

Chapter 10

The Boltzmann Distribution Law

1. The statistical thermodynamics of a cooperative system.

Perhaps the simplest statistical mechanical system having ‘cooperativity’ is the three-level system in the following table:

Energies	$2\varepsilon_0$	ε_0	0
Degeneracies	γ	1	1

- Write an expression for the partition function q as a function of energy ε , degeneracy γ , and temperature T .
- Write an expression for the average energy $\langle \varepsilon \rangle$ versus T .
- For $\varepsilon_0/kT = 1$ and $\gamma = 1$, compute the populations, or probabilities, p_1^* , p_2^* , p_3^* of the three levels.
- Now if $\varepsilon_0 = 2 \text{ kcal mol}^{-1}$ and $\gamma = 1000$, find the temperature T_0 at which $p_1 = p_3$.
- Under condition (d), compute p_1^* , p_2^* , and p_3^* at temperature T_0 .

$$(a) \quad q = 1 + e^{-\varepsilon_0/kT} + \gamma e^{-2\varepsilon_0/kT}.$$

$$(b) \quad \begin{aligned} \langle \varepsilon_0 \rangle &= 0p_0 + \varepsilon_0 p_1 + 2\varepsilon_0 p_2 \\ &= \frac{1}{q} \left(\varepsilon_0 e^{-\varepsilon_0/kT} + 2\varepsilon_0 \gamma e^{-2\varepsilon_0/kT} \right) = -\frac{\partial \ln q}{\partial \beta}. \end{aligned}$$

$$\begin{aligned}
\text{(c)} \quad q &= 1 + e^{-1} + e^{-2} = 1.5032, \\
p_1 &= \frac{1}{q} = 0.6652, \\
p_2 &= \frac{e^{-1}}{q} = 0.2447, \\
p_3 &= \frac{e^{-2}}{q} = 0.0900.
\end{aligned}$$

(d) Since $p_1 = 1/q$ and $p_3 = \gamma e^{-2\varepsilon_0/kT}/q$, we want

$$\begin{aligned}
\gamma e^{-2\varepsilon_0/kT_0} = 1 &\implies -\frac{2\varepsilon_0}{kT_0} = \ln(1/\gamma) = -6.9078 \\
\implies T_0 &= \frac{2(2000 \text{ cal mol}^{-1})}{6.9078(2 \text{ cal mol}^{-1})} = 289.5 \text{ K}.
\end{aligned}$$

(Use R in place of k for molar calculations.)

$$\text{(e)} \quad \frac{\varepsilon_0}{kT} = \frac{2000 \text{ cal mol}^{-1}}{(2 \text{ cal K}^{-1} \text{ mol}^{-1})(289.5 \text{ K})} = 3.4539.$$

$$\text{Now } q = 1 + e^{-3.45} + 1000e^{-6.9078} = 2.0317,$$

$$\begin{aligned}
p_1 &= \frac{1}{q} = 0.4922 = p_3, \\
p_2 &= e^{-3.45}/q = 0.0156.
\end{aligned}$$

5. Entropy depends on distinguishability.

Given a system of molecules at $T = 300 \text{ K}$, $q = 1 \times 10^{30}$, and $\Delta U = 3740 \text{ J mol}^{-1}$,

- (a) What is the molar entropy if the molecules are distinguishable?
- (b) What is the molar entropy if the molecules are indistinguishable?

(a) For *distinguishable* particles, where $Q = q^N$, the molar entropy is

$$\begin{aligned}\frac{S}{n} &= R \ln q + \frac{\Delta U}{nT}, \\ \frac{\Delta U}{n} &= 3740 \text{ J mol}^{-1} \implies \frac{S}{n} = (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \ln(10^{30}) + \frac{3740 \text{ J}}{300 \text{ mol K}} \\ \implies \frac{S}{n} &= 586.8 \text{ J K}^{-1} \text{ mol}^{-1}.\end{aligned}$$

(b) For *indistinguishable* particles,

$$Q = \frac{q^N}{N!} \approx \frac{q^N}{(N/e)^N} \implies \ln Q \approx N \ln q - N(\ln N - 1),$$

so

$$\frac{S}{n} = R(\ln q - \ln N + 1) + \frac{\Delta U}{nT}.$$

$N = n\mathcal{N}_A$, where N = number of molecules, n = number of moles and \mathcal{N}_A = Avogadro's number.

$$\begin{aligned}\implies \frac{S}{n} &= R \ln \left(\frac{q}{n\mathcal{N}_A} + 1 \right) + \frac{\Delta U}{nT} \\ &= (8.31 \text{ J K}^{-1} \text{ mol}^{-1}) \left[\ln \left(\frac{10^{30}}{6 \times 10^{23}} \right) + 1 \right] + \frac{3740}{300} = 139.9 \text{ J K}^{-1} \text{ mol}^{-1}.\end{aligned}$$

Note that S is larger if particles are distinguishable.

so

$$\Delta U = -\left(\frac{\partial \ln Q}{\partial \beta}\right) \approx -\frac{\partial}{\partial \beta}(N \ln q - N \ln N + N) = -N \left(\frac{\partial \ln q}{\partial \beta}\right),$$

so

$$\begin{aligned} \langle \varepsilon \rangle &= \frac{\Delta U}{N} = \frac{\Delta U}{N} = -\left(\frac{\partial \ln q}{\partial \beta}\right) \\ \implies \langle \varepsilon \rangle &\text{ doesn't depend on distinguishability.} \end{aligned}$$

$$\begin{aligned} \text{Now } S &= k \ln Q + \frac{\Delta U}{T} = Nk(\ln q - \ln N + 1) - \frac{N}{T} \left(\frac{\partial \ln q}{\partial \beta}\right) \\ &= S_{\text{distinguishable}} - \ln N + 1 < S_{\text{distinguishable}} \text{ for } N > 2 \text{ particles.} \end{aligned}$$

As seen in Problem 5, the entropy is larger for distinguishable systems.

9. Computing the Boltzmann distribution.

You have a thermodynamic system with three states. You observe the probabilities $p_1 = 0.9$, $p_2 = 0.09$, $p_3 = 0.01$ at $T = 300$ K. What are the energies ε_2 and ε_3 of states 2 and 3 relative to the ground state?

$$\begin{aligned} q &= 1 + e^{-\varepsilon_2/kT} + e^{-\varepsilon_3/kT}, \\ p_1 &= \frac{1}{q} = 0.9 \implies q = \frac{10}{9}, \\ p_2 &= \frac{e^{-\varepsilon_2/kT}}{q} = 0.9e^{-\varepsilon_2/kT} = 0.09 \implies e^{-\varepsilon_2/kT} = \frac{1}{10} \\ \implies \varepsilon_2 &= kT \ln 10 = (2 \text{ cal K}^{-1} \text{ mol}^{-1})(300 \text{ K}) \ln 10 = 1.38 \text{ kcal mol}^{-1}, \\ p_3 &= \frac{e^{-\varepsilon_3/kT}}{q} = 0.9e^{-\varepsilon_3/kT} = 0.01 \implies e^{-\varepsilon_3/kT} = \frac{1}{90}, \\ \implies \varepsilon_3 &= kT \ln 90 = (2 \text{ cal K}^{-1} \text{ mol}^{-1})(300 \text{ K}) \ln 90 = 2.70 \text{ kcal mol}^{-1}. \end{aligned}$$

10. The pressure reflects how energy levels change with volume.

If energy levels $\varepsilon_i(V)$ depend on the volume of a system, show that the pressure is the average

$$p = -N \left\langle \frac{\partial \varepsilon}{\partial V} \right\rangle.$$

From the fundamental energy equation, $p = -(\partial \Delta U / \partial V)_{S,N}$. But $\Delta U = N \langle \varepsilon \rangle$, so

$$\begin{aligned} p &= -N \left(\frac{\partial \langle \varepsilon \rangle}{\partial V} \right)_{S,N} = -N \left[\frac{\partial}{\partial V} \sum_1^N \varepsilon_i(V) p_i \right] = -N \left[\sum_1^N \frac{\partial}{\partial V} \varepsilon_i(V) p_i \right] \\ &= -N \left[\sum_1^N \left(\frac{\partial \varepsilon_i(V)}{\partial V} \right) p_i \right] = -N \left\langle \frac{\partial \varepsilon}{\partial V} \right\rangle. \end{aligned}$$

11. The end-to-end distance in polymer collapse.

Use the two-dimensional four-bead polymer of Example 10.3. The distance between the chain ends is 1 lattice unit in the compact conformation, 3 lattice units in the extended conformation, and $\sqrt{5}$ lattice units in each of the other three chain conformations. Plot the average end-to-end distance as a function of temperature, if the energy is

(a) $\varepsilon = 1 \text{ kcal mol}^{-1}$.

(b) $\varepsilon = 3 \text{ kcal mol}^{-1}$.

To get the average end-to-end length $\langle d \rangle$, use the Boltzmann probabilities p_j for each of the $j = 1, 2, \dots, 5$ conformations:

$$\langle d \rangle = \sum_{j=1}^5 p_j d_j = (1) \left(\frac{1}{q} \right) + \sqrt{5} \left(\frac{3e^{-\varepsilon/kT}}{q} \right) + 3 \left(\frac{e^{-\varepsilon/kT}}{q} \right),$$

where $q = 1 + 4e^{-\varepsilon/kT}$, so

$$\langle d \rangle = \frac{1 + 9.71e^{-\varepsilon/kT}}{1 + 4e^{-\varepsilon/kT}}.$$

The maximum end-to-end distance ($T \rightarrow \infty$) is

$$\frac{1 + 3\sqrt{5} + 3}{5} = 2.14.$$

The midpoint is at $\langle d \rangle = 1.57$. You can find the midpoint temperature T_0 from

$$\begin{aligned} (1.57) \left(1 + 4e^{-\varepsilon/kT_0}\right) &= 1 + 9.71e^{-\varepsilon/kT_0} \\ \implies \frac{0.57}{3.43} &= e^{-\varepsilon/kT_0}. \end{aligned}$$

$$(a) \quad T_0 = \frac{(1000 \text{ cal mol}^{-1})}{(2 \text{ cal K}^{-1} \text{ mol}^{-1}) \ln\left(\frac{3.43}{0.57}\right)} = 278 \text{ K}.$$

$$(b) \quad T_0 = 835 \text{ K}.$$

12. The lattice model of dimerization.

Use the lattice model for monomers bonding to form dimers, and assume large volumes $V \gg 1$.

- Derive the partition function.
- Compute $p_1(T)$ and $p_2(T)$, the probabilities of monomers and dimers as a function of temperature, and sketch the dependence on temperature.
- Compute the bond breakage temperature T_0 at which $p_1 = p_2$.

- If you choose the convention that the ground state (dimer) has zero energy and the dissociated state has energy $\varepsilon > 0$, then the partition function is

$$\begin{aligned} Q &= \sum_{\varepsilon} g(\varepsilon) e^{-\varepsilon/kT} \\ &= (V - 1) + \left(\frac{1}{2}V - 1\right) (V - 1) e^{-\varepsilon/kT}. \end{aligned}$$