Theme Music: Jake Shimabukuro

Shake it up

Cartoon: Steve Kelley & Jeff Parker

Justin
Boltzmann Probability

\[ P(\Delta E, T) = P_0 W(\Delta E, T) e^{-\frac{\Delta E}{k_B T}} \]
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 2\textsuperscript{nd} 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?)
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 $\Delta E$ is proportional to the Boltzmann factor

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

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

- At 300 K,

  $$k_B T \sim 1/40 \text{ eV} = 25 \text{ meV/molecule}$$

  $$N_A k_B T = RT \sim 2.4 \text{ kJ/mol}$$
The Boltzmann probability

- The probability of finding an additional energy $\Delta E$ 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.

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