

# Notes: Thermal Physics and Statistical Mechanics

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# Chapter 0

## Introduction

### 0.1 First Law

The first law of thermodynamics states that energy is conserved in a thermodynamic process. Or in math

$$\Delta U = Q + W$$

In differential form we can write this as

$$dU = TdS - pdV + \mu dN$$

Where  $T$  is the temperature,  $\mu$  is the chemical potential, and  $S$  is the entropy. From this the consequences are immediate

$$\begin{aligned}\left(\frac{\partial S}{\partial U}\right)_{V,N} &= \frac{1}{T} \\ \left(\frac{\partial U}{\partial V}\right)_{S,N} &= -p \\ \left(\frac{\partial U}{\partial N}\right)_{S,V} &= \mu\end{aligned}$$

In addition there are useful thermodynamic potentials. For the extent of investigating them we will assume  $N$  to be constant so that  $dU = TdS - pdV$ . First we may define the Enthalpy:

$$\begin{aligned}H &:= U + pV \\ dH &= dU + pdV + Vdp \\ &= TdS + Vdp\end{aligned}$$

From here we find the relations

$$T = \left( \frac{\partial H}{\partial S} \right)_p \quad V = \left( \frac{\partial H}{\partial p} \right)_S$$

Next we utilize a mathematical fact that  $\frac{\partial^2 f}{\partial x \partial y} = \frac{\partial^2 f}{\partial y \partial x}$ . This gives us what we call the Maxwell Relation.

$$\left( \frac{\partial T}{\partial p} \right)_S = \left( \frac{\partial V}{\partial S} \right)_p$$


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Now we may define the Helmholtz free energy:

$$\begin{aligned} F &:= U - TS \\ dF &= dU - TdS - SdT \\ &= -pdV - SdT \end{aligned}$$

From here we find the relations

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

And our Maxwell relation is

$$\left( \frac{\partial p}{\partial T} \right)_V = \left( \frac{\partial S}{\partial V} \right)_T$$


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Now we may define the Gibbs free energy:

$$\begin{aligned} G &:= U + pV - TS \\ dG &= dU + pdV + Vdp - TdS - SdT \\ &= Vdp - SdT \end{aligned}$$

From here we find the relations

$$V = \left( \frac{\partial G}{\partial p} \right)_T \quad -S = \left( \frac{\partial G}{\partial T} \right)_p$$

And our Maxwell relation is

$$\left( \frac{\partial V}{\partial T} \right)_p = - \left( \frac{\partial S}{\partial p} \right)_T$$

## 0.2 The Partition Theorem

The partition theorem provides a powerful tool for many tasks in thermodynamics and statistical mechanics. Chief among them it gives us an easy method to calculate the probability that a system is in any given state so long as it is in thermal equilibrium with its reservoir.

The probability of finding a system in a particular macrostate is obviously tied to the multiplicity of the reservoir given the macrostate

$$\frac{P(s_2)}{P(s_1)} = \frac{\Omega_R(s_2)}{\Omega_R(s_1)}$$

And since  $S = k \ln \Omega$  we can say

$$\frac{P(s_2)}{P(s_1)} = \frac{e^{S_R(s_2)/k}}{e^{S_R(s_1)/k}} = e^{[S_R(s_2) - S_R(s_1)]/k}$$

Using the first law of thermodynamics we have

$$dS_R = \frac{1}{T}(dU_R + pdV_R - \mu dN_R)$$

We may neglect the term  $pdV_R$  since it will be small and  $\mu dN_R$  since it will be zero. We then get

$$S_R(s_2) - S_R(s_1) = \frac{1}{T}[U_R(s_2) - U_R(s_1)] = -\frac{1}{T}[E(s_2) - E(s_1)]$$

Going back to our expression with the probabilities we have

$$\frac{P(s_2)}{P(s_1)} = e^{-[E(s_2) - E(s_1)]/kT} = \frac{e^{-E(s_2)/kT}}{e^{-E(s_1)/kT}}$$

We call a term like  $e^{-E(s)/kT}$  a Boltzmann factor. And clearly this is directly proportional to the probability of the given state with some factor or relation  $1/Z$ .

$$P(s) = \frac{1}{Z}e^{-E(s)/kT}$$

Where  $Z = \sum_s e^{-E(s)/kT}$ . For simplicity we write  $\beta = 1/kT$ . We can use the partition function to write the average energy of a particle in the system

$$\bar{E} = \frac{\sum_s E(s)N(s)}{N} = \sum_s E(s) \frac{N(s)}{N} = \sum_s E(s)P(s) = \frac{1}{Z} \sum_s E(s)e^{-\beta E(s)}$$

This is the same as saying

$$\overline{E} = -\frac{1}{Z} \frac{\partial Z}{\partial \beta} = -\frac{\partial}{\partial \beta} \ln Z$$

Similarly we can say for any variable that depends on state  $X(s)$

$$\overline{X} = \sum_s X(s) P(s) = \frac{1}{Z} \sum_s X(s) e^{-\beta E(s)}$$

To measure the deviation in a variable we can use the standard deviation where

$$\sigma_E^2 = \overline{E^2} - (\overline{E})^2$$

and

$$\overline{E^2} = \frac{1}{Z} \frac{\partial^2 Z}{\partial \beta^2} \quad \overline{E} = -\frac{1}{Z} \frac{\partial Z}{\partial \beta}$$

Together these give us

$$\sigma_E = kT \sqrt{\frac{C}{k}}$$

where  $C = \partial \overline{E} / \partial T$

## Part I

# 3 Models of Matter





We may begin our study of thermal mechanics with three simplified models of matter. The Einstein Solid will allow us to study solids. The Ising Model will allow us to study magnets. The Ideal Gas model will allow us to study gases.



# Chapter 1

## Ideal Gas

The ideal gas is one which obeys the ideal gas law

$$PV = Nk_B T$$

The question of its multiplicity seems at first somewhat pointless, surely in a given volume a molecule would have infinitely many positions it could take on and momentum vectors it could take on. If we entertain the idea for a bit longer, and start with just one monatomic molecule, it becomes clear that the multiplicity should be proportional to the volume in position space and the volume in momentum space

$$\Omega_1 \propto VV_p$$

By conservation of energy we know

$$U = \frac{1}{2m}(p_x^2 + p_y^2 + p_z^2) \implies p_x^2 + p_y^2 + p_z^2 = 2mU$$

This is clearly a sphere in momentum space with radius  $\sqrt{2mU}$ . The volume of momentum space would then be the surface area of this sphere. We can develop this idea further if we discretize with the Heisenberg Uncertainty Principle

$$(\Delta x)(\Delta p) \approx h$$

If we consider the number of distinct “spots” in position space as  $L/\Delta x$  and in momentum space as  $L_p/\Delta p_x$  we combine these to find

$$\frac{L}{\Delta x} \frac{L_p}{\Delta p_x} = \frac{LL_p}{h}$$

So in 3 dimensions

$$\Omega_1 = \frac{VV_p}{h^3}$$

For 2 particles we have a 6 dimensional momentum hypersphere, but must also divide by 2 to factor in that the two particles are indistinguishable to get

$$\Omega_2 = \frac{1}{2} \frac{V^2}{h^6} \times (\text{area of hypersphere})$$

If we continue this process we get the general case

$$\Omega_N = \frac{1}{N!} \frac{V^N}{h^{3N}} \frac{\pi^{3N/2}}{(3N/2)!} (\sqrt{2mU})^{3N} = f(N) V^N U^{3N/2}$$

## 1.1 Entropy

The entropy of the ideal gas is given by the **Sackur-Tetrode equation**

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

This equation can come in very handy, take for example quistatic isothermal expansion where  $N, U$  are constant. We find

$$\Delta S = Nk \ln \frac{V_f}{V_i}$$

## 1.2 Temperature

The entropy can be simplified to the form

$$S = Nk_B (\ln V + \ln U^{3/2}) + (\text{a function of } N)$$

And so we can calculate temperature

$$T = \left( \frac{\partial S}{\partial U} \right)^{-1} = \left( \frac{\frac{3}{2} Nk_B}{U} \right)^{-1}$$

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

Notice how this agrees with the equipartition theorem since every molecule in the gas will have 3 degrees of freedom (from the 3 directions of motion).

## Chapter 2

# Ising Model

We may think of the Ising model as arrows either pointing up or down. Clearly the multiplicity of the system with  $N$  arrows and  $N_\uparrow$  pointing up is

$$\Omega(N, N_\uparrow) = \binom{N}{N_\uparrow} = \frac{N!}{N_\uparrow!(N - N_\uparrow)!}$$

### 2.1 Entropy

$$\begin{aligned} S &:= Nk_B \Omega \\ S/k_B &= \ln N! - \ln N_\uparrow! - \ln(N - N_\uparrow)! \\ &\approx N \ln N - N_\uparrow \ln N_\uparrow - (N - N_\uparrow) \ln(N - N_\uparrow) \end{aligned}$$

### 2.2 Magnetism

If we imagine each arrow as a magnetic dipole  $\mu$  under the influence of some external field  $B$  it makes sense to define the total energy as

$$U = \mu B(N_\downarrow - N_\uparrow) = \mu B(N - 2N_\uparrow)$$

It then also makes sense to define the magnetization as the total moment of the whole system.

$$M = \mu B(N_\uparrow - N_\downarrow) = -\frac{U}{B}$$

## 2.3 Temperature

From this equation for the internal energy we can calculate the temperature. Here we will use the chain rule to make calculations simpler

$$\frac{1}{T} = \left( \frac{\partial S}{\partial U} \right)_{N,B} = \frac{\partial N_{\uparrow}}{\partial U} \frac{\partial S}{\partial N_{\uparrow}} = -\frac{1}{2\mu B} \frac{\partial S}{\partial N_{\uparrow}} = -\frac{k}{2\mu B} \ln \left( \frac{N - U/\mu B}{N + U/\mu B} \right)$$

Some algebra gives us

$$U = -N\mu B \tanh \left( \frac{\mu B}{kT} \right)$$

## 2.4 Partition function

Looking at one dipole we know it has two states: “up” with energy  $-\mu B$  and “down” with energy  $+\mu B$ . Thus the partition function yields

$$Z = \sum_s e^{-\beta E(s)} = e^{\beta\mu B} + e^{-\beta\mu B} = 2 \cosh(\beta\mu B)$$

We can then also write the probability of the states

$$P_{up} = \frac{e^{\beta\mu B}}{Z} = \frac{e^{\beta\mu B}}{2 \cosh(\beta\mu B)} \quad P_{down} = \frac{e^{-\beta\mu B}}{Z} = \frac{e^{-\beta\mu B}}{2 \cosh(\beta\mu B)}$$

We can then also calculate the average energy of our single dipole.

$$\begin{aligned} \bar{E} &= \sum_s E(s)P(s) \\ &= (-\mu B)P_{up} + (\mu B)P_{down} \\ &= -\mu B(P_{up} - P_{down}) \\ &= -\mu B \frac{e^{\beta\mu B} - e^{-\beta\mu B}}{2 \cosh(\beta\mu B)} \\ &= -\mu B \tanh(\beta\mu B) \end{aligned}$$

And this is in agreement with what we previously derived for the total internal energy

$$U = -N\mu B \tanh \left( \frac{\mu B}{kT} \right)$$

## Chapter 3

# Einstein Model

Consider a set of  $N$  oscillators, each able to hold an arbitrary number of units of energy, where there are in total  $q$  units. We can calculate the multiplicity as lining up  $q + N - 1$  dots and choosing  $q$  of them to be energy and the remaining  $N - 1$  will be “walls” partitioning the system into our  $N$  oscillators. So

$$\Omega(N, q) = \binom{q + N - 1}{q} = \frac{(q + N - 1)!}{q!(N - 1)!}$$

If the system is sufficiently large we may say

$$\Omega(N, q) \approx \frac{(q + N)!}{q!N!}$$

### 3.1 Entropy

We now can move to calculate the entropy, which is defined as  $S := k_B \ln \Omega$ , and also making use of Stirling’s approximation  $\ln n! \approx n \ln n - n$

$$\begin{aligned} \ln \Omega &= \ln \left( \frac{(q + N)!}{q!N!} \right) \\ &= \ln(q + N)! - \ln q - \ln N \\ &\approx (q + N) \ln(q + N) - q \ln q - N \ln N \end{aligned}$$

If we assume that  $q \gg N$  (i.e. the temperature is high) we can use the approximation  $\ln(1 + x) = x$  when  $x \ll 1$

$$\begin{aligned} \ln(q + N) &= \ln[q(1 + N/q)] \\ &= \ln q + \ln(1 + N/q) \\ &= \ln q + N/q \end{aligned}$$

If we plug this into our formula for  $\ln \Omega$  we find

$$\begin{aligned}
 \ln \Omega &\approx (q + N) \ln(q + N) - q \ln q - N \ln N \\
 &\approx (q + N)(\ln q + N/q) - q \ln q - N \ln N \\
 &= N \ln \frac{q}{N} + N + \frac{N^2}{q} \\
 &\approx N \ln \frac{q}{N} + N \\
 \Omega &\approx e^{N \ln(q/N)} e^N = \left(\frac{eq}{N}\right)^N
 \end{aligned}$$

### 3.2 Sharpness of the Multiplicity

We can see just how unlikely large deviations in the multiplicity are for large  $N$  by calculating the “sharpness” of the multiplicity function. Let’s say we have two blocks each with  $N$  oscillators and in the high temperature limit so that  $q \gg N$ . We then get

$$\Omega = \left(\frac{eq_A}{N}\right)^N \left(\frac{eq_B}{N}\right)^N = \left(\frac{e}{N}\right)^{2N} (q_A q_B)^N$$

We know that  $q_A + q_B = q$  and we know that the multiplicity will peak when  $q_A = q_B = q/2$ . So

$$\Omega_{max} = \left(\frac{e}{N}\right)^{2N} \left(\frac{q}{2}\right)^{2N}$$

We can investigate some deviation from the maximum by saying

$$q_A = \frac{q}{2} + x \qquad q_B = \frac{q}{2} - x$$

We then get the multiplicity as

$$\Omega = \left(\frac{e}{N}\right)^{2N} \left[\left(\frac{q}{2}\right)^2 - x^2\right]^N$$



We can then manipulate this as

$$\begin{aligned}
 \ln \left[ \left( \frac{q}{2} \right)^2 - x^2 \right]^N &= N \left[ \left( \frac{q}{2} \right)^2 - x^2 \right] \\
 &= N \left[ \left( \frac{q}{2} \right)^2 \left( 1 - \left( \frac{2x}{q} \right)^2 \right) \right] \\
 &= N \left[ \ln \left( \frac{q}{2} \right)^2 + \ln \left( 1 - \left( \frac{2x}{q} \right)^2 \right) \right] \\
 &\approx N \left[ \ln \left( \frac{q}{2} \right)^2 + \left( \frac{2x}{q} \right)^2 \right]
 \end{aligned}$$

If we exponentiate we get

$$\Omega = \left( \frac{e}{N} \right)^N e^{N \ln(q/2)^2} e^{-N(2x/q)^2} = \Omega_{max} e^{-N(2x/q)^2}$$

This is a Gaussian and its value falls to  $1/e$  of its maximum at

$$N(2x/q)^2 = 1 \qquad x = \frac{q}{2\sqrt{N}}$$

### 3.3 Temperature

We can define the internal energy of Einstein Solid as  $q\epsilon$ . The entropy will be

$$S = Nk_B \left( \ln \frac{q}{N} + 1 \right) = Nk_B \ln U - Nk \ln(\epsilon N) + Nk$$

From the definition of temperature we can calculate the temperature of the Einstein Solid.

$$\begin{aligned}
 T &= \left( \frac{\partial S}{\partial U} \right)^{-1} \\
 &= \left( \frac{Nk_B}{U} \right)^{-1} \\
 U &= Nk_B T
 \end{aligned}$$

Note this is exactly what the equipartition theorem would predict since each oscillator has 2 degrees of freedom (potential energy and kinetic). We can go on to calculate the heat capacity too.

$$C_V := \left( \frac{\partial U}{\partial T} \right)_{N,V} = Nk_B$$



## Part II

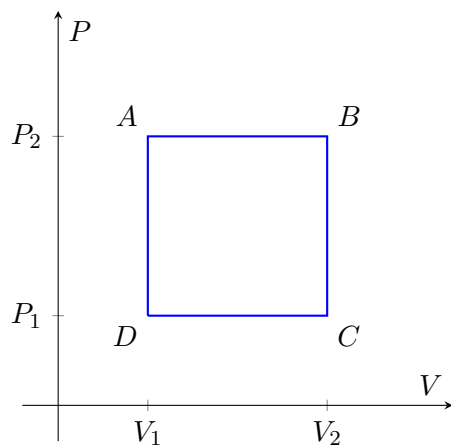
# 2 Heat Engine Cycles



## Chapter 4

# Square Cycle

Let us imagine a thermodynamic process comprised of four steps. We can plot the process and say that the order is clockwise starting at A.



We can find the heat flow, energy, and work at each step. Assume the substance is an ideal monatomic gas and thus has internal energy  $U = \frac{3}{2}NkT$ . We will also use the expressions  $W = -pdV$  and  $\Delta U = Q + W$ .

$\overline{AB} :$	$W = -P_2(V_2 - V_1)$	$Q = \frac{5}{2}P_2(V_2 - V_1)$	$\Delta U = \frac{3}{2}P_2(V_2 - V_1)$
$\overline{BC} :$	$W = 0$	$Q = \frac{3}{2}(P_1 - P_2)V_2$	$\Delta U = \frac{3}{2}(P_1 - P_2)V_2$
$\overline{CD} :$	$W = -P_1(V_1 - V_2)$	$Q = \frac{5}{2}P_1(V_1 - V_2)$	$\Delta U = \frac{3}{2}P_1(V_1 - V_2)$
$\overline{DA} :$	$W = 0$	$Q = \frac{3}{2}(P_2 - P_1)V_1$	$\Delta U = \frac{3}{2}(P_2 - P_1)V_1$
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$\sum :$	$W = (P_1 - P_2)(V_2 - V_1)$	$Q = -(P_1 - P_2)(V_2 - V_1)$	$\Delta U = 0$

Beyond just the calculation we can lend some physical intuition to the system. Since the system ends up where it starts the change in the internal energy must be 0. If it didn't we could examine exactly how many times the cycle had been performed by how much internal energy the system had, and so it would not have truly returned to its initial state.

The heat and work cannot be thought of in this way. The system can be idealized to be reversible, meaning it does not cause an increase in the total entropy of the universe.

## Chapter 5

# Carnot Cycle

The Carnot cycle consists of 2 adiabats and 2 isotherms. It then makes sense to discuss these separately before we discuss them together.

### 5.1 Adiabatic Processes

A process is said to be adiabatic if no heat is added to the system, in other words  $dQ = 0$ . So our first law becomes

$$dU = dQ + dW \implies dU = dW$$

In the case of expansion and no other work  $dW = -pdV$  and if we recall our definition of the heat capacity  $C_V = \frac{dU}{dT}$ , together

$$\begin{aligned} dU &= C_V dT = -pdV \\ C_V dT &= -\frac{RT}{V} dV && (\text{by } pV = nRT) \\ \frac{1}{T} dT &= -\frac{R}{C_V} \frac{1}{V} dV \\ \ln\left(\frac{T_2}{T_1}\right) &= -\frac{R}{C_V} \ln\left(\frac{V_2}{V_1}\right) \end{aligned}$$

Here we define  $\gamma := C_p/C_V$  and since  $C_p = C_V + R$  we get that  $-(R/C_V) = 1 - \gamma$ .

$$\begin{aligned}\ln\left(\frac{T_2}{T_1}\right) &= \gamma \ln\left(\frac{V_2}{V_1}\right) \\ \frac{T_2}{T_1} &= \frac{V_2^{1-\gamma}}{V_1^{1-\gamma}} = \frac{V_1^{\gamma-1}}{V_2^{\gamma-1}} \\ T_2 V_2^{\gamma-1} &= T_1 V_1^{\gamma-1}\end{aligned}$$

And by the ideal gas law we can say that  $pV \propto T$  and get the famous result

$$pV^\gamma = \text{constant}$$

We can arrive at the same result with a slightly different approach

$$\begin{aligned}dU &= \frac{f}{2} N k_B dT = -P dV \\ \frac{f}{2} N k_B dT &= -\frac{N k_B T}{V} dV \\ \frac{f}{2} \frac{1}{T} dT &= -\frac{1}{V} dV \\ \frac{f}{2} \ln\left(\frac{T_2}{T_1}\right) &= -\ln\left(\frac{V_2}{V_1}\right) \\ \frac{T_2^{f/2}}{T_1^{f/2}} &= \frac{V_1}{V_2} \\ T_2^{f/2} V_2 &= T_1^{f/2} V_1\end{aligned}$$

And if we substitute in  $T \propto pV$

$$\begin{aligned}(p_1 V_1)^{f/2} V_1 &= (p_2 V_2)^{f/2} V_2 \\ \left[p_1^{f/2} V_1^{1+f/2}\right]^{2/f} &= \left[p_2^{f/2} V_2^{1+f/2}\right]^{2/f}\end{aligned}$$

And if we define  $\gamma = \frac{f+2}{f}$  we arrive at

$$pV^\gamma = \text{constant}$$



## 5.2 Isothermic Processes

An isothermic process is one in which the temperature is constant or  $dT = 0$ . Since we know that in an ideal gas  $dU = C_V dT$  it must then also be that  $dU = 0$ . And so by our first law (conservation of energy) we get

$$dU = 0 = dQ + dW \implies dW = -dQ$$

We can then use  $dW = -pdV$  to look at isothermic expansion

$$\begin{aligned} \Delta Q &= \int dQ \\ &= \int -dW \\ &= \int_{V_1}^{V_2} p dV \\ &= \int_{V_1}^{V_2} \frac{RT}{V} dV \\ &= RT \ln \left( \frac{V_2}{V_1} \right) \end{aligned}$$

## 5.3 Carnot Cycle

We are now prepared to talk about the Carnot cycle, which can be defined by 4 points  $A, B, C, D$  in  $PV$ -space.  $\overline{AB}$  and  $\overline{CD}$  will be our adiabats.  $\overline{BC}$  and  $\overline{DA}$  will be our isotherms. Heat will only flow into and out of the system during the isotherms, so we can call the heat inflow as  $Q_h$  and outflow as  $Q_l$ . By our rules of adiabatic expansion and isothermic expansion we know:

$$\begin{aligned} \overline{AB} : Q_h &= RT_h \ln \frac{V_B}{V_A} \\ \overline{BC} : \left( \frac{T_h}{T_l} \right) &= \left( \frac{V_C}{V_B} \right)^{\gamma-1} \\ \overline{CD} : Q_l &= RT_l \ln \frac{V_D}{V_C} \\ \overline{DA} : \left( \frac{T_l}{T_h} \right) &= \left( \frac{V_A}{V_D} \right)^{\gamma-1} \end{aligned}$$

The statements about the adiabats tells us

$$\frac{V_B}{V_A} = \frac{V_C}{V_D}$$

And the statements on the isotherms tell us

$$\frac{Q_h}{Q_l} = \frac{T_h}{T_l}$$

We can now define the efficiency of the Carnot engine as the amount of work done by the system over the energy input

$$\epsilon := \frac{W}{Q_h}$$

By conservation of energy we know that  $W = Q_h - Q_l$

$$\epsilon_{Carnot} = \frac{Q_h - Q_l}{Q_h} = 1 - \frac{Q_l}{Q_h} = 1 - \frac{T_l}{T_h}$$

## 5.4 Carnot's Theorem

Carnot's theorem states that given two temperatures the Carnot engine is the most efficient engine possible.

To prove this by contradiction we can imagine some engine  $E$  such that  $\epsilon_E > \epsilon_{Carnot}$ . Since the Carnot engine is reversible we can hook it up to  $E$  so that the work from  $E$  causes the Carnot engine to run in reverse. Let's label the heat into  $E$  as  $Q'_h$  and out as  $Q'_l$ , and since the Carnot engine is in reverse the heat in will be  $Q_l$  and the heat out will be  $Q_h$ . By our assumption about the efficiencies

$$\frac{W}{Q'_h} > \frac{W}{Q_h} \implies Q_h > Q'_h$$

And by the first law of thermodynamics

$$W = Q'_h - Q'_l = Q_h - Q_l$$

which gives us

$$Q_h - Q'_h = Q_l - Q'_l$$

And since the LHS is positive so in the RHS. So all the heat extracted from  $T_l$  is dumped into the reservoir at  $T_h$ . This violates Clausius's statement of the second law: "No process is possible whose sole result is the transfer of heat from a colder to a hotter body."

Similarly we may show that any reversible engine working between two temperatures will have the same efficiency as the Carnot engine. We can show this by simply running it in reverse connected to a Carnot engine, and

it will violate Clausius's statement as before unless it has the same efficiency as the Carnot engine.

Kelvin's statement of the second law says: "No process is possible whose sole result is the complete conversion of heat into work." This is equivalent to Clausius's statement. We can first show that a system that violates Kelvin's statement also violates Clausius's. Say our Kelvin violator takes in a heat  $Q'_h$  and turns it entirely into work so  $W = Q'_h$ . We can hook it up to a Carnot engine in reverse which then pumps energy from  $T_l$  to  $T_h$  using the work. So the Carnot engine is pumping in a heat

$$Q_h = W + Q_l$$

And so the net heat being pumped into the high temperature reservoir is

$$Q_h - Q'_h = Q_l$$

This combined process is then turning all the heat from  $T_l$  and pumping it into  $T_h$ , violating Clausius's statement.

Similarly, a violating of Clausius's statement violates Kelvin's statement. We do this by having a Clausius violator that moves  $Q_l$  from  $T_l$  to  $T_h$  and then a Carnot engine that takes in  $Q_h$  and outputs  $Q_l$  as well as work  $W$ . Thus turning  $Q_h - Q_l$  entirely into work and violating Kelvin's statement.

## 5.5 Ideal Refrigerator

Most of the proofs we just went through hinted at a very crucial idea, that the Carnot engine is able to run backwards. This is not just crucial from a theoretical standpoint, it is also approximately how a refrigerator functions. A work  $W$  is input causing a flow of heat  $Q_l$  from a cold body to a hot body. Since the goal of the refrigerator is to remove heat it then makes sense to define the efficiency as

$$\epsilon_{fridge} = \frac{Q_l}{W} = \frac{T_l}{T_h - T_l}$$

It's clear that this can yield an efficiency above 100%.

## 5.6 Heat Pump

Similarly we can define the heat pump, this is essentially a refrigerator where the goal is to pump heat  $Q_h$  into a hot body (e.g. from the cold outdoors

into a house). The efficiency can then be defined

$$\epsilon_{pump} = \frac{Q_h}{W} = \frac{T_h}{T_h - T_l}$$

## 5.7 Clausius's Theorem

Recall we showed for the Carnot cycle (or any reversible cycle)

$$\frac{Q_h}{Q_l} = \frac{T_h}{T_l}$$

If we define  $\Delta Q_{rev}$  as the heat flow at some small point along the cycle. Over the whole cycle

$$\sum_{cycle} \frac{\Delta Q_{rev}}{T} = \frac{Q_h}{T_h} + \left(-\frac{Q_l}{T_l}\right) = 0$$

In the limiting case we can write

$$\oint \frac{dQ_{rev}}{T} = 0$$

If we generalize this beyond the case for a reversible cycle we get Clausius theorem which states

$$\oint \frac{dQ}{T} \geq 0$$

This naturally leads us to the definition of entropy as

$$dS = \frac{dQ}{T}$$

Reversible processes have  $dS = 0$  and are called isentropic.