Notes for today:

- Homework 2 to present 2 problems: #1 and 4

  I need 2 volunteers!

Einstein oscillators:

- Approximately correct model for energy of (insulating) solid; exact QM solution in chapter 7.

- Recall crystal modeled as $3N$ independent oscillators, each with energy quanta $\hbar\omega_o$

q indistinguishable quanta, distribute among $3N$ oscillators:

$$\Omega = \frac{(3N+q-1)!}{(q)!(3N-1)!}$$

- maps onto binomial problem but with #bins changing as total energy changes.
- Subdivided system, # accessible microstates peak value for equal distribution of energy among oscillators.

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Vibrational energy flows as heat between connected systems until this condition achieved (***irreversible spontaneous process***)

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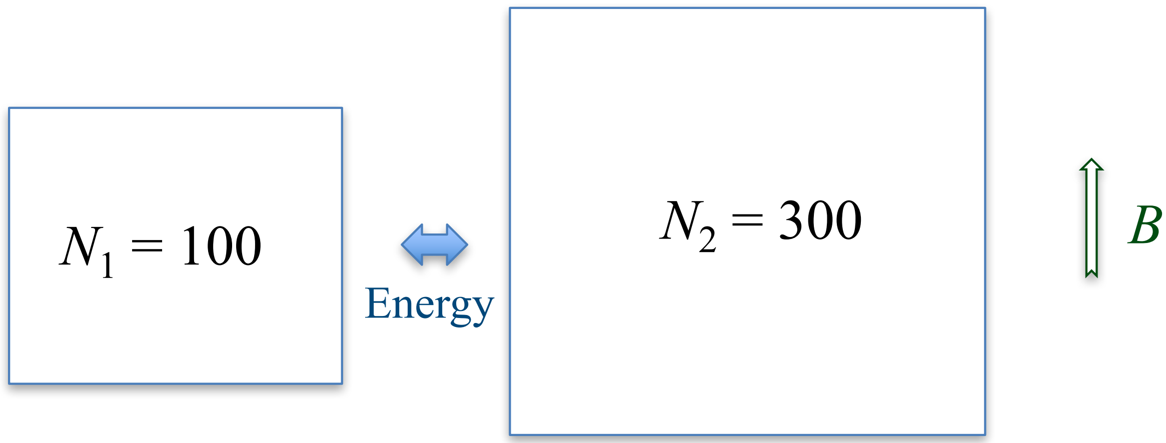
as total energy changes.
- Subdivided system, # accessible microstates peak value for <u>equal distribution of energy among oscillators</u>.

Imbalanced example (spin-1/2 paramagnet case):



Suppose 20 total quanta ($\Delta E = 20\ \mu B$), expected distribution?

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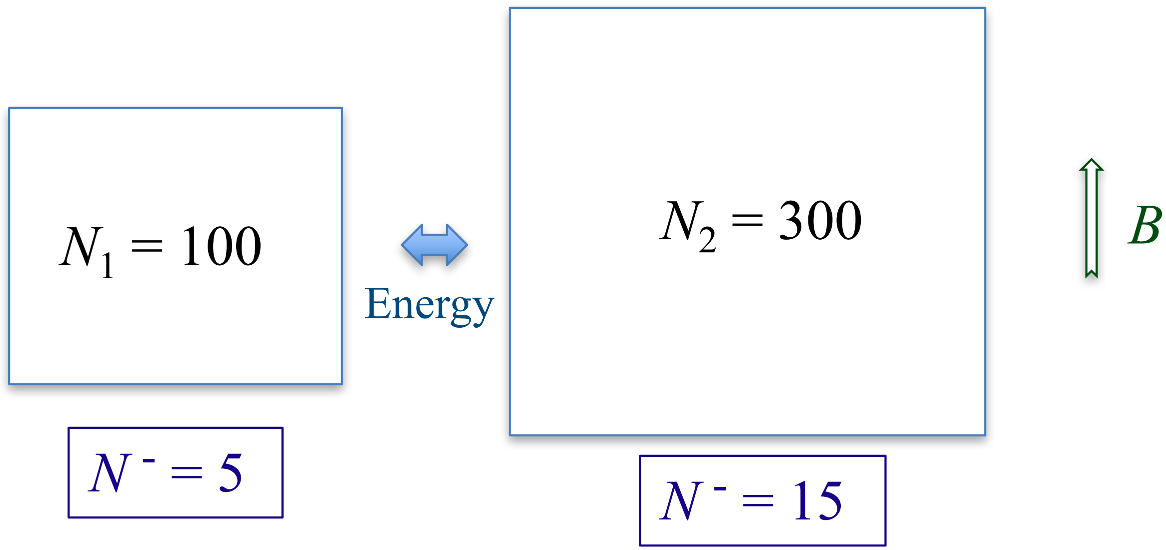

Suppose 20 total quanta ($\Delta E = 20\ \mu B$), expected distribution?

peak value based on maximum multiplicity (e.g. <u>not</u> same amount of energy each side)

In[1]:= $N\left[\frac{100! \times 300!}{5! \times 95! \times 15! \times 285!}\right]$

Out[1]= 5.78801×10^{32}

In[2]:= $N\left[\frac{100! \times 300!}{4! \times 96! \times 16! \times 284!}\right]$

Out[2]= 5.36974×10^{32}

In[3]:= $N\left[\frac{100! \times 300!}{6! \times 94! \times 14! \times 286!}\right]$

Out[3]= 4.80648×10^{32}

Further note on Binomial distribution, large N:

Recall $P_{n_1} = \binom{N}{n_1} p^{n_1}(1-p)^{N-n_1}$ normalized probability, n_1 successes.

Binomial theorem, $(p+q)^N = \sum_{n_1=0}^{N} \binom{N}{n_1} p^{n_1} q^{N-n_1}$

- So: $\langle n_1 \rangle = p \frac{\partial}{\partial p} \sum_{n_1=0}^{N} \binom{N}{n_1} p^{n_1} q^{N-n_1} = \mathrm{Np}$ easy to show.

- width of peak: $\langle {n_1}^2 \rangle = p \frac{\partial}{\partial p} p \frac{\partial}{\partial p} \sum_{n_1=0}^{N} \binom{N}{n_1} p^{n_1} q^{N-n_1}$

$$= p \frac{\partial}{\partial p} [Np(p+q)^N]$$

$$\rightarrow Np[Np+q] = \langle n_1 \rangle^2 + Npq$$

Further note on Binomial distribution, large N:

Multiplicity alone: sufficient for fixed-energy systems (microcanonical ensemble).

Recall $P_{n_1} = \binom{N}{n_1} p^{n_1}(1-p)^{N-n_1}$ normalized probability, n_1 successes.

Probabilities important when considering distribution of possible energies (Boltzmann distribution, see later)

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RMS width $\propto \sqrt{N}$

4th moment can treat in similar way: find ratio of 2nd and 4th moments identical for binomial, Gaussian distribution.

Entropy define:

$$S \equiv k_B ln(\Omega)$$

- Quantity maximized in spontaneous processes
- State function for system in equilibrium
- Rough measure of "disorder"

  e.g. paramagnet case
- Extensive property: can see from definition.

Recall:

Irreversible Process:

Spontaneous process with change of external parameters; will not occur spontaneously in reverse.

Or, spontaneous process in which number of accessible microstates (Ω) increases.

Fundamental Postulate of Statistical Mechanics:

Over time an isolated system in equilibrium will be found in each accessible microstate with equal probability.

Second Law of Thermodynamics:

Spontaneous processes always tend toward a macrostate with the largest number of accessible microstates.

Or, Ω always increases.

New (equivalent) definitions:

Irreversible Process:

Spontaneous process with change of external parameters; will not occur spontaneously in reverse.

Or, spontaneous process in which number of accessible microstates (Ω) increases.

Irreversible process: $\Delta S > 0$
Reversible process: $\Delta S = 0$

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Or, Ω always increases.

Or, Spontaneous processes have $\Delta S \geq 0$ (total for all interacting systems)

Temperature define:

- Recall for 2 interacting but independent systems,

$$\Omega = \Omega_1 \Omega_2 \quad \text{or,} \quad \Omega = \Omega_1(E_1)\Omega_2(E_{total} - E_1)$$

- Maximize Ω; $\frac{\partial \Omega}{\partial E_1} = 0$ leads to,

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- & can define,

$$\frac{1}{T} = \frac{\partial S}{\partial U}$$

$T_1 = T_2$

Equilibrium condition