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# Phys 359

## STATISTICAL MECHANICS

University of Waterloo

Course notes by: TC Fraser

Instructor: Michel Gingras

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[tcfraser@tcfraser.com](mailto:tcfraser@tcfraser.com)

Version: 1.0

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## Disclaimer

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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  $N \rightarrow \infty$ , 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 Josiah 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
<ul style="list-style-type: none"> <li>• great because they are totally general</li> <li>• relationship's (Maxwell's relations) between <math>c_p, c_v, \alpha, \kappa</math></li> </ul>	<ul style="list-style-type: none"> <li>• does not tell us how to compute anything</li> <li>• does not tell us what entropy is</li> </ul>

The 2<sup>nd</sup> law of Thermodynamics reveals  $dU = dQ - dW$  where  $dQ = TdS$ .

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  $dU, dN, dV = 0$
- 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 $N_H$ $N_T$		Microstate A B C D				Thermo Probability	True Probability
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 let's get a general expression for  $\Omega$  where  $\Omega$  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  $\Omega$  can be considered a function of  $N_H$  and nothing else.

Recall from probability that the form for  $\Omega$  is given by,

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

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

$$\left( \frac{d\Omega}{dN_H} \right) \Big|_{N_H=N_H^*} = 0 \quad \left( \frac{d^2\Omega}{dN_H^2} \right) \Big|_{N_H=N_H^*} < 0$$

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

### 2.4 Stirlings Formula and Gaussian Integrals

Consider the integral,

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

This can be evaluated using integration by parts,

$$I = N \int_0^{\infty} x^{N-1} e^{-x} dx = \dots = N! \quad (2.1)$$

### 2.4.1 Differentiation Trick

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

$$\int_0^{\infty} e^{-ax} dx = \left( -\frac{1}{a} e^{-ax} \right) \Big|_0^{\infty} = \frac{1}{a} \quad (2.2)$$

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

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

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

If one explores the  $N^{\text{th}}$  derivative of (2.2) with respect to  $a$ , you will derive the expression,

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

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),

$$\int_0^{\infty} x^N e^{-x} dx = N! \quad (2.4)$$

How can we approximate  $N!$  using the left hand 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,

$$N! = \int_0^{\infty} \sqrt{N} e^{-N} e^{N \ln(N + \sqrt{N}y)} e^{-\sqrt{N}y} dy$$

The approximation begins by expanding the logarithm for large  $N$ ,

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

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

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

Thus,

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

The lower bound can be approximated as  $\infty$  since  $N$  is so large,

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

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

$$\int_{-\infty}^{\infty} e^{-\frac{y^2}{2}} dy = \sqrt{\frac{\pi}{a}} \quad (2.5)$$

Thus letting  $a = 1/2$ ,

$$N! \approx \sqrt{2\pi N} e^{-N} N^N \quad (2.6)$$

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,

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

$$\ln(N!) \approx N \ln N - N \quad (2.7)$$

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  $\Omega$  (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,

$$I_x = \int_{-\infty}^{\infty} e^{-ax^2} dx$$

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

$$I_x I_y = \int_{-\infty}^{\infty} e^{-ax^2} dx \int_{-\infty}^{\infty} e^{-ay^2} dy$$

$$I^2 = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} e^{-a(x^2+y^2)} dx dy$$

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

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

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  $\text{Cu}^{2+}$  atoms. In a lattice the  $\text{Cu}^{2+}$  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,

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

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,

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

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  $\Omega$  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  $j = 0, 1, 2, 3, \dots$

How many microstates are there subject to the constraint that the total energy is  $3\varepsilon$ ?

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	$3\varepsilon$	3	3/10
					0	$3\varepsilon$	0		
					$3\varepsilon$	0	0		
2	0	1	1	0	0	$\varepsilon$	$2\varepsilon$	6	6/10
					$\varepsilon$	$2\varepsilon$	0		
					$2\varepsilon$	0	$\varepsilon$		
					0	$2\varepsilon$	$\varepsilon$		
					$2\varepsilon$	$\varepsilon$	0		
					$\varepsilon$	0	$2\varepsilon$		
3	0	3	0	0	$\varepsilon$	$\varepsilon$	$\varepsilon$	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 thermodynamic variables of the system and *not its history*, is called a *function of state*.

We will first focus on  $U_{\text{total energy}}$  first and then  $S_{\text{entropy}}$  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

$$dG = \frac{\partial G}{\partial x} dx + \frac{\partial G}{\partial y} dy \quad (3.1)$$

in the case of functions of state like  $U$ ,  $dU = dQ - dW$  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

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

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.

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

$\Delta G$  does not depend on the path from point  $(x_1, y_1)$  to  $(x_2, y_2)$ . 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

Configurational work is denoted  $\mathrm{d}W$  where the symbol  $\mathrm{d}$  represents that it is **not** an exact differential.

$$\mathrm{d}W = \sum_i y_i \mathrm{d}x_i$$

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

### 3.4.3 Sign Convention

$\mathrm{d}W > 0$  work done by the system

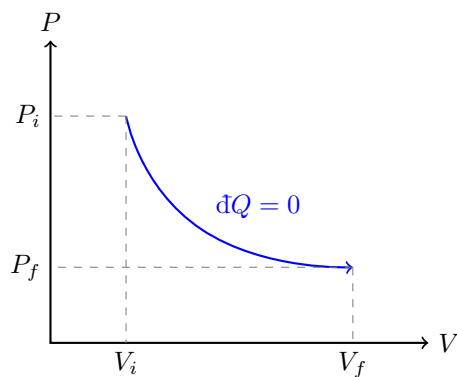
$\mathrm{d}W < 0$  work done on the system

Note:

- work is **not** a property of the system
- work is **not** a function of state
- integration on a closed loop is not degenerate  $\oint \mathrm{d}W \neq 0$

### 3.4.4 Adiabatic Work

Adiabatic 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. Let's define this as the total internal energy of the system.

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

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  $\mathrm{d}W$ . 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 ( $Q$ ).

$$dU = dW + dQ \quad (3.3)$$

Equation (3.3) is using the following convention:

$$\begin{aligned} dQ < 0 & \text{ heat flow } \mathbf{in} \\ dQ > 0 & \text{ heat flow } \mathbf{out} \\ dW < 0 & \text{ work is done } \mathbf{by} \text{ system} \\ dW > 0 & \text{ work is done } \mathbf{on} \text{ system} \end{aligned}$$

#### 3.5.2 Heat Capacities

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

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

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

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  $n = 1$  mol for convenience. How can we relate  $C$  to the properties of the substance? Let us write (noting the '-' convention),

$$dU = dQ - dW$$

Switch to specific (per mole) quantities,

$$du = dq - dw$$

$$du = \left( \frac{\partial u}{\partial T} \right)_v dT + \left( \frac{\partial u}{\partial v} \right)_T dv$$

$$dq = du + dw$$

$$dq = \left( \frac{\partial u}{\partial T} \right)_v dT + \left\{ \left( \frac{\partial u}{\partial v} \right)_T dv + P dv \right\}$$

However,

$$c_v = \lim_{dT \rightarrow 0} \frac{dq}{dT} \quad \text{At constant } V$$

Thus,

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

Which gives us,

$$\mathfrak{d}q = c_v dT + P dv$$

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 ( $U = U(T)$ ).

$$\mathfrak{d}q = c_v dT + P dv + (v dp - v dp)$$

$$\mathfrak{d}q = (c_v + R) dT - v dp$$

Thus,

$$\lim_{dT \rightarrow 0} \left( \frac{\mathfrak{d}q}{dT} \right)_{p=\text{const.}} = c_v + R$$

Thus we can define a new quantity,

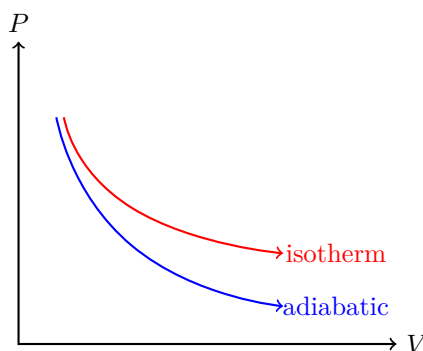
$$c_p \equiv \left( \frac{\mathfrak{d}q}{dT} \right)_{p=\text{const.}} = c_v + R$$

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),



$$\mathfrak{d}q = c_v dT + P dv$$

$$\mathfrak{d}q = c_p dT - v dP$$

And let's set  $\mathfrak{d}q = 0$  (adiabatic),

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

Which gives,

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

Or integrating along a curve,

$$\int_1^2 \frac{dP}{P} = - \int_1^2 \gamma \frac{dv}{v}$$

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

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  $dU = -PdV|_{\text{adiabatic}}$  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,

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

$$dQ = \left( \frac{\partial U}{\partial T} \right)_V dT + \left\{ \left( \frac{\partial U}{\partial V} \right)_T + P \right\} dV$$

$$\frac{dQ}{T} = \frac{1}{T} \left( \frac{\partial U}{\partial T} \right)_V dT + \frac{1}{T} \left\{ \left( \frac{\partial U}{\partial V} \right)_T + P \right\} dV$$

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

**Math Interlude:**

$$dG = A(x, y)dx + B(x, y)dy$$

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

$$d\tilde{G} = \mu \cdot dG$$

Thus,

$$d\tilde{G} = \mu A dx + \mu B dy$$

Making,

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

**Example:**

$$dG = \sin(y)dx + \cos(y)dy$$

$$d\tilde{G} = \mu \sin(y)dx + \mu \cos(y)dy$$

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

$$\begin{aligned}\frac{\partial(\mu \sin(y))}{\partial y} &= \frac{\partial(\mu \cos(y))}{\partial x} \\ \mu(x) \cos(y) &= \frac{d\mu}{dx} \cos(y) + \mu \frac{d \cos y}{dx} \\ \mu(x) \cancel{\cos(y)} &= \frac{d\mu}{dx} \cancel{\cos(y)} + \mu \frac{d \cos y}{dx} \xrightarrow{0}\end{aligned}$$

Thus,

$$\mu(x) = \frac{du}{dx}$$

Which gives,

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

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

$$\frac{dQ}{T} = \underbrace{\frac{1}{T} \left( \frac{\partial U}{\partial T} \right)_V}_A dT + \underbrace{\frac{1}{T} \left\{ \left( \frac{\partial U}{\partial V} \right)_T + P \right\}}_B dV$$

And thus,

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

Gives,

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

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

$$\begin{aligned}\frac{1}{T} \frac{\partial^2 U}{\partial V \partial T} &= -\frac{1}{T^2} \left( \frac{\partial U}{\partial V} + P \right) + \frac{1}{T} \frac{\partial^2 U}{\partial T \partial V} + \frac{1}{T} \frac{\partial P}{\partial T} \\ \cancel{\frac{1}{T} \frac{\partial^2 U}{\partial V \partial T}} &= -\frac{1}{T^2} \left( \frac{\partial U}{\partial V} + P \right) + \cancel{\frac{1}{T} \frac{\partial^2 U}{\partial T \partial V}} + \frac{1}{T} \frac{\partial P}{\partial T} \\ 0 &= -\frac{1}{T^2} \left( \frac{\partial U}{\partial V} + P \right) + \frac{1}{T} \frac{\partial P}{\partial T} \\ \frac{1}{T^2} \left( \frac{\partial U}{\partial V} + P \right) &= \frac{1}{T} \frac{\partial P}{\partial T} \\ \frac{1}{T^2} \frac{\partial U}{\partial V} + \frac{P}{T^2} &= \frac{1}{T} \frac{\partial P}{\partial T} \\ \frac{1}{T^2} \frac{\partial U}{\partial V} + \cancel{\frac{R}{TV}} &= \cancel{\frac{R}{TV}}\end{aligned}$$

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,

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

### 3.6.3 Summary of First Law

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

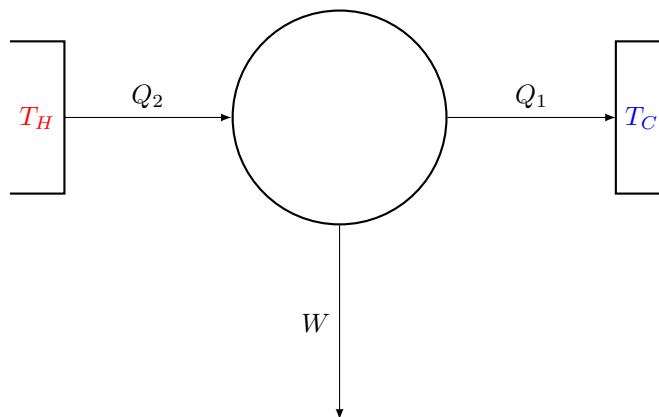
$$dU = dQ - dW$$

## 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 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,

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

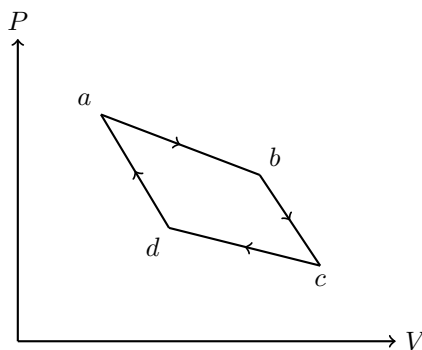
- $Q_2$  : injected into engine  $E$  and is  $> 0$
- $Q_1$  : extracted from engine  $E$  and is  $< 0$

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”.



$ab$	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:

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

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

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

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,

$$\begin{aligned} \eta_{\text{Carnot}} = \eta_C &= 1 + \frac{Q_1}{Q_2} \\ \eta_C &= 1 + \frac{RT_1 \ln(V_d/V_c)}{RT_2 \ln(V_b/V_a)} = 1 - \frac{T_1 \ln(V_c/V_d)}{T_2 \ln(V_b/V_a)} \\ \eta_C &= 1 - \frac{T_1}{T_2} \end{aligned}$$

### 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  $Q_2 = 100$  cal, performs  $W = 20$  cal of work and then dumps the remaining  $Q_1 = 80$  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  $Q_2 = 100$  cal,  $W = 40$  cal,  $Q_1 = 60$  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 cal to run. This can be supplied by our "better" engine. Therefore, this combined engine has the net effect of absorbing 100 cal from a cold reservoir at  $T_1$  and injecting 100 cal into a hot reservoir 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.

$$\eta_{\text{irreversible}} < \eta_{\text{Carnot}} \quad (3.6)$$

### 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,

$$\sum_{n=1}^k \frac{Q_n}{T_n} = 0 \quad (3.7)$$

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

$$dS = \frac{dQ}{T} \quad \text{with} \quad \oint dS_{\text{rev}} = 0$$

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  $\Delta S$ .

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

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

$$\begin{aligned} dS &= \frac{dQ}{T} = \frac{C_v}{T} dT \\ \int_1^2 dS &= \int_{T_1}^{T_2} \frac{C_v}{T} dT = c_v \ln \left( \frac{T_2}{T_1} \right) \\ (S_2 - S_1) &= C_v \ln \left( \frac{T_2}{T_1} \right) \end{aligned}$$

#### Example (Constant Temperature):

Let's consider change of entropy for an isothermal process.

$$S_2 - S_1 = \int_1^2 \frac{dQ}{T}$$

But from the first law we have for constant temperature,

$$dU = dQ - PdV = 0$$

Thus,

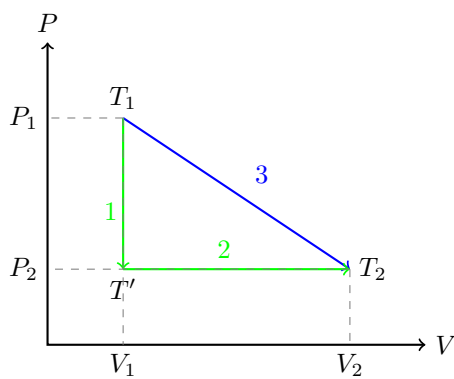
$$dQ = PdV$$

$$\int_1^2 dS = \int_1^2 \frac{P}{T} dV = \int_1^2 \frac{nR}{V} dV = nR \ln \left( \frac{V_2}{V_1} \right) \quad (3.8)$$

**Summarize:**

1. No engine is more efficient than Carnot.
2. As a by-product, we discovered a quantity  $\Delta S$  defined as:
  - $\Delta S = \frac{\Delta Q}{T}$  ( $dS = \frac{dQ}{T}$  for the infinitesimal)
  - $dS$ : defined at each point in  $(P, V, T)$  diagram
  - $dS$ : 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,

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

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

Thus the total change is given by,

$$\begin{aligned} \Delta S &= \Delta S_1 + \Delta S_2 \\ &= C_v \ln \left( \frac{T'}{T_1} \right) + C_p \ln \left( \frac{T_2}{T'} \right) \\ &= C_v \ln \left( \frac{T'}{T_1} \right) + (C_v + R) \ln \left( \frac{T_2}{T'} \right) \\ &= C_v \ln \left( \frac{T_2}{T_1} \right) + R \ln \left( \frac{T_2}{T'} \right) \\ &= \cancel{C_v \ln \left( \frac{T_2}{T_1} \right)}^0 + R \ln \left( \frac{T_2}{T'} \right) \\ &= R \ln \left( \frac{T_2}{T'} \right) \end{aligned}$$

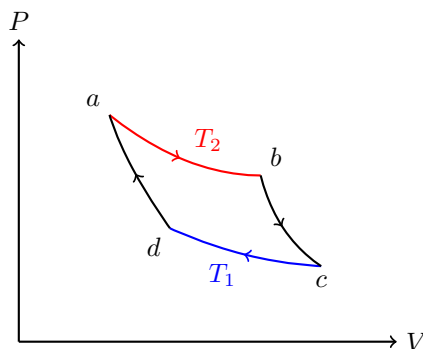
Note the cancellation  $T_1 = T_2$  since (3) is an isotherm.

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  $\Delta S$  is independent of path.

### 3.7.5 Clausius Inequality



Recall from equation (3.7), we have that for a reversible Carnot cycle,

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

Now consider the case of heat extraction and heat disposal along a *tiny Carnot cycle*.

$$\frac{dQ_2}{T_2} + \frac{dQ_1}{T_1} = 0$$

**TODO: Insert PV circle liney diagram from notes he said he'd upload**

The idea here is to consider any physical process or cycle as being made up of numerous tiny adiabatic curves and isotherms. We *approximate* the real cycle as being composed of a series of reversible processes. In the limit of the number of “switches” goes to infinity, the real engine process is made exactly reversible.

Essentially, we are mapping out the contour of any given cycle by following many isotherms and adiabats. Then for any given sub-process here,

$$\sum_{i=1}^n \frac{dQ_i}{T_i} = 0$$

Or in the limit as  $n \rightarrow \infty$ ,

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

Again we observe that  $Q_{\text{rev}}/T$  is an **exact** differential and we can call it  $dS$  as done before.  $S$  is a state variable.

Any reversible cycle must obey the following equation,

$$\oint \frac{dQ}{T} = 0 \quad \text{For a reversible cycle.}$$

What about for an irreversible cycle? An irreversible cycle is some process that somewhat has a step that can not be performed backward. What we have shown is that the efficiency of an engine with an irreversible cycle  $\eta'$  must be less than that of Carnot  $\eta_C$  (see (3.6)).

$$\eta' < \eta_C$$

Using equation (3.6), we can show that,

$$\frac{Q'_1}{Q'_2} < \left( \frac{Q_1}{Q_2} \right)_{\text{rev Carnot}}$$

Or that,

$$\frac{dQ'_1}{T_1} + \frac{dQ'_2}{T_2} < 0 \quad \text{For an irreversible cycle.}$$

Which lead to the generalization for an infinite number of steps as,

$$\sum_{i=1}^n \frac{dQ'_i}{T_i} < 0 \rightarrow \oint \frac{dQ'}{T} < 0$$

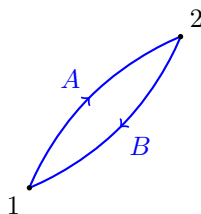
This leads to the Clausius Inequality:

$$\oint \frac{dQ'}{T} \leq 0$$

Which achieves equality only when the **entire** cycle is irreversible. Inequality is always maintained if any part of the cycle is irreversible. This can be understood as another formulation of the Second Law of Thermodynamics.

There are two cases “applications” of Clausius inequality:

1) Consider a single two-step *reversible* cycle



Therefore,

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

$$\int_1^2 \left( \frac{dQ}{T} \right)_A + \int_2^1 \left( \frac{dQ}{T} \right)_B = 0$$

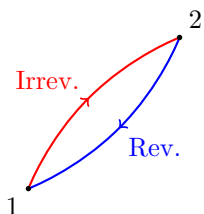
Rearrangement gives,

$$\int_1^2 \left( \frac{dQ}{T} \right)_A = - \int_2^1 \left( \frac{dQ}{T} \right)_B = \int_1^2 \left( \frac{dQ}{T} \right)_B$$

Which implies that entropy is conserved,

$$(S_2 - S_1)_A = (S_2 - S_1)_B$$

2) Consider a two-step *irreversible/reversible* process



Therefore by the Clausius Inequality we have,

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

$$\oint_1^2 \left( \frac{dQ}{T} \right)_{\text{irrev}} + \oint_2^1 \left( \frac{dQ}{T} \right)_{\text{rev}} \leq 0$$

$$\oint_1^2 \left( \frac{dQ}{T} \right)_{\text{irrev}} \leq - \oint_2^1 \left( \frac{dQ}{T} \right)_{\text{rev}} = \oint_1^2 \left( \frac{dQ}{T} \right)_{\text{rev}}$$

Thus we can conclude that with  $dS \left( \frac{dQ}{T} \right)_{\text{rev}}$ ,

$$\oint_1^2 \left( \frac{dQ}{T} \right)_{\text{irrev}} \leq \oint_1^2 (dS)_{\text{rev}} = S_2 - S_1$$

Which gives that our entropy increases each cycle,

$$(S_2 - S_1)_{\text{rev}} \geq \oint_1^2 \left( \frac{dQ}{T} \right)_{\text{irrev}}$$

Now suppose that our system is undergoing an adiabatic process along the whole path. This means that no heat is exchanged during the process ( $dQ = 0$ ). This gives us,

$$(S_2 - S_1)_{\text{irrev}} \geq 0 \quad \text{For an irreversible, adiabatic process.}$$

In conclusion, the entropy can only increase for an *isolated* (our adiabatic example) system undergoing an irreversible process. This is a restatement of the Second Law of Thermodynamics; entropy always increases for an isolated system. Of course this is all subject to the constraint imposed on the system:  $N, V, E$  might be constrained or imposed to be constant. Or more clearly:

At *equilibrium*, entropy must reach its maximum value. Otherwise it would increase because it has to.

### 3.7.6 Perspective on Entropy

Consider a container with two sub-sections. The left hand side will have a gas and the right hand side will have a vacuum (each side having volume  $V$ ). At time  $t = 0$ , the barrier between the two containers is removed and the gas has access to the entire container of volume  $2V$ . At equilibrium, the gas occupies the entire container. Evidently, this is an irreversible process (the gas does not have the luxury to return to its original state). Some comments:

- irreversible process
- gas does no work against the vacuum
- no heat exchange



- $\Delta U = \Delta Q - \Delta W = 0$  (Conservation of energy  $\implies$  temperature is constant)

This process is irreversible, so there is no way to directly compute its change in entropy throughout the entire process. However, the entropy can be calculated using properties about the two endpoints and a *reversible* process that connects these endpoints.

The *reversible* process we will consider as a replacement will be letting the gas expand via a piston held initially at the midway point of the container that is controlled externally. We will slowly move the piston until the gas fills the entire container. This new process is considered isothermal that takes us from state (1) (half gas, half vacuum) to state (2) (total gas). Along this process we can compute the change in entropy  $S_2 - S_1$  along the reversible path. Turns out we already computed this in equation (3.8).

$$\Delta S = S_2 - S_1 = nR \ln \left( \frac{V_2}{V_1} \right)$$

Let  $nR = k_B N_A$  where  $k_B$  is the Boltzmann constant and  $N_A$  is Avogadro's number. Note that  $V_1 = V$  and  $V_2 = 2V$ ,

$$\Delta S = k_B N_A \ln \left( \frac{2V}{V} \right) = k_B \ln (2^{N_A})$$

Thus we expect,

$$\Delta S \propto \underbrace{(\text{const.})}_{\text{units } J/K} \times \ln (2^N)$$

Note that the ' $2^N$ ' term measures the number of microstates that the system received or now has access to due to the process. Consider the microstates counted by the possibility that the particle can be on the left or the right of the container.

- All particles on left except 1
  - LLLLLL..LLRLLL..LLLLL
  - $N$  ways for this to occur
- All particles on the left except 2
  - LLLLLL..LLRLLL..LLRL..LLLLL
  - $N(N-1)/2$  ways for this to occur

The most probable macrostate occurs when the total number of microstates reaches a maximum. Using the Stirling's approximation, this occurs when there is a 50/50 split between the left and right with total number of microstates,

$$\Omega \sim 2^N + \text{small corrections}$$

Note that disordered ("mixed") states (50/50) can be realized in so many more ways than "ordered states".

With this view, entropy can be viewed as a measure of the number of microstates through the relation of the second law. These ideas are what lead Boltzmann to consider the possibility,

$$S \sim \ln \Omega$$

With further corrections and units,

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

Where the constant  $S_0$  can be shown to be zero with the Third Law of Thermodynamics.

### 3.7.7 Conclusion

The Second Law of Thermodynamics is very much a manifestation of the probability/statistics of the large number of states microscopic objects can realize.

The law  $\Delta S \geq 0$  spontaneously for an isolated system means that we must seek microscopic configurations that *maximize*  $S$ , as when this is achieved, the system must have reached equilibrium.

## 4 S.M. Basis for T.D.

Statistical Mechanics Basis for Thermodynamics.

### 4.1 Contact Between S.M. & T.D.

1. Systems where  $V \rightarrow \infty$  and  $N \rightarrow \infty$  and the density  $N/V$  remains constant
  - Thermodynamically large system
2. Equilibrium Thermodynamics / S.M.
  - Consider two regions of a container separated by a diathermal wall
  - $(N_1, V_1, E_1)$  and  $(N_2, V_2, E_2)$  number of particles, volume, energy respectively
  - Interested in total number of microstates
  - Composite system  $\Omega^{(0)} = \Omega^{(1)} \times \Omega^{(2)}$