

Entropy and Maxwell Relations

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We finally talk about the spooky “entropy” that everyone has heard of, count microstates, and use Stirling’s approximation to get interesting results from a statistical mechanics point of view. We also derive Maxwell’s relations of thermodynamic potentials, which are useful because they relate difficult-to-measure quantities to others than can be easily measured.

1 The Second Law of Thermodynamics

Recall that if the First Law of Thermodynamics is essentially a statement about what *can* happen in a thermodynamical system, addressing energy and its conservation, then the Second Law is the one that dictates what will happen. We can think of the Second Law of Thermodynamics as giving a direction to time, philosophically, as it distinguishes processes that can happen while time progresses. The law itself can be phrased in a multitude of different ways, two of which are Clausius’ and Kelvin’s Postulates. Today, we’ll phrase it differently:

Law 2 (The Second Law of Thermodynamics). In a physical system, the *entropy* S of the system is non-decreasing, approaching a maximum value.

We will be focused mostly on the nature of *entropy*, our final state variable. Recall that a *state variable* is one that only depends on the current configuration of particles in a system, and not on how the configuration was generated.

2 Entropy and Statistical Mechanics

To investigate entropy from a statistical mechanics perspective, we appeal to one of Boltzmann’s results. First, define Ω to be the number of ways a state can be achieved/populated by the particles in the system. That is, given the energy distribution of the particles, Ω is the number of ways the atoms can be arranged to satisfy the conditions of the system. Boltzmann defines the entropy S as

$$S = k_B \ln \Omega,$$

where k_B is the *Boltzmann constant*. This allows one to derive the Third Law of Thermodynamics, where when we have one state ($\Omega = 1$) in a crystal lattice, the entropy of the system is zero. Not super relevant or particularly useful, but it’s an interesting little corollary.

We will now work in a *micro-canonical ensemble*, where we fix the number of atoms N , the total energy of the system E , and the number of atoms in each of the r energy states n_k , each associated with energy ε_k . In

variables, we have the following two constraints on our system:

$$N = \sum_{k=1}^r n_k \quad E = \sum_{k=1}^r \varepsilon_k n_k$$

In general, in statistical mechanics (while working in equilibrium states), the micro-canonical ensemble is one of three main models used to describe a thermodynamical system. The others are the *grand canonical ensemble* and the *We can compute Ω and the entropy S explicitly now:*

$$\Omega = \frac{N!}{n_1! n_2! \dots n_r!} \implies S = k_B \ln \Omega = k_B \ln N! - k_B \sum_{k=1}^r \ln n_k!$$

To maximize S , we have to use...Lagrange multipliers! Consider the Lagrangian function

$$\mathcal{L} = S + \lambda \left(N - \sum_{k=1}^r n_k \right) + \mu \left(E - \sum_{k=1}^r \varepsilon_k n_k \right)$$

and plugging in, we get

$$\mathcal{L} = k_B \ln N! - k_B \sum_{k=1}^r \ln n_k! + \lambda \left(N - \sum_{k=1}^r n_k \right) + \mu \left(E - \sum_{k=1}^r \varepsilon_k n_k \right)$$

We now compute $\frac{\partial \mathcal{L}}{\partial n_j}$ and set it equal to 0:

$$\frac{\partial \mathcal{L}}{\partial n_j} = -k_B \frac{\partial}{\partial n_j} \ln n_j! - \lambda - \mu \varepsilon_j = 0$$

So far, we've let the n_i s be integers, but in order to differentiate with respect to an n_i , we have to differentiate a factorial function. Since we're physicists, we're allowed to approximate, and so we can use *Stirling's approximation*:

$$n! \approx \left(\frac{n}{e} \right)^n \sqrt{2\pi n} \implies \ln n! \approx n \ln n - n + \frac{1}{2} \ln 2\pi + \frac{1}{2} \ln n$$

We're allowed to use this approximation that gets much better as n_i gets very large (as we want them to be, usually), and so we can "differentiate" $\ln n!$:

$$\frac{\partial}{\partial n} \ln n! \approx \ln n + 1 - 1 + \frac{1}{2n} \approx \ln n$$

This gives us

$$\frac{\partial \mathcal{L}}{\partial n_j} = -k_B \ln n_j - \lambda - \mu \varepsilon_j = 0$$

If we pick different n_j , n_k , and we subtract them from each other, we have:

$$\frac{\partial \mathcal{L}}{\partial n_j} - \frac{\partial \mathcal{L}}{\partial n_k} = -k_B \ln \frac{n_j}{n_k} - \mu(\varepsilon_j - \varepsilon_k) = 0 \implies k_B \ln n_j + \mu \varepsilon_j = k_B \ln n_k + \mu \varepsilon_k$$

Out of nowhere, we've found the invariant $k_B \ln n_k + \mu \varepsilon_k$! With some foresight, let's let this constant be $k_B \ln A$:

$$k_B \ln n_k + \mu \varepsilon_k = k_B \ln A \implies \ln \frac{n_k}{A} = -\frac{\mu \varepsilon_k}{k_B} \implies n_k = A e^{-\frac{\mu \varepsilon_k}{k_B}}$$

This means the number of particles occupying state k with energy ε_k is proportional to $e^{-\frac{\mu \varepsilon_k}{k_B}}$ in equilibrium, derived from the fact that the entropy has to be maximized by the system. All we have to do now is to figure out what exactly μ is.

The way we figure out what μ is by considering what happens what happens to the entropy S when we move an atom from state i to j .

$$dS = k_B \ln \frac{N!}{n_1! n_2! \dots (n_i - 1)! \dots (n_j + 1)! \dots n_r!} - k_B \ln \frac{N!}{n_1! n_2! \dots n_i! \dots n_j! \dots n_r!}$$

$$= k_B \ln \frac{n_i}{n_j + 1} \approx k_B \ln \frac{n_i}{n_j} = k_B \ln e^{\frac{\mu}{k_B}(\varepsilon_j - \varepsilon_i)} = \mu(\varepsilon_j - \varepsilon_i)$$

This means that the change in entropy is directly proportional to the change in energy that the atom experiences, which is also the infinitesimal change in heat δQ ! Assuming the process is reversible, we have $dS = \mu \delta Q$. We can make the final leap to claim that $\mu = \frac{1}{T}$, if we believe our definition of entropy from looking at Carnot cycles and heat engines.

This directly gives the most important thermodynamic fact in reversible processes, by way of the First Law of Thermodynamics:

Theorem 1

The change in the internal energy U is given by $dU = TdS - pdV$.

This is a cool fact to tinker with and one can get all sorts of interesting relations amongst the state variables p, V, T , and S .

From this statistical perspective, entropy can be seen to be a measure of the “disorder” of a system - the more ways a system can be populated, the higher the Ω , and the higher the entropy. This can be interpreted (poorly) as the amount of “chaos” present in the system, which is not a very useful way to think about the entropy.

With this analysis of entropy, what we’ve also found is this underlying probability distribution of atoms occupying energy states, proportional to $e^{-\frac{\varepsilon}{k_B T}}$, where ε is the energy of the state. This gives us an interesting probability distribution for ideal gases and how fast the atoms within them are moving. If we recall that the energy of a particle is $\frac{1}{2}mv^2$, where v is the velocity, the probability distribution we have is now proportional to $e^{-\frac{mv^2}{2k_B T}}$, normalized by some constant., which turns out to be

$$P(\vec{v}, d\vec{v}) = \left(\frac{m}{2\pi k_B T} \right)^{\frac{3}{2}} e^{-\frac{mv^2}{2k_B T}}$$

However, if we want to be working with a speed distribution, in our phase space, we have to “integrate” this velocity distribution over all spheres of constant speed v , which gives us an extra term:

$$P(v, dv) = \left(\frac{m}{2\pi k_B T} \right)^{\frac{3}{2}} 4\pi v^2 e^{-\frac{mv^2}{2k_B T}}$$

This gives us the *Maxwell-Boltzmann speed distribution* for ideal gases, which is fairly accurate in real life and also gives us the energy for ideal gases as $U = \frac{3}{2}k_B T$, interestingly enough.

3 Thermodynamic Potentials

A *thermodynamic potential* is a quantity used to represent some thermodynamic state in a system. Each thermodynamic potential represents a different “type” of energy that the system has. There are *natural variables* for each thermodynamic potential. When these variables are held constant, the associated potential is conserved.

3.1 Internal Energy

One example of a thermodynamic potential is *internal energy*, which, as we know, is the energy of the system due to the motion of its constituent particles. Based on Theorem 1, U is conserved when S and V are both constant. Therefore, entropy and volume are the natural variables of internal energy.

3.2 Enthalpy

The *enthalpy* H is another thermodynamic potential defined as

$$H = U + PV.$$

The enthalpy is the total heat content of the system - it measures the capacity to do non-mechanical or release heat.

We can derive dH as follows. We have

$$dH = dU + PdV + VdP = TdS + VdP. \quad (1)$$

Based on equation 1, we can conclude that entropy and pressure are the natural variables of enthalpy.

3.3 Helmholtz Free Energy

Another thermodynamic potential is the *Helmholtz free energy*

$$F = U - TS.$$

This is the capacity to do useful work of any kind (mechanical and non-mechanical).

The differential form is

$$dF = dU - TdS - SdT = -PdV - SdT. \quad (2)$$

From equation 2, we see that the natural variables of the Helmholtz free energy are volume and temperature.

3.4 Gibbs Free Energy

The final thermodynamic potential we will consider is the Gibbs free energy

$$G = H - TS.$$

This measures how much non-mechanical work the system could do. We find that the differential form is

$$dG = dH - TdS - SdT = VdP - SdT, \quad (3)$$

so the natural variables of the Gibbs free energy are pressure and temperature.

4 Derivation of Maxwell Relations

4.1 Internal Energy

We write the internal energy U as a function of its natural variables, S and V , so the total differential is

$$dU = \left(\frac{\partial U}{\partial S} \right)_V dS + \left(\frac{\partial U}{\partial V} \right)_S dV.$$

Equating this to the differential form from Theorem 1 gives

$$\left(\frac{\partial U}{\partial S} \right)_V dS + \left(\frac{\partial U}{\partial V} \right)_S dV = TdS - PdV,$$

so

$$\begin{aligned} \left(\frac{\partial U}{\partial V} \right)_S &= -P, \\ \left(\frac{\partial U}{\partial S} \right)_V &= T. \end{aligned}$$

Then we have

$$\begin{aligned}\left(\frac{\partial}{\partial S}\right)_V \left(\frac{\partial U}{\partial V}\right)_S &= -\left(\frac{\partial P}{\partial S}\right)_V, \\ \left(\frac{\partial}{\partial V}\right)_S \left(\frac{\partial U}{\partial S}\right)_V &= \left(\frac{\partial T}{\partial V}\right)_S.\end{aligned}$$

By Clairaut, we conclude that

$$-\left(\frac{\partial P}{\partial S}\right)_V = \left(\frac{\partial T}{\partial V}\right)_S. \quad (4)$$

Equation 4 is our first Maxwell relation.

4.2 Enthalpy

We use the same logic to derive the second Maxwell relation. Consider the enthalpy as a function of its natural variables, so that $H = H(S, P)$. Then we have

$$dH = \left(\frac{\partial H}{\partial S}\right)_P dS + \left(\frac{\partial H}{\partial P}\right)_S dP = TdS + VdP,$$

so

$$\begin{aligned}\left(\frac{\partial H}{\partial S}\right)_P &= T, \\ \left(\frac{\partial H}{\partial P}\right)_S &= V.\end{aligned}$$

Then

$$\begin{aligned}\left(\frac{\partial}{\partial P}\right)_S \left(\frac{\partial H}{\partial S}\right)_P &= \left(\frac{\partial T}{\partial P}\right)_S, \\ \left(\frac{\partial}{\partial S}\right)_P \left(\frac{\partial H}{\partial P}\right)_S &= \left(\frac{\partial V}{\partial S}\right)_P,\end{aligned}$$

so

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P. \quad (5)$$

This is the second Maxwell relation.

4.3 Helmholtz Free Energy

We now consider the Helmholtz free energy as a function of its natural variables, so that $F = F(V, T)$. Then we have

$$dF = \left(\frac{\partial F}{\partial V}\right)_T dV + \left(\frac{\partial F}{\partial T}\right)_V dT = -PdV - SdT,$$

so

$$\begin{aligned}\left(\frac{\partial F}{\partial V}\right)_T &= -P, \\ \left(\frac{\partial F}{\partial T}\right)_V &= -S.\end{aligned}$$

Then

$$-\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial}{\partial T}\right)_V \left(\frac{\partial F}{\partial V}\right)_T = \left(\frac{\partial}{\partial V}\right)_T \left(\frac{\partial F}{\partial T}\right)_V = -\left(\frac{\partial S}{\partial V}\right)_T,$$

so

$$\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T. \quad (6)$$

This is the third Maxwell relation.

4.4 Gibbs Free Energy

Finally, we consider the Gibbs free energy as a function of its natural variables, so that $G = G(P, T)$. Then we have

$$dG = \left(\frac{\partial G}{\partial P}\right)_T dP + \left(\frac{\partial G}{\partial T}\right)_P dT = VdP - SdT,$$

so

$$\begin{aligned} \left(\frac{\partial G}{\partial P}\right)_T &= V, \\ \left(\frac{\partial G}{\partial T}\right)_P &= -S. \end{aligned}$$

Then

$$\left(\frac{\partial V}{\partial T}\right)_P = \left(\frac{\partial}{\partial T}\right)_P \left(\frac{\partial G}{\partial P}\right)_T = \left(\frac{\partial}{\partial P}\right)_T \left(\frac{\partial G}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T,$$

so

$$\left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T. \quad (7)$$

This is the last Maxwell relation.

5 Summary of Maxwell Relations

We have derived the following Maxwell relations.

$$\begin{aligned} -\left(\frac{\partial P}{\partial S}\right)_V &= \left(\frac{\partial T}{\partial V}\right)_S \\ \left(\frac{\partial T}{\partial P}\right)_S &= \left(\frac{\partial V}{\partial S}\right)_P \\ \left(\frac{\partial P}{\partial T}\right)_V &= \left(\frac{\partial S}{\partial V}\right)_T \\ \left(\frac{\partial V}{\partial T}\right)_P &= -\left(\frac{\partial S}{\partial P}\right)_T \end{aligned}$$

These equations are useful because they relate difficult to measure quantities like $\left(\frac{\partial S}{\partial P}\right)_T$ to more easily measurable quantities like $\left(\frac{\partial V}{\partial T}\right)_P$. Note that they are not the only Maxwell relations; others can be derived for different thermodynamic potentials.