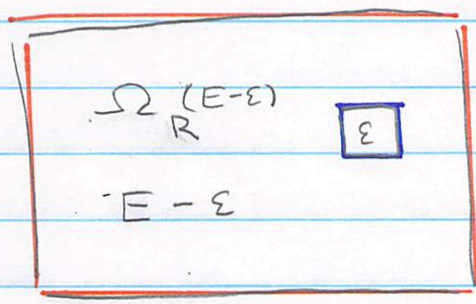
The Boltzmann Factor

- We can use notions of entropy to derive the Boltzmann Distribution

$$P_{\text{micro state } s} \propto e^{-\mathcal{E}_s/k_B T} \qquad \mathcal{E}_s \equiv \text{energy of microstate}$$

- Take a subsystem which is small compared to the total, Iteracting with a reservoir (the rest of the system)



- The total system has energy E. Let us require that the subsystem be in <u>one</u> microstate with energy ε. The remaining system has energy $E-\varepsilon$. The probability of this configuation is

$$P(E-\varepsilon;\varepsilon) \propto \Omega_R(E-\varepsilon)\ 1$$

(Before we had $\Omega_1(E_1)\,\Omega_2(E_2)$, now system 2 is in exactly one state). $\Omega_R(E-\varepsilon) = \Omega_1$ is the number of microstates associated with the reservoir.

- Take the log

$$\log P(\varepsilon) = \text{const} + \log \Omega_R(E-\varepsilon) + \cancel{\log 1}^{\,0}$$

- Now ε is small compared to the total system

$$\log \Omega_R(E-\varepsilon) = \log \Omega_R(E) - \left(\frac{\partial \log \Omega_R(E)}{\partial E}\right)\varepsilon$$

Or since

$$\frac{1}{k_B T} = \frac{\partial \log \Omega_R(E)}{\partial E}$$

- We have

$$\log P(\varepsilon) = \underbrace{\text{const} + \log \Omega_R(E)}_{\substack{\text{all const} \\ \text{indep of } \varepsilon}} - \frac{\varepsilon}{k_B T}$$

- So exponentiating

$$\boxed{P(\varepsilon) = (\text{Const})\, e^{-\varepsilon/k_B T}}$$

The constant can be found from normalization

$$\sum_s P(\varepsilon_s) = 1 \quad \text{or} \quad \sum_s C e^{-\varepsilon_s/kT} = 1$$

i.e.

$$C \equiv \frac{1}{Z} \quad \text{with} \quad \boxed{Z = \sum_s e^{-\varepsilon_s/kT}}$$

So finally

$$\boxed{P_{\substack{\text{state}\\ s}} = \frac{1}{Z} e^{-\varepsilon_s/kT}}$$

Einstein Model of Solid

N atoms connected by springs.

- As a simple picture of 1d solid, might consist of N oscillators. For simplicity take each of the oscillators to be independent

- integer $q \gg 1$

  Then the total Energy is $U = q\hbar\omega_0$.
  q is the total number of quanta of energy to be <u>shared</u> or partitioned amongst the N atoms

- For definiteness take $\underset{}{\overset{= N}{400}}$ atoms and $\overset{= q}{400}$ quanta of energy. $1 \text{ quanta} = 1\hbar\omega_0$

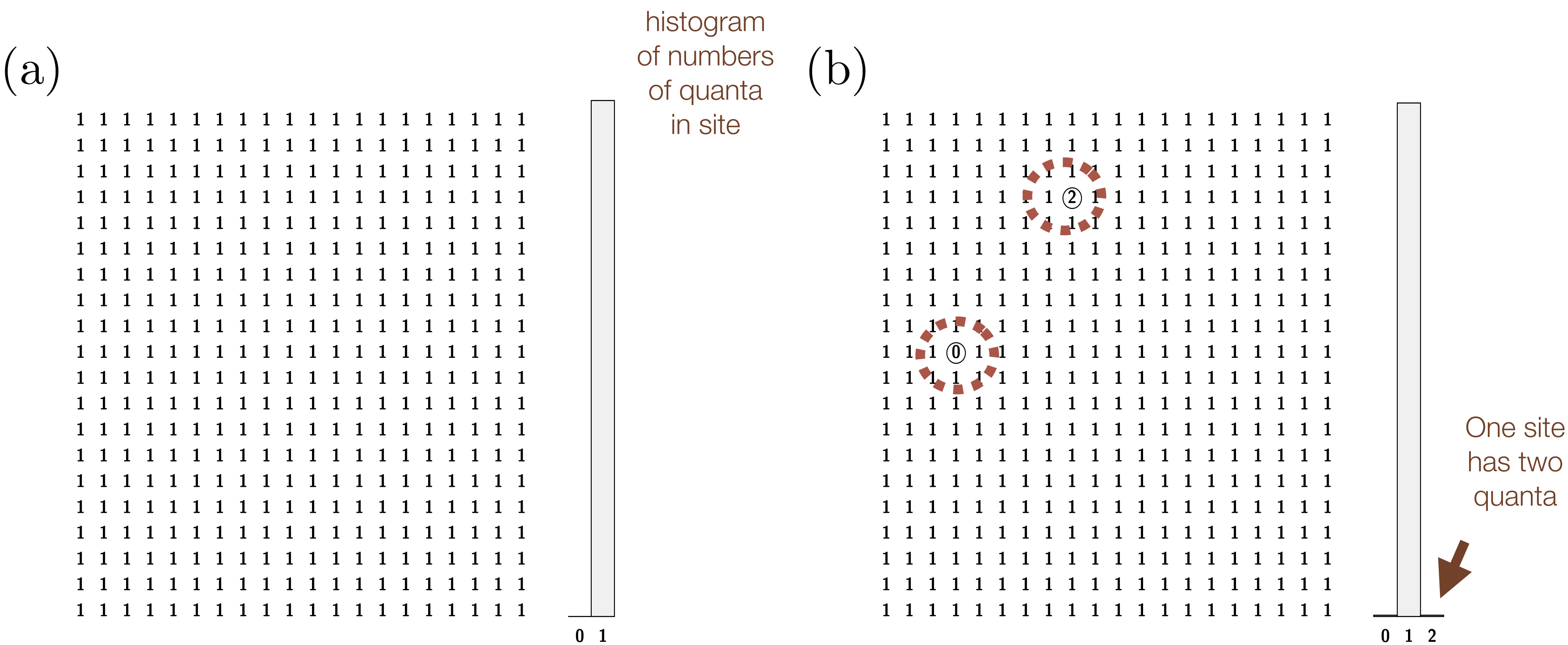
- One possible configuration is that each atom has one quanta of energy:

  This is shown on the slide below.

- Now pick one oscillator at random and transfer one quanta of energy to another randomly chosen site,

  We get another possible state see slide.

20x20 oscillators (sites), with 20x20 quanta of energy, one per site

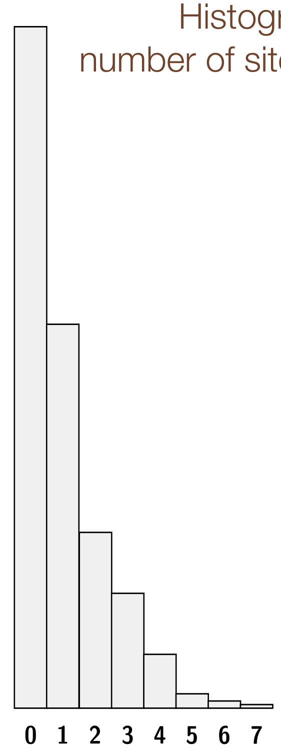


Start with initial state (a), pick two oscillators randomly, and transfer an energy quanta between the two sites. You find (b).

Now repeat the process: there are 10^{240} ways to share the energy

(c)

0	0	1	0	1	1	0	0	0	0	1	3	1	2	0	0	0	1	0	0
0	1	0	5	1	4	0	1	1	0	2	0	1	0	0	0	1	3	1	0
0	3	0	1	1	0	1	0	1	2	3	0	0	1	2	4	1	0	3	2
2	1	2	4	3	4	0	0	1	1	0	4	0	1	0	2	1	1	1	0
1	2	0	0	1	0	1	0	4	0	0	0	0	0	0	1	2	0	0	0
0	1	1	1	0	4	0	1	0	2	2	1	3	1	0	0	3	0	0	0
1	0	0	0	0	2	0	0	2	0	6	0	3	1	3	0	2	1	1	0
2	2	4	1	2	0	0	0	0	1	3	0	2	0	0	0	2	1	3	2
3	0	0	2	1	1	2	0	0	0	0	0	0	0	1	0	0	0	1	0
1	3	1	1	0	0	0	0	3	0	1	0	1	0	0	0	0	2	0	0
2	1	0	1	0	1	2	0	4	1	0	1	0	2	1	1	1	1	1	2
1	0	0	0	0	0	1	4	2	2	2	0	1	0	0	2	0	0	1	1
0	3	0	1	1	0	0	0	1	0	0	3	2	0	0	2	2	2	0	3
5	2	0	0	1	0	0	2	1	0	0	0	1	0	0	1	0	3	0	3
1	1	0	3	0	0	1	4	1	0	2	0	0	6	3	0	1	0	1	3
0	1	1	0	2	0	0	4	1	3	2	0	0	0	0	2	1	0	2	0
1	4	1	0	3	0	2	1	1	0	3	1	1	0	3	1	3	0	2	0
5	0	3	1	7	2	2	0	0	1	0	0	1	1	1	0	0	0	0	3
0	0	5	0	0	1	0	1	0	2	2	1	0	4	3	3	0	0	1	0
0	0	0	0	0	1	0	1	0	0	0	0	1	0	4	1	0	1	1	1



Histogram of N(n) :
number of sites N with n quanta

A typical distribution distribution is shown above: What is $N(n)$?

- Repeating the process, the system is equally likely to be in any of its accessible micro states. The system is thermalized:

$$P_m = C$$

probability to be in a microstate m

Normalizing, then $\sum_m P_m = 1$ or $C \sum_m 1 = 1$

this letterally counts all states

or

$$C\,\Omega(E) = 1 \quad \text{and} \quad \boxed{P_m = \frac{1}{\Omega(E)}}$$

This probability dist is known as the <u>micro-canonical ensemble</u>

- The entropy of the ensemble is

$$\boxed{S = k_B \ln \Omega = -k_B \ln P_m}$$

Micro-canonical only

- For the problem at hand, you will show for $N = q = 400$, that $\Omega = 10^{240}$. So

$$\frac{S}{k_B} = 240 \ln 10 \simeq 554.9$$

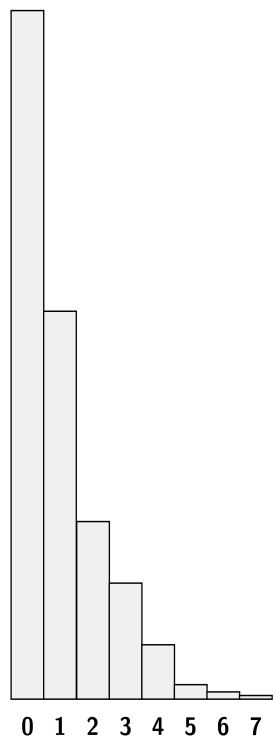
You will count the states and find $\Omega = 10^{240}$ in homework.

What is $N(n)$?

(c)

Histogram of energies
in units of $\epsilon_0 = \hbar\omega_0$

0	0	1	0	1	1	0	0	0	0	1	3	1	2	0	0	0	1	0	0
0	1	0	5	1	4	0	1	1	0	2	0	1	0	0	0	1	3	1	0
0	3	0	1	1	0	1	0	1	2	3	0	0	1	2	4	1	0	3	2
2	1	2	4	3	4	0	0	1	1	0	4	0	1	0	2	1	1	1	0
1	2	0	0	1	0	1	0	4	0	0	0	0	0	0	1	2	0	0	0
0	1	1	1	0	4	0	1	0	2	2	1	3	1	0	0	3	0	0	0
1	0	0	0	0	2	0	0	2	0	6	0	3	1	3	0	2	1	1	0
2	2	4	1	2	0	0	0	0	1	3	0	2	0	0	0	2	1	3	2
3	0	0	2	1	1	2	0	0	0	0	0	0	0	1	0	0	0	1	0
1	3	1	1	0	0	0	0	3	0	1	0	1	0	0	0	0	2	0	0
2	1	0	1	0	1	2	0	4	1	0	1	0	2	1	1	1	1	1	2
1	0	0	0	0	0	1	4	2	2	2	0	1	0	0	2	0	0	1	1
0	3	0	1	1	0	0	0	1	0	0	3	2	0	0	2	2	2	0	3
5	2	0	0	1	0	0	2	1	0	0	0	1	0	0	1	0	3	0	3
1	1	0	3	0	0	1	4	1	0	2	0	0	6	3	0	1	0	1	3
0	1	1	0	2	0	0	4	1	3	2	0	0	0	0	2	1	0	2	0
1	4	1	0	3	0	2	1	1	0	3	1	1	0	3	1	3	0	2	0
5	0	3	1	7	2	2	0	0	1	0	0	1	1	1	0	0	0	0	3
0	0	5	0	0	1	0	1	0	2	2	1	0	4	3	3	0	0	1	0
0	0	0	0	0	1	0	1	0	0	0	0	1	0	4	1	0	1	1	1



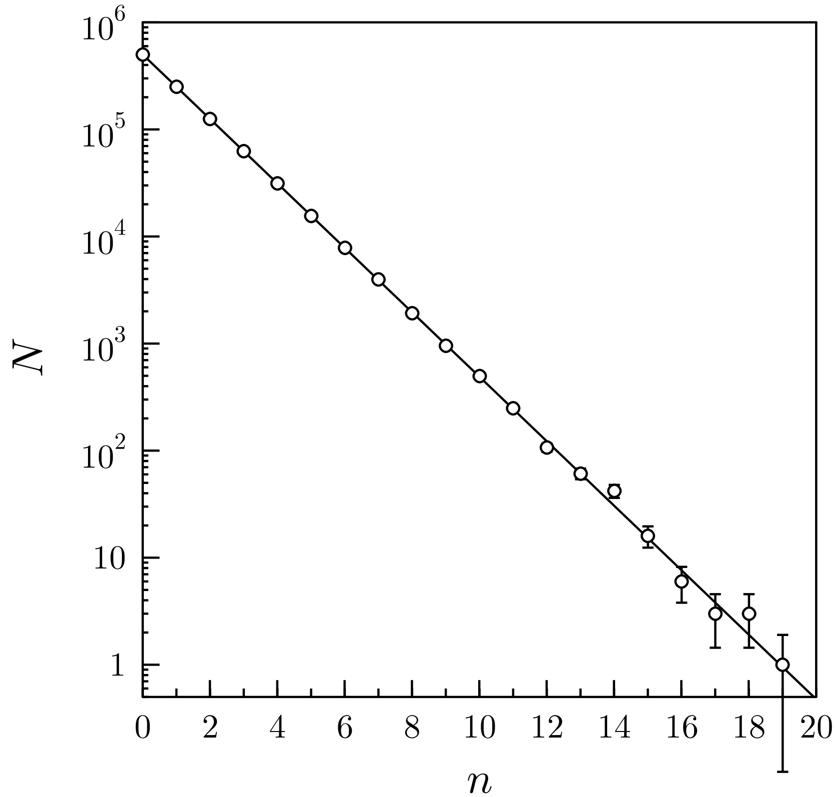
Pick a site:
The remaining sites are the reservoir

Expect the probability for a site to have n quanta to be

$$P(\epsilon_n) \propto e^{-\beta\epsilon_n} = e^{-n\beta\epsilon_0}$$

The histogram N(n) is the number of sites with n quanta, and should be P_n up to normalization

Numerical verification: number of sites, $N(n)$, with n quanta on 1000x1000 grid



What you are seeing (on a log scale) is

$$N(n) = C_1 e^{-C_2 n}$$

The log of $N(n)$ is

$$\ln N(n) = \ln C_1 - C_2 n$$

The constant $C_2 = \beta\epsilon_0$ determines the temperature

- Then the probability for a site / oscillator to have energy $\mathcal{E}_n$ is (see slide)

$$P_n \propto e^{-\mathcal{E}_n/kT} \quad \text{or} \quad \boxed{P_N = \frac{1}{Z} e^{-\mathcal{E}_n/kT}}$$

with $$\boxed{Z = \sum_{n=0}^{\infty} e^{-\mathcal{E}_n/kT}} = \sum_{n=0}^{\infty} e^{-n\hbar\omega_0/kT}$$

$$\boxed{Z = \frac{1}{1-e^{-\hbar\omega_0/kT}}}$$

see homework

magenta is general

green is for SHO

- The mean energy is:

calculated energy

$$\boxed{\langle E \rangle = N \langle \mathcal{E} \rangle = N \frac{\hbar\omega_0}{e^{\hbar\omega_0/kT}-1}}$$

input energy

- Now for the problem at hand $N = 200$ $E = 200\,\hbar\omega_0$

The temperature is adjusted so that the mean energy agrees with the input energy

$$200\,\hbar\omega_0 = \frac{200\,\hbar\omega_0}{e^{\hbar\omega_0/kT}-1}$$

or $$e^{\hbar\omega_0/kT} = 2 \implies \frac{\hbar\omega_0}{\ln 2} = k_B T$$

This example shows how the temperature is operationally defined in the canonical ensemble $P_n \propto e^{-E_n/kT}$. T is adjusted to reproduce the mean energy of the full system.

- The Einstein model gives a successful phenomenology of solids

$$dQ = dE + p\,\cancel{dV}^{\,0} \quad \text{at constant vol}$$

So at constant volume $dV = 0$

$$\left(\frac{\partial E}{\partial T}\right)_V = \frac{dQ_V}{dT} \longleftarrow \text{this is } C_V$$

So

$$C_V = \left(\frac{\partial E}{\partial T}\right)_V = N\,(\beta\hbar\omega_0)^2 \frac{e^{-\beta\hbar\omega_0}}{(1-e^{-\beta\hbar\omega_0})^2}$$

You will do this in homework! In fact you did it already!

We did it here in 1D.
In 3D the only change is

$$\boxed{C_V = 3N\,(\beta\hbar\omega_0)^2 \frac{e^{-\beta\hbar\omega_0}}{(1-e^{-\beta\hbar\omega_0})^2}}$$

Specific Heat of Einstein model

3 for 3 dimensions, each atom can oscillate in x, y, z

This is a one parameter model for the specific heats of solids. $\hbar\omega_0$ is adjusted to reproduce the data

- The Specific Heat of silver is shown on the slide. It is reasonably fit by taking $\hbar\omega_0 = 0.013\,eV$

- In the high temperature limit find

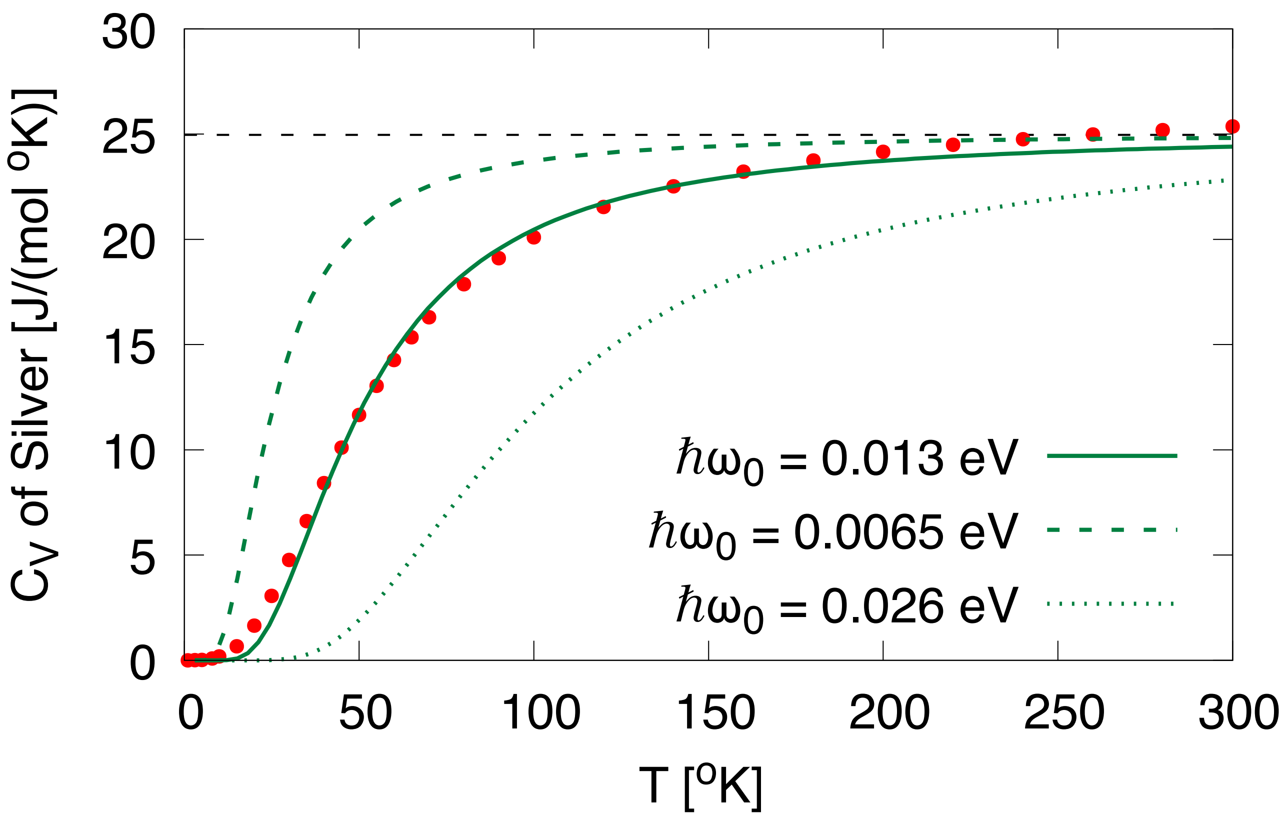
$$C_v = 3Nk_B$$

or for one mole $N = N_A$, $C_v^{1mol} = 3R$

Indeed at high temperatures the specific heats of solids approach 3R (see slide)

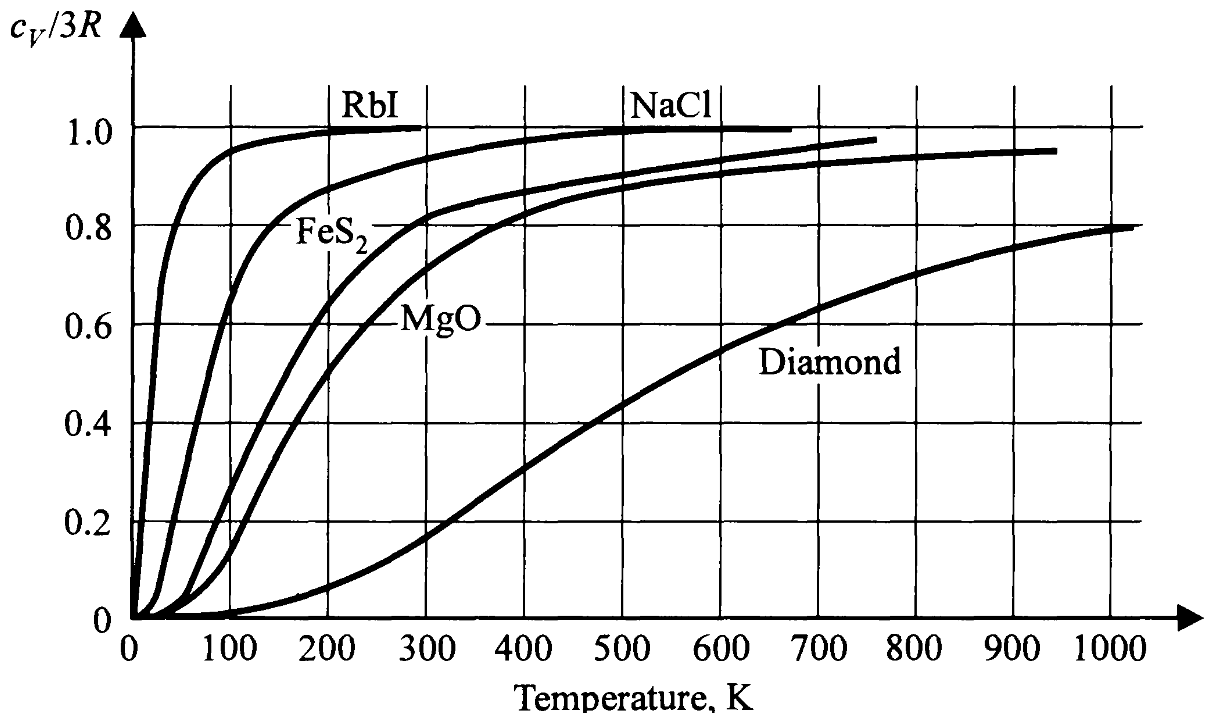
- Classically one finds $C_v = 3R$, and that the result is independent of temperature. Getting the specific heat to drop with temperature was a great early success of quatium mechanics

Specific Heat of Silver



Approaches 3R
at high temperature
where the dynamics
is classical

Specific Heats of Solids: (Taken from Zemansky and Dittman)



Approaches 3R
at high temperature
where the dynamics
is classical

The general shape of these curves agrees with the Einstein Model!

Entropy Revisited:

- Previously we considered each microstate of the full system to be equally likely. Thus

$$P_m = C$$

probability to be in microstate m is constant

Then $\sum_m P_m = 1$ or $C \sum_m 1 = 1$ this litterally counts the states

or

$C\,\Omega(E) = 1$ and $\boxed{P_m = \dfrac{1}{\Omega(E)}}$

Thus

$$S = k \ln \Omega = -k \ln P_m$$

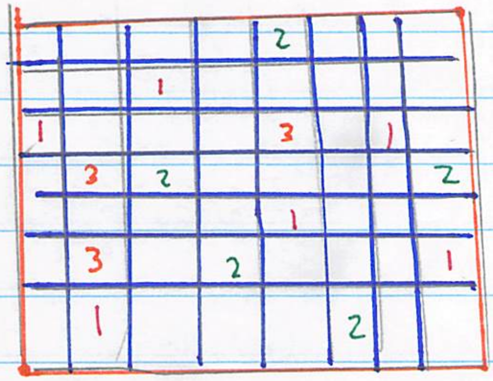
- Now we have a subsystem with probabilies $P_m \propto e^{-\mathcal{E}_m/kT}$. We would to find the mean Entropy for the subsystems, with this probability distribution

The generalzation is (as we show below)

$$\boxed{S = -\langle k \ln P_m \rangle = -k \sum_m P_m \ln P_m}$$

Let's work it out!

Consider a large number of subsystems



N subsystems: (blue boxes)

N_1 in state 1:

N_2 in state 2, etc

for example, probability to be in state 1 $\longrightarrow P_1 = \frac{N_1}{N} \propto e^{-\mathcal{E}_1/kT}$

- $S_{TOT} = k \ln(\#\text{ configurations with } N_1, N_2, \ldots \text{ fixed})$

$$= k \ln \frac{N!}{N_1!\, N_2! \ldots N_m!}$$

$$\simeq k\left(N \ln N - N - \sum_m (N_m \ln N_m - N_m)\right)$$

- So using $\sum_m N_m = N$ we have

$$S_{TOT} = k \sum_m N_m \ln N - N_m \ln N_m$$

Using $\ln N - \ln N_m = -\ln N_m/N = -\ln P_m$ we have

$$S_{TOT} = -k \sum_m N_m \ln P_m$$

- Finally the mean entropy for one subsystem is

$$S = \frac{S_{TOT}}{N} = -k \sum_m \frac{N_m}{N} \ln P_m = -k \sum_m P_m \ln P_m$$

So we have an important result:

$$\boxed{S = -k \sum_m P_m \log P_m}$$

this expression for S is valid for any probality distribution, P_m

<u>Notes</u>

① If $P_m = \frac{1}{\Omega}$ is the microcanonical (or equally likely distribution)

Then

$$S = -k \sum_m \frac{1}{\Omega} \log \frac{1}{\Omega} = -k \log \Omega \underbrace{\sum_m \frac{1}{\Omega}}$$

Sum over States divided by # of States

$$S = -k \log \Omega$$

This is what we had before:

② If $P_m = \frac{1}{Z} e^{-\beta E_m}$, this is the canonical ensemble

Then

$$S = -k \sum_m \frac{1}{Z} e^{-\beta E_m} \log \left(\frac{1}{Z} e^{-\beta E_m} \right)$$

$$= -k \frac{1}{Z} \sum_m (-\beta E_m) e^{-\beta E_m} + k \log Z \overbrace{\frac{1}{Z} \sum_m e^{-\beta E_m}}^{1}$$

$$\boxed{S = k\beta \bar{E} + k \log Z}$$

So

$$\boxed{S = \frac{\bar{E}}{T} + k \log Z}$$

this is how the entropy can be computed from the partition function Z

$$\bar{E} = \frac{-1}{Z}\frac{\partial Z}{\partial \beta}$$

- Finally lets calculate the entroply of the Einstein Model with $E = 400\hbar\omega$, $N = 400$

$$\boxed{S_{\substack{\text{one}\\\text{site}}} = \frac{\bar{E}}{T} + k \ln Z}$$

this is general.

$$\frac{S_{\substack{\text{one}\\\text{site}}}}{k} = \frac{\bar{E}}{kT} + \ln Z$$

- Putting in $\bar{E} = \hbar\omega/(e^{\hbar\omega/kT} - 1)$ $\quad Z = \dfrac{1}{1 - e^{-\hbar\omega/kT}}$

we have

$$\boxed{\frac{S_{\text{one}}}{k} = \frac{\beta\hbar\omega_0}{e^{\beta\hbar\omega_0} - 1} - \ln\left(1 - e^{-\hbar\omega_0\beta}\right)}$$

entropy of SHO at temperature T

Using $\hbar\omega_0/\ln 2 = k_B T$ and multiplying by $N = 400$

we have, $\beta\hbar\omega_0 = \ln 2$

$$\frac{S}{k} = N\frac{S_{\text{one site}}}{k} = N \; 2\ln 2 \simeq 554.$$

this is in agreement with the direct counting result we quoted earlier.