Phys 359

STATISTICAL MECHANICS

University of Waterloo

Course notes by: TC Fraser
Instructor: Michel Gingras

tcfraser@tcfraser.com

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Table Of Contents

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1   Introduction

1.1   What is Statistical Mechanics

Statistical Mechanics is the area of Physics interested in systems with a large number of degrees of freedom n. Note that these variables can be interacting or not.

There are two distinct class of Statistical Mechanics: equilibrium and non-equilibrium.

The Statistical part of Statistical Mechanics implies that it is inherently a study of probabilities and probability distributions. These laws must still remain fully consistent with physical laws.

Typically, systems are analyzed on a microscopic level. For a system of particles with charges $\{q_i\}$ and their positions $\{\vec{r}_i\}$, the dynamics are governed by the forces acting on each particle,

$$\vec{F}_i = m_i \vec{a}_i = \sum_{i \neq j} \frac{q_i q_j}{4\pi\epsilon_0} \frac{1}{|\vec{r}_{ij}|^2}$$

But does labeling the particles really matter? For the case of $N \to \infty$, the global phenomenology is of interest.

1.2   History

1738   Daniel Bernoulli

- molecules moving in container, they collide with one another
- collisions with walls explains pressure

1850   Gay Lussac, Joule, Thomson (Lord Kelvin), Carnot

1859   James Clerk Maxwell

- $D(\nu) \sim e^{-\frac{\nu^2}{2k_B T}}$

1884   Josiash Willard Gibbs

- ensemble averaging

1900   Planck, Einstein, Bose, Pauli, Fermi, Dirac

Today   Frontier is in non-equilibrium Statistical Mechanics

- cold atoms
- biology
- quantum information

2   Foundations

2.1   Essence of Statistical Mechanics

Laws of Thermodynamics:

Pros	Cons
• great because they are totally general • relationship's (Maxwell's relations) between c_p, c_v, α, κ	• does not tell us how to compute anything • does not tell us what entropy is

The 2nd law of Thermodynamics reveals $\mathrm{d}U = \dbar Q - \dbar W$ where $\dbar Q = T\mathrm{d}S$.

But what is S and what does it **physically** mean? Boltzmann reveals the relation:

$$S = k_B \ln(\Omega)$$

Which we will come back to.

2.2 Postulate of Statistical Mechanics

There is only one postulate of Statistical Mechanics:

For an isolated system in equilibrium, all microstates accessible to the system are equally probable.

In order to digest this postulate, we will require some definitions.

Definitions:

- system

    - part of the universe we care about
    - only weakly coupled to the rest of the universe
    - the dynamics/mechanics are dominated by the internal degrees of freedom and forces

- isolated

    - idealization
    - eliminates all external influences; no force, no energy/heat flux and no particle flux
    - quantities such as the energy, number of particles and volume assumed constant forever $\mathrm{d}U, \mathrm{d}N, \mathrm{d}V = 0$

- equilibrium

    - everything is no-longer changing

- microstate

    - a complete/total description of everything at the microscopic level $\{\vec{r}_i, \vec{p}_i\}$ for each i

- macrostate

    - a description at the macroscopic level in accordance with the external constraints
    - $U, P, T, \bar{M}$

- equally probable

    - we are dealing with probabilities and statistics
    - microstates are somehow describing probabilistically the properties at the macroscopic level

- accessible

    - consistency with the macroscopic constraints imposed by the conservation laws (fixed energy, fixed number of particles)

Postulate Follow-up:

We assume that the observed/realized macrostate is the one with the most microstates.

2.3 Perspective from Coin Tossing

Consider 4 coins tossed many, many times. What are the microstates describing this system?

Macrostate Label	Macrostate		Microstate				Thermo Probability	True Probability
	N_H	N_T	A	B	C	D		
1	4	0	H	H	H	H	1	1/16
2	3	1	H	H	H	T	4	4/16
			H	H	T	H		
			H	T	H	H		
			T	H	H	H		
3	2	2	H	H	T	T	6	6/16
			H	T	T	H		
			T	T	H	H		
			T	H	H	T		
			H	T	H	T		
			T	H	T	H		
4	1	3	T	T	T	H	4	4/16
			T	T	H	T		
			T	H	T	T		
			H	T	T	T		
5	0	4	T	T	T	T	1	1/16

We note that the most probable macrostate 3 is the one with the most microstates 6.

How do we deal with very large N, N_H, N_T in order to locate the most likely macrostate? First likes get a general expression for Ω were Ω is the number of microstates. Since $N = N_H + N_T$ and N is considered fixed, there is only one free parameter N_H (taken by choice). Thus Ω can be considered a function of N_H and nothing else.

Recall from probability that the form for Ω is given by,

$$\Omega = \frac{N!}{N_H! \, (N - N_H)!}$$

The most likely macrostate is given when Ω (the number of microstates) is maximized. This means that we are interested in finding values of N_H, namely N_H^* where,

$$\left(\frac{\mathrm{d}\Omega}{\mathrm{d}N_H} \right)\Big|_{N_H = N_H^*} = 0 \qquad \left(\frac{\mathrm{d}^2\Omega}{\mathrm{d}N_H^2} \right)\Big|_{N_H = N_H^*} > 0$$

In order to do this, we will need to explore some mathematics ideas.

2.4 Stirlings Formula and Gaussian Integrals

Consider the integral,

$$I = \int_0^\infty x^N e^{-x} \mathrm{d}x$$

This can be evaluated using integration by parts,

$$I = N \int_0^\infty x^{N-1} e^{-x} \mathrm{d}x = \cdots = N! \tag{2.1}$$

2.4.1 Differentiation Trick

However, integration by parts N times on (2.1) is annoying. There is a nice trick. Notice that,

$$\int_0^\infty e^{-ax}\mathrm{d}x = \left(-\frac{1}{a}e^{-ax}\bigg|_0^\infty \right) = \frac{1}{a} \tag{2.2}$$

One can treat a as a *dummy* variable, and examine (2.2)'s derivative with respect to a,

$$\frac{\partial}{\partial a}\int_0^\infty e^{-ax}\mathrm{d}x = \int_0^\infty \frac{\partial}{\partial a}e^{-ax}\mathrm{d}x = \int_0^\infty -xe^{-ax}\mathrm{d}x = \frac{\partial}{\partial a}\left(\frac{1}{a}\right) = -\frac{1}{a^2}$$

The reason for doing this is to simplify the process of (2.1).

If one explores the Nth derivative of (2.2) with respect to a, you will derive the expression,

$$\left[(-1)^N \frac{\partial^N}{\partial a^N}\int_0^\infty e^{-ax}\mathrm{d}x \right]_{a=1} = N! \tag{2.3}$$

The $(-1)^N$ term is a result of the alternating sign induced by bringing down a $-x$ each time you take a derivative.

2.4.2 Stirling's Formula

Looking back at the integral (2.1),

$$\int_0^\infty x^N e^{-x}\mathrm{d}x = N! \tag{2.4}$$

How can we approximate $N!$ using the left had side of (2.4)? To derive Stirling's Formula, we need to make a change of variables $x = N + \sqrt{N}y$. Substituting into (2.4) gives,

$$N! = \int_0^\infty \sqrt{N}e^{-N}e^{N\ln\left(N+\sqrt{N}y\right)}e^{-\sqrt{N}y}\mathrm{d}y$$

The approximation begins by expanding the logarithm for large N,

$$\ln\left(N+\sqrt{N}y\right) = \ln\left(N\left[1+\frac{y}{\sqrt{N}}\right]\right) = \ln\left(N\right) + \ln\left(1+\frac{y}{\sqrt{N}}\right)$$

Take $\epsilon = \frac{y}{\sqrt{N}} << 1$ and apply Taylor series,

$$\ln\left(1+\epsilon\right) \approx \epsilon - \frac{\epsilon^2}{2}$$

Thus,

$$N! \approx \sqrt{N}e^{-N}N^N \int_{-\sqrt{N}}^\infty e^{-\frac{y^2}{2}}\mathrm{d}y$$

The lower bound can be approximated as ∞ since N is so large,

$$N! \approx \sqrt{N}e^{-N}N^N \int_{-\infty}^\infty e^{-\frac{y^2}{2}}\mathrm{d}y$$

Notice the remaining integral term. It is called the *Gaussian Integral* and has solution (see Gaussian Integrals),

$$\int_{-\infty}^{\infty} e^{-\frac{y^2}{2}} \, \mathrm{d}y = \sqrt{\frac{\pi}{a}} \tag{2.5}$$

Thus letting $a = 1/2$,

$$N! \approx \sqrt{2\pi N} e^{-N} N^N \tag{2.6}$$

Equation (2.6) is known as *Stirling's Formula*. However, there is a much more useful form of Stirling's Formula. It is obtained by taking the logarithm of both sides,

$$\ln (N!) \approx \left(N + \frac{1}{2}\right) \ln (N) - \left(N - \underbrace{\frac{1}{2} \ln (2\pi)}_{\text{small compared to large } N}\right)$$

$$\ln (N!) \approx N \ln N - N \tag{2.7}$$

Note that the remaining N is not dropped. This is because for $N \sim 10^{23}$, $N \ln N - N$ and $N \ln N$ differ by about 2%.

Now we can apply this to the problem of maximizing Ω (which is equivalent to maximizing $\ln \Omega$) because the logarithm is monotonically increasing.

$$0 = \frac{\partial \ln \Omega}{\partial N_H} = \frac{\partial}{\partial N_H} \left[\ln \left(\frac{N!}{N_H! \, (N - N_H)!} \right) \right]$$

Through some manipulation, and applying (2.7), one obtains the expected result,

$$N_H = \frac{N}{2}$$

2.4.3   Gaussian Integrals

Before continuing, we should take a moment to explore how (2.5) is solved. Let,

$$I_x = \int_{-\infty}^{\infty} e^{-ax^2} \, \mathrm{d}x$$

Here comes the trick. Multiply I_x by itself and switch from rectangular coordinates to polar coordinates,

$$I_x I_y = \int_{-\infty}^{\infty} e^{-ax^2} \, \mathrm{d}x \int_{-\infty}^{\infty} e^{-ay^2} \, \mathrm{d}y$$

$$I^2 = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} e^{-a(x^2 + y^2)} \, \mathrm{d}x \mathrm{d}y$$

Where we take $\mathbb{R}^2(x, y) \mapsto \mathbb{R}^2(r, \phi)$

$$I^2 = \int_0^{2\pi} \int_0^{\infty} r e^{-ar^2} \, \mathrm{d}r \mathrm{d}\phi$$

Which reveals that $I^2 = \pi/a$. Thus,

$$I = \sqrt{\frac{\pi}{a}}$$

2.5 Connections between Thermodynamics and Statistical Mechanics

Consider a lattice of Cu^{2+} atoms. In a lattice the Cu^{2+} atoms are distinguishable because they have unique locations. Now apply an external magnetic field.

$$H_{\text{Zeeman}} = -\vec{\mu} \cdot \vec{B}$$

Recall that $\vec{u} = g\mu_B \vec{s}$ has units J/T where T is Tesla. Where for an electron,

$$\mu_B = \frac{e\hbar}{2m} = 9 \times 10^{-24} \, \text{JT}^{-1} \qquad g \approx 2$$

For $\vec{B} = B\hat{z}$, $H_{\text{Zeeman}} = 2\mu_B B s_z \equiv b s_z$. The splitting of the two spin states $s_z = \pm 1$ for $B = 1\,\text{T}$ has characteristic temperature of,

$$\frac{H_{\text{Zeeman}}}{k_B} = \frac{\varepsilon}{k_B} = \frac{10 \times 10^{-23} \, \text{J}}{1.4 \times 10^{23} \, \text{JK}^{-1}} \approx 0.6\,\text{K}$$

Now consider N electrons subject to the field $\vec{B}$ where there are N_+ spins "up" and N_- spins "down". This is completely analogous to the coin flipping example. The total energy of the system is given by,

$$U = -N_- \varepsilon + N_+ \varepsilon$$

Note that $N = N_+ + N_-$ and thus,

$$\frac{U}{N} = \varepsilon - 2\varepsilon \frac{N_-}{N}$$

Constraining U and using the substitution,

$$\frac{N_-}{N} = \frac{1-x}{2} \qquad \frac{N_+}{N} = \frac{1+x}{2}$$

Then the microstate measure is given by,

$$\Omega = \frac{N!}{N_+! N_-!}$$

Becomes (after some manipulation as using (2.7))

$$\ln \Omega = -N \left[\left(\frac{1+x}{2} \right) \ln \left(\frac{1+x}{2} \right) + \left(\frac{1-x}{2} \right) \ln \left(\frac{1-x}{2} \right) \right]$$

Now recall that for fixed volume $dV = 0$,

$$\frac{1}{T} = \left(\frac{\partial S}{\partial U} \right)_V$$

But since U depends only on x, we can write,

$$\frac{1}{T} = \left(\frac{\partial S}{\partial x} \right) \left(\frac{\partial x}{\partial U} \right)$$

Thus reveals a slight connection between S the entropy and Ω through x in this example. Further analysis with motivate Boltzmann's equation,

$$S = k_B \ln \Omega + S_0$$

2.6   Example of a Physical System with Constraint

Suppose you have 3 particles called A, B, C such that each particle can have $\varepsilon_j = j\varepsilon$ where $j = 0, 1, 2, 3, \ldots$.

How many microstates are there subject to the constraint that the total energy is 3ε?

Macrostate Label	Macrostate				Microstate			Thermo Probability	True Probability
	N_0	N_1	N_2	N_3	A	B	C		
1	2	0	0	1	0	0	3ε	3	3/10
					0	3ε	0		
					3ε	0	0		
2	0	1	1	0	0	ε	2ε	6	6/10
					ε	2ε	0		
					2ε	0	ε		
					0	2ε	ε		
					2ε	ε	0		
					ε	0	2ε		
3	0	3	0	0	ε	ε	ε	1	1/10

3   Review of Thermodynamics

3.1   Definitions

Recall Boyle's Law $PV = nRT$.

- processes
    - constant T, isothermal process
    - constant P, isobaric process
    - constant V, isochoric process or isovolumetric process
    - constant S, adiabatic process
        * Comes from greek *diabatos* which means *to go through*
        * No heat exchange between system and surroundings
        * Can also be an approximation for processes that occur really quickly over a short period of time
- processes reversible/irreversible
    - reversible process happens over a number of discrete steps and that are each reversible
    - irreversible processes are like poking a hole in a balloon or a gas expanding in a vacuum
- thermodynamic variables T, P, V, U where U is the *total energy*

3.2   Zeroth Law of Thermodynamics

If systems A and B are in equilibrium with one another and systems B and C are in equilibrium then A is in equilibrium with C.

3.3   Functions of State

Thermodynamic variables are not independent. They are often related by an equation of state. For example $PV = nRT$ for an ideal gas. Other variables might come into an equation of state. For example $\rho, \mathcal{T}, E$ are all important for the equation of state for a liquid crystal sample.

Equations of state with typically look like

$$f(P, V, T) = 0$$

Another important notion is the notion of *function of state*. A quantity that depends only on the thermo-dynamic variables of the system and *not it's history*, is called a *function of state*.

We will first focus on $U_{\text{total energy}}$ first and then S_{entropy} as our functions of state.

Mathematically, $G = g(x, y)$ where x, y are the thermodynamic variables and G is a function of state analytic everywhere and obeys some properties:

- $dG = \left(\frac{\partial G}{\partial x}\right)_y dx + \left(\frac{\partial G}{\partial y}\right)_x dy$

- at most values of the thermodynamic variables $g(x, y)$ is "smooth".

- for example: $\left(\frac{\partial^2 G}{\partial x^2}\right)_y$ or $\left(\frac{\partial^2 G}{\partial y^2}\right)_x$ or $\left(\frac{\partial}{\partial x}\left(\frac{\partial G}{\partial y}\right)_x\right)_y$ are all continuous

- the order of discontinuities is determined by whether or not the system or substance is undergoing transitions of state or not

For functions of state that are analytical everywhere, the order of derivatives is inconsequential.

$$\left(\frac{\partial}{\partial x}\left(\frac{\partial G}{\partial y}\right)\right) = \left(\frac{\partial}{\partial y}\left(\frac{\partial G}{\partial x}\right)\right)$$

What can we say about G in cases where

$$dG = \frac{\partial G}{\partial x}dx + \frac{\partial G}{\partial y}dy \tag{3.1}$$

in the case of functions of state like U, $dU = \text{d}Q - \text{d}W$ and the inexact differentials and how they relate to exact differentials like dV and dS? In particular, when can we integrate dU?
Answer: equation (3.1) can be integrated in situations where

$$\left(\frac{\partial}{\partial y}\left(\frac{\partial G}{\partial x}\right)_y\right)_x = \left(\frac{\partial}{\partial x}\left(\frac{\partial G}{\partial y}\right)_x\right)_y \tag{3.2}$$

When equation (3.2) is held for a physical system, one can say that dG is an **exact differential**. Review 12,13 in notes on "Review of Thermodynamics".

The difference in the function $G(x, y)$ between two sufficiently close pairs of points (x_1, y_1) and (x_2, y_2) depends only on the difference in $G(x, y)$ evaluated at those two points.

$$\Delta G = G(x_2, y_2) - G(x_1, y_1)$$

ΔG does not depend on the path from point (x_1, y_1) to (x_1, y_1). In practice, one can assign such a function G to the values of the thermodynamic variables at the points (x, y). For example, $U(P, V)$ is such a function of state. It depends only on the description through the thermodynamic variables and not the history.

By counter example, heat Q is not a function of state. No one can say, "that substance has X units of heat in it".

3.4 Work

There are two types of work. One is called *configuration work* and the other is called *dissipative work*.

3.4.1 Configuration Work

Configuational work is denoted $\dđ W$ where the symbol $\dđ$ represents that it **is not** and exact differential.

$$\dđ W = \sum_i y_i \mathrm{d}x_i$$

where y_i is an intensive variable (not proportional to N, V; examples: pressure, surface tension). It can be thought of as a generalized force. Here $\mathrm{d}x_i$ is the generalized displacement which is an extensive variable.

3.4.2 Dissipative Work

Dissipative work can be thought of as "stirring work". Examples include a mixer in a liquid or an electrical wire/resistor.

- electrical power:

  - $P = V \cdot I$
  - $\dđ W_{\mathrm{dis}} = P \cdot \mathrm{d}t = RI^2 \mathrm{d}t$

3.4.3 Sign Convention

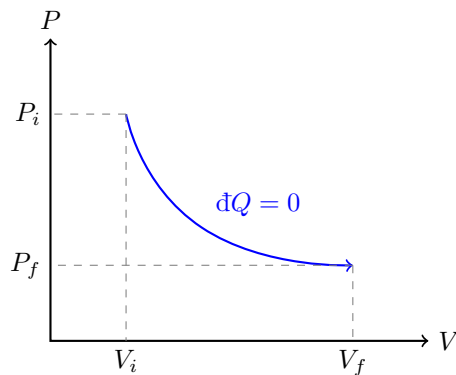$$\dđ W > 0 \quad \text{work done by the system}$$
$$\dđ W < 0 \quad \text{work done on the system}$$

Note:

- work is **not** a property of the system

- work is **not** a function of state

- integration on a closed loop is not degenerate $\oint \dđ W \neq 0$

3.4.4 Abiabatic Work

Abiabatic work occurs with no heat exchange.

Adiabatic work is done between any two equilibrium states and is *independent of path*. One can define a function of state as the total adiabatic work done on a system. Lets define this a the total internal energy of the system.

$$\mathrm{d}U = -\mathrm{d}W_{\mathrm{adiabatic}}$$

Note the minus '$-$' sign is due to the fact that the total energy of the system increases when work is done **on** this system. Along adiabatic paths, there is an exact differential associated with $\dđ W$. It is called internal energy $\mathrm{d}U$.

3.5   First of Law of Thermodynamics

3.5.1   Heat

In systems such as boiling a pot of water, there is no work performed on the system however the state of the system changes (not boiling to boiling). The mechanism that causes this change of state is heat (Q).

$$\mathrm{d}U = \text{đ}W + \text{đ}W \tag{3.3}$$

Equation (3.3) is using the following convention:

$$
\begin{aligned}
\text{đ}Q &:< 0 \quad \text{heat flow } \mathbf{in} \\
\text{đ}Q &:> 0 \quad \text{heat flow } \mathbf{out} \\
\text{đ}W &:< 0 \quad \text{work is done } \mathbf{by} \text{ system} \\
\text{đ}W &:> 0 \quad \text{work is done } \mathbf{on} \text{ system}
\end{aligned}
$$

3.5.2   Heat Capacities

Use the convention that C is the heat capacity (extensive) and c is the specific heat capacity (intensive).

$$c = \frac{C}{n}$$

$$C \equiv \lim_{\Delta T \to 0} \frac{\Delta Q}{\Delta T}$$

Heat capacity C is very important. Measuring C in a metal at low temperatures reveals very important intrinsic properties of the material. Also note that heat capacity is always $C \sim \frac{1}{T}$ and not some other power than -1.

Relationship Between c_v, c_p for an Ideal Gas:

$$PV = nRT$$

Using Boyle's law, work with $n = 1\,\mathrm{mol}$ for convenience. How can we relate C to the properties of the substance? Let us write (noting the '-' convention),

$$\mathrm{d}U = \text{đ}Q - \text{đ}W$$

Switch to specific (per mole) quantities,

$$\mathrm{d}u = \text{đ}q - \text{đ}w$$

$$\mathrm{d}u = \left(\frac{\partial u}{\partial T}\right)_v \mathrm{d}T + \left(\frac{\partial u}{\partial v}\right)_T \mathrm{d}V$$

$$\text{đ}q = \mathrm{d}u + \text{đ}w$$

$$\text{đ}q = \left(\frac{\partial u}{\partial T}\right)_v \mathrm{d}T + \left\{ \left(\frac{\partial u}{\partial v}\right)_T \mathrm{d}V + P\mathrm{d}v \right\}$$

However,

$$c_v = \lim_{\mathrm{d}T \to 0} \frac{\text{đ}q}{\mathrm{d}T} \quad \text{At constant V}$$

Thus,

$$c_v = \left(\frac{\partial u}{\partial T}\right)_v \tag{3.4}$$

Which gives us,

$$đq = c_v dT + P dv$$

Note that this formula uses the fact that,

$$\left(\frac{\partial U}{\partial v}\right)_T = 0 \quad \text{For ideal gas.}$$

Which we will prove momentarily, but can be taken as an experimental fact discovered by Guy-Lussac. Namely U is only a function of T for an ideal gas ($U = U(T)$).

$$đq = c_v dT + P dv + (v dp - v dp)$$

$$đq = (c_v + R) \, dT - v dp$$

Thus,

$$\lim_{dT \to 0} \left(\frac{dq}{dT}\bigg|_{p=\text{const.}}\right) = c_v + R$$
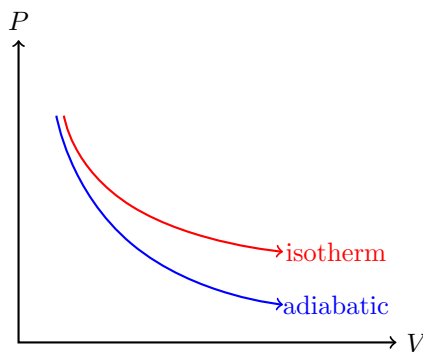
Thus we can define a new quantity,

$$c_p \equiv \left(\frac{đq}{dT}\bigg|_{p=\text{const.}}\right) = c_v + R$$

For an monoatomic gas ($U = \frac{3}{2}RT$),

$$\gamma \equiv \frac{c_p}{c_v} = \frac{5}{3}$$

3.6 Adiabatic Work Continued

Let us examine an isotherm (red) next to an adiabatic curve (blue),

$$đq = c_v dT + P dv$$
$$đq = c_P dT - v dP$$

And let's set $đq = 0$ (adiabatic),

$$c_v dT + P dv = c_P dT = v dP$$

Which gives,

$$\frac{\mathrm{d}P}{P} = -\gamma \frac{\mathrm{d}v}{v} \quad \text{Using } \gamma = c_P/c_v$$

Or integrating along a curve,

$$\int_1^2 \frac{\mathrm{d}P}{P} = -\int_1^2 \gamma \frac{\mathrm{d}v}{v}$$

$$\ln\left(\frac{P_2}{P_1}\right) = -\gamma \ln\left(\frac{v_2}{v_1}\right)$$

Which gives the relationship,

$$P_1 V_1^\gamma = P_2 V_2^\gamma$$

Which holds true along an adiabatic curve. However, $PV = RT$. Thus using the expression $\mathrm{d}U = -P\mathrm{d}V|_{\text{adiabatic}}$ gives the result,

$$W = \left\{\frac{P_2 V_2 - P_1 V_1}{1 - \gamma}\right\}_{\gamma > 1}$$

3.6.1 Gay-Lussac Experiment

For an ideal gas,

$$\left(\frac{\partial U}{\partial V}\right)_T = 0$$

$$đQ = \left(\frac{\partial U}{\partial T}\right)_V \mathrm{d}T + \left\{\left(\frac{\partial U}{\partial V}\right)_T + P\right\}\mathrm{d}V$$

$$\frac{đQ}{T} = \frac{1}{T}\left(\frac{\partial U}{\partial T}\right)_V \mathrm{d}T + \frac{1}{T}\left\{\left(\frac{\partial U}{\partial V}\right)_T + P\right\}\mathrm{d}V$$

Employ an integrating factor for the inexact differentials. It will take us from and inexact differential to an exact differential.

Math Interlude:

$$đG = A(x,y)\mathrm{d}x + B(x,y)\mathrm{d}y$$

Multiply G by $\mu(x,y)$ and unknown function of x and y,

$$\mathrm{d}\tilde{G} = \mu \cdot đG$$

Thus,

$$\mathrm{d}\tilde{G} = \mu A \mathrm{d}x + \mu B \mathrm{d}y$$

Making,

$$\frac{\partial(\mu A)}{\partial y} = \frac{\partial(\mu B)}{\partial x} \tag{3.5}$$

Example:

$$\mathrm{d}G = \sin(y)\mathrm{d}x + \cos(y)\mathrm{d}y$$

$$\mathrm{d}\tilde{G} = \mu \sin(y)\mathrm{d}x + \mu \cos(y)\mathrm{d}y$$

Let us look for a μ such that $\mu(x,y) = \mu(x)$ and plugging into equation (3.5),

$$\frac{\partial \left(\mu \sin(y)\right)}{\partial y} = \frac{\partial \left(\mu \cos(y)\right)}{\partial x}$$

$$\mu(x)\cos(y) = \frac{\mathrm{d}\mu}{\mathrm{d}x}\cos(y) + \mu\frac{\mathrm{d}\cos y}{\mathrm{d}x}$$

$$\mu(x)\cancel{\cos(y)} = \frac{\mathrm{d}\mu}{\mathrm{d}x}\cancel{\cos(y)} + \mu\cancel{\frac{\mathrm{d}\cos y}{\mathrm{d}x}}^{\,0}$$

Thus,

$$\mu(x) = \frac{\mathrm{d}u}{\mathrm{d}x}$$

Which gives,

$$\mu(x) = e^x$$

The purpose of introducing the notion of an integrating factor is to reveal that although đQ is an inexact differential, we can introduce an integrating factor $\frac{1}{T}$ that makes the quantity $\frac{\mathrm{d}Q}{T}$ an **exact** differential. This quantity is somehow more important that Q as it describes a property of the system. We will see that this quantity is the motivation for entropy. Let us examine this,

$$\frac{\mathrm{d}Q}{T} = \underbrace{\frac{1}{T}\left(\frac{\partial U}{\partial T}\right)_V \mathrm{d}T}_{A} + \underbrace{\frac{1}{T}\left\{\left(\frac{\partial U}{\partial V}\right)_T + P\right\}\mathrm{d}V}_{B}$$

And thus,

$$\frac{\partial A}{\partial V} = \frac{\partial B}{\partial T}$$

Gives,

$$\frac{\partial A}{\partial V} = \frac{\partial}{\partial V}\left\{\frac{1}{T}\frac{\partial U}{\partial T}\right\} = \frac{1}{T}\frac{\partial^2 U}{\partial V \partial T}$$

$$\frac{\partial B}{\partial T} = \frac{\partial}{\partial T}\left\{\frac{1}{T}\left(\frac{\partial U}{\partial V} + P\right)\right\} = -\frac{1}{T^2}\left(\frac{\partial U}{\partial V} + P\right) + \frac{1}{T}\frac{\partial^2 U}{\partial T \partial V} + \frac{1}{T}\frac{\partial P}{\partial T}$$

Equating these two expressions (noticing that $\frac{\partial^2 U}{\partial T \partial V} = \frac{\partial^2 U}{\partial V \partial T}$ and that $PV = RT \implies \frac{P}{T^2} = \frac{R}{TV}$),

$$\frac{1}{T}\frac{\partial^2 U}{\partial V \partial T} = -\frac{1}{T^2}\left(\frac{\partial U}{\partial V} + P\right) + \frac{1}{T}\frac{\partial^2 U}{\partial T \partial V} + \frac{1}{T}\frac{\partial P}{\partial T}$$

$$\frac{1}{\cancel{T}}\cancel{\frac{\partial^2 U}{\partial V \partial T}} = -\frac{1}{T^2}\left(\frac{\partial U}{\partial V} + P\right) + \frac{1}{\cancel{T}}\cancel{\frac{\partial^2 U}{\partial T \partial V}} + \frac{1}{T}\frac{\partial P}{\partial T}$$

$$0 = -\frac{1}{T^2}\left(\frac{\partial U}{\partial V} + P\right) + \frac{1}{T}\frac{\partial P}{\partial T}$$

$$\frac{1}{T^2}\left(\frac{\partial U}{\partial V} + P\right) = \frac{1}{T}\frac{\partial P}{\partial T}$$

$$\frac{1}{T^2}\frac{\partial U}{\partial V} + \frac{P}{T^2} = \frac{1}{T}\frac{\partial P}{\partial T}$$

$$\frac{1}{T^2}\frac{\partial U}{\partial V} + \frac{\cancel{R}}{\cancel{T}V} = \frac{\cancel{R}}{\cancel{T}V}$$

Therefore Gay-Lussac was destined to find this relationship through experiment:

$$\frac{\partial U}{\partial V} = 0$$

3.6.2   Joule-Thomson(Kelvin) Experiment

Using $\frac{1}{T}$ as the integrating factor, one can go through a similar derivation as in section 3.6.1 to understand that the quantity S is a state function of a system with,

$$\mathrm{d}S \equiv \frac{\text{đ}Q}{T}$$

3.6.3   Summary of First Law

In summary, the first law of thermodynamics is really just conservation of energy with expression,

$$\mathrm{d}U = \text{đ}Q - \text{đ}W$$

3.7   Second Law of Thermodynamics

Physical laws on the microscopic scale always are found to have an inherent time-reversal symmetry. The physics behaves the same running forward in time and backward in time. However, a semi-paradox of real-world phenomenology seems to suggest that there are some processes can not occur moving backward in time. They still satisfy the conservation of energy, but there is another law that governs these macroscopic phenomena.

3.7.1   Heat Engines

Imagine a an engine E that runs from temperature T_2 to T_1 (two heat baths), where it extracts heat Q_2 and disposes heat Q_1 and does some work W.
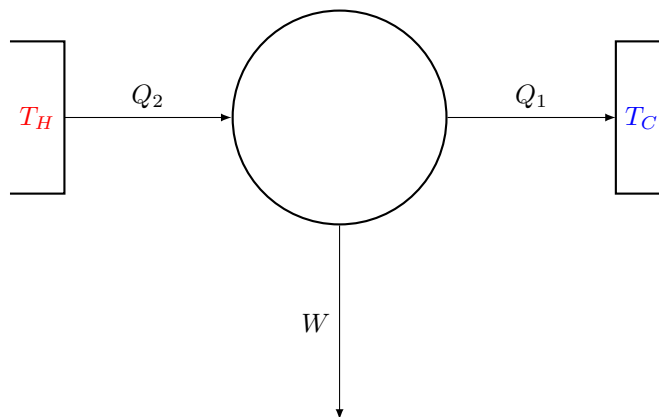
The efficiency of the engine is defined as,

$$\eta \equiv \frac{\text{output}}{\text{input}} = \frac{W}{Q_2}$$

Note that on a cyclic process $\Delta U = 0$ since U is a function of state. However it is also equal to,

$$\Delta U = (Q_1 + Q_2) - W$$

Therefore typically the efficiency is given by,
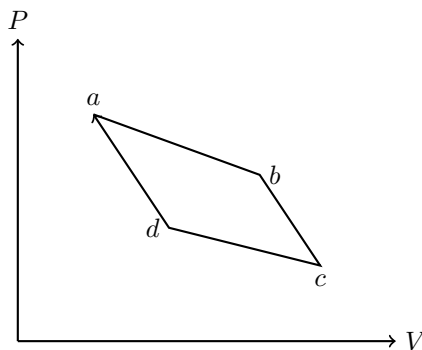
$$\eta = 1 + \frac{Q_1}{Q_2}$$

- Q_2 : injected into engine E and is > 0

- Q_1 : extracted from engine E and is < 0

This can be re-written as,

$$\eta = 1 + \frac{Q_1}{-|Q_2|} = 1 - \frac{|Q_1|}{|Q_2|}$$

3.7.2 Carnot Cycle/Engine

It can be shown that no engine is more efficient than a Carnot engine. Upon considering this, one can use entropy to expose the Second Law of Thermodynamics and the natural "arrow of time".

TODO: labels and arrows

ab	isotherm (T_2)	$Q_2 > 0$	$W^{ab} > 0$
bc	adiabat	$Q = 0$	$W^{bc} > 0$
cd	isotherm (T_1)	$Q_1 < 0$	$W^{cd} < 0$
da	adiabat	$Q = 0$	$W^{da} < 0$

The total work is given by,

$$W_{\text{tot}} = W^{ab} + W^{bc} + W^{cd} + W^{da}$$

1) First the isotherms:

$$W \sim \int P \mathrm{d}V \quad \text{Use } PV = RT \text{ (1 mole)}$$

$$W = \int_1^2 \frac{RT}{V} \mathrm{d}V = RT \ln\left(\frac{V_2}{V_1}\right)$$

ab	$RT_2 \ln\left(\frac{V_b}{V_a}\right) > 0$	$\implies Q_2$
cd	$RT_1 \ln\left(\frac{V_d}{V_c}\right) < 0$	$\implies Q_1$

This is to be expected because we are on isotherms and $\Delta U = 0$.

2) Second the adiabats:
Along an adiabat,

$$PV^\gamma = \text{const.}$$
$$P_1 V_1^\gamma = P_2 V_2^\gamma$$

Furthermore, relating this to $PV = RT$,

$$\frac{RT_1}{V_1} V_1^\gamma = \frac{RT_2}{V_2} V_2^\gamma$$

$$T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1}$$

Applying this to our diagram,

$$T_2 V_b^{\gamma-1} = T_1 V_c^{\gamma-1} \quad \text{and} \quad T_1 V_d^{\gamma-1} = T_2 V_a^{\gamma-1}$$

Which after rearrangement yields a constraint for the volumes,

$$\frac{V_b}{V_a} = \frac{V_c}{V_d}$$

Therefore,

$$\eta_{\text{Carnot}} = \eta_C = 1 + \frac{Q_1}{Q_2}$$

$$\eta_C = 1 + \frac{RT_1 \ln(V_d/V_c)}{RT_2 \ln(V_b/V_a)} = 1 - \frac{T_1}{T_2} \frac{\ln(V_c/V_d)}{\ln(V_b/V_c)}$$

$$\eta_C = 1 - \frac{T_1}{T_2}$$

3.7.3 Second Law Statements

1. **Clausius:** You can not build a machine or engine operating in a cycle can be constructed whose sole effect is to transfer heat from a cold to hot.

2. **Kelvin-Planck:** It is impossible to construct a device whose sole effect is to produce work by only absorbing heat from a single reservoir. Two reservoirs are needed.

Now let us use Clausius statement to prove Carnot's theorem as per the Carnot Engine; the most efficient engine is a Carnot engine.

Example:
Suppose we have an engine E that extracts heat from a hot T_2 reservoir $Q_2 = 100\,\text{cal}$, performs $W = 20\,\text{cal}$ of work and then dumps the remaining $Q_1 = 80\,\text{cal}$ calories of heat into a cold reservoir T_1. This is our Carnot engine.

$$\eta_C = \frac{W}{Q_2} = \frac{20}{100} = 20\%$$

Now suppose we had a better engine with $\eta_y > \eta_C$. Namely, this new engine has specs $Q_2 = 100\,\text{cal}, W = 40\,\text{cal}, Q_1 = 60\,\text{cal}$.

$$\eta_y = \frac{W}{Q_2} = \frac{40}{100} = 40\%$$

Now to prove is can not be the case, let us take our Carnot engine and reverse it's processes (making it a fridge), and doubling it's size. Therefore this Carnot fridge will require $40\,\text{cal}$ to run. This can be supplied by our "better" engine. Therefore, this combined engine will absorb $100\,\text{cal}$ from a cold reservoir at T_1 and inject it into a hot reservoir $100\,\text{cal}$ at temperature T_2, **with no other effect.** This violates the Clausius hypothesis.

Corollary:
All engines operating reversibly between two temperatures T_1 and T_2 have the same efficiency. In other words, the presence of any irreversible process degrades the efficiency $\eta_{\text{irreversible}} < \eta_{\text{Carnot}}$.

3.7.4   Entropy

We have found that,

$$\eta_C = 1 + \frac{Q_1}{Q_2} = 1 - \frac{T_1}{T_2}$$

Or equivalently,

$$\frac{Q_1}{T_1} + \frac{Q_2}{T_2} = 0$$

For a single Carnot engine, the sum of heat at step n over the temperature at step n has sum,

$$\sum_{n=1}^{k} \frac{Q_n}{T_n} = 0$$

Which gives that $\Delta Q/T$ over the whole cycle is zero. Taking the limit as $k \to \infty$, it suggests that the quantity $đQ/T$ is an exact differential. Introduce the label of entropy,

$$\mathrm{d}S = \frac{đQ}{T} \quad \text{with} \quad \oint \mathrm{d}S_{\mathrm{rev}} = 0$$

As you can see, considering a Carnot engine also suggests the presence of a quantity S call entropy. Just as before, S is a state function.

How can we compute entropy?

Example (Constant Volume):
Let's consider heat injected at constant volume, and attempt to calculate ΔS.

$$\Delta U = \Delta Q - \Delta W \quad \text{At constant volume, } \Delta W = 0$$

But we also have $\Delta Q = C_v \Delta T$ where C_v is the heat capacity of the material. This combination yields,

$$\mathrm{d}S = \frac{đQ}{T} = \frac{C_v}{T}\mathrm{d}T$$

$$\int_{1}^{2} \mathrm{d}S = \int_{T_1}^{T_2} \frac{C_v}{T}\mathrm{d}T = c_v \ln\left(\frac{T_2}{T_1}\right)$$

$$(S_2 - S_1) = C_v \ln\left(\frac{T_2}{T_1}\right)$$

Example (Constant Temperature):
Let's consider change of entropy for an isothermal process.

$$S_2 - S_1 = \int_{1}^{2} \frac{đQ}{T}$$

But from the first law we have for constant temperature,

$$\mathrm{d}U = đQ - P\mathrm{d}V = 0$$

Thus,

$$đQ = P\mathrm{d}V$$

$$\int_{1}^{2} \mathrm{d}S = \int_{1}^{2} \frac{P}{T}\mathrm{d}V = \int_{1}^{2} \frac{nR}{V}\mathrm{d}V = nR\ln\left(\frac{V_2}{V_1}\right)$$

Summarize:

1. No engine is more efficient than Carnot.

2. As a by-produce, we discovered a quantity ΔS defined as:

   - $\Delta S = \frac{\Delta Q}{T}$ ($\mathrm{d}S = \frac{\mathrm{d}Q}{T}$ for the infinitesimal)
   - $\mathrm{d}S$: defined at each point in (P, V, T) diagram
   - $\mathrm{d}S$: is exact differential. $S_2 - S_1$ only depends on the **endpoints** not the **path**

Let us show this by comparing two paths,
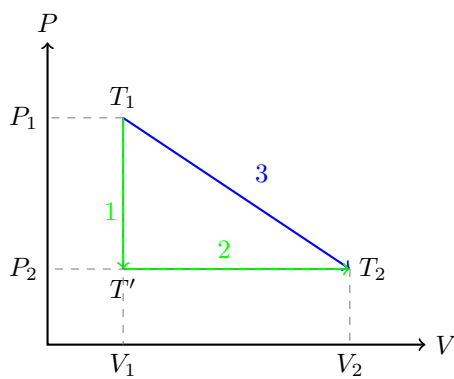
Along the green path,

$$\Delta S_1 = \int \left(\frac{\mathrm{d}Q}{T}\right)_1 = C_v \int_{T_1}^{T'} \frac{\mathrm{d}T}{T} = C_v \ln\left(\frac{T'}{T_1}\right)$$

$$\Delta S_2 = \int \left(\frac{\mathrm{d}Q}{T}\right)_2 = C_p \int_{T'}^{T_2} \frac{\mathrm{d}T}{T} = C_p \ln\left(\frac{T_2}{T'}\right)$$

Thus the total change is given by,

$$\Delta S = \Delta S_1 + \Delta S_2$$

$$= C_v \ln\left(\frac{T'}{T_1}\right) + C_p \ln\left(\frac{T_2}{T'}\right)$$

$$= C_v \ln\left(\frac{T'}{T_1}\right) + (C_v + R)\ln\left(\frac{T_2}{T'}\right)$$

$$= C_v \ln\left(\frac{T_2}{T_1}\right) + R\ln\left(\frac{T_2}{T'}\right)$$

$$= C_v \underbrace{\ln\left(\frac{T_2}{T_1}\right)}_{0} + R\ln\left(\frac{T_2}{T'}\right)$$

$$= R\ln\left(\frac{T_2}{T'}\right)$$

Note the cancellation $T_1 = T_2$ since (3) is an isotherm.

Since path (2) is at constant P

$$\Delta S = R \ln \left(\frac{V_2}{V_1} \right)$$

Which is identical to the change in entropy along the isotherm derived above. Thus confirming that ΔS is independent of path.