Agenda: Information, Probability, Statistical Entropy

- Information and probability
  - simple combinatorics, random variables.
  - Probability distributions, joint probabilities, correlations
  - Statistical entropy
  - Monte Carlo simulations
- Partition of probability
  - Multiple partitions, max entropy, stationary states, stability
  - Canonical and grand canonical ensembles
  - Applications to chem. reactions
  - Decomposition of partition functions for independent particles, external & internal degrees of freedom
  - Gibbs' stability criteria, equilibrium
- Phase space evolution (Eta Theorem)

Reading Assignments
Weeks 6 & 7
LN III.1- III.6:

Kondepudi Ch. 20, 4,9

McQuarrie & Simon Ch. 3 & 4

Math Chapters
MC B, E

Decomposition of PF into Independent Components

Decomposition of PF for independent *d.o.f.* (different types of energy)

Decomposition of PF for independent particles (different particles)

Systems with multiple independent degrees of freedom (***i*** = translational, rotational, vibrational, electronic, nuclear,...),
Total energy equals sum over the individual energies $E = \langle E \rangle = \sum_i \langle E_i \rangle$

Total number of states $\Omega = \prod_i \Omega_i$, corresponding Ω_i for individual d.o.f.

$$Q(\beta) = \prod_i Q_i(\beta) = \prod_i \sum_n^{\Omega_i} e^{-\beta \cdot E_n(i)}$$

i **=** degree of freedom
n = # of μ state

Molecules, Atoms, Nuclei ⇨ $Q = Q^{trans} \cdot Q^{rot} \cdot Q^{vib} \cdot Q^{electr} \cdot Q^{nucl} \cdot \cdot \cdot$

Decomposition of the Partition Function

***i* = degree of freedom, *n* =1,2 # of particle. Start with 2-particle system**
N=2 identical classical particles (can be numbered)

$$q_1(\beta) = \sum_n^{\Omega} e^{-\beta\cdot E_n(1)} = e^{-\beta\cdot E_1(1)} + e^{-\beta\cdot E_2(1)} + e^{-\beta\cdot E_3(1)} + \ldots$$

$$\beta = 1/k_B T$$

$$q_2(\beta) = \sum_n^{\Omega} e^{-\beta\cdot E_n(2)} = e^{-\beta\cdot E_1(2)} + e^{-\beta\cdot E_2(2)} + e^{-\beta\cdot E_3(2)} + \ldots$$

set of possible μstate energies : $\{E_N\} = \{E(1+2)\} = \{E_{n1}(1) + E_{n2}(2),\ all\ n1, n2\}$

$$\begin{aligned} Q_{12} &= e^{-\beta[E_1(1)+E_1(2)]} + e^{-\beta[E_1(1)+E_2(2)]} + e^{-\beta[E_1(1)+E_3(2)]} + \ldots \\ &+ e^{-\beta[E_2(1)+E_1(2)]} + e^{-\beta[E_2(1)+E_2(2)]} + \ldots \\ &+ e^{-\beta[E_3(1)+E_1(2)]} + e^{-\beta[E_3(1)+E_2(2)]} + \ldots \\ &= \sum_j e^{-\beta E_j(1)} \cdot \sum_k e^{-\beta E_k(2)} = q_1 \cdot q_2 \end{aligned}$$

For N identical classical particles

$$Q = \prod_{n=1}^{N} q_n = q^N$$

For N identical indistinguishable quantal particles :

$$Q = \frac{1}{N!}\prod_{n=1}^{N} q = \frac{q^N}{N!}$$

Continuous Degrees of Freedom

Classical motion (linear and angular) through space etc. is continuous→ d.o.f.

1D, M particles $\{x_1, x_2, x_3, \ldots, x_M\}$ → energy $\varepsilon = \varepsilon(x_1, x_2, x_3, \ldots, x_M)$

For example, particle kinetic energy $\boxed{\varepsilon = (m/2)\upsilon^2}$

$$\text{Canonical PF}: Q_{trans} = \sum_n e^{-\beta\cdot\varepsilon_n} \rightarrow Q = \int dx_1 \cdots dx_M \, e^{-\beta\cdot\varepsilon(x_1,\cdots,x_M)} = \left(q_{trans}\right)^M$$

$$\text{Independent particles } \varepsilon(x_1,\cdots,x_M) = \sum_{n=1}^{M} \varepsilon(x_n). \quad \text{Free space } \varepsilon = \varepsilon(\upsilon)$$

$$q_{trans} = \int d\upsilon \, e^{-\beta\cdot\varepsilon(\upsilon)} = \int d\upsilon \, e^{-\varepsilon(\upsilon)/k_B\cdot T} = \int d\upsilon \, e^{-m\cdot\upsilon^2/2k_B\cdot T}$$

$$\langle\varepsilon\rangle = -\frac{\partial}{\partial\beta}\ell n Q = \frac{-1}{Q}\frac{\partial Q}{\partial\beta} = \frac{1}{Q}\int dx_1 \cdots dx_M \, \varepsilon(x_1,\cdots,x_M)\cdot e^{-\beta\cdot\varepsilon(x_1,\cdots,x_M)}$$

Continuous Degrees of Freedom

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For example, particle kinetic energy $\varepsilon = (m/2)\upsilon^2$

$$q_{trans} = \int d\upsilon\, e^{-m\cdot\upsilon^2/2k_B\cdot T} \rightarrow Q_{trans} = (q_{trans})^M \leftarrow M \text{ independent particles}$$

$$\langle\varepsilon\rangle = -\frac{\partial}{\partial\beta} Ln(q_{trans}) = \frac{-1}{q_{trans}}\frac{\partial q_{trans}}{\partial\beta} = -\frac{\partial}{\partial\beta} Ln\left[\int d\upsilon\, e^{-\beta\cdot m\cdot\upsilon^2/2}\right] \qquad \underline{\textit{per particle}}$$

$$\textit{Variable transform } v := \sqrt{\beta}\cdot\upsilon \rightarrow d\upsilon/dv = 1/\sqrt{\beta} \rightarrow \langle\varepsilon\rangle = -\frac{\partial}{\partial\beta} Ln\left[\frac{1}{\sqrt{\beta}}\cdot\int dv\, e^{-m\cdot v^2/2}\right]$$

$$\langle\varepsilon\rangle = -\frac{\partial}{\partial\beta}\left\{Ln\left(\beta^{-1/2}\right) + Ln\int dv\, e^{-m\cdot v^2/2}\right\} = -\frac{\partial}{\partial\beta}\left\{-\frac{1}{2}Ln(\beta)\right\} = \frac{1}{2\beta} = \frac{1}{2}(k_B\cdot T)$$

$$\boxed{\langle\varepsilon\rangle = \frac{1}{2}(k_B\cdot T)} \quad \textit{per particle and d.o.f.}$$

Equipartition of Thermal Energy

A similar conclusion can be drawn for any d.o.f. ***x*** for which the energy ε depends quadratically on ***x***: $\varepsilon(x) \propto x^2$

Canonical ensembles, systems (N, V, T) at constant temperature, at maximum entropy (stationary, equilibrium states):

Any degree of freedom *i* with a quadratic energy dependence carries in thermal equilibrium a mean energy of

$$\langle \varepsilon_i \rangle = \frac{1}{2}\left(k_B \cdot T\right)$$

Particles moving freely in 3D space (3 independent d.o.f.) kept at ***T***

$$\langle \varepsilon \rangle = \langle \varepsilon_x \rangle + \langle \varepsilon_y \rangle + \langle \varepsilon_z \rangle = \frac{3}{2}\left(k_B \cdot T\right)$$

Quantum mechanics

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