Week 1

The Boltzmann Factor and Partition Functions

1.1 Overview of Major Results

1/10:
- In this course, we will review thermochemistry from intro chem, but go deeper with statistical mechanics.

- TA: Haozhi.
  - Did his undergrad at Oxford.
  - Has already taught this class in the PME.

- **Boltzmann constant**: The following constant. *Denoted by $\boldsymbol{k_B}$. Given by*

$$k_B = 1.381 \times 10^{-23}\,\text{J/K}$$

  - Equal to the quotient of the ideal gas constant and Avogadro's constant.

- **Ideal gas law**: The following relationship between the pressure P, volume V, number of moles n, and temperature T of an ideal gas, and the ideal gas constant R.

$$PV = nRT$$

  - Multiplying by the quotient of Avogadro's constant with itself yields

$$PV = nN_A \frac{R}{N_A} T$$
$$PV = Nk_B T$$

    where N is the number of molecules in the system.
  - The unit for PV is Joules.
  - Thus, the above form states that PV is equal to the number of particles times a tiny unit of energy.

- Relating PV to the kinetic energy of gas molecules/atoms[1].

  - Pressure originates microscopically from the collisions of particles with the walls of their container.
  - As such, we first seek to derive an expression for the number of collisions per second per area.

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[1]This derivation differs from that on Labalme (2021a, pp. 3–4) and Labalme (2021b, pp. 18–19), in that its approach is from a flux perspective.

- ■ Consider the number $N(v_x)$ particles with speed v_x in the x-direction.
- ■ The quotient $N(v_x)/V$ is the density in the container of particles with speed v_x.
- ■ Thus, the flux "through"/to/at the wall is this density, times the area of the wall, times the x-velocity of the particles.
- − Assume an elastic collision of each particle with the wall. Thus, when each particle of mass m collides with the wall, it transfers $2mv_x$ of momentum.
- − Therefore, since $F = \mathrm{d}p/\mathrm{d}t$, the overall force exerted on the wall by the gas particles moving with speed v_x is $2mv_x$, $N(v_x)/V \cdot v_x \cdot \text{Area}$ times per second.
- − But, of course, we must sum over all possible v_x, so the total force

$$F = \int_{v_x > 0} 2mv_x \cdot \frac{N(v_x)}{V} \cdot v_x \cdot \text{Area} \, \mathrm{d}v_x$$

- − It follows that

$$P = \frac{F}{\text{Area}}$$
$$= \int_{v_x > 0} 2mv_x^2 \cdot \frac{N(v_x)}{V} \, \mathrm{d}v_x$$

The factor of $1/2$ in the following line comes from the fact that we are only integrating over half of the possible v_x^2s (i.e., the positive ones).

$$= 2m \cdot \frac{N}{V} \cdot \frac{1}{2} \langle v_x^2 \rangle$$
$$= \frac{N}{V} m \langle v_x^2 \rangle$$
$$PV = Nm \cdot \langle v_x^2 \rangle$$

Assuming that the gas is not moving in any one direction means that $\langle v_x^2 \rangle = \langle v_y^2 \rangle = \langle v_z^2 \rangle = \frac{1}{3} \langle v^2 \rangle$. Therefore,

$$= Nm \cdot \frac{1}{3} \langle v^2 \rangle$$
$$= \frac{2}{3} N \cdot \frac{1}{2} m \langle v^2 \rangle$$
$$= \frac{2}{3} N \cdot \langle E_{KE} \rangle$$
$$\langle E_{KE} \rangle = \frac{3}{2} \frac{PV}{N}$$
$$\langle E_{KE} \rangle = \frac{3}{2} k_B T$$

- − Note that this applies to all sorts of regimes — we used no properties of the particles (e.g., atom vs. molecule) to derive this relationship.

- • Getting the distribution of the gas energies or speed is the next logical step.

- • First, though, we consider alternate occurrences of $k_B T$.

- − The activation energy of Arrhenius (1889): "To collide is to react" is inaccurate; it must collide with sufficient energy. The molecule must be "activated."

$$k = A\mathrm{e}^{-E_a/RT} = A\mathrm{e}^{-E_a/k_B T}$$

- ■ The first E_a is the molar energy of activation; the second is the molecular energy of activation.
- ■ Yields the probability distribution of a molecule reacting.
 - Nernst equation:
$$E_{\text{cell}} = E_{\text{cell}}^0 - \frac{RT}{nF} \ln Q$$
- ■ $\ln Q$ is the ratio inside vs. outside the membrane.
- ■ $F = N_A e$ where e is the charge of an electron.
- ■ Thus,
$$\Delta E = \frac{RT}{nF} = \frac{k_B T}{ne}$$
- ■ If the potential across the membrane is approximately $k_B T$, then $\ln Q \approx 1$, so $Q \approx \mathrm{e}$.
- ■ Thus, at body temperature ($T = 310\,\text{K}$), $k_B T/\mathrm{e} = 26\,\text{mV}$.
 - The speed of sound: Certainly sound cannot travel faster than the molecules. Therefore, we can derive the following approximation for the speed of sound.
$$\frac{1}{2} m \left\langle v^2 \right\rangle = \frac{3}{2} k_B T$$
$$\sqrt{\langle v^2 \rangle} = \sqrt{\frac{3 k_B T}{m}}$$
$$v_{\text{rms}} = \sqrt{\frac{3 k_B T}{m}}$$
- ■ This estimate is within $20-30\,\%$ — take m to be the average mass of air.
 - de Broglie wavelength: A molecule has a kinetic energy approximately equal to $k_B T$. Additionally, the quantum mechanical kinetic energy of a molecule aligns with this, as $\hbar^2 k^2/2m \approx k_B T$. Furthermore, the particle-wave duality relates the momentum to wavelength by $p = \hbar k = h/\lambda$. Therefore,
$$\lambda \approx \sqrt{\frac{h^2}{2 m k_B T}}$$
- ■ Thus, a gas at STP has a very small de Broglie wavelength and behaves classically.
- ■ Only at very low temperatures with very light gasses do quantum considerations come into play.
- ■ A H_2 molecule at $300\,\text{K}$ has de Broglie wavelength $\lambda = 1.78\,\text{Å}$.
- ■ Note that the quantum mechanical kinetic energy of a free particle is derived as follows.
$$\hat{H}\psi = E\psi$$
$$-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2}\left(\mathrm{e}^{ikx}\right) = E\mathrm{e}^{ikx}$$
$$\frac{\hbar^2 k^2}{2m} \mathrm{e}^{ikx} = E\mathrm{e}^{ikx}$$
$$E = \frac{\hbar^2 k^2}{2m}$$

- **Boltzmann factor**: Gives the relative probability p_2/p_1 of two states E_1, E_2, provided their respective energies E_1, E_2. *Given by*
$$\frac{p_2}{p_1} = \mathrm{e}^{-(E_2 - E_1)/k_B T}$$
 - Consider states $E_1, E_2, E_3, \dots$, denoted by their energies.

– Consistency check: Given

$$\frac{p_2}{p_1} = e^{\frac{-(E_2 - E_1)}{k_B T}} \qquad\qquad \frac{p_3}{p_2} = e^{\frac{-(E_3 - E_2)}{k_B T}}$$

we do indeed have

$$\frac{p_3}{p_1} = \frac{p_3}{p_2} \cdot \frac{p_2}{p_1} = e^{\frac{-(E_3 - E_2)}{k_B T} + \frac{-(E_2 - E_1)}{k_B T}} = e^{\frac{-(E_3 - E_1)}{k_B T}}$$

– We'll take this as God-given for now. Boltzmann derived it with a very good knowledge of the thermodynamics of freshman chemistry.

- We're starting with the above exciting result, and then going back and building up to it over the next three weeks.

- We write the Boltzmann factor for degenerate states as follows.

  – Consider four states at E_2 and one state at E_1.
  – The Boltzmann factor still tells us that $p_2/p_1 = e^{-(E_2 - E_1)/k_B T}$, but we have to make the following adjustment. Indeed, the total probability of being in one of the four states at energy E_2 is $p(E_2) = 4p_2$, while the total probability of being in the one state at energy E_1 is still just $p(E_1) = 1p_1$.
  – In each state E_2,
  $$\frac{p(E_2)}{p(E_1)} = \frac{N_2}{N_1} e^{-(E_2 - E_1)/k_B T}$$

- The weekly quiz.

  – The first quiz will be next week.
  – A Canvas quiz – we'll have 24 hours to take it, but only 1 hour to take it.

1.2 Boltzmann Factor Examples / Partition Function

1/12:
- We will apply the Boltzmann factor to electronic, magnetic, translational, rotational, and vibrational molecular states.

- Example: Sodium lamp – two lines at 589.6 nm and 589.0 nm with intensity ratio 1:2.
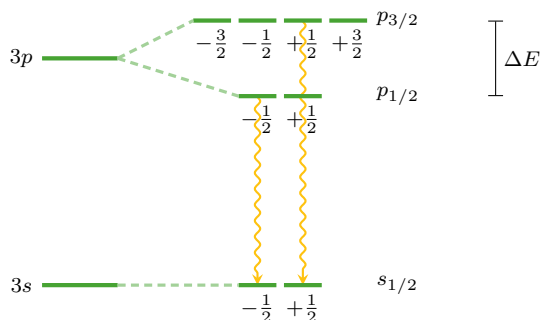

Figure 1.1: Sodium lamp energy levels.

– Street lamps use this (very efficient).
– Also used in astronomy.
– In the sodium atom, there are two energy levels ($3s$ and $3p$).
– The states have a spin-orbit coupling effect.

- 3s (with $S = 1/2$) splits into two degenerate states $s_{\pm 1/2}$ based on spin.
- 3p (with $L = 1$ and $S = 1/2$) splits into two nondegenerate states ($l = \pm 1$ [called $p_{3/2}$] and $l = 0$ [called $p_{1/2}$]), which further subdivide into four (resp. two) degenerate states ($-3/2, -1/2, 1/2, 3/2$ and $-1/2, 1/2$).

- Let ΔE be the difference in energy between the $p_{3/2}$ and $p_{1/2}$. Then

$$\frac{\Delta E}{k_B} = \frac{1}{k_B}\left(\frac{hc}{\lambda_1} - \frac{hc}{\lambda_2}\right) = 25\,\text{K}$$

where $\lambda_1 = 589.6\,\text{nm}$ and $\lambda_2 = 589.0\,\text{nm}$.

- Thus, $e^{-\Delta E/k_B T} \approx 1$ for $T = 300\,\text{K}$ (the temperature in the sodium vapor lamp).
- Therefore,

$$\frac{p(E_2)}{p(E_1)} = \frac{4}{2} \cdot 1$$
$$p(E_2) = 2p(E_1)$$

- Example: MRI.

  - The magnetic field polarizes the spins of the hydrogen protons in our body with $\Delta E = \mu_B B$.
  - If we also take $B = 6\,\text{T}$ and $T = 310\,\text{K}$ (body temperature), then

$$\frac{\mu_B B}{k_B T} = 2 \times 10^{-5}$$

  - Thus, very few protons actually flip, but with modern technology we can still measure this.

- **Proton magnetic moment**: The magnetic moment of a proton. *Denoted by $\boldsymbol{\mu_B}$. Given by*

$$\mu_B = 1.4 \times 10^{-26}\,\text{J/T}$$

- Example: Rotational.

  - The rotational energy E_J of a molecule depends on the angular momentum quantum number J and the moment of inertia of the molecule $I = \mu R^2$ via the following relation.

$$E_J = \frac{\hbar^2}{2I} J(J+1)$$

  - Microwave spectroscopy can be used to find molecules out in the universe.
  - At $300\,\text{K}$,

$$\frac{p(J=1)}{p(J=0)} = \frac{3}{1} e^{\frac{-(E_1 - E_0)}{k_B T}} = 2.95$$

    - As before $J = 1$ corresponds to states $j = -1, 0, 1$.
  - See Figure 18.5 in the textbook.
  - There is a range of angular momenta due to the temperature that for $T = 300\,\text{K}$ peaks around $J = 5$.

- Example: Vibrational.

  - Here, $\Delta E = E_n - E_{n-1} = h\nu$ for every energy level since $E_n = h\nu(n + 1/2)$.
  - It follows that

$$\frac{h\nu}{k_B} = 2800\,\text{K}$$

for CO, meaning that at $300\,\text{K}$, CO will be largely in its ground state.

- The partition function tells us everything we wanna know about a system.

$$Q = \sum_i e^{-E_i/k_B T}$$

  - All we need to know is the energy of every state in the system.
  - This is impossible for an infinite system, but the Schrödinger equation gives us the energy of a system, so its a great place to start.

- Calculating the total energy from the partition function.

  - To construct it, start with

$$Q = \frac{p_1}{p_1} + \frac{p_2}{p_1} + \frac{p_3}{p_1} + \cdots = 1 + e^{\frac{-(E_2-E_1)}{k_B T}} + e^{\frac{-(E_3-E_1)}{k_B T}} + \cdots$$

  - The total energy is equal to

$$\langle E \rangle = E_1 p_1 + E_2 p_2 + E_3 p_3 + \cdots$$

  - Taking $E_1 = 0$ gives

$$\langle E \rangle = p_1 \left[E_2 \frac{p_2}{p_1} + E_3 \frac{p_3}{p_1} + \cdots \right]$$

  - Note that

$$\frac{\partial}{\partial T} \left(e^{-E_2/k_B T} \right) = \frac{E_2}{k_B T^2} e^{-E_2/k_B T} = \frac{1}{k_B T^2} \left(E_2 \frac{p_2}{p_1} \right)$$

  - Additionally,

$$p_1 = 1 - (p_2 + p_3 + \cdots)$$
$$= 1 - p_1 \left(\frac{p_2}{p_1} + \frac{p_3}{p_1} + \cdots \right)$$
$$= 1 - p_1(Q - 1)$$
$$p_1 = \frac{1}{Q}$$

  - Therefore,

$$\langle E \rangle = p_1 k_B T^2 \frac{\partial}{\partial T} \left(\frac{p_1}{p_1} + \frac{p_2}{p_1} + \cdots \right)$$
$$= p_1 k_B T^2 \frac{\partial Q}{\partial T}$$
$$= \frac{1}{Q} k_B T^2 \frac{\partial Q}{\partial T}$$
$$\langle E \rangle = k_B T^2 \frac{\partial}{\partial T} (\ln Q)$$

  - The above is an important result.

- Changing the origin of energy.

  - We know that

$$Q(E_0) = Q(E_0') e^{-(E_0'-E_0)/k_B T}$$
$$\ln Q(E_0) = \ln Q(E_0') - \frac{E_0' - E_0}{k_B T}$$

– Thus,

$$\langle E \rangle_{E_0} = k_B T^2 \frac{\partial}{\partial T} (\ln Q(E_0))$$

$$= k_B T^2 \left(\frac{\partial}{\partial T} (\ln Q(E_0')) - \frac{\partial}{\partial T} \left(\frac{E_0' - E_0}{k_B T} \right) \right)$$

$$= \langle E \rangle_{E_0'} + (E_0' - E_0)$$

$$\langle E \rangle_{E_0} + E_0 = \langle E \rangle_{E_0'} + E_0'$$

– So the change of the energy origin does indeed change the total energy by the same amount.

1.3   Calculating Average Energies

- We derived that for an ideal gas, $\langle E \rangle = 3k_B T / 2$. But this may change at higher pressures.

- Calculating the average kinetic energy at higher temperatures.

  – Use the main result from last time, which gives us the energy in terms of the partition function.

  – We have different degrees of freedom since KE and PE are on different coordinates (KE is on speed and PE is on position).

  – When we write the Boltzmann factor, we'll have an exponential with the sum of the kinetic and potential energy.

  $$Q = \sum_{ij} e^{-(E_{KE_i} - E_{PE_j})/k_B T} = \sum_{ij} e^{-E_{KE_i}/k_B T} e^{-E_{PE_j}/k_B T} = Q_{KE} Q_{PE}$$

  ■ The second equality holds because KE depends on the velocity coordinates and PE depends on position coordinates; thus, they are independent.

  – Kinetic energy partition function.

  $$E_{KE} = \frac{1}{2} m v_x^2$$

  ■ Thus,

  $$Q_{KE_{v_x}} = \int_{-\infty}^{\infty} e^{-\frac{1}{2} m v_x^2 / k_B T} \, dv_x = \sqrt{\frac{2\pi k_B T}{m}}$$

  ■ This function doesn't depend on anything of significant import.

  – It follows that

  $$\langle KE_x \rangle = k_B T^2 \frac{\partial}{\partial T} \left(\ln Q_{KE_{v_x}} \right) = k_B T^2 \frac{\partial}{\partial T} \left(\ln \sqrt{\frac{2\pi k_B}{m}} + \frac{1}{2} \ln T \right) = \frac{k_B T}{2}$$

  and

  $$\langle KE \rangle = \langle KE_x \rangle + \langle KE_y \rangle + \langle KE_z \rangle = \frac{3}{2} k_B T$$

  – Therefore, this result holds beyond the specific case of an ideal gas!

- Now for the potential energy of a harmonic oscillator.

  – $PE = \frac{1}{2} k x^2$; calculate the partition function for the coordinate x.

  $$Q_x = \int_{-\infty}^{\infty} e^{-\frac{1}{2} k x^2 / k_B T} \, dx = \sqrt{\frac{2\pi k_B T}{k}}$$

- Thus,
$$\langle PE_x \rangle = \frac{k_B T}{2}$$

- For a 3D harmonic oscillator,
$$\langle PE \rangle = \frac{3}{2} k_B T$$

- Average potential energy of a gravitational potential.

  - Apply the virial theorem (relates the average kinetic energy of a system in a conservative potential to the potential energy).
  - Since we've shown that for any system, the average kinetic energy in one dimension is $k_B T/2$, the potential in any system will be related (i.e., have a factor of $k_B T$).

- What it means to cool something down, if KE always follows the same formula.

  - Although the formula does not change, $\langle KE \rangle \propto T$, so decreasing the temperature decreases the kinetic energy.
  - Similarly, as things change phase, more and more potentials take hold (e.g., in the gas phase, there is no potential energy, but there is significant potential energy in the solid and liquid phases).

- Rotational kinetic energy.

  - Consider N_2, with its two rotational degrees of freedom.
  - Classically,
$$E_{\text{rot}} = \frac{1}{2} I \omega^2$$

  - Thus, once again,
$$Q_\omega = \int_{-\infty}^{\infty} e^{-\frac{1}{2} I \omega^2 / k_B T} \, d\omega = \sqrt{\frac{2\pi k_B T}{I}}$$
  making
$$\langle E_{\text{rot}} \rangle = \frac{k_B T}{2}$$
  for one degree of freedom.

- **Law of Dulong and Petit**: The heat capacity of elemental solids is about $3nR$.

  - Observed in 1819.
  - A major result in an era where atomic structure was just emerging.
  - Imagine an atom bound in a three-dimensional (octahedral) potential. It's energy is thus
$$\frac{1}{2} mv^2 + \frac{1}{2} kr^2$$

  - Thus,
$$\langle E_{\text{atom}} \rangle = \frac{3}{2} k_B T + \frac{3}{2} k_B T = 3 k_B T$$
$$\langle E_{\text{solid}} \rangle = 3N k_B T = 3n N_A k_B T = 3nRT$$

  - Some heat capacities are lower than $3nR$ (solids of rare gases that are heavier and need more heat to behave ideally), and some are higher (the potential is not a harmonic potential).

- As experiments got better, people realized that heat capacity, as a function of temperature, decreases as $T \to 0\,\text{K}$, and was only asymptotic at $3nR$ at temperatures sufficiently close to room temperature.

- – Quantum mechanics, especially the work of Einstein, solved this mystery.
- – Atomic motion is quantized in units of energy.
    - ■ If the temperature is much higher than the quantized energies, the system behaves classically.
    - ■ If the temperature drops below the quantization energies of the vibration, we will not have equal population of energy levels (most will be in the ground state, making the energy 0; thus, there is no derivative of it and no heat capacity).

- Partition function of a quantum harmonic oscillator and the energy of the oscillator.

    - – Recall that the energies are given by $(n + 1/2)h\nu$.
    - – The partition function of the vibration of the quantum harmonic oscillator is

$$Q = 1 + \mathrm{e}^{-h\nu/k_B T} + \mathrm{e}^{-2h\nu/k_B T} + \cdots$$
$$Q = (\mathrm{e}^{-h\nu/k_B T})^0 + (\mathrm{e}^{-h\nu/k_B T})^1 + (\mathrm{e}^{-h\nu/k_B T})^2 + \cdots$$
$$Q - Q\mathrm{e}^{-h\nu/k_B T} = 1$$
$$Q = \frac{1}{1 - \mathrm{e}^{-h\nu/k_B T}}$$

    when we take the zero point energy as our zero of energy.
    - – It follows that

$$\langle E \rangle = k_B T^2 \frac{\partial}{\partial T}\left[\ln\left(\frac{1}{1 - \mathrm{e}^{-h\nu/k_B T}}\right)\right]$$
$$= \frac{h\nu}{\mathrm{e}^{h\nu/k_B T} - 1}$$

    - – As $T \to \infty$, $h\nu/k_B T$ gets very small. But since $\mathrm{e}^x \approx 1 + x$ at small x, as $T \to \infty$, we have that

$$\langle E \rangle \approx \frac{h\nu}{(1 + h\nu/k_B T) - 1} = k_B T$$

    - – Therefore, as $T \to \infty$, we recover the energy of a classical harmonic oscillator.
    - – On the other hand, as $T \to 0$, $E \to 0$.

- Note that heat capacity $C = \partial E/\partial T$.