# 3.020 Lecture 29

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# 1 Maximum entropy condition and the Boltzmann distribution

- from last time
  - optimizing S' for isolated system
  - $dS^{'} = 0$ subject to constraints $dU^{'} = 0$, $dn_{TOT} = 0$
  - method of Lagrange multipliers: $\alpha$, $\beta$

$$\sum_i \underbrace{(\dots)}_{\textbf{set coefficients to 0}} \quad dn_i = 0$$

  - determine $\alpha$ by normalization

$$\frac{n_i}{n_{TOT}} = \frac{e^{\beta\epsilon_i/k_B}}{Q}, \qquad Q = \sum_i e^{\beta\epsilon_i/k_B}$$

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- Determine $\beta$ by considering microscopic, reversible process $dn_i$

$$\begin{aligned} dS^{'} &= -k_B \sum_i \ln\left(\frac{n_i}{n_{TOT}}\right) dn_i = -k_B \sum_i \ln\left(\frac{e^{\beta\epsilon_i/k_B}}{Q}\right) dn_i \\ &= -\beta \sum_i \epsilon_i dn_i + k_B \ln Q \sum_i dn_i \\ &= -\beta \; dU^{'} + k_B \ln Q \; dn_{TOT} \quad \textbf{=0 by construction} \end{aligned}$$

- Compare this to

$$dS^{'} = \frac{1}{T}\, dU^{'} + \frac{P}{T} dV^{'} - \frac{\mu}{T} dn$$
$$\Downarrow$$
$$\beta = -1/T$$

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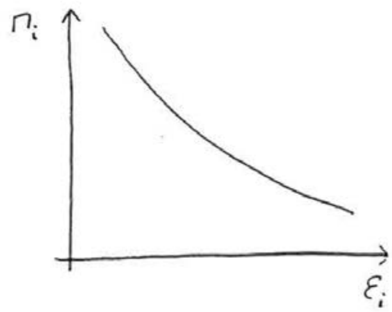
- With $\beta = -1/T$, we have the <u>Boltzmann distribution</u>

$$\frac{n_i}{n_{TOT}} = \frac{e^{\epsilon_i/k_BT}}{Q}$$
$$Q = \sum_i e^{-\epsilon_i/k_BT}$$



$\Longrightarrow$ Distribution that maximizes entropy for an isolated system with $n_{TOT}$ particles distributed over states with energy $\epsilon_i$ according to $\{n_i\}$

- Describes equilibrium state

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- Maxwell distribution and likelihood
  e.g. How much less likely is it to find particle in state with energy $\epsilon_m = \epsilon_l + \Delta\epsilon$ than in state with energy $\epsilon_l$

$$\frac{n_m}{n_l} = \frac{e^{-(\epsilon_l+\Delta\epsilon)/k_BT}}{e^{-\epsilon_l/k_BT}} = e^{-\Delta\epsilon/k_BT}$$

  - Depends on $\Delta\epsilon/k_BT$
  - Becomes less likely with energy splitting $\Delta\epsilon$
  - Becomes more likely with temperature $T$

- Thermal energy $k_BT$

$$k_B = R/N_A = 1.380 \times 10^{-23}\ J/k = 8.617 \times 10^{-5}\ eV/k$$

  - sets energy scale for likely fluctuations $\Delta\epsilon$
    $\Delta\epsilon \approx k_BT$ are likely
    $\Delta\epsilon >> k_BT$ are unlikely

    thermally activated processes

  - at $T = 298\ K$, $k_BT = 4.112 \times 10^{-21}\ J = 0.0257\ eV = 25.7\ meV$
  - foundation for Arrhenius rate equation (hello 3.091 !!)

$$k = A\ e^{-E_a/kT}$$

  k: rate; $E_a$ : activation energy

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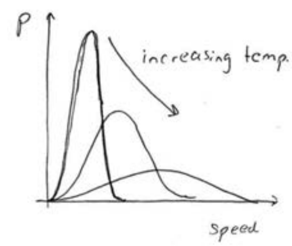
## 2 Maxwell-Boltzmann distribution

- Consider particles with kinetic energy $\mathbf{p}^2/2m = (p_x^2 + p_y^2 + p_z^2)/2m$
- Distribution of energy $f_E$ depends on both
  - Maxwell distribution $n_i/n_{TOT} = Q^{-1}\ exp(-\mathbf{p}_i^2/2mk_BT)$
  - Density of states in momentum space

$$d^3\mathbf{p} = 4\pi p^2 dp = 4\pi m\sqrt{2mE}dE$$

$$f_E = 2\sqrt{\frac{E}{\pi}}(\frac{1}{kT})^{3/2}e^{-E/kT}$$

$\longrightarrow$ more faster particles at higher temp
$\longrightarrow$ vanishing number of particles with $p = 0$

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## 3 Ensembles

A group of things or people acting or taken together as a whole

- Microcanonical ensemble: Set of all possible microstates of an isolated system with fixed $U'$, $V'$, n
  - Microcanonical partition function $Q = \sum_i e^{\epsilon_i/k_BT}$, (sum over all possible single particle states)
  - Equilibrium (S maximized) for Boltzmann probability distribution

$$\mathcal{P}_i = \frac{n_i}{n_{TOT}} = \frac{e^{-\epsilon_i/k_BT}}{Q}$$

probability $\mathcal{P}_i$ of finding single particles in state $i$, with energy $\epsilon_i$

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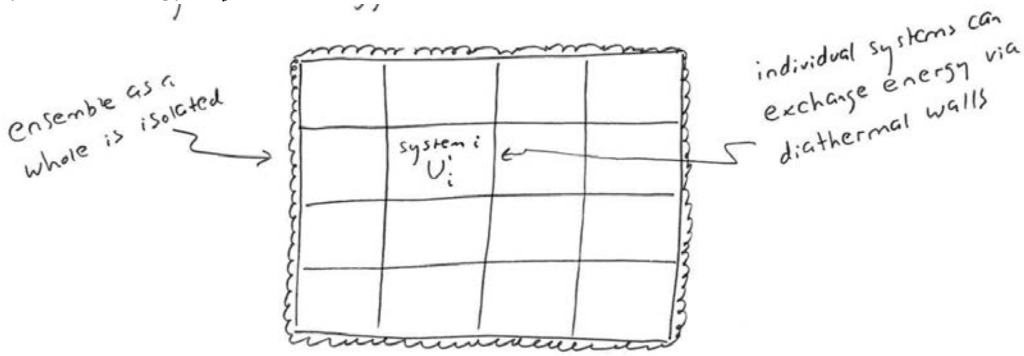
- Canonical ensemble: Set of all possible microstates of a system with fixed $V'$, n
  - System is closed and rigid, but can exchange energy with surroundings, i.e. diathermal walls

– System energy $U'_\nu$ can fluctuate

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– canonical partition function $Z = \sum_\nu e^{-U'_\nu/kT}$
sum over possible states of the system

– equilibrium (F minimized) for distribution

$$P_\nu = \frac{e^{-U'_\nu/k_BT}}{Z}$$ **Boltzmann distribution for canonical ensemble**

$P_\nu$: prob. of finding system in state $\nu$ with energy $U'_\nu$

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# 4 The partition functions

- Describe equilibrium properties and fluctuations
- Basis for calculating thermodynamic potentials and properties

$$\textbf{e.g.} < U > = -\frac{\partial \ln Z}{\partial(1/kT)}$$

$$C_V = \frac{1}{kT^2}\ \frac{\partial^2 lnZ}{\partial(1/kT)^2}$$

$$S' = \frac{< U >}{T} + k_B \ln Z$$

$$F' = -k_B T \ln Z$$

$$< U^2 > - < U >^2 = kT^2\ \frac{\partial < U >}{\partial T}$$

$$\ldots$$