Entropy and Energy representations. Thermodynamic states

Friday, September 8, 2017
BME/CHE/PHY 558, Physical & Quantitative Biology
Rutgers University: Chemical Thermodynamics
Lecturer: Gábor Balázsi
Determine Max W and MaxEnt!

Spin an arrow around a disk with 4 colors N=12 times.

\[
\frac{S_{\text{Boltzmann}}}{k} = \ln(W) = \ln \left( \frac{N!}{n_r!n_y!n_g!n_b!} \right)
\]

\[
\frac{S_{\text{Shannon}}}{k} \approx - \sum_{\{r,y,g,b\}} p_i \ln(p_i)
\]

(a) Ordered  
(b) Biased  
(c) Biased  
(d) Random

\[
\begin{align*}
W &= ? \\
S &= ?
\end{align*}
\]

\[
\begin{align*}
W &= ? \\
S &= ?
\end{align*}
\]

\[
\begin{align*}
W &= ? \\
S &= ?
\end{align*}
\]

\[
\begin{align*}
W &= ? \\
S &= ?
\end{align*}
\]
Max W is equivalent to MaxEnt. But Maxwell ≠ Shannon

Spin an arrow around a disk with 4 colors N=12 times.
What is the MaxEnt distribution for coin flips?

Flip a coin $N$ times. If Heads=1 occur $n_1$ times, with probability $p = n_1/N$:

MaxW:

$$W = \frac{N!}{n_1!n_0!} \quad \Rightarrow \quad W \text{ is maximum if: } n_1 = n_0$$

MaxEnt:

$$\frac{S}{k} \approx -p \ln(p) - (1-p) \ln(1-p)$$

$$\frac{dS}{kdp} = -\frac{dp}{k} \left[ p \ln p + (1-p) \ln(1-p) \right] = \ln \left( \frac{1-p}{p} \right)$$

$$\ln \frac{1-p}{p} = 0 \Rightarrow p = 1 - p = \frac{1}{2}$$

MaxEnt and MaxW imply a flat distribution.
Maximum Entropy without constraints

\[ S(p_1, p_2, \ldots p_M) = -\sum_i p_i \ln(p_i) \]  

Goal: maximize \( S \).

Constraint: \( \sum_i p_i = 1 \rightarrow \sum_i dp_i = 0 \)

\[ \frac{\partial S}{\partial p_i} = -\frac{\partial [p_i \ln(p_i)]}{\partial p_i} = -\ln(p_i) - 1 \]

Applying Lagrange multipliers.

\[-\ln(p_i) - 1 - \alpha = 0 \rightarrow p_i = e^{-1-\alpha} = \text{const} \]

\[ \sum_i p_i = \sum_i e^{-1-\alpha} = Me^{-1-\alpha} = 1 \rightarrow p_i = e^{-1-\alpha} \frac{e^{-1-\alpha}}{\sum_i e^{-1-\alpha}} = \frac{1}{M} \]

Conclusion: a flat (uniform) distribution maximizes \( S \).
Maximum Entropy + Average fixed

\[ S(p_1, p_2, \ldots p_M) = -\sum_i p_i \ln(p_i) \]

Goal: to maximize \( S \).

Constraints:
\[ \sum_i p_i = 1 \quad \rightarrow \quad \sum_i dp_i = 0 \]
\[ \sum_i \varepsilon_i p_i = \mu \quad \rightarrow \quad \sum_i \varepsilon_i dp_i = 0 \]

Applying Lagrange multipliers:
\[-\ln(p_i) - 1 - \alpha - \beta \varepsilon_i = 0 \quad \rightarrow \quad p_i = e^{-1-\alpha-\beta \varepsilon_i} \]

Application: How would particles distribute on energy levels if their average energy is given?

Conclusion: the \textbf{exponential distribution} maximizes \( S \).
Example: estimating the bias of loaded dice

For a die, \( i = 1 \ldots 6 \)

\[
\varepsilon_i = i \\
x = e^{-\beta}
\]

\[
p_i = \frac{x^i}{x + x^2 + \ldots + x^6}
\]

\[
\langle \varepsilon \rangle = \langle i \rangle = \frac{x + 2x^2 + \ldots + 6x^6}{x + x^2 + \ldots + x^6}
\]
Example: estimating the bias of coins

For a coin, \( i=1,2 \) (Heads=1, Tails=2)

\[
\begin{align*}
\epsilon_i &= i \\
x &= e^{-\beta}
\end{align*}
\]

\[
\begin{align*}
p_1 &= p(\text{Heads}) = \frac{x}{x + x^2} \\
p_2 &= p(\text{Tails}) = \frac{x^2}{x + x^2}
\end{align*}
\]

\[
\begin{align*}
\langle \epsilon \rangle = \langle i \rangle &= \frac{x + 2x^2}{x + x^2} = \frac{1 + 2x}{1 + x}
\end{align*}
\]

\[
x = \frac{\langle \epsilon \rangle - 1}{2 - \langle \epsilon \rangle} \quad \text{if} \quad \langle \epsilon \rangle = 1.8 \quad \Rightarrow \quad x = \frac{0.8}{0.2} = 4
\]

\[
\begin{align*}
p_1 &= \frac{1}{5} \\
p_2 &= \frac{4}{5}
\end{align*}
\]
Thermodynamic systems

Thermodynamic system = collection of matter, delineated by real or imaginary boundaries.
Types of thermodynamic systems

- **Open system**: Can exchange volume, matter and energy with its surroundings.
- **Closed system**: Can exchange volume and energy, but not matter with its surroundings.
- **Adiabatically isolated system**: Heat cannot cross its boundaries.
- **Isolated system**: Neither volume, nor matter, nor energy can cross its boundaries.
- **Simple system**: Homogeneous, with only a single phase, no boundary effects, no changes due to external fields.
  - **Semipermeable membrane**: Certain molecules can cross it, others cannot.
  - **Phase**: Homogeneous part of a system that is separable. Pressure, temperature, concentration uniform or continuous within the phase.
Extensive properties of thermodynamic systems

**Extensive property**: when a system’s property is the sum of its subsystems’ properties:

\[ \text{Prop}(S_1+S_2+S_3) = \text{Prop}(S_1) + \text{Prop}(S_2) + \text{Prop}(S_3). \]

Spatial extent (volume, surface, length): Extensive.

**Number of particles**: Extensive.

**Internal energy**: Extensive. For non-interacting particles:

\[ U = \sum_{i=1}^{M} N_i \varepsilon_i \]

**Entropy**: Extensive.
Intensive properties of thermodynamic systems

**Intensive property**: when a system’s property is equal to its subsystems’ properties:

\[ \text{Prop}(S_1+S_2+S_3) = \text{Prop}(S_1) = \text{Prop}(S_2) = \text{Prop}(S_3). \]

**Temperature**: Intensive.

**Pressure**: Intensive.

**Chemical potential**: Intensive.

**Concentration**: Intensive.
The Postulates of Thermodynamics
by Herbert B. Callen

*Postulate* (or *axiom*) = A statement considered true without proof.
Basic Problem of Thermodynamics

Determine the equilibrium state that eventually results after the removal of internal constraints in a closed system.
Basic Problem of Thermodynamics

Determine the equilibrium state that eventually results after the removal of internal constraints in a closed system.

$U^{(F)}$, $V^{(F)}$, $N_1^{(F)}$, $N_2^{(F)}$, $\ldots$, $N_M^{(F)}$
Postulate #1

There exist particular states (called equilibrium states) of simple systems that, macroscopically, are characterized completely by the internal energy $U$, the volume $V$, and the amounts of the $M$ components $n_1, n_2, \ldots, n_M$.

$$S^{(1)} = S^{(1)}(U^{(1)}, V^{(1)}, N_1^{(1)}, N_2^{(1)}, \ldots, N_M^{(1)})$$
Postulate #2

For all equilibrium states there exists a function (the entropy $[S]$) such that: In the absence of constraints, the extensive parameters $U, V, n_1, n_2, \ldots, n_M$ take on values that maximize the entropy $S$ over all microstates.

\[
S_{\text{max}} = S(U^{(F)}, V^{(F)}, N_1^{(F)}, N_2^{(F)}, \ldots, N_M^{(F)})
\]
Fundamental thermodynamic equation: Entropy representation

System completely characterized by:
\[ U^{(F)}, V^{(F)}, N_1^{(F)}, N_2^{(F)}, \ldots, N_M^{(F)} \]

Entropic Fundamental Equation: Entropy \( S \) depends on extensive properties of the system.

\[ S = S(U,V,N) = S(U,V,[N_1,N_2,\ldots,N_M]) \]

=maximized when \( U \) is constant

Everything (all thermodynamics) results from here.

Differential form: defines how \( dS \) depends on \( dU, dV, dN \).

\[ dS = \left( \frac{\partial S}{\partial U} \right)_{V,N} dU + \left( \frac{\partial S}{\partial V} \right)_{U,N} dV + \sum_{j=1}^{M} \left( \frac{\partial S}{\partial N_j} \right)_{U,V,N_{i\neq j}} dN_j \]
Postulate #3.1

The entropy \( S \) of a composite system is additive over the constituent subsystems.

\[
S^{(1+2)} = S^{(1)} + S^{(2)}
\]
Postulate #3.2

The entropy $S$ is continuous, differentiable and monotonically increasing function of the energy.

If $U$ increases, $S$ must increase as well.
If $S$ increases, $U$ must increase as well.

This means that $S(U)$ is invertible.

$$S = S(U, V, N) = S(U, V, [N_1, N_2, \ldots, N_M])$$

$$U = U(S, V, N) = U(S, V, [N_1, N_2, \ldots, N_M])$$
The fundamental thermodynamic equation:

**Energy representation**

System completely characterized by:

\[ S^{(F)}, V^{(F)}, \]
\[ N_1^{(F)}, N_2^{(F)}, \ldots, N_M^{(F)} \]

**Energetic Fundamental Equation**: Energy \( U \) depends on extensive properties of the system.

\[ U = U(S, V, N) = U(S, V, [N_1, N_2, \ldots, N_M]) \quad \text{=minimum when } S \text{ is constant} \]

Everything (all thermodynamics) results from here.

**Differential form**: defines how \( dU \) depends on \( dS, dV, dN \).

\[
dU = \left( \frac{\partial U}{\partial S} \right)_{V,N} dS + \left( \frac{\partial U}{\partial V} \right)_{S,N} dV + \sum_{j=1}^{M} \left( \frac{\partial U}{\partial N_j} \right)_{S,V,N_{i\neq j}} dN_j
\]
When U is fixed: Maximum entropy
When S is fixed: Minimum energy

‘MaxEnt’

‘MinEnerg’

Equilibrium corresponds to maximum entropy when energy is controlled.
Equilibrium corresponds to minimum energy when entropy is controlled.

(Find the minimum rope length to cover a given rectangular area.
Find the maximum area that can be covered by a given rope.)

Remember: Rope problem!
Postulate #4

The entropy of any system vanishes in the state for which:

$$\left( \frac{\partial U}{\partial S} \right)_{V,N_1, N_2, \ldots, N_M} = 0$$

(that is, at the zero of temperature).