February 17, 2016 Physics 132 Prof. E. F. Redish

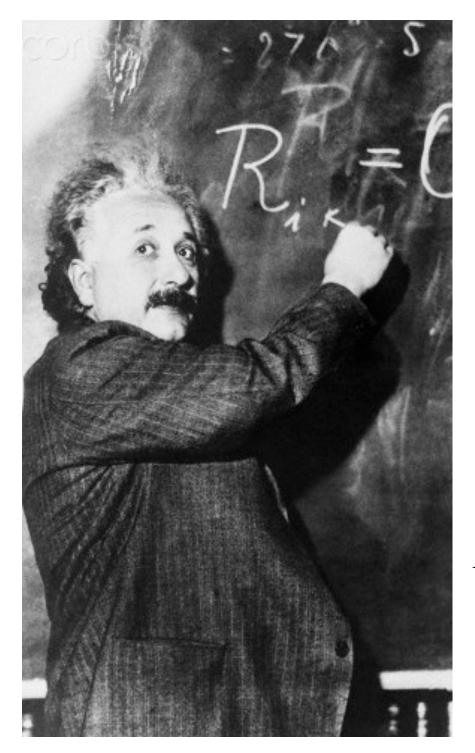
■ <u>Theme Music:</u> Jake Shimabukuro

Shake it up

■ <u>Cartoon:</u> Steve Kelley & Jeff Parker

Justin







Boltzmann Probability

 $P(\Delta E,T) = P_0 W(\Delta E,T) e^{-\Delta E/k_B T}$

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Foothold ideas: The Second Law of Thermodynamics

- Systems spontaneously move toward the thermodynamic (macro)state that correspond to the largest possible number of particle arrangements (microstates).
 - The 2nd law is probabilistic. Systems show fluctuations violations that get proportionately smaller as N gets large.
- Systems that are not in thermodynamic equilibrium will spontaneously transform so as to increase the entropy.
 - The entropy of any particular system can decrease as long as the entropy of the rest of the universe increases more.
- The universe tends towards states of increasing chaos and uniformity. (Is this contradictory?)

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Foothold ideas: Energy distribution

- Due to the randomness of thermal collisions, even in (local) thermal equilibrium the energy in each DoF fluctuates, so a range of energy will be found in each degree of freedom.
- The probability of adding an energy ΔE is proportional to the Boltzmann factor

 $P(\Delta E) \propto e^{-\Delta E/k_B T}$ (for one DoF)

$$P(\Delta E) \propto e^{-\Delta E/RT}$$
 (for one mole)

■ At 300 K,

 $k_{\rm B}T \sim 1/40 \text{ eV} = 25 \text{ meV/molecule}$ $N_{\rm A}k_{\rm B}T = RT \sim 2.4 \text{ kJ/mol}$ Physics 132

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The Boltzmann probability

- The probability of finding an additional energy ΔE in a DoF is proportional to the number of ways that that energy can be distributed, *W*.
- The overall probability has to be normalized so that the sum (integral) over all energies is 1.

$$P(\Delta E,T) = P_0 W(\Delta E,T) e^{-\Delta E/k_B T}$$