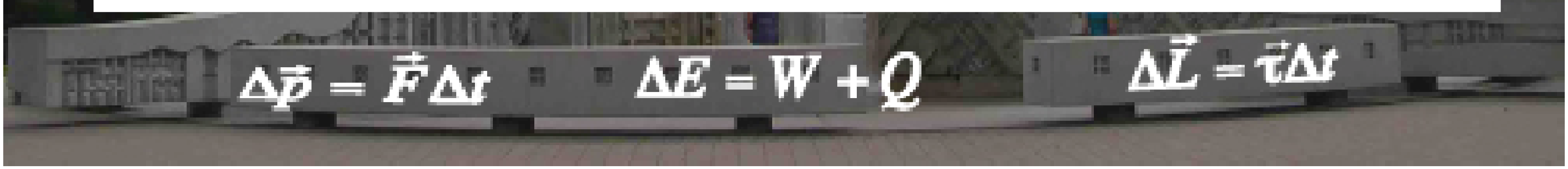
Exam 3 multiple-choice part on CHIP

Please check your scores/answers on CHIP – if you see ‘0’, let us know ASAP.

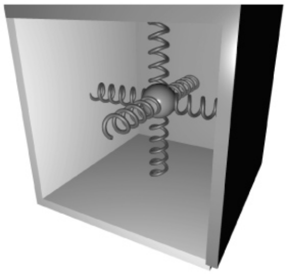
Finalizing iClicker scores 10-22

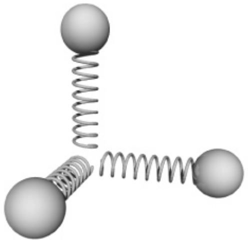
Scores for **Lectures 10-22** have been uploaded. Deadline for requesting corrections is <u>**5 PM this Friday**</u> (April 20).

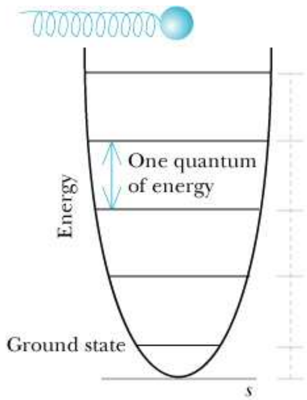


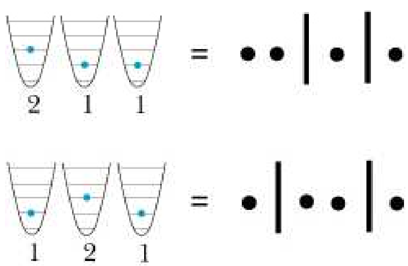
Summary: Foundations

Einstein Model of Solids









 # microstates

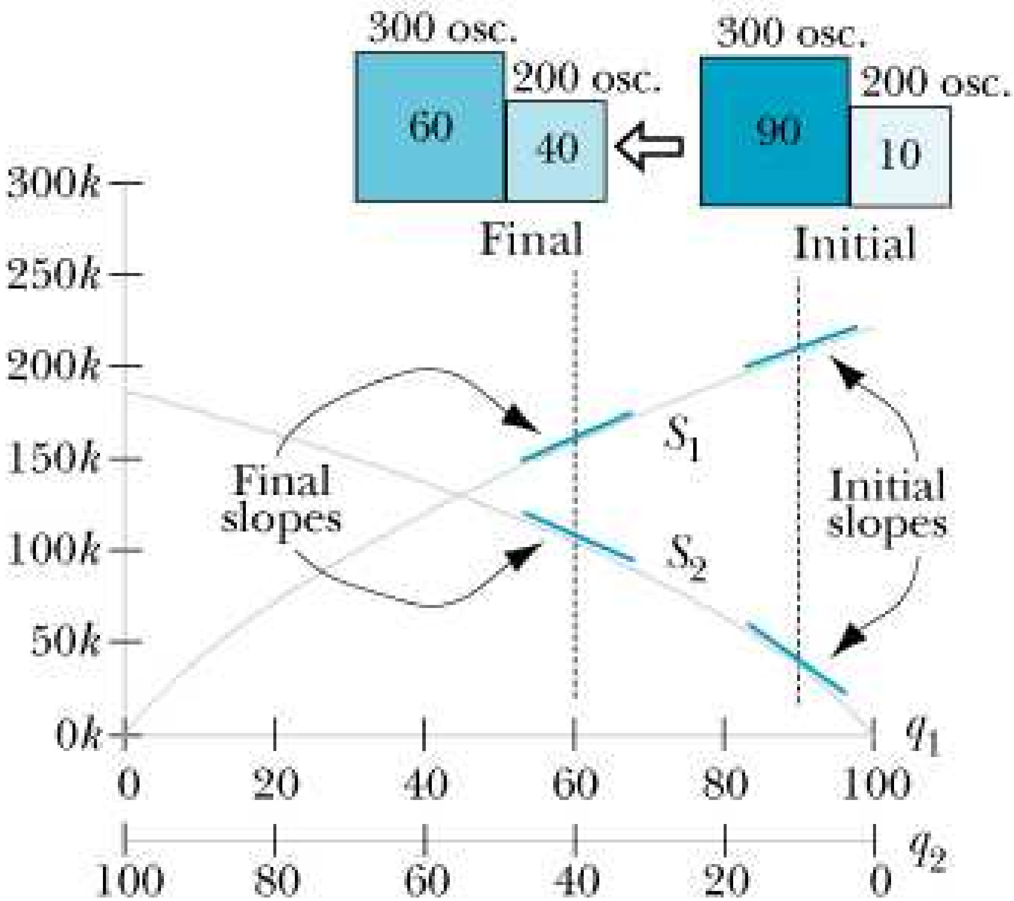
(N oscillators, q quanta)

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

Fundamental assumption of statistical mechanics

Over time, an isolated system in a given macrostate (total energy) is equally likely to be found in any of its microstates (microscopic distribution of energy).

Summary: Entropy and Temperature



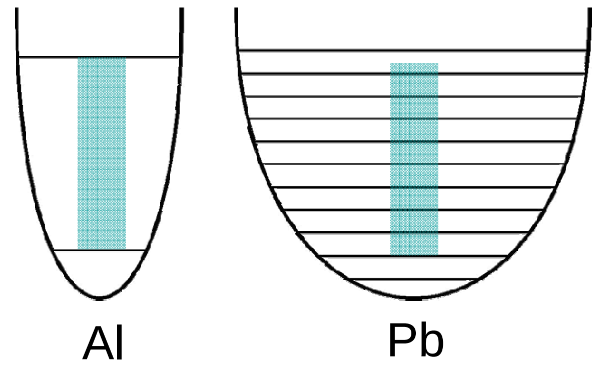
$$S \equiv k \ln \Omega$$

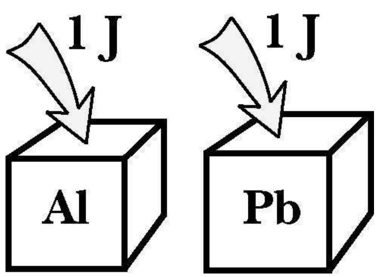
$$\frac{1}{T} \equiv \frac{dS}{dE_{\text{int}}}$$

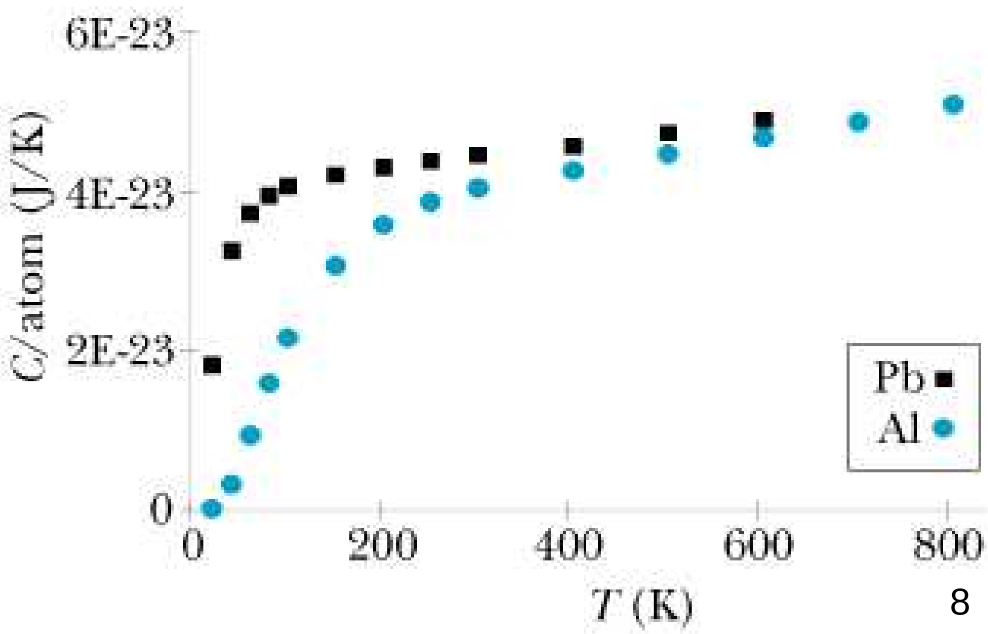
If the initial state is not the most probable, energy is exchanged until the most probable distribution is reached.

Summary: Specific Heat

$$C_{atom} = \frac{\Delta E_{atom}}{\Delta T} \equiv \frac{\Delta E_{system} / N_{atoms}}{\Delta T}$$







Today: The Boltzmann Distribution

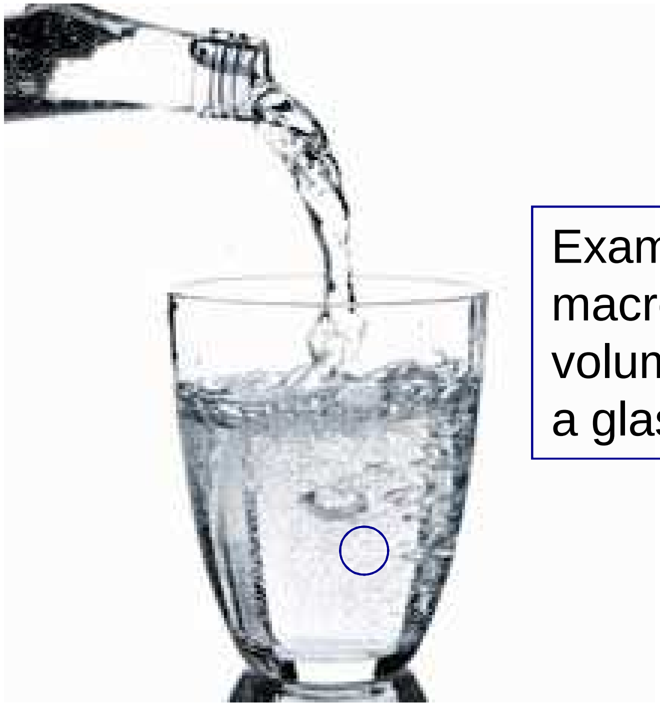
- **Derivation: Choose Your System Wisely**
- **Many Systems or Many Observations?**
- **Simple Applications:**
  - **Probabilities for Atomic Excitations**
  - **Block of Lead**
  - **Biological Physics**

Boltzmann Distribution

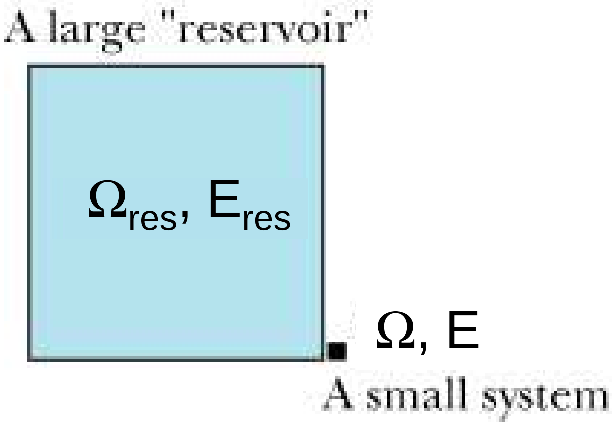
The Boltzmann distribution comes about by cleverly picking our system.

Say that we want to analyze a cup of water.

What system do we pick? A tiny volume of the water!

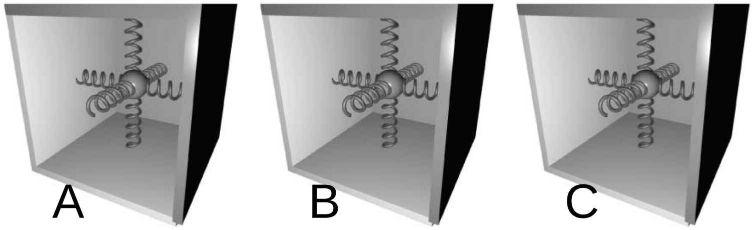


Example: a macroscopic volume of water in a glass of water



$E_{tot} = E_{res} + E = \text{constant}$

Recall the Pb Nanoparticle (3 atoms) from Ch 11, p 392-393:



q	Ω	ln Ω	S
4	465	6.20	$6.20k_B$
5	1287	7.16	$7.16k_B$
6	3003	8.01	$8.01k_B$

q	T(K)
4-5	58.9
5	62.5
5-6	66.6

Temperature: $\frac{1}{T} \equiv \frac{\partial S}{\partial E_{\text{int}}}$

$$T_q \approx \frac{\Delta E}{\Delta S} = \frac{\Delta q \times \hbar\omega_o}{k\Delta(\ln\Omega)}$$

$$C = \frac{1}{3}\frac{\Delta E(3\text{ atoms})}{\Delta T} = \frac{1}{3}\frac{8\times 10^{-22}}{(66.6-58.9)} = 3.4\times 10^{-23}\text{ J/K per atom}$$

What if we wanted to know what is happening on **<u>one</u>** of the three atoms? For example, with q=6, how often is atom A found with q_A=2?

What if we wanted to know what is happening on **one** of the three atoms?
For example, with q=6, how often is atom A found with q_A=2?

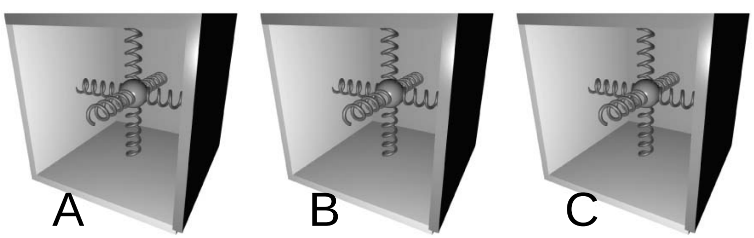
We can simply count the states with 2 quanta on atom A:

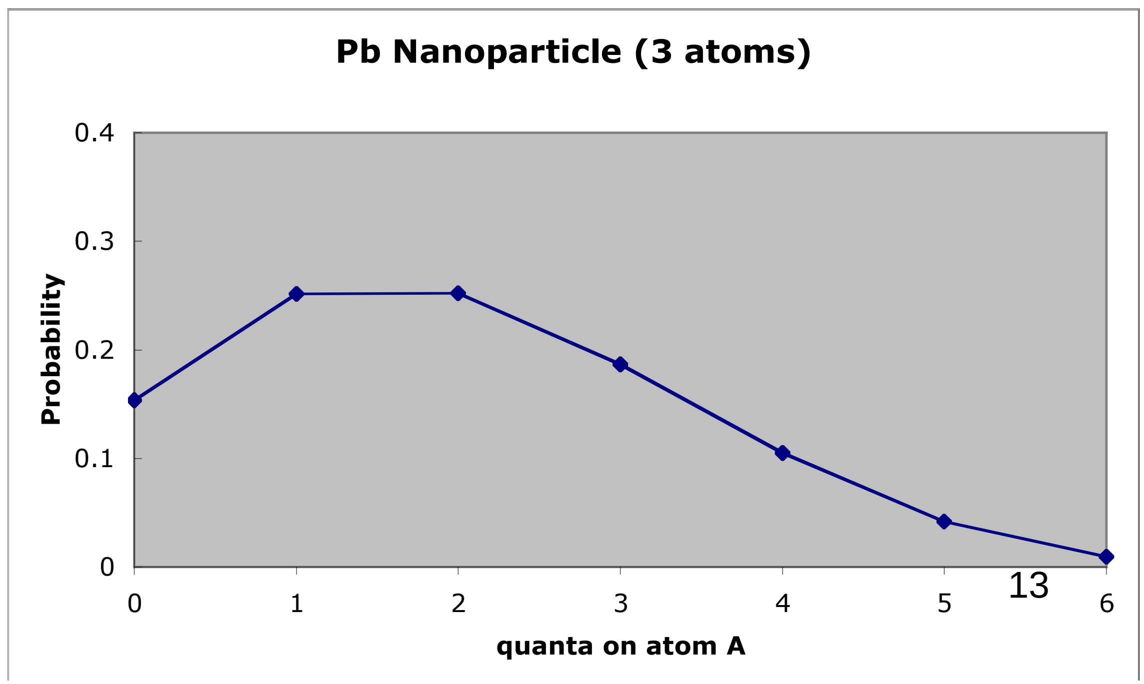
$$\Omega_A(q_A = 2) = \frac{(2+3-1)!}{2!(3-1)!} = 6$$

$$\Omega_{BC}(q_{BC} = 6-2) = \frac{(4+6-1)!}{4!(6-1)!} = 126$$

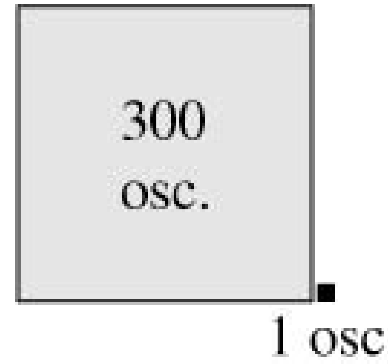
$$\Omega_A(2)\Omega_{BC}(4) = 6 \times 126 = 756$$

$$P = \frac{\Omega_A(2)\Omega_{BC}(4)}{\Omega_{total}(6)} = \frac{756}{3003} \approx 0.25$$

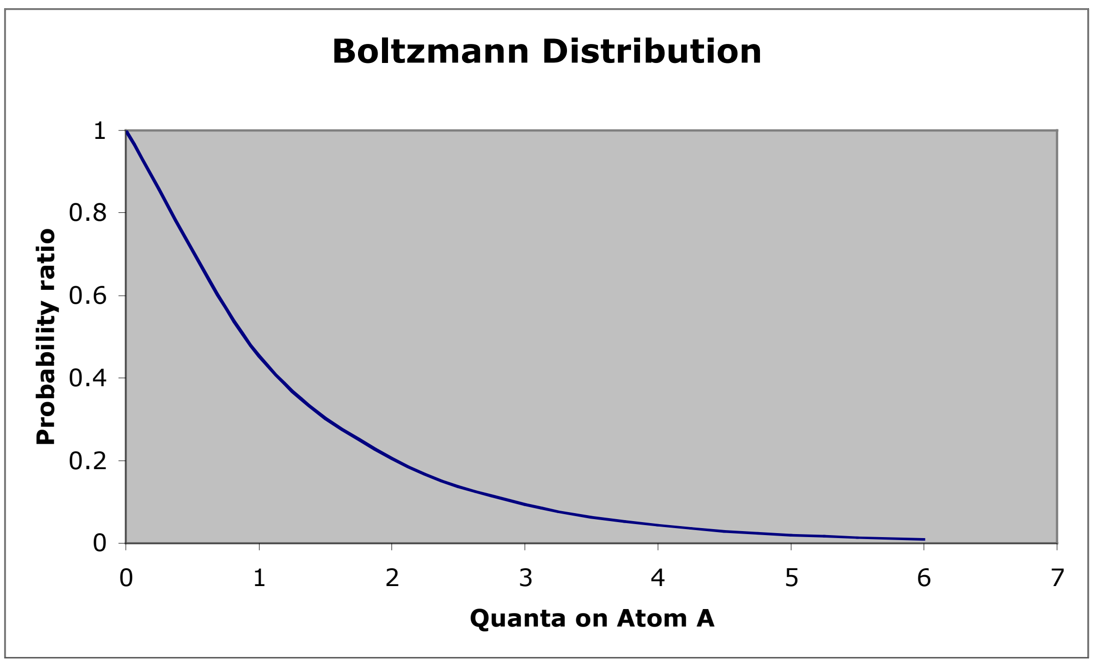




Now, a more interesting question: What is the probability of finding 2 quanta on atom A if it is in contact with a large Pb block? (Assume same T as before.)

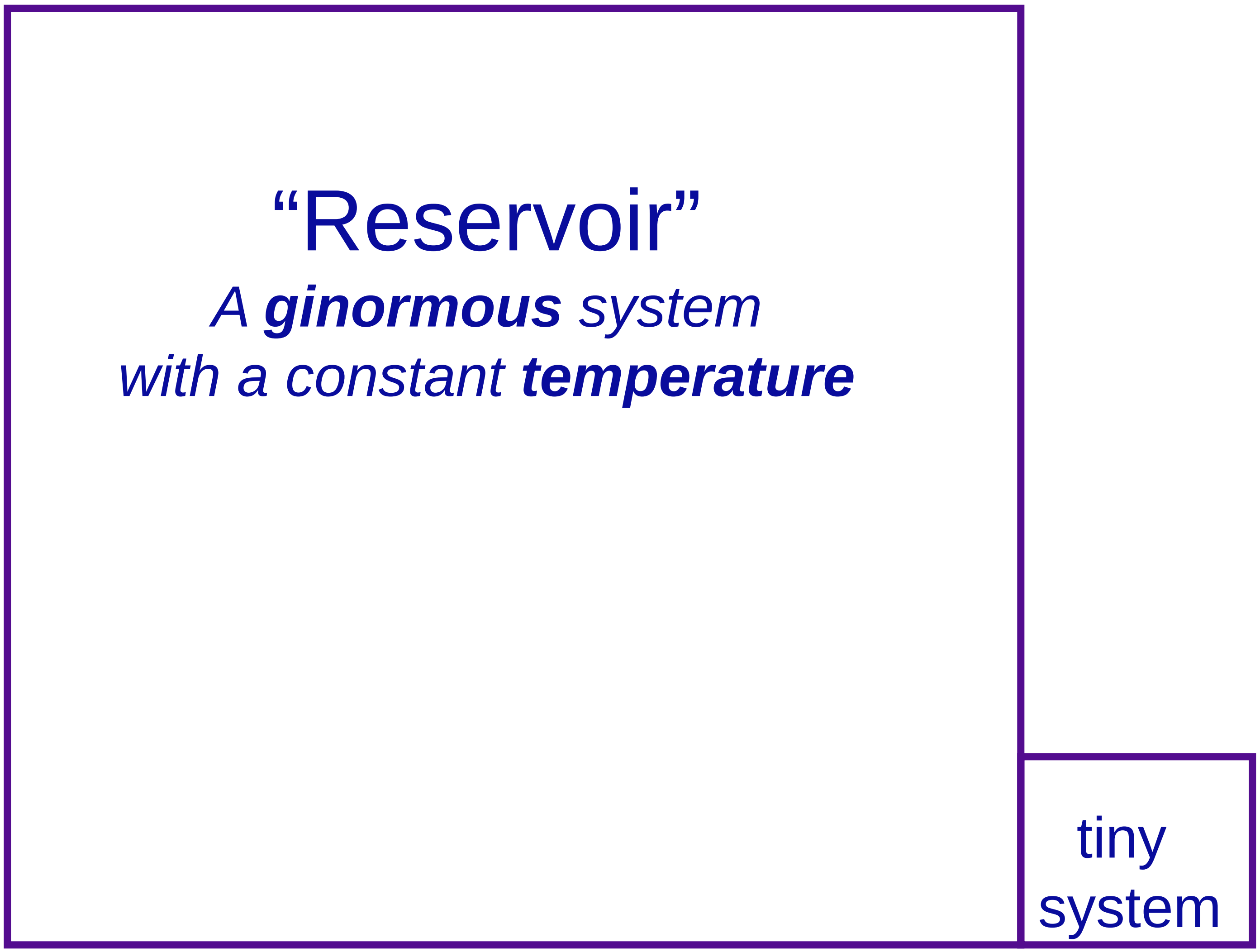


$$\frac{\text{Probability of }\Delta\text{E above ground state}}{\text{Probability of being in ground state}} \sim \Omega_A(\Delta E)e^{-\frac{\Delta E}{kT}} \sim e^{-\frac{\Delta E}{kT}}$$

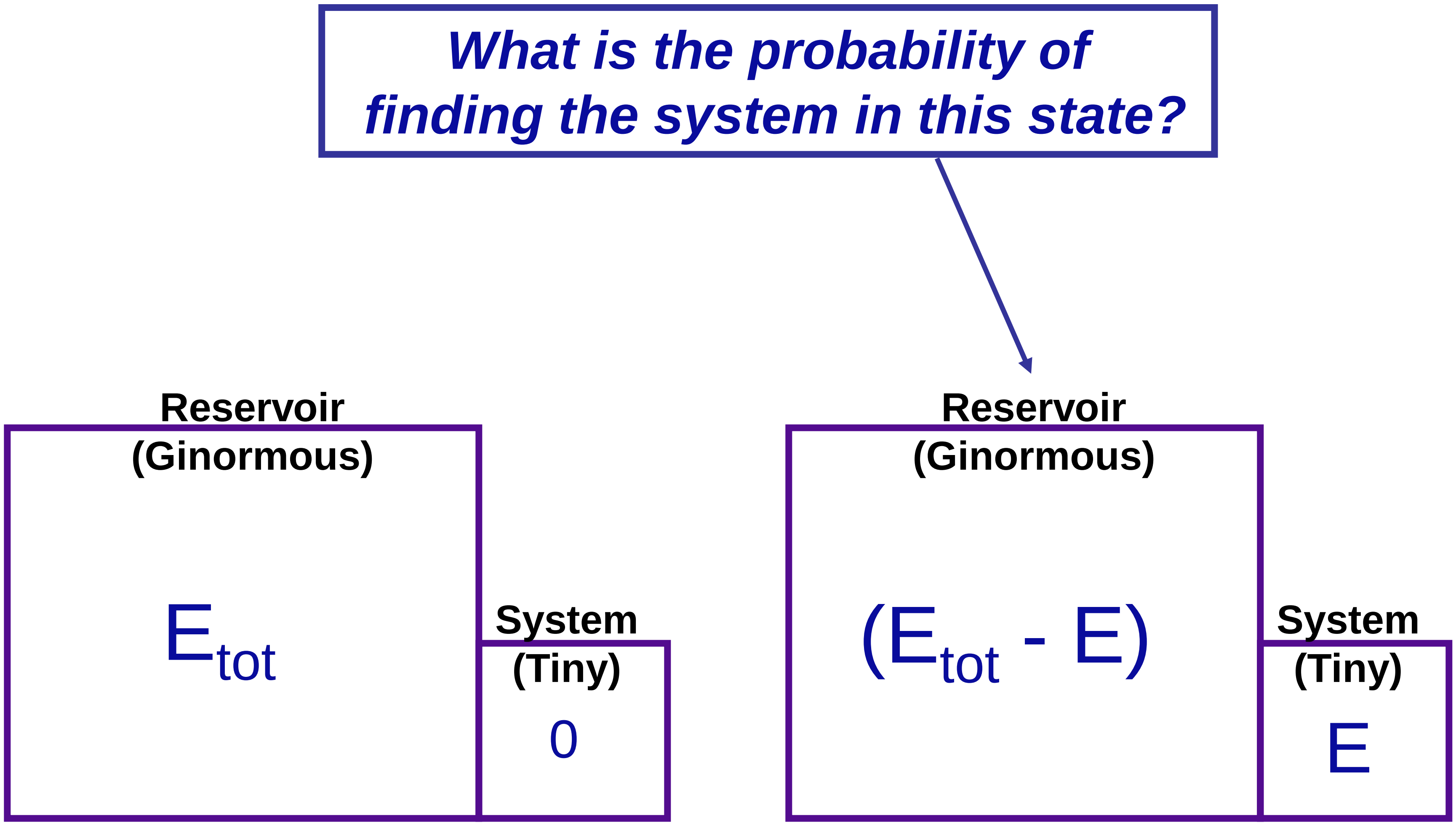


This is a property of **<u>any</u>** small system in thermal equilibrium with a large reservoir at a fixed temperature.

Proof (next few slides)



Probabilities



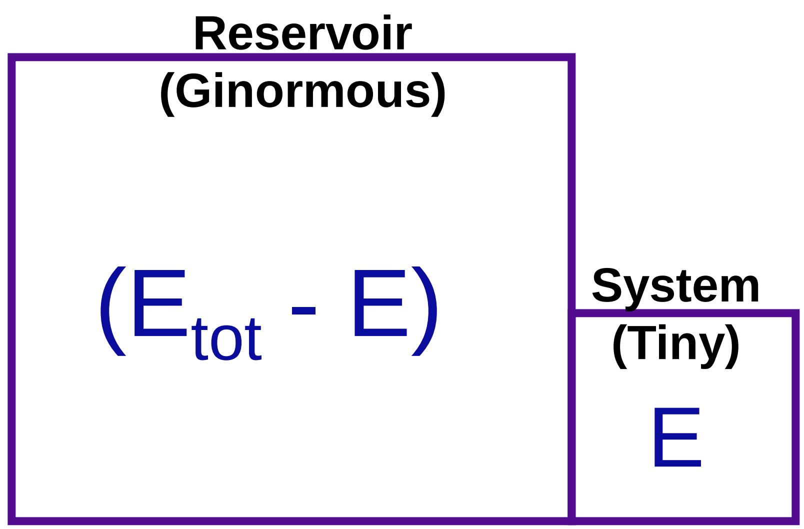
Probabilities

Number of ways of having $E_{sys} = E$

$$P(E) = \frac{\overbrace{\Omega_{res}(E_{res})\Omega(E)}}{\Omega_{tot}(E_{tot})}$$

Total number of ways of arranging energy in combined system: Tot = Res + Sys

We can find the probability from the number of ways of arranging the energy.



Now Do Some Math...

$$P(E) = \frac{\Omega_{res}(E_{res})\Omega(E)}{\Omega_{tot}(E_{tot})}$$

We can find the probability from the number of ways of arranging the energy.

$$S = k\ln(\Omega)$$

$$k\ln P = k\ln\left(\frac{\Omega_{res}(E_{res})\Omega(E)}{\Omega_{tot}(E_{tot})}\right)$$

$$= k\ln(\Omega_{res}(E_{res})) + k\ln(\Omega(E)) - k\ln(\Omega_{tot}(E_{tot}))$$

$$= \quad S_{res}(E_{res}) \quad + \quad S(E) \quad - \quad S_{tot}(E_{tot})$$

More Math...

$$k\ln P = S_{res}(E_{res}) + S(E) - S_{tot}(E_{tot}) \qquad E_{\text{res}} = E_{\text{tot}} - E$$

Use a Taylor Expansion for the Ginormous Reservoir: *($E << E_{res}$)*

$$S_{res}(E_{res}) \approx S_{res}(E_{tot}) - \frac{dS_{res}}{dE_{res}}E + \cdots = S_{res}(E_{tot}) - \frac{E}{T}$$

$$\frac{1}{T}$$

Spot The Temperature!

$$k\ln P = S_{res}(E_{tot}) - \frac{E}{T} + S(E) - S_{tot}(E_{tot})$$

$$= k\ln(\Omega_{res}(E_{tot})) - \frac{E}{T} + k\ln(\Omega_{sys}(E)) - k\ln(\Omega_{tot}(E_{tot}))$$

More Math...

$$k \ln P = k \ln(\Omega_{res}(E_{tot})) - \frac{E}{T} + k \ln(\Omega_{sys}(E)) - k \ln(\Omega_{tot}(E_{tot}))$$

Exponentiate Everything...

$$P = e^{\ln P} = e^{\text{const.}} e^{-E/kT} \Omega_{sys}(E)$$

$$\boxed{P \propto e^{-E/kT}}$$

BOLTZMANN FACTOR

Very very important!

Boltzmann Distribution

The probability of finding energy E in a small system in contact with a large reservoir is

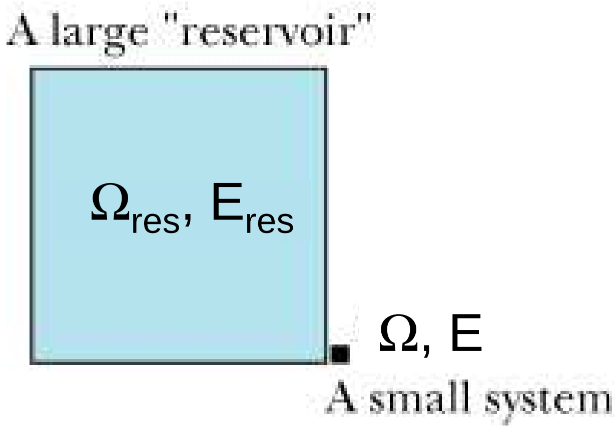
$$P(E) \propto \Omega(E) \cdot e^{-\frac{E}{kT}}$$

The exponential part, $e^{-E/kT}$, is called the “Boltzmann factor.”

Ω(E) is the number of microstates in the small system at energy E.

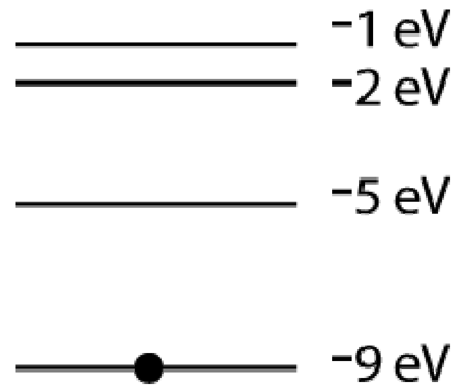
In many circumstances, Ω(E) changes so slowly compared to $e^{-E/kT}$ that it is essentially constant:

$$P(E) \approx const \cdot e^{-\frac{E}{kT}}$$



Application: Atomic Excitations

How likely is an atom to be in 1st excited, compared to odds of being in ground state?



$$\frac{P(E_1)}{P(E_0)} = \frac{e^{-E_1/kT}}{e^{-E_0/kT}} = e^{-\Delta E/kT}$$

NOTE: kT at room temp = 1/40 eV.

For the above atom, odds of being in first excited state are

$$P\left(1^{\text{st}} \text{ excited state}\right) = \frac{1}{e^{\Delta E / 1/40 \text{ eV}}} = \frac{1}{e^{40\Delta E}} = \frac{1}{e^{40\times 4}} = 3\times 10^{-70}$$

Typical atomic energy gaps are big compared to room temp.

A room-temperature box of neon doesn't glow! (Unless you add energy)

Application: Block of Lead

$$\frac{\hbar\omega}{k} = \frac{8 \times 10^{-22} J}{k} = 57K$$

T=300K at room temperature

$$\boxed{P \propto e^{-E/kT}}$$

BOLTZMANN FACTOR
Very very important!

Think of adding q quanta of energy to one lead atom...

At room temperature, the Boltzmann factors for exciting vibrations are:

$$q = 0 \qquad P \propto e^{-q\hbar\omega/kT} = e^{0/300} = 1$$

Most probable state

$$q = 1 \qquad P \propto e^{-q\hbar\omega/kT} = e^{-57/300} = 0.83$$

$$q = 2 \qquad P \propto e^{-q\hbar\omega/kT} = e^{-2*57/300} = 0.68$$

$$q = 3 \qquad P \propto e^{-q\hbar\omega/kT} = e^{-3*57/300} = 0.57$$

Watch out!
These are *relative* probabilities

Application: Block of Lead

$\hbar\omega = 8 \times 10^{-22} J = 57K$

T=300K at room temperature

Think of adding q quanta of vibrational energy to one lead atom...

The actual probabilities use a normalization factor "Z" (partition function).

$$q = 0 \qquad P = e^{-q\hbar\omega/kT}/Z = 17\%$$

$$q = 1 \qquad P = e^{-q\hbar\omega/kT}/Z = 14\%$$

$$q = 2 \qquad P = e^{-q\hbar\omega/kT}/Z = 12\%$$

$$q = 3 \qquad P = e^{-q\hbar\omega/kT}/Z = 9.8\%$$

$$q = 4 \qquad P = e^{-q\hbar\omega/kT}/Z = 8.1\%$$

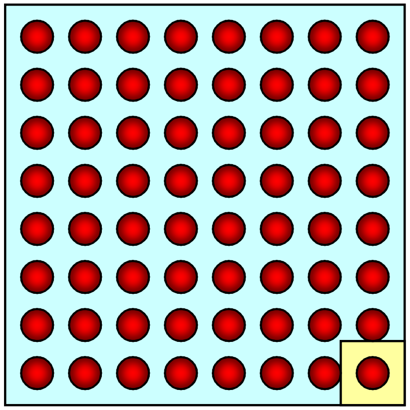
$$q = 5 \qquad P = e^{-q\hbar\omega/kT}/Z = 6.7\%$$

$$q = 6 \qquad P = e^{-q\hbar\omega/kT}/Z = 5.5\%$$

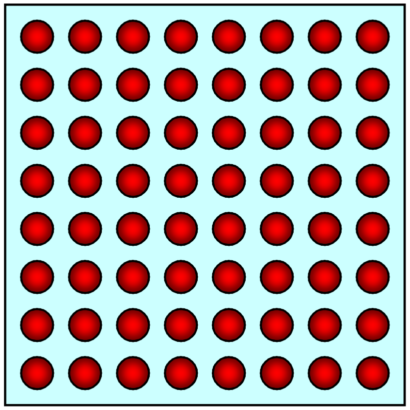
Most likely to find the vibrations are excited.

On average, q=5.

Boltzmann distribution arises in 2 ways



Measure energy on a single oscillator at many different times. Number of measurements at energy E is proportional to: $e^{-\frac{E}{kT}}$



Measure energy on each oscillator in a system at one single time. Number of oscillators at energy E is proportional to: $e^{-\frac{E}{kT}}$

Distribution of oscillator energies in a large system <u>also</u> follows Boltzmann distribution!

Today: The Boltzmann Distribution

- Derivation: Choose Your System Wisely
- Many Systems or Many Observations?
- Simple Applications:
  - Probabilities for Atomic Excitations
  - Block of Lead
  - Biological Physics

Next Time: Boltzmann Applications

- Speed Distribution in a Gas
- Energy Equipartition and Specific Heat
- Pressure and the Ideal Gas Law