

Agenda: Information, Probability, Statistical Entropy

- Information and probability
 - simple combinatorics, stochastic variables.
 - Probability distributions, joint probabilities, correlations
 - Statistical entropy
 - Statistical entropy for bi- & multi-partitions
 - Microstates,
 - Stationary states defined by extreme statistical entropy, asymptotic stationary states
 - Constraints: in particle number, total energy,...
 - The Boltzmann factor, probability distribution
- Partition of probability, thermodynamic connection
 - Canonical Observables, Free Energy A
- Gibbs stability criteria, equilibrium
 - Grand Canonical Observables, Free Energy G
 - Application to chemical reactions
- Partition functions for other degrees of freedom
- Phase space evolution (Eta Theorem)

Reading Assignments

Weeks 5 & 6

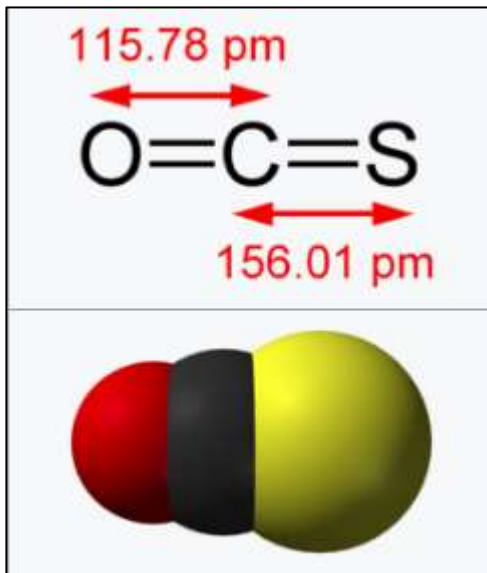
LN III.1- III.6:

Kondepudi Ch. 20
Additional Material

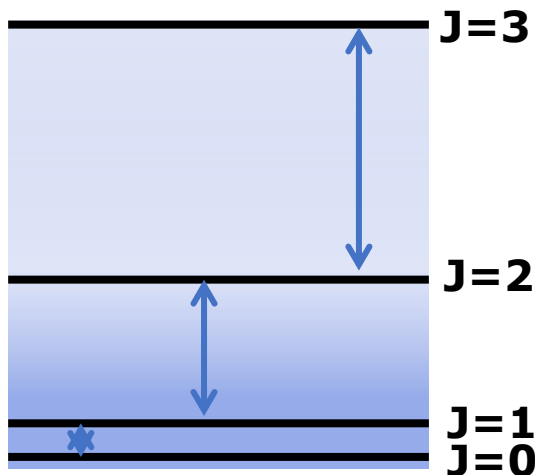
McQuarrie & Simon
Ch. 3 & 4

Math Chapters
MC B, E

Example: Carbonyl Sulfide OCS, Rot. Spectrum



El dipole moment 0.65 D
(1D = ≈ 0.020819434 e·nm)



Bond lengths R_{CO} and R_{CS} . Finite el. dipole moment,

Rotational spectrum $E_J = B \cdot J \cdot (J + 1)$; $J = 0, 1, \dots$

Rotational constant $B = \frac{\hbar^2}{2\mathcal{I}}$, \mathcal{I} = moment of inertia

$B(\text{OCS}) = 4.03 \cdot 10^{-24} \text{ J} \hat{=} 6.08 \text{ GHz} \hat{=} 0.203 \text{ cm}^{-1}$

Rotational transitions $J_i(\text{e.g. } 0^+) \xrightarrow{h\nu_{if}} J_f(\text{e.g. } 1^-)$

Transition frequency: $\nu_{J,J+1} = 2 \cdot B \cdot (J + 1) \sim 0.4 \text{ cm}^{-1}$

Thermal $k_B T \sim 200 \text{ cm}^{-1} \rightarrow$ **thermal excitation**

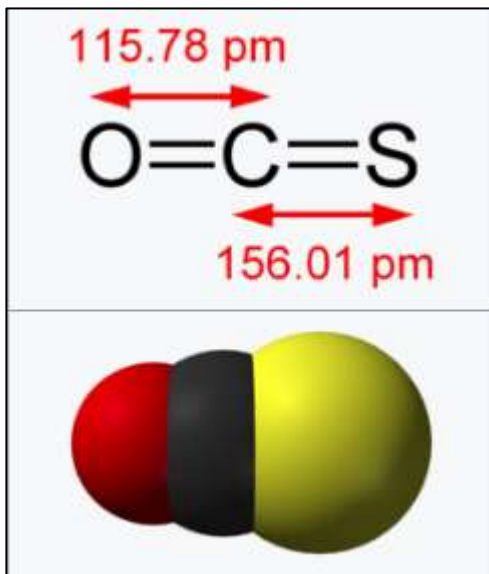
\rightarrow Molecules in heat bath (T) are not in g.s.

\rightarrow thermal populations of spectrum.

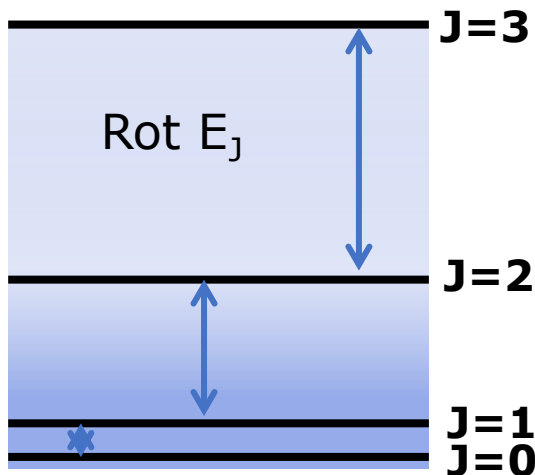
Equilibrium populations $p(J, T)$ given by

Canonical part. funct. $Q(T) = \sum_J (2J + 1) \cdot e^{-E_J / (k_B \cdot T)}$

Example: Carbonyl Sulfide OCS, Rot. Ensemble



El dipole moment 0.65 D
 (1D ≈ 0.020819434 e·nm)



OCS molecules in *heat bath*, temp. $T = 400\text{K}$.

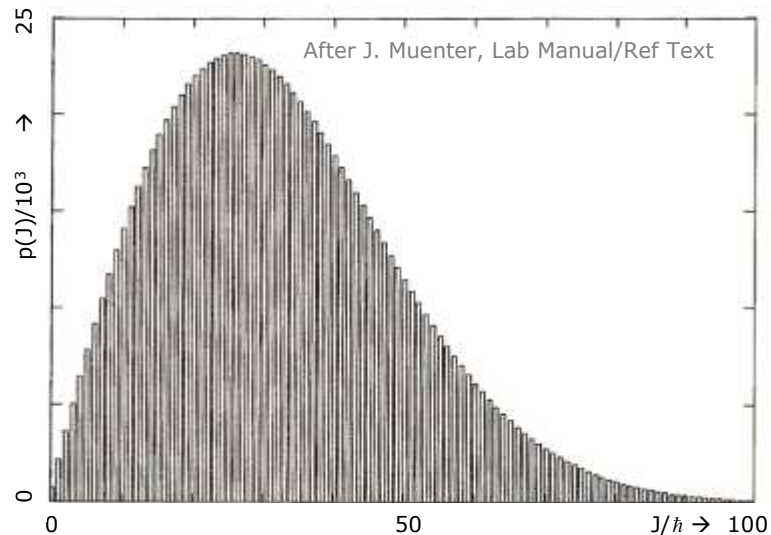
$$E_J = 0.203\text{cm}^{-1} \cdot J \cdot (J + 1); \quad J = 0, 1, \dots, 100$$

Boltzmann const. $k_B = 0.695\text{cm}^{-1}/\text{K}$

Canonical partition function :

$$Q(400\text{K}, J_{\max} = 100) = \sum_{j=0}^{100} (2J + 1) \cdot e^{-E_J/(k_B \cdot T)} \approx 1.4 \cdot 10^3$$

$$\text{Thermal population } p(J) = \frac{1}{Q} (2J + 1) \cdot e^{-E_J/(k_B \cdot T)}$$



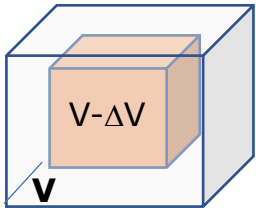
OCS Rotational
 Partition Function,
 $k_B T = 400\text{K}$.

→ Many quantum
 states are
 populated at room
 temp.

More Thermodynamic Connections

Macroscopic ensemble (system) parameters : (N, V, T)

$S = S(N, V, T) \rightarrow Q = Q(N, V, T)$ change with $V \rightarrow V \pm \Delta V$? Expansion/
Compression



$$Q(N, V, T) = \sum_n \exp \left\{ -\frac{E_n(V)}{k_B \cdot T} \right\} \rightarrow \text{internal (quantal) property } E_n(V)$$

$$\frac{\partial}{\partial V} Q(N, V, T) = \sum_n \frac{\partial}{\partial V} \exp \left\{ -\frac{E_n(V)}{k_B \cdot T} \right\} = \frac{1}{k_B \cdot T} \sum_n \left(-\frac{\partial E_n(V)}{\partial V} \right) \exp \left\{ -\frac{E_n(V)}{k_B \cdot T} \right\}$$

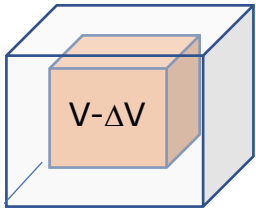
$$(-k_B \cdot T) \cdot \frac{\partial}{\partial V} [\ln Q(N, V, T)] = \frac{1}{Q} \sum_n \left(\frac{\partial E_n(V)}{\partial V} \right) \exp \left\{ -\frac{E_n(V)}{k_B \cdot T} \right\} = \left\langle \frac{\partial E(V)}{\partial V} \right\rangle_T$$

$\langle \partial E(V) / \partial V \rangle = ?$ compression $[\partial V < 0]$ increases internal energy
at conserved relative population of μ states ($S = S_{max} = \text{const}$) \rightarrow

Thermodynamic Connection

Macroscopic ensemble (system) parameters : (N, V, T)

$S = S(N, V, T) \rightarrow Q = Q(N, V, T)$ change with $V \rightarrow V \pm \Delta V$?



$$Q(N, V, T) = \sum_n \exp \left\{ -\frac{E_n(V)}{k_B \cdot T} \right\} \rightarrow \text{internal (quantal) property } E_n(V)$$

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$[-\partial E_n(V)/\partial V] = ?$ compression $[\partial V < 0]$ increases internal energy at conserved population of μ states ($S = \text{const}$) \rightarrow

TD meaning $-\frac{\partial E_n(V)}{\partial V} = p(N, V, T)$ external pressure Note sign !

$$dE_n(V) = -p(N, V, T) \cdot dV$$

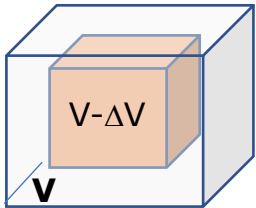
If **S** = constant, population does not change in compression/expansion \rightarrow internal excitation (external pressure work on system) is reversible.

More Thermodynamic Connections

Macroscopic ensemble (system) parameters : (N, V, T)

$S = S(N, V, T) \rightarrow Q = Q(N, V, T)$ change with $V \rightarrow V \pm \Delta V$? *Expansion/Compression*

TD meaning of variation of energy with volume?



$$-\left\langle \frac{\partial E(V)}{\partial V} \right\rangle_{\tau} = p(N, V, T) \text{ external pressure}$$

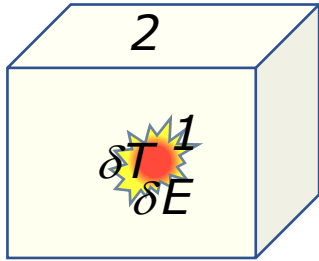
$$d\langle E(V) \rangle = -p(N, V, T) \cdot dV$$

Note sign !

If $S = \text{constant}$, population does not change in compression/expansion \rightarrow internal excitation (external pressure work on system) is reversible.

Thermal Stability of Canonical System

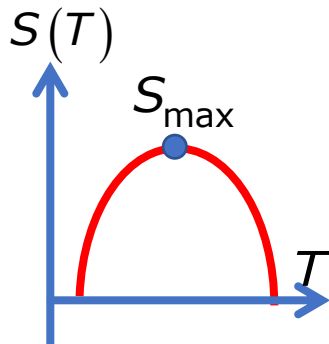
Is stationary system with max entropy stable? Consider thermal fluctuations δT about extremum $S \approx S_{\max}$ small disturbance #1 inside large system #2



$$S/k_B = \ln Q + \beta \cdot E \rightarrow \left(\frac{\partial S/k_B}{\partial E} \right)_{N,V,\beta} = \beta = \frac{1}{k_B \cdot T}$$

Stationary state at $S = S_{\max} = S_{\max,1} + S_{\max,2}$

Constant $E \rightarrow \delta E_1 = -\delta E_2, \beta_1 = \beta_2 \rightarrow T_1 \approx T_2 = T$



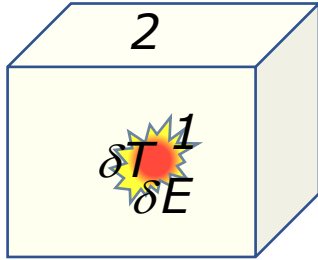
Q: Do small thermal δT fluctuations make the total system more stable or less stable? Driving force expected toward more stable configurations ($S \approx S_{\max}$)

Taylor expansion of $\Delta S = S - S_{\max}$

$$\Delta S = \sum_{i=1}^2 \left(\frac{\partial S}{\partial E_i} \right) \cdot \delta E_i + \frac{1}{2} \sum_{i=1}^2 \left(\frac{\partial^2 S}{\partial E_i^2} \right) \cdot (\delta E_i)^2 + \dots \text{mixed etc}$$

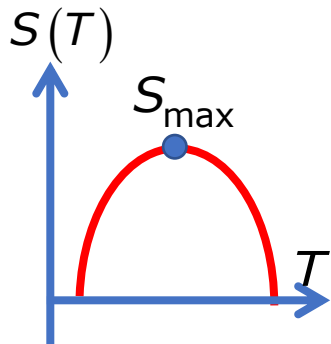
Thermal Stability of Canonical System

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$$S/k_B = \ln Q + \beta \cdot E \rightarrow \left(\frac{\partial S/k_B}{\partial E} \right)_{N,V,\beta} = \beta = \frac{1}{k_B \cdot T}$$

$$\Delta S \approx 0 + \frac{1}{2} \sum_{i=1}^2 \left(\frac{\partial^2 S}{\partial E_i^2} \right) \cdot (\delta E_i)^2 = \frac{1}{2} \sum_{i=1}^2 \left(\frac{\partial}{\partial E_i} \frac{1}{T_i} \right) \cdot (\delta E_i)^2 = \frac{1}{2} \delta^2 S$$



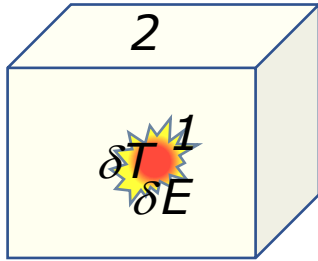
$$\frac{\partial}{\partial E_i} \frac{1}{T_i} = - \frac{1}{T_i^2} \frac{\partial T_i}{\partial E_i} \quad \leftarrow \quad \text{"heat capacity"}$$

$$C_{Vi} = \frac{\partial E_i}{\partial T_i} \rightarrow \delta E_i = C_{Vi} \cdot \delta T_i$$

$$\delta^2 S \approx - \frac{(C_{V1} + C_{V2})}{T^2} (\delta T)^2 < 0$$

Also: mechanical stability if $\kappa > 0$. $\rightarrow S = S_{max} \rightarrow$ stable, "equilibrium" state

Canonical Stability and Free Energy

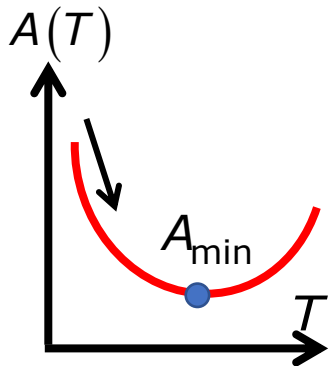


Is stationary system with max entropy stable ?
 Consider thermal fluctuations δT about extremum $\mathbf{S} \approx \mathbf{S}_{max}$ small disturbance #1 inside large system #2

$$S = k_B \cdot \ln Q + \beta \cdot E = k_B \cdot \ln Q + \frac{E}{T}$$

$$T \cdot S = k_B \cdot T \cdot \ln Q + E \quad \rightarrow \quad -k_B T \cdot \ln Q = (E - T \cdot S)$$

"Helmholtz Free Energy" $A = (E - T \cdot S)$



$$\ln Q = -\frac{A}{k_B T} \quad \rightarrow \quad Q = e^{-A/k_B T}$$

Helmholtz free energy $A(N, V, T)$ represents a driving potential, driving system to maximum stability \rightarrow
 $\rightarrow S = S_{max} \rightarrow$ stable, "equilibrium" state

Extremum-Maximum Entropy \leftrightarrow Minimum of Free Energy

Summary Canonical/ μ Canonical PF

Canonical PF

$$Q = Q(N, V, T)$$

Free energy

$$A = -k_B T \cdot \ln Q$$

Entropy

$$S = k_B \cdot \ln Q + \frac{E}{T}$$

$$S = - \left(\frac{\partial \ln A}{\partial T} \right)_V$$

Pressure

$$p = - \left(\frac{\partial \ln A}{\partial V} \right)_T$$

Internal (heat) energy

$$U = k_B T^2 \left(\frac{\partial \ln Q}{\partial T} \right)_V$$

Partition function = generating function for the probability distribution of all macroscopic thermodynamic observables.

Expectation values for the internal energy, pressure, entropy, and free energy can be derived from Q using differential operators.

Closed-form expression derived for Q in terms of a macroscopic Free Energy A and temperature T.

$$\lim_{T \rightarrow 0} (Q) = \lim_{T \rightarrow 0} \left(\sum_E \varpi(E) \exp\{-E/T\} \right) = \varpi(E)$$



For a **microcanonical ensemble**, degeneracy $\varpi(E)$ directly determines expectation values for all observables.

Summary Canonical PF

Canonical PF

$$Q = Q(N, V, T)$$

Entropy

$$S = k \left(\ln Q + T \frac{\partial \ln Q}{\partial T} \right)$$

Internal (heat) energy

$$U = kT^2 \left(\frac{\partial \ln Q}{\partial T} \right); \text{ rel. } E_{g.s.}$$

Pressure

$$p = kT \left(\frac{\partial \ln Q}{\partial V} \right)$$

Free energy

$$A = -kT \cdot \ln Q$$

Partition function = generating function for the probability distribution of all macroscopic thermodynamic observables.

Expectation values for the internal energy, pressure, entropy, and free energy can be derived from Q using differential operators.

Closed-form expression derived for Q in terms of a macroscopic Free Energy A and temperature T.

For a microcanonical ensemble, the degeneracy ω determines expectation values for all observables.