Lecture 16 – Thermodynamics from Ensembles

A. Boltzmann's Formula and Entropy

So far we have had two major ideas from Gibbs. These are two of the three fundamental postulates of statistical thermodynamics.

1) Ergodicity – we can consider ensemble averages instead of time averages
2) A priori equal probability – the probability of equal energy microstates is uniform and therefore the probability of microstate is inversely proportional to its degeneracy (number of states w/ same energy).

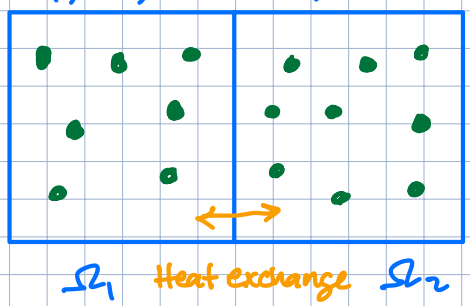
To make the final leap to connect microstates to thermodynamic macrostates we need one more postulate: Boltzmann's formula,

$$S \propto \ln \Omega$$

S: entropy; Ω: # of microstates

This idea is probably so familiar to you that you undoubtedly fail to appreciate its significance and revolutionary impact. In classical thermodynamics, entropy is an abstract quantity that systems posess that always increases. With Boltzmann's and Gibbs' insights we see that entropy is inherently statistical in nature. Entropy is a count of the number of ways a system can exist – the volume of its phase space. It is something about how "disordered" a system is. How many different ways it can be arranged. How much information the system has ($S \propto \ln(1/p)$, $p \approx 1$ we have high information / low surprise).

To get Boltzmann's equation more precisely, consider the following thought experiment,



constant

Total Energy: $E_0 = E_1 + E_2$

Total microstates: $\Omega_0 = \Omega_1 \Omega_2$

We suppose that the equilibrium state is the one with the most microstates. So, let's maximize Ω_0 with respect to the energy,

$$\left.\frac{\partial \Omega_0}{\partial E_1}\right|_{E_1 = E_1^*} = 0 \quad \text{at } E_1 = E_1^* \text{ the equilibrium energy of 1}$$

Using the product rule for Ω_0,

$$\left.\frac{\partial \Omega_0}{\partial E_1}\right|_{E_1^*} = \left.\frac{\partial \Omega_1}{\partial E_1}\right|_{E_1^*} \Omega_2(E_1^*) + \Omega_1(E_1^*) \left.\frac{\partial \Omega_2}{\partial E_1}\right|_{E_1^*}$$

$E_2^* = E_0 - E_1^*$ (constant)

Chain rule $\frac{\partial \Omega_2}{\partial E_1} = \frac{\partial \Omega_2}{\partial E_2}\frac{\partial E_2}{\partial E_1}$

$\frac{\partial E_2}{\partial E_1} = \frac{\partial}{\partial E_1}(E_0 - E_1) = -1$

$$\left.\frac{\partial \Omega_0}{\partial E_1}\right|_{E_1^*} = \left.\frac{\partial \Omega_1}{\partial E_1}\right|_{E_1^*} \Omega_2(E_2^*) + \Omega_1(E_1^*)(-1) \left.\frac{\partial \Omega_2}{\partial E_2}\right|_{E_2^*} = 0$$

Divide both sides by $\Omega_1 \Omega_2$

$$\frac{1}{\Omega_1(E_1^*)} \left.\frac{\partial \Omega_1}{\partial E_1}\right|_{E^*} - \frac{1}{\Omega_2(E_2^*)} \frac{\partial \Omega_2}{\partial E_2^*} = 0$$

$$\left.\frac{\partial \ln \Omega_1}{\partial E_1}\right|_{E_1^*} = \left.\frac{\partial \ln \Omega_2}{\partial E_2}\right|_{E_2^*}$$

Equilibrium criteria!

$$\beta_1 = \beta_2 \qquad \text{Let } \beta = \frac{\partial \ln \Omega}{\partial E}$$

What is the criteria for thermal equilibrium in classical thermodynamics?

$T_1 = T_2$

$\left.\frac{\partial S}{\partial E}\right|_{N,V} = \frac{1}{T}$ Definition of temperature

$\beta = \frac{1}{k_B T}$

needs units of 1/energy

$k_B = 1.38 \times 10^{-23}$ J/K

$S = k_B \ln \Omega$

B. Connecting Ensembles to thermodynamics

Boltzmann's equation for connecting the number of microstates to entropy is also consistent with the laws of thermodynamics.

0th law: Definition of temperature, thermal equilibrium

we just proved this.

1st law: Conservation of Energy

If we do work on the system (e.g. reversibly change volume), we add internal energy, $dE = PdV$. From our relation above, we know $dE = TdS$. From thermodynamics, we know that

$$dE = TdS + PdV = \delta Q + \delta W$$

Thus we can identify TdS from the microstates as the heat energy.

2nd law: Entropy of a closed system increases

The equilibrium is the maximum number of microstates. This means the system evolves from small Ω to large Ω. $S = k_B \ln \Omega$ means we evolve from small S to large S, which is the 2nd law.

Stability: Perturbations from equilibrium return to it ($\frac{\partial^2 S}{\partial E^2} < 0$)

Because the point (E_i^*, E_v^*) is a maximum, the second derivative $\frac{\partial^2 S}{\partial E^2}$ must be negative (concave down).

Practically, what does this mean? How do we connect information about microscopic interactions to thermodynamic quantities?

Step 1: Determine the Hamiltonian for the system of interest, $H(q_i, p_i)$ using molecular potentials.

$$H = \sum_i \frac{p_i^2}{2m_i} + \sum_{i<j}\sum u_{ij}(q_i, q_j)$$

Step 2: Compute the density of states $\Omega(N, V, E)$.

$$\Omega(N,V,E) = \frac{1}{h^{3N} N!} \int_\Gamma \delta(H(\underline{x}) - E)\, d\underline{x} \qquad \underline{x} = (\underline{q}, \underline{p})$$

↖ usually the hard step

Step 3: Compute S using Boltzmann's formula

$$S = k_B \ln \Omega$$

Step 4: Use thermodynamic relations to find other quantities of interest.

- Legendre transforms

  $F = E - TS \qquad H = E + PV \qquad G = H - TS$

- Fundamental equations & maxwell relations

  $dS = \frac{1}{T} dE + \frac{P}{T} dV$ Fundamental equation for S

  $P = T\left(\frac{\partial S}{\partial V}\right)_E$ Pressure (By inspection)

  $C_V = \left(\frac{\partial E}{\partial T}\right)_V = \underbrace{\left(\frac{\partial E}{\partial S}\right)_V \left(\frac{\partial S}{\partial T}\right)_V}_{\text{chain rule}} = T\left(\frac{\partial S}{\partial T}\right)_V$ Heat capacity

Step 4 (alternate): Use ensemble averages to compute quantities of interest

$$\langle M \rangle = \int_\Gamma M(\underline{x})\,\rho(\underline{x})\,d\underline{x} \qquad \rho_{NVE}(\underline{x}) = \frac{1}{\Sigma}\,\delta(H(\underline{x}) - E)$$

$$\Sigma = \int_\Gamma \delta(H(x) - E)\,d\underline{x}$$

This is sometimes written with the PMF instead.

$$\langle M \rangle = \frac{1}{h^{3N} N!} \int M(\underline{x})\,P(\underline{x})\,d\underline{x} \qquad P(\underline{x}) = \frac{1}{\Omega}\,\delta(H(\underline{x}) - E)$$

$$\Omega = \frac{1}{h^{3N} N!} \int \delta(H(\underline{x}) - E)\,d\underline{x}$$

C. Example: Ideal Gas

Let's apply our procedure to compute the equation of state and the heat capacity of an ideal gas of N particles of equal mass m.

(i) Step 1: Determine $H(p, q)$

For an ideal gas there is no potential between the atoms of the gas, $U(q_i) = 0$. So, the Hamiltonian is

$$H(q_i, p_i) = \sum_{i=1}^{3N} \frac{p_i^2}{2m}$$

$i = 1 \to 1x$
$2 \to 1y$
$3 \to 1z$
$4 \to 2x$

(ii) Step 2: Compute Ω (the long step)

$$\Omega = \frac{1}{h^{3N} N!} \int_\Gamma \delta\left[\sum_{i=1}^{3N} \frac{p_i^2}{2m} - E\right] d\underline{p}\,d\underline{q}$$

$\underline{p} = \{p_i\}$ $i \in [1, 3N]$

$\underline{q} = \{q_i\}$ $i = [1, 3N]$

This is independent of $\underline{q}$

$$\Omega = \frac{\Gamma}{h^{3N} N!} \int d\underline{q} \int \delta\left[\sum_{i=1}^{3N} \frac{p_i^2}{2m} - E\right] d\underline{p}$$

Lets do the $d\underline{q}$ integral

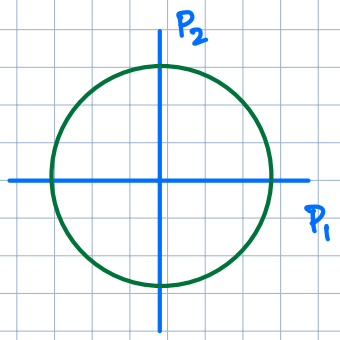
$$\int d\underline{q} = \int dq_1 \int dq_2 \int dq_3 \cdots \int dq_{3N}$$

$$= \underbrace{\int dx_1 \int dy_1 \int dz_1}_{V} \underbrace{\int dx_2 \int dy_2 \int dz_2}_{V} \cdots \underbrace{\int dx_N \int dy_N \int dz_N}_{V} = V^N$$

Substitute back into Ω

$$\Omega = \frac{V^N}{h^{3N} N!} \int \delta\left[\sum_{i=1}^{3N} \frac{p_i^2}{2m} - E\right] d\underline{p}$$

Now, let's do the $d\underline{p}$ integral. The delta function reduces us to a $(3N-1)$-dimensional hypersurface in the p phase space. In 2D,



$p_1^2 + p_2^2 = 2mE$

A circle of radius $p = \sqrt{2mE}$

$S = 2\pi p = 2\pi\sqrt{2mE}$

In 3D we get a sphere with a radius $p = \sqrt{2mE}$ and surface area

$$S = 4\pi p^2 = 4\pi (2mE)$$

For $3N$ dimensions we get a hypersphere in $3N$ dimensions. The surface area of a hypersphere in n dimensions of radius R is given by

$$S = \frac{2\pi^{n/2}}{\Gamma(n/2)} R^{n-1}$$

$\Gamma(n)$: Gamma function

$\Gamma(n) = (n-1)!$ when $n \in \mathbb{N}$

↑ annoying to write as factorials b/c of the $n/2$.

The 2 is not raised to the power $3N/2$, the π is.

Using this formula gives for $3N$ dimensions

$$S = \frac{2\pi^{3N/2}}{\Gamma(3N/2)} p^{(3N-1)/2} = \frac{2\pi^{3N/2}}{\Gamma(3N/2)} (2mE)^{(3N-1)/2}$$

For large N, $\frac{3N-1}{2} \approx 3N/2$

$$= \frac{2\pi^{3N/2}}{\Gamma(3N/2)} (2mE)^{3N/2}$$

We can now put it all together,

$$\Omega = \frac{V^N}{h^{3N} N!} \cdot \frac{(2\pi m E)^{3N/2}}{\frac{1}{2}\Gamma(3N/2)}$$

Awesome!

(iii) Step 3: Get the Entropy

$$S = k_B \ln \Omega = k_B \ln \left[\frac{V^N}{h^{3N} N! \frac{1}{2}\Gamma(3N/2)} (2\pi m E)^{3N/2} \right]$$

Let's simplify this expression

$$S = k_B \ln \left[\frac{2V^N}{N!\Gamma(3N/2)} \left(\frac{2\pi m E}{h^2}\right)^{3N/2} \right]$$

$$S/k_B = \ln 2 + \ln V^N - \ln N! - \ln \Gamma(3N/2) + \ln \left(\frac{2\pi m E}{h^2}\right)^{3N/2}$$

Stirling's formula for the factorial $N!$: For $N \to \infty$

$$\ln N! \simeq (N+\tfrac{1}{2}) \ln N - N + \tfrac{1}{2} \ln(2\pi) \simeq N \ln N - N$$

Stirling's formula for the Gamma function:

note the minus sign b/c $(n-1)!$

$$\ln \Gamma(z) = (z - \tfrac{1}{2}) \ln z - z + \tfrac{1}{2} \ln(2\pi)$$

$$\ln \Gamma\left(\frac{3N}{2}\right) = \left(\frac{3N}{2} - \frac{1}{2}\right) \ln \frac{3N}{2} - \frac{3N}{2} + \frac{1}{2} \ln 2\pi \approx \frac{3N}{2} \ln \frac{3N}{2} - \frac{3N}{2}$$

Also valid for continuous numbers and in the complex plane.

Using Stirling's formula:

$$S/k_B = \ln 2 + N \ln V - N \ln N + N - \frac{3N}{2} \ln \frac{3N}{2} + \frac{3N}{2}$$

$$+ \frac{3N}{2} \ln \left(\frac{2\pi m E}{h^2}\right)$$

$$\frac{S}{Nk_B} = \cancel{\ln\frac{2}{N}} + \ln V - \ln N + 1 - \frac{3}{2}\ln\left(\frac{3N}{2}\right) + \frac{3}{2} + \frac{3}{2}\ln\left(\frac{2\pi m\bar{E}}{h^2}\right)$$

goes to 0 as $N\to\infty$

$$= \ln(V/N) + \frac{5}{2} + \frac{3}{2}\ln\left(\frac{2\pi mE}{h^2}\cdot\frac{2}{3N}\right)$$

$$\boxed{\frac{S}{Nk_B} = \ln(V/N) + \frac{3}{2}\ln\left(\frac{4\pi mE}{3Nh^2}\right) + \frac{5}{2}}$$

Sackur-Tetrode Equation

The quantity in parentheses is related to a quantity called the thermal wavelength. This is the average de Broglie wavelength of ideal gas atoms (derivation in appendix).

$$\lambda_{th} = \langle\lambda\rangle = \frac{h}{\langle p\rangle} = \frac{h}{\sqrt{\frac{4}{3}\pi m E/N}} = \sqrt{\frac{3Nh^2}{4\pi mE}}$$

$$\frac{S}{Nk_B} = \ln\left(\frac{V}{N}\right) + \frac{3}{2}\ln\left(\frac{1}{\lambda_{th}^2}\right) + \frac{5}{2} = \ln\left(\frac{V}{N}\right) + \ln\left(\frac{1}{\lambda_{th}^3}\right) + \frac{5}{2}$$

$$\boxed{\frac{S}{Nk_B} = \ln\left(\frac{V}{N\lambda_{th}^3}\right) + \frac{5}{2}}$$

(iv) Step 4: Get the quantities we care about

Let's get the pressure first,

$$P = T\left(\frac{\partial S}{\partial V}\right)_E \quad \leftarrow \text{evaluate } \frac{\partial S}{\partial V}$$

$$\frac{\partial S}{\partial V} = \frac{\partial}{\partial V}\left[Nk_B\left(\ln V - \cancel{\ln N} - \cancel{\ln\lambda_{th}^3}\right) + \cancel{\frac{5}{2}Nk_B}\right] = \frac{Nk_B}{V}$$

Plug into formula for P

$$P = T\,\frac{k_B N}{V} \quad \text{or} \quad \boxed{P = \frac{Nk_BT}{V}}$$

Now for the heat capacity. Let's use the fact that

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_V \leftarrow \text{from fundamental equation (other term)}$$

$$\frac{1}{T} = \frac{\partial}{\partial E}\left[N k_B \ln\left(\frac{V}{N\lambda_{th}^3}\right) + \frac{5}{2}\right] \qquad \lambda_{th} = h\left(\frac{4}{3}\pi m \frac{E}{N}\right)^{-1/2}$$

$$= N k_B \frac{\partial}{\partial E}\left[\ln\frac{V}{N} - 3\ln\lambda_{th} + \frac{5}{2}\right]$$

$$= N k_B \left(-3\,\frac{1}{\lambda_{th}}\frac{\partial \lambda_{th}}{\partial E}\right) \qquad \frac{\partial \lambda_{th}}{\partial E} = -\frac{1}{2}h\left(\frac{4\pi m E}{3N}\right)^{-\frac{3}{2}}\frac{4\pi m}{3N}$$

$$= N k_B \left(-\frac{3}{\lambda_{th}}\cdot -\frac{\lambda_{th}}{2E}\right) \qquad = -\frac{h}{2}\left(\frac{4\pi m E}{3N}\right)^{-1/2}\frac{1}{E} = \frac{-\lambda_{th}}{2E}$$

$$\frac{1}{T} = \frac{3}{2}N k_B \frac{1}{E} \qquad \boxed{E = \frac{3}{2}N k_B T}$$

The heat capacity is defined as

$$C_V = \left(\frac{\partial E}{\partial T}\right)_V = \frac{\partial}{\partial T}\left(\frac{3N}{2}k_B T\right) = \frac{3N k_B}{2}$$

$$\boxed{C_V = \frac{3N k_B}{2}}$$

What did we do? We derived all of the thermodynamic properties of a monoatomic ideal gas from first principles! Molecules to bulk properties. Complete theory! Matches empirical results with dilute gases. Teaches us what an ideal gas is! It is a gas with $U = 0$.

D. Appendix: Thermal Wavelength

Recall that the total momentum p is given by,

$$p^2 = p_{1x}^2 + p_{1y}^2 + p_{1z}^2 + p_{2x}^2 + \ldots = 2mE \leftarrow \text{total system energy}$$

What is the average momentum per atom $\langle p \rangle$? It is given by

$$\langle p \rangle = \sqrt{\frac{2\pi}{3}}\, p_{rms}$$ ← root-mean square

$$p_{rms} = \sqrt{p^2/N}$$ ← p^2 is the "square" and divide by N to get the "mean"

$$\langle p \rangle = \sqrt{\frac{2\pi}{3}\frac{2mE}{N}} = \sqrt{\frac{4\pi}{3}\frac{mE}{N}}$$

If we know the average momentum, we can define the average de Broglie wave length,

$$\lambda_{th} = \langle \lambda \rangle = \frac{h}{\langle p \rangle} = \frac{h}{\sqrt{\frac{4\pi}{3}\frac{mE}{N}}} = \sqrt{\frac{3Nh^2}{4\pi mE}}$$

The thermal wavelength is the de Broglie wavelength of gas atoms with energy E/N. We substitute $E = \frac{3}{2}Nk_BT$ to get

$$\lambda_{th}^2 = \frac{3Nh^2}{4\pi mE} = \frac{3Nh^2}{2 \cdot 4\pi m\left(\frac{3}{2}Nk_BT\right)} = \frac{h^2}{2\pi mk_BT}$$

$$\boxed{\lambda_{th} = \frac{h}{\sqrt{2\pi mk_BT}}}$$

size of wavepacket of an atom with mass m and temperature T

E. Appendix: Quantum Corrections

When is the Sackur-Tetrode – the equation for a classical ideal gas – valid? When the de Broglie wave length is small? How "small"? We have another natural length scale. The average distance between atoms in the gas

$$\ell = \left(\frac{V}{N}\right)^{1/3}$$ $\frac{V}{N}$: volume per atom. units length^3.

So when $\ell \gg \lambda_{th}$, the quantum effects should be small. If $\ell \sim \lambda_{th}$ then I can have quantum effects.

If $\ell \sim \lambda_{th}$ then I have to take into account spin degrees of freedom. If they have integer spin, they are bosons (e.g., photons) and the gas is a "bose gas." If they have half-integer spin, they are fermions (e.g., electrons) and the gas is a "fermi" gas. Most matter (e.g., atoms) are fermions. But some can be bosons (e.g., sodium atoms can form a Bose-Einstein condensate).

Wait a minute, then is our Ω wrong? If so, why doesn't it matter? The answer is that Ω neglects smaller scale degrees of freedom. So in this sense it is "wrong." We could get a new Ω with more microstates,

$$\Omega_{corrected} = \Omega_{ST} \cdot \Omega_{spin} \leftarrow \text{Bose or Fermi}$$

But it turns out this doesn't matter at large $(V/N)^{1/3}$. Why? One of the most important points to learn here is that there are always smaller D.O.F we could account for! We can have more microstates for string theory too! By ignoring these, AKA by setting $\Omega_{spin} = 1$ (or any small DOF), we are choosing a reference state. We are saying that $S=0$ at some point.

As we know, in thermodynamics, our results don't depend on the reference state! So, we are ok when we do this. What matters is how $\Omega = \Omega(N,V,E)$. Or how Ω depends on the system constraints.

So, in the case of a Bose/Fermi gas, the dependence of Ω on $N, V, \& E$ is only affected when $\ell \sim \lambda$. Otherwise those D.O.F. are irrelevant.

F. Appendix: Absolute Density of States

The other point to make here is that the absolute value of Ω is not very important. We really only care about Ω/Ω_0, where Ω_0 is our reference state (where $S=0$).

Finally, it is impractical to count microstates numerically, those are impossibly large numbers. Lets do a quick calculation with the Sackur-Tetrode equation to see why.

Example: Size of Ω for He atoms at 300K and 1 bar in $1\,cm^3$

$m = 4\ g/mol \qquad h = 6.626 \times 10^{-34}\ Js \qquad P = 1\ bar = 10^5\ J/m^3$

$k_B = 8.314\ J/mol\,K \qquad T = 300K$

$$S = k_B \ln \Omega \rightarrow \Omega = \exp(S/k_B)$$

$$\frac{S}{k_B N} = \ln\left(\frac{V}{N\lambda_{th}^3}\right) + \frac{5}{2} \qquad \lambda_{th} = \frac{h}{\sqrt{2\pi m k_B T}}$$

$$\frac{N}{V} = \frac{P}{k_B T} = \frac{10^5\ J/m^3}{8.314 \cdot 300\ \frac{J}{mol}} = 40.09\ \frac{mol}{m^3} \cdot \frac{6.02\times10^{23}}{1\,mol} = 2.41 \times 10^{25}\ m^{-3}$$

$$\lambda_{th} = \frac{h}{\sqrt{2\pi m k_B T}} = \frac{6.626\times10^{-34}\ Js}{\sqrt{2\cdot\pi\cdot 4\,g/mol \cdot 8.314\,\frac{J}{mol\,K}\cdot 300K \cdot \left(\frac{1\,mol}{6.02\times10^{23}}\right)^2 \frac{kg}{1000\,g}}}$$

$$= 6.626\times10^{-34}\ kg\,m^2/s \left(\frac{2\cdot\pi\cdot 4\cdot 8.314\cdot 300}{(6.02\times10^{23})^2\,10^3} \cdot kg\cdot kg\,m^2/s^2\right)^{1/2}$$

$$= \frac{6.626\times10^{-34}\ kg\,m^2/s}{1.315\times10^{-23}\ kg\,m/s} = 5.04\times10^{-11}\ m$$

$$\lambda_{th}^3 = 1.28\times10^{-31}\ m^3$$

$$\frac{S}{N k_B} = \ln\left(\frac{k_B T / P}{\lambda_{th}^3}\right) + \frac{5}{2} = \ln\left(\frac{4.14 \times 10^{-26}\ m^3}{1.28 \times 10^{-31}\ m^3}\right) + \frac{5}{2}$$

$$= \ln(3.24 \times 10^6) + 5/2 = 15.1 \quad \leftarrow \text{intensive entropy } S/k_B$$

Assume $5/2 \ll \ln\left(\frac{V}{N}\frac{1}{\lambda_{th}^3}\right)$ for a minute.

$$\frac{PV}{k_B T} = \frac{10^6\ J/m^3 \cdot (10^{-2})^3\ m^3}{8.314\ \frac{J}{mol\,K} \cdot 300\,K \cdot \frac{mol}{6.02 \cdot 10^{23}}} = 2.41 \times 10^{19}$$

$$\Omega = \exp(S/k_B) = \left(\frac{k_B T / P}{\lambda_{th}^3}\right)^N = \left(\frac{k_B T / P}{\lambda_{th}^3}\right)^{PV/k_B T} = (12.6)^{2.41 \cdot 10^{19}}$$

$$\boxed{\Omega \sim 10^{10^{19}}}$$

In summary:

- Absolute density of states is not necessary and impractical.
  - There are always smaller scale degrees of freedom.
  - Thermodynamics depends on the difference between two states.
  - The density of states is an impossibly large number.
- By setting the degrees of freedom we are neglecting, we are setting the reference state.
- The dependence of Ω on the constraints $\Omega(N, V, E)$ determines the thermodynamic behavior.