

Statistical/Thermal Physics

Based on lectures by Dr. Steve Presse

Notes taken by Daniel Moore

Fall 2019

These notes are not endorsed by the lecturers, and I have modified them (often significantly) after lectures. They are nowhere near accurate representations of what was actually lectured, and in particular, all errors are almost surely mine.

Contents

0	Introduction	3
1	Thermodynamics	4
1.1	Energy in Thermal Physics	4
1.1.1	Temperature	4
1.1.2	The Ideal Gas	4
1.1.3	The First Law of Thermodynamics	7
1.1.4	Compression and Expansion Work	7
1.1.5	Heat Capacities	11
1.1.6	Phase Transitions and Latent Heat	12
1.1.7	Enthalpy	13
1.2	The Second Law, Engines, and Refrigerators	13
1.2.1	The Carnot Engine	13
1.2.2	Two-State and Multi-State Systems	15
1.2.3	The Second Law of Thermodynamics	16
1.2.4	Large Systems	16
1.2.5	The Ideal Gas	16
1.2.6	Entropy	16
1.3	Interactions and Implications	16
1.3.1	Temperature	16
1.3.2	Entropy and Heat	16
1.3.3	Mechanical Equilibrium and Pressure	16
1.3.4	Diffusive Equilibrium and Chemical Potential	16
1.4	Free Energy and Chemical Thermodynamics	16
1.4.1	Free Energy as Available Work	16
1.4.2	Free Energy as a Force Toward Equilibrium	16
1.4.3	Phase Transformations of Pure Substances	16
2	Statistics	17
3	Statistical Mechanics	18
3.1	Boltzmann Statistics	18
3.1.1	The Boltzmann Factor	18
3.1.2	Average Values	18
3.1.3	Partition Functions and Free Energy	18
3.1.4	Partition Functions for Composite Systems	18
3.1.5	Ideal Gas Revisited	18
3.1.6	Monte Carlo, Metropolis-Hastings	18
3.2	Quantum Statistics	18
3.2.1	The Gibbs Factor	18
3.2.2	Bosons and Fermions	18
3.2.3	Degenerate Fermi Gases	18
3.2.4	Blackbody Radiation	18
3.2.5	Debye Theory of Solids	18

0 Introduction

There are four primary branches of physics:

- (i) Classical Mechanics
- (ii) Quantum Mechanics
- (iii) Electricity & Magnetism
- (iv) Statistical Mechanics

We've already seen a fair amount of the first three things, but now we're going to take a dive into something we haven't seen much of before: statistical mechanics, or mechanics for many-particle systems (usually on the order of 10^{23} or more). What we talk about in this class will actually cover two topics, often lumped together under the name "thermal physics:"

- (i) Thermodynamics – that is, thermal physics which makes average statements about most probable configurations of molecules or other degrees of freedom.
- (ii) Statistical Mechanics – that is, thermal physics which makes more detailed statements about fluctuations across averages.

They'll be covered in that order, with a short section in the middle to talk about statistics in general, since that's something we've never quite got around to in a physics course so far for some reason.

1 Thermodynamics

1.1 Energy in Thermal Physics

1.1.1 Temperature

We're basically familiar with temperature by now, but we will talk about some basic properties:

- Temperature (T) is related to the average kinetic energy of the microscopic motion of electrons, atoms, and molecules that make up some material.
- There is such a thing as a “zero” temperature.
- After long enough, two things at different temperatures will find equilibrium at the same temperature.

1.1.2 The Ideal Gas

We can make two observations about gases in general:

- The pressure of a gas is proportional to its density (n/V).
- The pressure of a gas is proportional to its temperature (T).

If $P \propto \frac{n}{V}$ and $P \propto T$, then $P \propto \frac{n}{V}T$, or

$$P = R \frac{n}{V} T$$

Where R is the “ideal gas constant.”

If we want to take a look at the units of this relationship:

$$\begin{aligned} P : [\text{Pa}] &= \frac{\text{N}}{\text{m}^2} = \frac{\text{kg}}{\text{m} \cdot \text{s}^2} \\ T : [\text{K}] \\ n : [\text{mol}] \\ V : [\text{m}^3] \\ \implies R : \left[\frac{\text{J}}{\text{mol} \cdot \text{K}} \right] \end{aligned}$$

In fact, we know that

$$R = 8.31 \frac{\text{J}}{\text{mol} \cdot \text{K}}$$

There are two ways we usually see the ideal gas law written. The first is the way chemists (and many statistical physicists) write it, which is just a slightly shifted version of what we've already seen:

$$PV = nRT$$

The other is a way that's more “physics-y.” We can multiply the right-hand side of this by N_A/N_A , where $N_A = 6.02 \times 10^{23}$ is Avogadro's number:

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

nN_A is simply the number of molecules, which we can write as N , and R/N_A is just a combination of constants, which we can write as another constant, Boltzmann's constant k_B (or sometimes just k), with units of J/K. This way, we can write the ideal gas law as

$$PV = Nk_B T$$

A fix for interacting particles

What makes a gas ideal? Well, namely, that it follows the two observations we noted earlier. Most importantly, we call a gas an ideal gas if its pressure is proportional to temperature.

For example, for water, as T decreases from 150°C to 100°C, the pressure drops proportionally. However, as the temperature drops from 100°C to 99°C, the pressure drops to basically 0. This means that for high enough temperatures, water does, in fact, behave as an ideal gas. But when water molecules are at low enough temperatures to interact, those interactions break the ideal gas assumption that

$$P \propto N \propto \rho$$

Where ρ is the density, or $\rho = N/V$.

Obviously, the ideal gas law is only approximately true. To try to fix it for interacting particles, we can try to assume that what we write as the ideal gas law is, in fact, only the first term in a Taylor expansion, and to get a better approximation, we can try to add more terms. Thus, expanding around ρ , we can say that there must be some \mathbb{C} such that

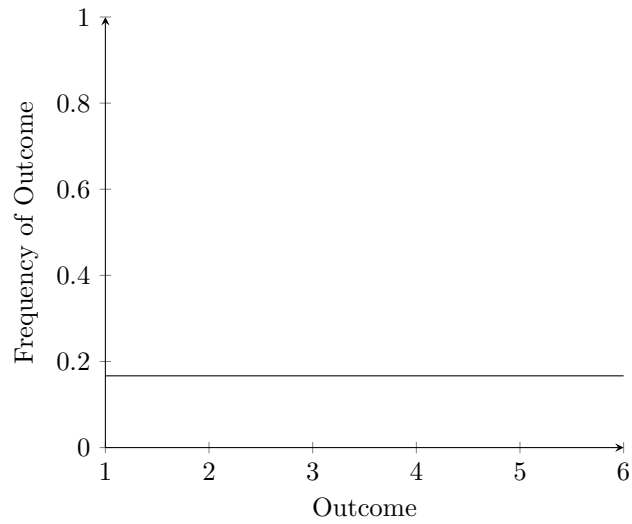
$$P = \rho k_B T + \mathbb{C} \rho^2 + \dots$$

For attractive interactions (bosons, as we will see), $\mathbb{C} < 0$, and for repulsive interactions (fermions, as we will see), $\mathbb{C} > 0$. If $\mathbb{C} = 0$ (at least approximately), then we're dealing with something that behaves like an ideal gas.

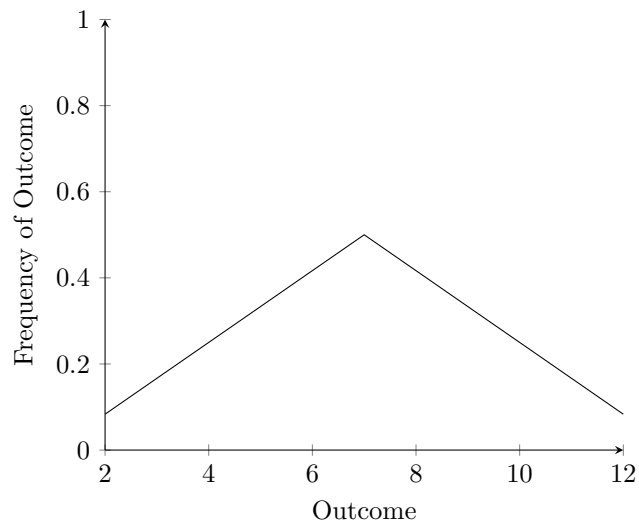
Questioning our assumptions

In writing the ideal gas law, we've made the assumption that the molecules of this gas are homogeneously distributed (that is, evenly distributed) in space. How good is this assumption?

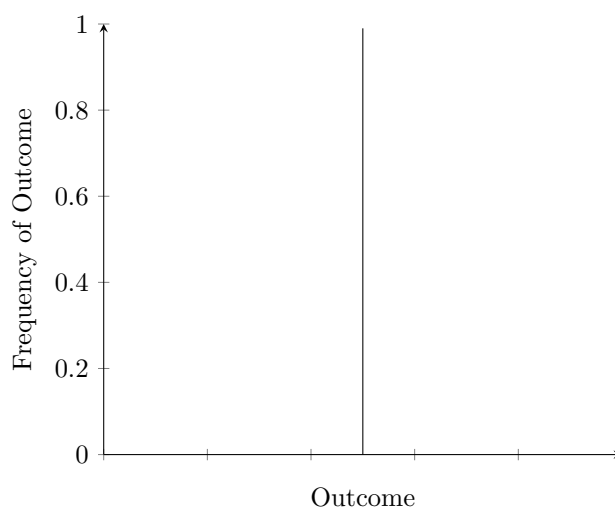
Let's lay the groundwork for answering that question using dice. If we roll one die a sufficient number of times, and we graph the frequency of each side landing face-up, we'd end up with a straight line, because each side is equally likely to land face-up (assuming the die is fair, of course):



If we roll 2 dice, we'll get something that looks slightly different. There are more configurations that result in numbers like 6, 7, or 8, than there are that result in numbers like 2, 11, or 12, so it will be triangle-shaped:



If we scale this up a ton to, say, N_A dice, then we see a sharp spike at the halfway point, and basically zero everywhere else:



Similarly, if we consider atom configurations in a room, with the number of atoms we care about (at N_A or more atoms), there are so many more configurations that result in a uniform distribution of atoms, than those that don't, that it's an incredibly good assumption to say that ρ is always uniform.

1.1.3 The First Law of Thermodynamics

We've heard of energy conservation before, but the first law of thermodynamics puts the law of energy conservation in the language of thermodynamics. Mathematically, we write this as:

$$\Delta U = Q + W$$

Where:

- ΔU is the average change of energy in a system.
- Q is the heat flowing into the system, or the spontaneous flow of energy from one object to another caused by temperature differences.
- W is the work done on the system, or energy flow into the system actively caused by a (usually) identifiable agent.

All three of these are generally measured in Joules, $J = \text{kg} \cdot \text{m}^2/\text{s}^2$, although heat, Q , is sometimes measured in calories (cal), where 1 cal is defined as the heat needed to raise the temperature of one gram of water by $1^\circ\text{C} = 1\text{K}$.

1.1.4 Compression and Expansion Work

There are a few types of compressions and expansions that we will consider, each with their own features. I'll list the types, meanings, and features here now, and I'll prove them later in this section:

- (i) Isobaric: Constant pressure,

$$W = -P \int_{V_i}^{V_f} dV = -P\Delta V$$

(ii) Isothermal: Constant temperature,

$$\begin{aligned}\Delta U &= 0 \\ \Rightarrow W &= -Q\end{aligned}$$

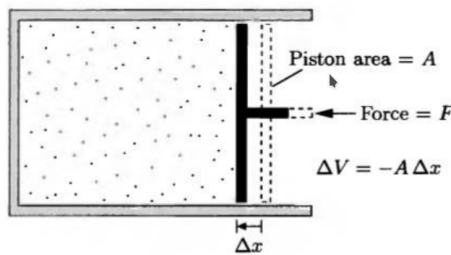
(iii) Adiabatic: Isolated system,

$$\begin{aligned}Q &= 0 \\ \Rightarrow \Delta U &= W \\ VT^{3/2} &= \text{const.} \\ V^{5/2}P &= \text{const.}\end{aligned}$$

Consider a piston with an ideal gas in it. Recall from earlier classical physics classes that when we have a gas that is compressed, the work done on something is given by the force exerted on the gas dotted into the displacement, or

$$W = \mathbf{F} \cdot d\mathbf{r}$$

For a gas in a piston, we can simplify things a bit.



The only way we can exert a force on this gas system is by moving the piston in what we'll define as the x direction by some amount Δx . This means that we can take the work equation we had before to be

$$W = F\Delta x$$

Where a positive Δx means the piston moves inward. We can write this instead in terms of the volume and pressure, things that are more apparent from the ideal gas law we've been working with:

$$\begin{aligned}W_{on} &= P\Delta x \\ &= PA\Delta x \\ &= -P\Delta V\end{aligned}$$

Not that we made two big assumptions here:

(i) **Quasistatic change**

We assumed that as the piston moved, the gas was at equilibrium at every point in time. This is an idealization, but usually a good enough approximation.

(ii) **Isobaric**

We assumed that the pressure in the piston was constant. That is, we could pull the pressure out of an integral like so:

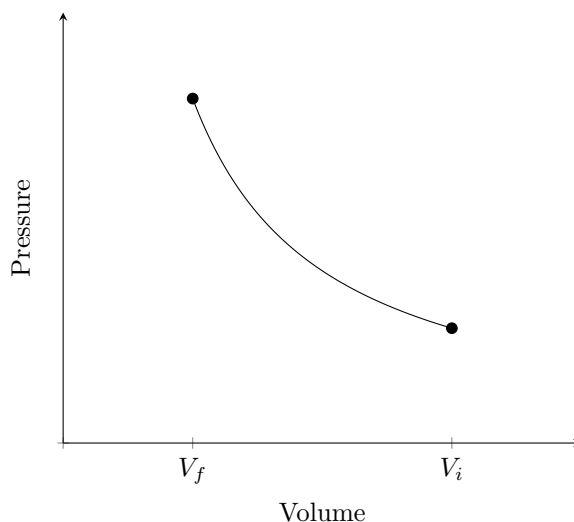
$$\begin{aligned} W &= -P\Delta V \\ &= -\int_{V_i}^{V_f} P(V)dV \\ &= -P \int_{V_i}^{V_f} dV \end{aligned}$$

For this isobaric assumption to be true, according to the ideal gas law, the temperature T must be changing.

Now, suppose we did some compression, but we kept the temperature constant (ie. we did an *isothermal* compression). What must be the work done on the system now?

$$\begin{aligned} W &= -\int_{V_i}^{V_f} P(V)dV \\ &= -\int_{V_i}^{V_f} \frac{nRT}{V} dV \\ &= -nRT \ln \left(\frac{V_f}{V_i} \right) \end{aligned}$$

We can no longer rely on a constant pressure, but we can rely on a constant temperature and knowing the initial and final volumes. If we graph such an isothermal compression on a Pressure-Volume plot, we can see what we call an isotherm:



For reasons we'll prove later, the total internal energy of a monatomic ideal gas at any time is given by

$$U = \frac{3}{2}Nk_B T = \frac{3}{2}nRT$$

Note that the 3 in the numerator of that fraction comes from the number of degrees of freedom for a single atom (all 3 translational degrees of freedom). Note that the only non-constant term here is T . That means that if T doesn't change, as in an isothermic compression or expansion, then the total internal energy should be the same at the beginning as it is at the end, or

$$\Delta U = 0$$

We can use the first law of thermodynamics to conclude, then, that

$$\begin{aligned}\Delta U &= 0 \\ Q + W &= 0 \\ Q &= -W\end{aligned}$$

This means that in order to maintain constant temperature during a compression, heat must flow out of the system.

Lastly, we'll look at an adiabatic system: one where we compress or expand our ideal gas in a chamber which is isolated from its environment (the most important meaning of this: heat can't flow between the system and its environment). If Q can't flow at all, then that means we must have $Q = 0$, so

$$\begin{aligned}\Delta U &= \cancel{Q} + W \\ &= W\end{aligned}$$

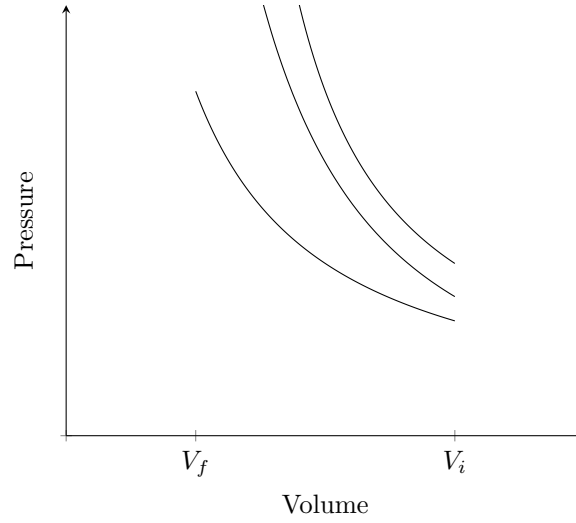
We can use an infinitesimal change in energy for an ideal gas undergoing adiabatic compression or expansion to show some interesting features:

$$\begin{aligned}dU &= \frac{3}{2}Nk_B dT = -PdV \\ \frac{3}{2}\cancel{N}\cancel{k_B} dT &= -\frac{\cancel{N}\cancel{k_B}T}{V}dV \\ \frac{3}{2}\frac{dT}{T} &= -\frac{dV}{V} \\ \frac{3}{2}\ln\left(\frac{T_f}{T_i}\right) &= -\ln\left(\frac{V_f}{V_i}\right) \\ V_f T_f^{3/2} &= V_i T_i^{3/2}\end{aligned}$$

In other words, when an isolated system undergoes a change in volume (ie. a compression or expansion), the quantity $VT^{3/2}$ is always constant. By extension,

$$\begin{aligned}VT^{3/2} &= \text{const.} \\ V^{2/3}T &= \text{const.}' \\ V^{2/3}\frac{PV}{nR} &= \text{const.}' \\ V^{5/3}P &= \text{const.}''\end{aligned}$$

If we plot an isothermic compression (or expansion) along a Volume-Pressure graph, we find that along an adiabat, $P \propto \frac{1}{V^{5/3}}$



1.1.5 Heat Capacities

Heat capacity is defined as the amount of heat needed to raise the temperature of an object per temperature degree increase (or the amount of heat needed to raise the temperature of an object by 1°C or 1K). Mathematically,

$$C \equiv \frac{Q}{\Delta T} = \frac{\Delta U - W}{\Delta T}$$

Note that this is definitionally context-dependent: doing work on an object changes its heat capacity. Practically, there are two types of heat capacity that we talk about: heat capacity at constant volume, where no work is being done on the system and therefore the volume of the container does not change, and heat capacity at constant pressure, where the pressure in the container is held constant (implying that the volume is changing).

Mathematically, we can write heat capacity at constant volume easily as a differential, and solve it for the case of the monatomic ideal gas:

$$\begin{aligned} C_V &= \left(\frac{\Delta U}{\Delta T} \right)_V = \left(\frac{\partial U}{\partial T} \right)_V \\ &= \frac{3}{2} N k_B \left. \frac{\partial T}{\partial T} \right|_V \\ &= \frac{3}{2} N k_B \end{aligned}$$

Similarly, at constant pressure, we can write the heat capacity using our energy-work definitions:

$$\begin{aligned}
 C_P &= \left. \frac{\Delta U - W}{\Delta T} \right|_P \\
 &= \left. \frac{\Delta U - (-P\Delta V)}{\Delta T} \right|_P \\
 &= \left(\frac{\partial U}{\partial T} \right)_P + P \left(\frac{\partial V}{\partial T} \right)_P \\
 &= \frac{3}{2} N k_B \left. \frac{\partial T}{\partial T} \right|_P + P \left(\frac{N k_B}{P} \right) \left. \frac{\partial T}{\partial T} \right|_P \\
 &= \frac{5}{2} N k_B
 \end{aligned}$$

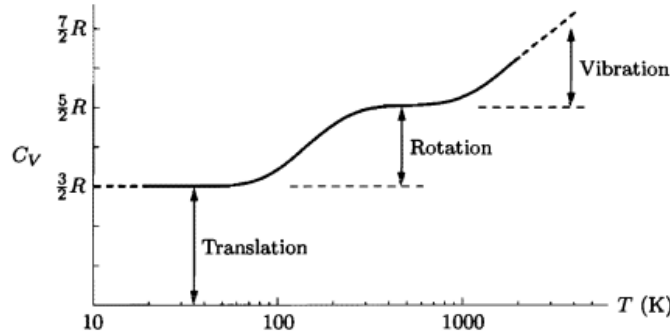
We can see that $C_P > C_V$ by a difference of Nk_B (or, more mathematically, $C_P - C_V = Nk_B$). Here's an intuitive reason why: If the volume can't expand and we put in energy, it takes much less energy to increase the heat than it would if some of that energy had to go towards the work of expansion or contraction. For non-monatomic ideal gases, we can extend these. In general, we can write the internal energy of a system as a function of the degrees of freedom f :

$$U = \frac{f}{2} N k_B T = \frac{f}{2} n R T$$

In the case of a monatomic ideal gas, where there are 3 (translational) degrees of freedom, we have the internal energy equation that we've seen already. In a case like H_2 , we have 3 translational degrees of freedom, 2 vibrational degrees of freedom (kinetic and potential energy stored in bond vibrations), and 2 rotational degrees of freedom (note that axis rotation isn't included because in quantum mechanics, these particles aren't distinguishable and we can't keep track of axis rotation, so no energy can be stored there). In this case,

$$U = \frac{7}{2} N k_B T = \frac{7}{2} n R T$$

We can see the effects of this on C_V in the graph below:



1.1.6 Phase Transitions and Latent Heat

At phase transitions, we can heat without necessarily increasing temperature. This means two things. First, we can find that $C_V \rightarrow \infty$ as the temperature

approaches the critical temperature (ie. the temperature at which the phase transition occurs). Second, this means that we need to introduce a new quantity that specifies the amount of heat required to increase the temperature and change the phase of a material with mass m . We call this the latent heat, L , where

$$L = \frac{Q}{m}$$

1.1.7 Enthalpy

We run into constant-pressure processes a lot. In constant-pressure processes, it can be time-consuming to keep track of the work done after a while, but we can introduce something to make that easier: rather than talking about the energy of a system, we can find it convenient to talk about the enthalpy. The enthalpy is defined as

$$H \equiv U + PV$$

At constant pressure, the enthalpy is just the heat flowing into the system:

$$\begin{aligned}\Delta H &= \Delta U + P\Delta V \\ &= Q - P\Delta V + P\Delta V \\ &= Q\end{aligned}$$

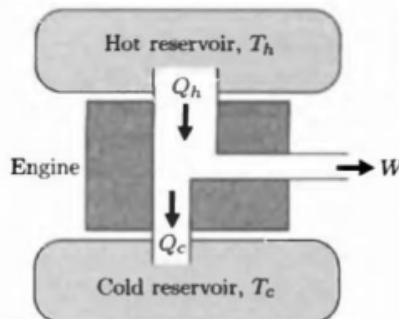
And thus,

$$C_P = \left. \frac{\partial Q}{\partial T} \right|_P = \left. \frac{\partial H}{\partial T} \right|_P$$

1.2 The Second Law, Engines, and Refrigerators

1.2.1 The Carnot Engine

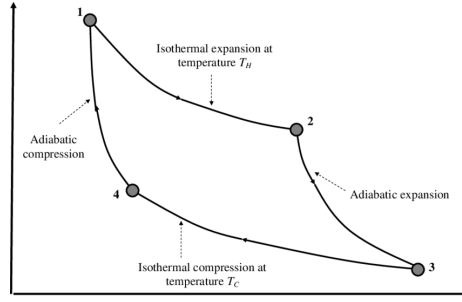
A heat engine is a device which absorbs heat and converts that energy into work. But not all absorbed heat can be converted into work (this is one way of stating the second law of thermodynamics). We'll explain why a little later when we introduce entropy. Here's a brief energy-flow diagram of what a heat engine looks like: energy flows from the hot reservoir to generate work, with the leftover heat flowing into the cold reservoir:



We define the efficiency, ϵ , of a system as the ratio of useful work, to heat absorbed:

$$\epsilon = \frac{W}{Q_H} = \frac{Q_H^{the.} - Q_C^{the.}}{Q_H^{the.}} \leq \frac{Q_H^{act.} - Q_C^{act.}}{Q_H^{act.}}$$

We can draw the cycle of an engine on a graph of pressure vs. volume, where the work done would be given by the area between the curves describing the pressure as a function of volume. We can deform the path on the diagram to be in terms of adiabats and isotherms, while keeping the area (work) constant.



We call the cycle thus described the Carnot cycle. Here's a description:

1 \rightarrow 2 : Isotherm

$$U = Q_h + W = 0$$

$$W = -Q_h$$

$$Q_h = T_h(S_2 - S_1)$$

2 \rightarrow 3 : Adiabatic expansion

$$\begin{aligned} \Delta U &= \frac{3}{2} N k_B (T_c - T_h) \\ &= W \end{aligned}$$

3 \rightarrow 4 : Isothermal compression

$$\begin{aligned} Q &= T_c(S_4 - S_3) \\ &= T_c(S_1 - S_2) \\ &= -Q_C \end{aligned}$$

4 \rightarrow 1 : Adiabatic compression

$$\Delta U = \frac{3}{2} N k_B (T_h - T_c)$$

We defined a state variable S here—there must be some internal variable that defines the difference of state between 1 and 2. We call this entropy.

Using the relations we see in that cycle, we can re-write the efficiency of an engine as

$$\begin{aligned} \epsilon &= \frac{Q_h - Q_c}{Q_h} \\ &= \frac{T_h - T_c}{T_h} \\ &= 1 - \frac{T_c}{T_h} \end{aligned}$$

We can see here clearly that even in the limit where we consider only theoretical Q_h and Q_c , the efficiency must be less than 1. We can also say that

$$Q_h^{act.} \leq T\Delta S = Q_h^{theo.}$$

Refrigerators

We can reverse this cycle/process and get what we call a refrigerator. In this case, we say that we take heat out of the cold reservoir and put it in the hot reservoir, but in order to do so, we must use some work. Rather than talking about the efficiency of a refrigerator, we usually talk about the coefficient of performance:

$$\text{COP} = \frac{Q_c}{W} = \frac{T_c}{T_h - T_c}$$

1.2.2 Two-State and Multi-State Systems

We'll need to take a brief statistical interlude. Suppose we flip a coin 3 times. If we get two heads and one tails, we call this a macrostate. There are 3 possible ways to get this macrostate: HHT, HTH, and THH. These three ways are called microstates. In a full sentence, we might say that there are 3 microstates consistent with our macrostate. Alternatively, we might say that the multiplicity, Ω , of the macrostate is 3. We can find the multiplicity generally by taking the binomial coefficient. To find the multiplicity of a macrostate with N number of events (ie. flips) and n of a certain outcome (ie. heads), we would do:

$$\Omega = \binom{N}{n} = \frac{N!}{n!(N-n)!}$$

If there are more than 2 possible outcomes (or, really, we could do this with 2 possible outcomes), we write this as

$$\Omega = \binom{N}{n_1 \cdots n_i} = \frac{N!}{n_1! \cdots n_i!}$$

As long as the sum of the small n comes out to N .

1.2.3 The Second Law of Thermodynamics

1.2.4 Large Systems

1.2.5 The Ideal Gas

1.2.6 Entropy

1.3 Interactions and Implications

1.3.1 Temperature

1.3.2 Entropy and Heat

1.3.3 Mechanical Equilibrium and Pressure

1.3.4 Diffusive Equilibrium and Chemical Potential

1.4 Free Energy and Chemical Thermodynamics

1.4.1 Free Energy as Available Work

1.4.2 Free Energy as a Force Toward Equilibrium

1.4.3 Phase Transformations of Pure Substances

2 Statistics

3 Statistical Mechanics

3.1 Boltzmann Statistics

3.1.1 The Boltzmann Factor

3.1.2 Average Values

3.1.3 Partition Functions and Free Energy

3.1.4 Partition Functions for Composite Systems

3.1.5 Ideal Gas Revisited

3.1.6 Monte Carlo, Metropolis-Hastings

3.2 Quantum Statistics

3.2.1 The Gibbs Factor

3.2.2 Bosons and Fermions

3.2.3 Degenerate Fermi Gases

3.2.4 Blackbody Radiation

3.2.5 Debye Theory of Solids