Physics 114 Statistical Mechanics Spring 2018
Seminar 2

Overview:

This week, the new idea is entropy, S, a function which fully characterizes an equilibrium state. (So does the energy E; they have equivalent information content.) The partial derivatives of S define functions of state. Postulates about S (stated carefully in the Callen reading) give mathematical rigor to thermodynamics. The second and third laws of thermo are both about entropy: that S must increase in any real process, and at zero temperature, $S = 0$.

Also equal to zero at $T = 0$ are the partial derivatives of S with respect to functions of state. This makes it impossible to bring a thermodynamic system to $T = 0$ in any real process. Recently, a temperatures of only $0.006K$ was reached for a chunk of solid copper, and gas atoms have been cooled to within a billionth of a degree above $T = 0$. But $T = 0$ is not obtainable. (Or is it? See `https://www.quantum-munich.de/research/negative-absolute-temperature/`.) Practical consequences of the second and third laws are that we can envision heat engines which turn some heat into work, and refrigerators which work to pump heat against the "natural" thermodynamic direction. Both of these can be made optimally efficient, which means that input heat or work are used with as little waste as possible. However, it is impossible for any machine to convert heat entirely into work, without some heat being shed to increase the entropy of the universe.

Required Reading:

G&T Sections

- 2.12 - 2.20, 2.23.1 and 2.24.1

B&B sections

- Chapter 13,
- 14.1-14.4
- Chapter 18

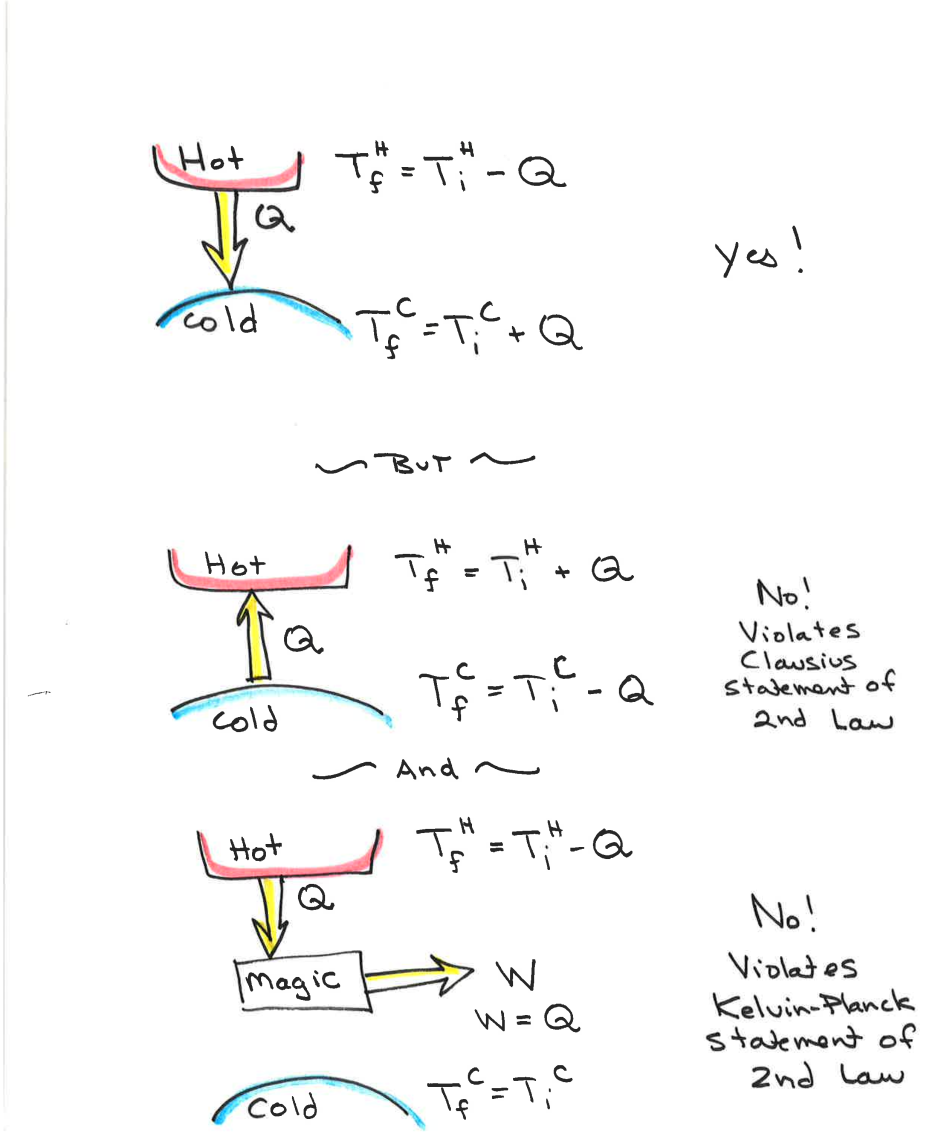
Recommended Reading:

- Callen's Chapters 1 & 2 are linked to our Moodle site. Recommended for this week are sections 1.9 - 2.7. (Ch. 1 up to 1.9 is a good elaboration on last week's reading.)
- Callen's Appendix A is a summary of the kinds of partial derivative relations we need to use, and a compliment to G&T 2.241 (also B&B A.6 from last week).

Concept checklist from Readings:

- *Notation alert:* I will interchangeably use E and U below, since our readings differ in which they use. That's life.
- Last week, we read about problems in "calorimetry", which envision heat flowing between two systems at different starting temperatures, with different heat capacities $C_A(T)$ and $C_B(T)$. Conservation of energy implied $Q_A + Q_B = 0$; and using $Q = \int C(T)dT$ allowed us to calculate T_f, the final temperature of A and B. This week, we learn that the *change in entropy* for a system is $dS = dQ/T$ for an *infinitesimal, reversible* way of adding heat dQ. Putting two systems in thermal contact fits this definition. Thus, $\Delta S = \int_i^f C(T)/T \; dT$ can be applied separately to systems A and B, leading to $\Delta S_{total} = \Delta S_A + \Delta S_B$. If the thermal energy flows from warmer to colder object, then $\Delta S_{total} > 0$, a manifestation of the *second law* of thermodynamics.
- G&T Section 22.4.1 and Appendix A of Callen (as well as last week's C.6 of B&B) are reminders of the kinds of partial derivative identities we will need in thermo. Some are not intuitive (e.g. the minus sign that shows up in G&T 2.238 and B&B Eq. C.42) but all are derivable beginning with basic ideas of taking partial derivatives of a multivariate function, and the chain rule of calculus.
- The terms isentropic process, reversible process, quasistatic process, have the potential to be confusing, so do your best to think carefully about them. For example, all reversible, isentropic processes are adiabatic. But not all adiabatic processes are isentropic; for example, a free expansion into a vaccuum. (This process is not reversible!)
- Another source of confusion is that sometimes when books make arguments about S they are talking about the system, and sometimes about the system+surroundings. Yikes! For the system+surroundings, it is always the case that $\Delta S_{system+surroundings} \geq 0$. For just a system, it is always the case that $TdS_{system} \geq dQ_{system}$ where equality means the process is reversible.

- The first law is about conservation of energy: Nonconservative processes are impossible. The second law further restricts processes. Here it is in pictures:



- The *thermodynamic temperature* is found by thinking of entropy as a function: $S(E, V, N)$. Then

$$\frac{1}{T} \equiv \left(\frac{\partial S}{\partial E}\right)_{V,N}$$

This T is equivalent to the ideal gas temperature θ, as is argued in G&T section 2.16.

- A little more about $S(E,V,N)$ ... inspired by Callen and B&B, so I'll switch to using U for energy ...
  - The *natural* variables for S are actually $U, V, N_1, N_2, ...$ where we are being very general to subscript N ... in case we have different kinds of molecules , ... if we are doing chemistry for example.
  - These *natural variables* for entropy are extensive, as is S itself.
  - For simplicity, consider a system with just two parts, A and B. Then $S_A + S_B = S$ for composite system. In other words, entropies are additive.
  - In equilibrium, extensive parameters evolve to where $S(U_A, U_B, V_A, V_B, N_{1A}, ...)$ is maximized - subject to any constraints. E.g. if a wall is "adiabatic", energy can't cross. If it is "conductive" (also called "diathermy") it can; so U_A and U_B can repartition themselves, as long as their sum remains a constant.
  - $S(U,V,N)$ is monotonically increasing with U . This is key, b/c it means that we can invert $S(U,V,N)$ to write $U(S,V,N)$. You can consider entropy as the starting point of your argument, your most important *thermodynamic potential*, or you can consider energy to be the important one. (We will meet other thermodynamic potentials next week, and see how to mathematically convert one to the other.)
  - It follows that $S(\lambda U, \lambda V, \lambda N_1, ...) = \lambda S(U, V, N_1, ...)$. So S is a homogeneous, first order function of the extensive parameters of the system.
  - Entropy vanishes* so $S = 0$ for the zero temperature state ... i.e. when $(\partial U / \partial S) = 0$.

* Well ... S doesn't strictly have to vanish. It can go to some small nonzero constant if the lowest energy state state of the system is "degenerate" and there are a couple of configurations that have the same energy.

- The intensive parameters are *partial derivatives of the entropy* with respect to the extensive parameters. Please review the argument around, and perhaps even sketch a picture of, sides A and B of a box separated by a diathermal wall. Maximizing entropy means $(\partial S_A / \partial U_A) = (\partial S_B / \partial U_B)$ and this allows us to make the important leap to defining:

$$1/T \equiv (\partial S / \partial U)_{V,N}$$

As mentioned above, this is our *thermodynamic definition of temperature*. It lets us make an argument (as in G&T section 2.13) that if the two systems evolve and entropy changes, since $\Delta S > 0$ it must be that the hotter system always loses energy to the colder.

- A similar argument with a wall that can move to give more/less volume to A or B gives us *pressure*:

$$P/T \equiv (\partial S/\partial V)_{U,N}$$

- Ditto with particle numbers. This defines a new quantity that will be important in later weeks, *chemical potential*:

$$\mu/T \equiv -(\partial S/\partial N)_{U,V}$$

- If we take the view that that U(S,V,N) is our fundamental thermodynamic potential, we arrive at a similar set of partial derivatives. Be aware of new placements of minus signs. Eg. $P/T \equiv -(\partial U/\partial V)_{S,N}$.

- G&T section 2.18 is a great summary of what we should know about entropy, $S(E,V,N)$. The partial derivatives for intensive properties defined above lead us to

  $dS = dE/T + P/TdV - \mu/TdN \;\; Change\ in\ Entropy\ in\ quasistatic\ process$

- If we take the view that E(S,V,N) is our fundamental thermodynamic potential, we arrive at

  $dE = TdS - PdV + \mu dN \;\; the\ Fundamental\ Thermodynamic\ Relation$

- What is an "equation of state"? Is it $S = S(E,V,N)$ or equivalently, $E = E(S,V,N)$? No. Admittedly, this is all just terminology. But an "equation of state" carries *less information*. Callen tells us that the relationship between one intensive and three (or more) extensive variables is an "equation of state". For example, $T = (\partial S/\partial E)_{V,N}$ is a function S, V, N. There are three different functional relationships, *each* of which we'd call an equation of state:

$$T = T(S,V,N) \;\; ; \;\; P = P(S,V,N) \;\; ; \;\; \mu = \mu(S,V,N)$$

  If we know *all* of these, then we have as much information as is contained by the original function, $S(E,V,N)$.

- Equations of state are homogeneous zero order ... rescaling each extensive parameter by a factor, λ, leaves the equation of state unchanged. This is cool because it means we can take $\lambda = N$ and write our equation of state in "reduced variables" like $s = S/N$ and $v = V/N$. In a problem this week, you are asked to write the van der Waals equation of state in the form $P = f(T,\rho)$.

- We can put together the fundamental thermodynamic relation and the ideal gas energy equation and equation of state to find the *entropy change for a monatomic ideal gas*:

$$\Delta S = \frac{3}{2} Nk \; ln \frac{T_2}{T_1} + Nk \; ln \frac{V_2}{V_1}$$

- We have talked about the free expansion of a gas ... so simple yet so rich that it has a name: *Joule Expansion*. Please understand this case, that it is one where gas entropy increases, pressure decreases, but no energy enters or leaves, and the universe as a whole gains entropy (unlike the case of a reversible isothermal expansion, where $\Delta S_{system} = -\Delta S_{surroundings}$.). Joule expansion is an adiabatic, non-isentropic, irreversible process :-p (There will be more details about the Joule expansion next week, in a reading from B&B Ch. 27.1.)

- Engines, refrigerators and heat pumps are discussed in G&T reading section 2.14 and B&B Ch. 13 There are new notations now ... one is that W is the work done *by* the engine. In other words, W in the sections of G&T about engines is $-W$ of earlier sections. Aargh. We also read about Q_h or Q_{hot} for heat taken from a hot place, and Q_l or Q_{cold} sent to the cold place. All of these numbers should be interpreted as *positive*. They are the sum of all heats entering or leaving the working substance. For example: On Fig. 2.4 of G&T, there are two legs on which heat comes in (Q_{hot}) , and two on which heat leaves (Q_{cold}) the working substance. Be sure you can use the first law to identify which ones.

- So for example, it is true in this section to write:

$$W_{out} = Q_{hot} - Q_{cold} \quad the \; first \; law$$

  Question: What is ΔE on this cycle? Answer: Because engines operate in cycles, it is zero.

- There can be reversible engines (or reversible cycles). B&B section 13.7 has a good discussion where all cycles are claimed to obey *Clausius' theorem:* $\oint đQ/T \leq 0$. Please know that a cycle like Fig. 2.4 on G&T is *not* reversible, but the cycle of Fig. 2.9 is. This is subtle ... reversible engines do not increase the entropy of the system+surroundings. Needless to say, they are an impossible idealization :-)

- Know the details of the Fig. 2.9 engine, which is the *Carnot Engine*. It is reversible. Its *efficiency* is the highest possible working between two given temperatures.

- Every engine has an efficiency of *what you get / what you pay for*= $\eta = 1 - Q_{cold}/Q_{hot}$. Acting between two extreme temperatures T_{hot} and T_{cold}, a reversible engine has an efficiency of $\eta = 1 - T_{cold}/T_{hot}$.

- There is a COP for a heat pump or refrigerator. Like engines, it is (*what you get / what you pay for*) But in these cases, what you get is different; heat. What you pay for is work. Thus for a fridge, $COP = Q_{cold}/W$. (The symbol W has now come back to referring to the work put *into* the system.) For a heat pump, a way of keeping warm by working to reversing the natural direction of heat flow, you'd want to define $COP = Q_{hot}/W$.

- The *third law* of thermodynamics states that the $T = 0$ state of a system is unique. Often you will read that $S(T = 0) = 0$. But really, the important thing is that $S(T = 0)$ it is *a unique value*, independent of pressure, chemical potential, ... any other thermodynamic function you could vary. Here is a picture from wikipedia where X plays the role of this other parameter.

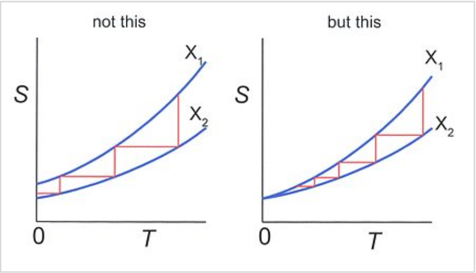


Fig.1 Left side: Absolute zero can be reached in a finite number of steps if $S(0,X_1) \neq S(0, X_2)$. Right: An infinite number of steps is needed since $S(0,X_1) = S(0,X_2)$.

- In summary, G&T quotes Einstein saying:
  A theory is the more impressive the greater the simplicity of its premises, the more different kinds of things it relates, and the more extended its area of applicability. Therefore ... classical thermodynamics ...is the only physical theory of universal content which I am convinced will never be overthrown, within the framework of applicability of its basic concepts.
  Here are some postulates and theorems which Einstein probably knew, and you should probably know also :-)
  - The Clausius statement of the second law
  - The Kelvin statement of the second law
  - The Nernst statement of the third law
  - Carnot's theorem
  - Callen's entropy Postulate II
  - Callen's entropy Postulate III
  - The maximum work theorem (see Callen Ch. 4)

Warmup Problems: *Due before seminar, Monday at 5 pm*

1. **entropy of an ideal gas** G&T 2.24
2. **heat pump: possible or impossible?** B&B 13.1

Held-over-from-last-week problems

We may not have done problems 10 and 11 last week (depending on what section you are in). We want to do them ... Amy can field them in the sections where they were not done.

Regular problems

Which problem is yours to present? Which is yours to introduce? Section Wed A is deciding this themselves - and I'll create a document for Wed B and Thurs, which you all are free to alter in any way you see fit! We just want coverage on all problems.
1: Ideal refrigerator G&T problem 2.19

2: partial derivatives
a) G&T Problem 2.31
b) Using the definition of $z(x, y)$ in part a), find $\left(\frac{\partial z}{\partial x}\right)_u$ where $u(x, y) = xy$.

3: Establishing equilibrium
a) Callen 2.6-3
b) Callen 2.7-2

4: An equation of state Write the van der Waals equations of state in the form $P = f(T, \rho)$ (Hey, wasn't this a warmup last week? Yes :-) and thus show that this is an equation which is homogeneous and zero order in the extensive state variables.

5: Free expansion of a non-ideal gas G&T Problem 2.29

6: Realistic refrigerator B&B Problem 13.6

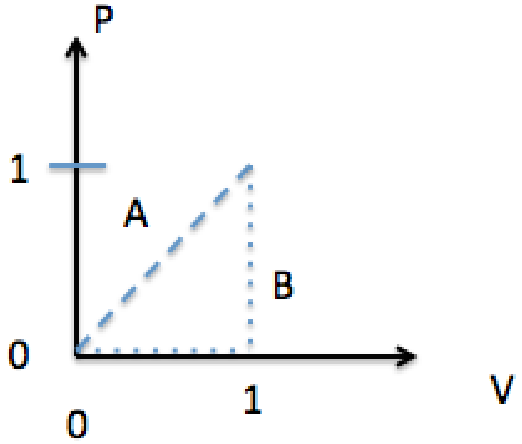
7: What's the change in entropy for the system?
How about the change in entropy for the system+surroundings?
Hint: Reference data can be found on the Web and pp. 404-405 of Schroder's book.

a) when solid copper is slowly cooled from 42^oC to 20^oC by a mechanism of your choice
b) when 100 g of ice at 0^oC melts into 100 g of water at 0^oC by a mechanism of your choice
c) when a magician goes "poof" and turns the crystal kyanite into a different crystal, andalusite; taking place at $T = 298K$ and atmospheric pressure.
d) when one mole of ideal gas at 0^oC does an isothermal expansion to twice its original volume.
e) when one mole of ideal gas at 0^oC does an adiabatic expansion (i.e. $Q = 0$, but happens quasi statically) to twice its original volume.
f) when one mole of ideal gas at 0^oC undergoes a free expansion (i.e. $Q = 0$, but happens quickly, and irreversibly) , also known as a "Joule expansion", to twice its original volume.

8: exact differentials
a) Given $df = F(P, V)dP + G(P, V)dV$ where $F = PV$ and $G = P^2$, is df an exact differential?
b) Whether your answer to a) is yes or no, please find

$$\int_{0,0}^{1,1} df$$

on the two paths, A (dashed) and B (dotted) shown below.



9: I think I just broke thermodynamics A scientist thinks they have found a system for which $S = NR\ ln(c\frac{UV}{N^2})$ where c is a constant. This violates the 3rd law. Why?

10: Positive change of entropy G&T Problem 2.61

11: The Otto cycle B&B problem 13.5. Is an Otto engine really less efficient than a Carnot engine? How so?

12: Removing a constraint Callen 1.10-3

13: Finding equations of state Callen 2.2-1
Note: θ *and* v_o *are just constants.*