

Physics 112 Notes

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1 January 17

1.1 Introduction

In this class, we cover the material in three main categories: Thermodynamics, Classical Statistical Mechanics, and Quantum Statistical Mechanics.

[Write some more later]

1.2 Part 1: Thermodynamics

When we have one or two particles, Newtonian Mechanics (or quantum mechanics) works just fine. But for larger numbers we cannot solve the equations analytically. To describe the behavior of massive collections of atoms such as a cup of water, we *could* model the system on a computer and run a simulation but... why bother? Most times, the properties we are actually interested in are bulk properties such as the temperature of the *cup* of water rather than the properties of, say, atom 264506. So, instead of trying to study the behavior of each individual particle, we will study the *emergent properties* of large collections of particles.

Now let's define some common terms:

System and environment

- System: A thermodynamic system is defined by the matter and radiation fields in a region of space.
- Everything not in the system is the environment.

Some good examples of systems and environments are pictured below:

[Insert diagrams]

Now, there are three different types of systems that we will often work with:

1. Isolated: No exchange at all with the environment.
2. Closed: Exchange of energy with the environment is allowed.
3. Open: Exchange of both energy and particles with the environment is allowed.

[Complete this day's notes]

2 January 22

Today we'll cover

- Equilibrium
- Pressure and temperature
- Chemical Potential
- State Variables
- Defining Temperature

2.1 Equilibrium

Equilibrium

Equilibrium between two systems occurs when the bulk properties remain (roughly) fixed and don't spontaneously change.

There are numerous *types* of Equilibrium, each one associated with some quantity which is exchanged until equilibrium is attained:

- Mechanical Equilibrium - Volume is exchanged but no direction is preferred.
- Thermal Equilibrium - Energy is exchanged but no direction is preferred.
- Diffusive Equilibrium - Particles are exchanged but no direction is preferred.

In order to **quantify** these equilibria, we define the following quantities:

- Preessure (P): For mechanical equilibrium (exchange of volume)

[Draw Diagram]

If there is a pressure differential, say $P_2 > P_1$, then there is an **exchange of volume from low to high pressure regions**. We then obtain two regions of equal pressure P_{eq} and the volumes adjust accordingly to $V_1 + \Delta V$ and $V_2 - \Delta V$. (Note that this has been phrased so as to frame the next few quantities analogously. We should really think of forces balancing out rather than the pressure coming to equilibrium.)

- Temperature (T): For thermal equilibrium.

[Draw Diagram]

If there is a temperature differential, say $T_2 > T_1$, then there is an **exchange of energy from high to low temperatures**. We then obtain two regions of equal temperature T_{eq} , with the regions having energies $U_1 - \Delta U$ and $U_2 + \Delta U$

- Chemical Potential (μ): For diffusive equilibrium.

[Draw Diagram]

Just like the two Potentials defined above, if there is a differential in Chemical Potential $\mu_2 > \mu_1$ then there is an **(net) exchange of particles from high to low potential**.

We specify that there is a net change in this direction because particles flow in both directions, it's just that more go from higher μ to lower μ until diffusive equilibrium is achieved.

Then, the number of particles in the two regions are adjusted and we obtain two regions of equal chemical potential μ_{eq} .

Note: Chemical Potential has units of energy – that's why it has potential in the name.

Example: Consider a sample of ideal gas in a gravitational field at height z . Then

$$\mu = k_B T \ln \left(\frac{n}{n_q} \right)$$

where $n = \frac{N}{V}$ and n_q is the **Quantum Concentration**.

- The closer the concentration gets to the Quantum Concentration, the worse the classical approximation becomes. At the Quantum Concentration, it becomes necessary to consider quantum mechanical effects.
- n_q is mass dependent, so particles of one kind will have the same Quantum Concentration.

Suppose we have a cylinder within which the temperature is a constant T throughout the volume. Let's look at the column of air [Finish this example when recording comes out].

Each type of particle gets its own chemical potential.

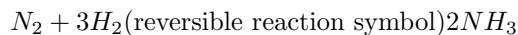
[Draw Diagram]

In the above setup, to have chemical equilibrium, we require

$$\mu_{A,1} = \mu_{A,2}$$

$$\mu_{B,1} = \mu_{B,2}$$

- Chemical Reactions allow particles of one kind to turn into particles of another kind. For instance,



This chemical reaction gives us a relation between each of the chemical potentials. In particular, the equation

$$\mu_{N_2} + 3\mu_{H_2} = 2\mu_{NH_3}$$

must hold in order for Chemical Equilibrium to be maintained. Otherwise, the reaction is driven one way or the other.

[Complete this when the recording comes out]

[Draw table of potentials and quantities]

When every type of equilibrium is simultaneously achieved, then we say the system is at **Thermo-**

dynamic Equilibrium.

2.2 Variables of State

3 February 7

3.1 Statements of the Second Law of Thermodynamics

Today, we'll cover

- The Second Law!
- Introducing... Entropy!
- Entropy and the 2nd Law
- The Third Law

Recap

- Last time we spoke about the Carnot Cycle and the Carnot *Theorem* which told us that the cycle depended only on the temperatures of the two heat baths.
- We derived the *Carnot Efficiency*

$$\eta_{\text{carnot}} = 1 - \frac{T_C}{T_H}$$

Now, there are *three* primary statements of the second law:

1. Carnot Statement: No heat engine operating between a high temperature of T_H and a low temperature of T_C can be more efficient than a reversible engine operating between just those two temperatures.

This statement tells us that there is no engine that can possibly be more efficient than the Carnot engine.

2. Clausius Statement: Heat can never pass from a colder to a hotter body without *some* change - connected therewith - occurring at the same time.

This statement basically says that if we want to pull heat from a cold thing and deposit it into a hot thing, we need to do work. Heat naturally flows from Hot to Cold, going the other way requires energy.

3. Kelvin-Planck Statement: It is impossible to construct a heat engine that produces *no* effect other than absorbing heat and performing an equal amount of work.

The third statement basically says that if we operate an engine, there must be some *waste* heat. There exist no perfectly efficient engines.

These three statements are all equivalent, and in fact, if one of them is violated then we can show that the others are violated too. For example, if we have an engine that violates the Clausius statement then we can couple that with the Carnot Cycle and obtain an engine that violates the Carnot Statement.

3.2 Revisiting the Carnot Cycle

Recall that the Carnot Cycle has four stages:

1. Isothermal heat input @ T_H

2. Adiabatic Cooling

3. Isothermal heat extraction @ T_C

4. Adiabatic Heating

And so we have

$$\oint_{\Gamma_{\text{circle}}} \frac{\delta Q}{T} = \oint_{(i)} \frac{\delta Q}{T} + \underbrace{\oint_{(ii)} \frac{\delta Q}{T}}_{=0, \text{adiabatic}} + \oint_{(iii)} \frac{\delta Q}{T} + \underbrace{\oint_{(iv)} \frac{\delta Q}{T}}_{=0, \text{adiabatic}}$$

$$= \frac{Q_{in}}{T_H} - \frac{Q_{out}}{T_C}$$

Recall that the Carnot Efficiency is given by

$$\eta_C = 1 - \frac{Q_{out}}{Q_{in}} = 1 - \frac{T_C}{T_H}$$

which means

$$\frac{Q_{out}}{Q_{in}} = \frac{T_C}{T_H}$$

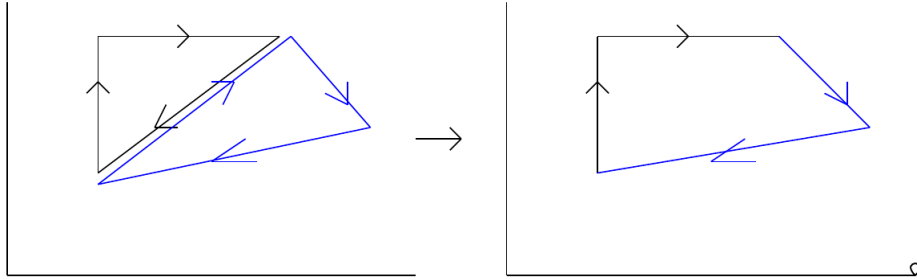
Thus,

$$\boxed{\oint_{\Gamma_{\text{circle}}} \frac{\delta Q}{T} = 0}$$

This leads us to two ideas:

Idea 1: For a Carnot cycle, $\oint \frac{\delta Q}{T} = 0$.

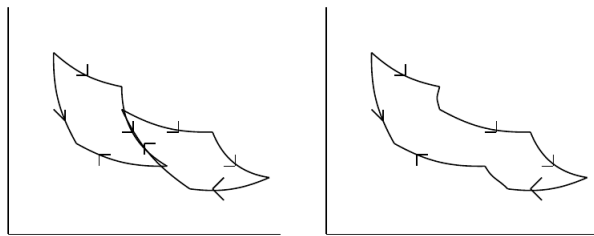
Idea 2: If one cycle has a reversible leg in one direction and another cycle has the "reversed" leg, then the two cycles can be combined with the shared leg **canceling out**.



$$\int_{\Gamma_{\text{combo}}} = \int_{\Gamma_1} + \int_{\Gamma_2}$$

Idea 3: Any cycle built out of the Carnot Cycles with shared legs will *also* have

$$\oint \frac{\delta Q}{T} = 0$$



By Idea 2, we have

$$\oint_{\Gamma_{\text{combo}}} \frac{\delta Q}{T} = \oint_{\Gamma_1} \frac{\delta Q}{T} + \oint_{\Gamma_2} \frac{\delta Q}{T} = 0$$

Idea 4: Any reversible process can be decomposed into a sequence of infinitesimal reversible sotherms and adiabats.

- So, for example, we can take any constant-pressure process and rather than breaking it up into a bunch of little isobars, we can use the concept of infinitessimals to break it up into a bunch of isotherms and adiabats.
- The smaller we make our isotherms and adiabats, the better the approximation will be.
- In this limit as our segments become infinitesimal, both our curves (the one consisting of isobars, and the one consisting of isotherms+adiabats) will have the same internal energy ΔU (since it's a state variable), the same work W (since work is the area under the curve, and the area gets closer and closer in the limit). Thus, the two curves will be characterized by the same Heat Q .
- Moreover, if we can do that, we get Idea 5.

Idea 5: Any reversible or quasi-static process can be decomposed into a sequence of combined Carnot Cycles.

- This follows from the combination of Ideas 2 (we can combine cycles by canceling internal legs) and 4 (any path can be broken into isotherms and adiabats).
- Insert diagram later

But recall that Idea 3 tells us that the loop integral for a Carnot cycle is zero. Therefore, Idea 5 + Idea 3 allow us to conclude that

For any reversible cycle, Γ ,

$$\oint_{\Gamma} \frac{\delta Q}{T} = 0$$

This has massive implications!!

3.3 Implications

Consider a reversible cycle Γ consisting of two paths Γ_1, Γ_2 . Then,

$$\begin{aligned} \int_{\Gamma} \frac{\delta Q}{T} &= 0 \\ \Rightarrow \int_{\Gamma_1} \frac{\delta Q}{T} + \int_{\Gamma_2} \frac{\delta Q}{T} &= 0 \\ \Rightarrow \boxed{\int_{\Gamma_1} \frac{\delta Q}{T} = \int_{\Gamma_2} \frac{\delta Q}{T}} \end{aligned}$$

That means that our paths Γ_1, Γ_2 don't matter. The quantity we're integrating is path independent. In other words,

$$\frac{\delta Q}{T} \text{ is } \textit{exact!}$$

So, this quantity is exact, *even if δQ is not exact* which means ***there is some state variable S such that***

$$\delta S = \frac{\delta Q}{T}$$

We've just invented a new state variable!

$$\begin{aligned} dS &= \frac{1}{T} \delta Q \\ \Delta S &= \int_{\Gamma} \frac{\delta Q}{T} \text{ for reversible } \Gamma \end{aligned}$$

This also gives us an analogous way of expressing δQ , similar to how we write δW :

$$\begin{aligned} \delta W &= -PdV \\ \delta Q &= TdS \end{aligned}$$

Entropy

We call S the ***entropy***.

- This is how it was discovered in Thermodynamics.
- Later, we'll take a *completely* different approach yet arrive at exactly the same expression in Statistical Mechanics.

Spoiler: We've really only defined the *Change in Entropy* δS , but there *does* exist an absolute scale for Entropy which has to do with the number of microstates associated with a certain thermodynamical configuration. We'll study this in about two weeks.

What does the Entropy Change look like for different processes?

- Reversible Isotherm: $\Delta S = \frac{Q}{T}$
- Reversible Adiabatic: $\Delta S = 0$ (This is why these processes are also called "*isentropic*").
- Reversible Isochor: $\Delta S = \int \frac{C_v dT}{T}$
- Reversible Isobar: $\Delta S = \int \frac{C_p dT}{T}$

What are the units of Entropy?

- $[S] = \frac{\text{energy}}{\text{temperature}} = [k_B]$.
- The Boltzmann Constant has the same units as Entropy, and serves as sort of a natural scale.
- Often, it's convenient to use their ratio, which is dimensionless. This is often denoted as

$$\sigma \equiv \frac{S}{k_B}$$

Let's do an explicit calculation

We undergo a reversible isothermal transformation at temperature T_0 in which our volume goes from V_0 to $2V_0$. Then

$$\Delta S = \frac{Q_0}{T_0}$$

And the first-law tells us

$$\Delta U = Q_0 + Q = 0$$

where the last inequality is because we're assuming the Equipartition Theorem and working with an Ideal gas. So,

$$\begin{aligned} Q_0 &= -W \\ &= \int_{V_0}^{2V_0} P dV \\ &= Nk_B T \ln \left(\frac{2V_0}{V_0} \right) \end{aligned}$$

So,

$$\boxed{\Delta S = Nk_B \ln(2)}$$

Note that this is *extensive*. Double the number of particles, double the entropy change.

3.4 Carnot yet again!

[Complete this later; too sleepy rn]