$r_n = r_B n^2 \qquad r_B = \text{Bohr radius} \cong 5\cdot 10^{-11}\,m$$

At some point, H atom is as big as container of gas (or even as big as universe) at which point the energy levels $E_n = R\left(1-\frac{1}{n^2}\right)$ are wrong, need to include interaction of fat H atom with walls. For large n, when electron is far from nucleus, better approximation to energy levels is free particle in box of size L:

$$E_n = \frac{h^2 n^2}{8mL^2} \propto n^2 \quad \propto \frac{1}{L^2}$$

(See Schroeder pages 368–369). For $E_n \propto n^2$, levels are not bounded and partition $f^{\underline{n}}$ easily seen to converge, e.g. by integral convergence test (giving Gaussian) or by ratio test $\lim_{n\to\infty} \frac{a_{n+1}}{a_n} = p = 0 < 1$ ✓

Let's see how this works:

$$r_n \simeq 1m = (5\cdot 10^{-11} m)\, n^2 \Rightarrow n \simeq 10^5$$

$r_n \simeq$ size of universe

$$= 14\cdot 10^9\, ly \times \frac{10^{16} m}{ly} = (5\cdot 10^{-11} m)\, n^2 \Rightarrow n \simeq 10^{18}$$

at room temp, $e^{-R/kT} \simeq 10^{-230}$ but $\sum_{i=1}^{10^{18}} n^2 \simeq \frac{(10^{18})^3}{3} \simeq 10^{54}$

$Z = 1 + 10^{-230}\cdot 10^{54} \simeq 1$ excellent approx