

# Thermodynamics

Josh Borrow

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## 0.1 Introduction

Thermodynamics predates the atomic model and was created so that we can get the most work out of machines for a given input. We began by studying bulk material properties (think of a black box), however this is generalistic and it's difficult to see the point. We can know a heat capacity, great. This doesn't tell us anything about the physics that's going on, though.

In this course we will open the black box and look at the microscopic picture. This really enriches our understanding, but we have to use statistical mechanics. In a lecture hall, there are about  $10^{30}$  atoms. With a 5Ghz processor, this would take over the age of the universe to count (one per clock cycle!) So what we really study is the average behaviour of many-bodied systems.

## 0.2 Definitions

Here we will use two systems to compare *extensive* and *intensive* variables.

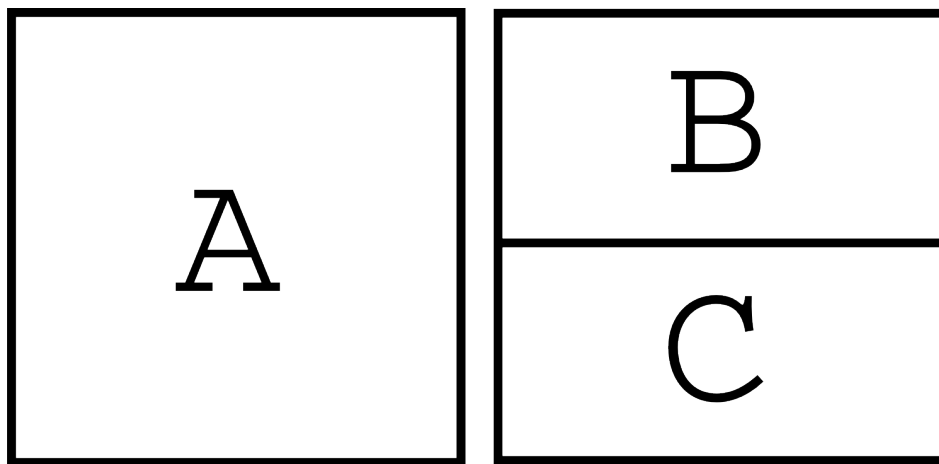


Figure 1: Three systems that start all with the same initial conditions

**Extensive variables** are ones which change when the system is split up. For example:

- Volume  $V_A = 2V_B = 2V_C$
- Energy  $U_A = 2U_B = 2U_C$

**Intensive variables** are independent of the size of the system:

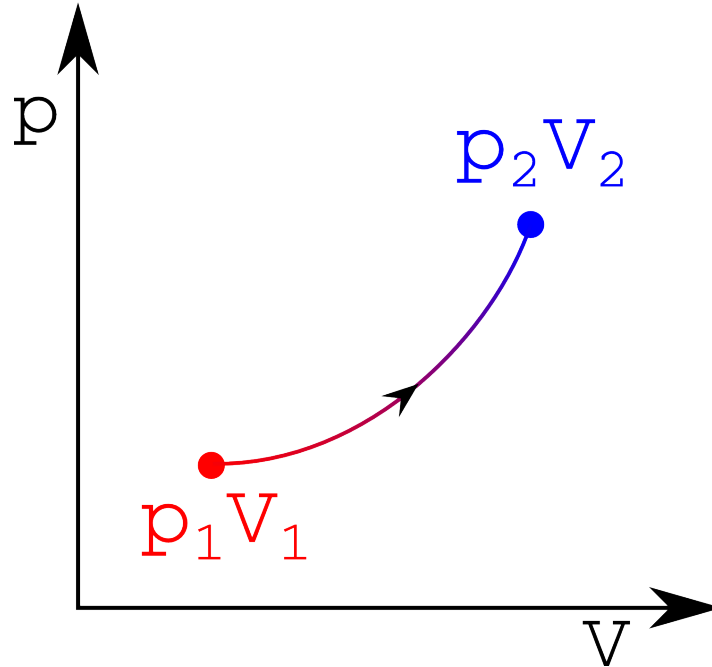
- Temperature  $T_A = T_B = T_C$
- Pressure  $P_A = P_B = P_C$

**The system** is the matter we're interested in.

**The surroundings** is the rest of the universe.

### 0.2.1 P-V Diagrams

P-V diagrams are favourites in the thermodynamics community. They show the path between two points of known pressure and volume:



**Temperature** is a measure of how hot something is.

**Heat** is energy in transit.

## 0.3 Equations of state

Equations of state describe a system mathematically:

$$f = f(p, V, T, \dots)$$

For example:

$$pV = RT \rightarrow f = f(p, V)$$

Here we have two independent variables, and we can always find the third.

## 0.4 Heat

Heat always travels from a hot body to a cold body, if there is no external influence.

### 0.4.1 Heat capacity

Heat capacity is a measure of how much energy is needed to increase the temperature of a system:

$$C_v = \left( \frac{\partial Q}{\partial T} \right)_v$$

We can then find the change in energy needed by integrating:

$$\Delta Q = \int_{T_1}^{T_2} C_v \cdot dT$$

There are two types of heat capacity that we use regularly. There is the heat capacity at constant volume ( $C_V$ ), and the heat capacity at constant pressure ( $C_p$ ). The heat capacity at constant pressure is always higher because we need to do work in increasing the volume of the gas, as well as the temperature.

## 0.5 The Zero<sup>th</sup> Law of Thermodynamics

This law is the basis of temperature. It says:

If we have three systems, A, B and C, and we begin by letting A and B thermally equilibrate, then we have two systems in thermal equilibrium. If we then move B to C and there is no net heat transfer, meaning that B and C are already in equilibrium, then this means that A and C are in thermal equilibrium too - meaning they must be the same *temperature*.

## 0.6 Relevant Mathematics

### 0.6.1 Total differentials

$$dZ = \left( \frac{\partial z}{\partial x} \right)_y dx + \left( \frac{\partial z}{\partial y} \right)_x dy$$

This lets us see what happens to the system when we make a small change to some variable(s). For large changes, it is best to add up small increments (i.e. integrate):

$$\Delta Q = \int C_p \cdot dT$$

In mathematics, partial derivatives are relatively straightforward. However, here, what about:

$$\left( \frac{\partial U}{\partial V} \right)_p ?$$

**Example:** Find the above:

$$U = \frac{1}{2}mv^2 = \frac{3}{2}Nk_B T = \frac{3}{2}pV$$

Now, if we differentiate:

$$\left( \frac{\partial U}{\partial V} \right)_T = \frac{\partial}{\partial V} \left[ \frac{3}{2}Nk_b T \right] = 0$$

$$\left(\frac{\partial U}{\partial V}\right)_p = \frac{\partial}{\partial V} \left[ \frac{3}{2} p V \right] = \frac{3}{2} p$$

It is important to remember which variable you are keeping constant in thermodynamics, or things can get out of hand quickly.

### 0.6.2 Some Relations

If we have that  $x$ ,  $y$  and  $z$  are related by  $f(x, y, z)$ , then we also have that  $x = x(y, z)$ ,  $y = y(x, z)$ .

#### Useful properties of 3D functions

There are two useful things to use:

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial x}\right)_z = 1$$

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1$$

*Proof.* Begin with the original partial above:

$$dx = \left(\frac{\partial x}{\partial y}\right)_z dy + \left(\frac{\partial x}{\partial z}\right)_y dz$$

We can also repeat it with a change of variables to  $y$ :

$$dy = \left(\frac{\partial y}{\partial x}\right)_z dx + \left(\frac{\partial y}{\partial z}\right)_x dz$$

Substituting:

$$dx = \left(\frac{\partial x}{\partial y}\right)_z \left[ \left(\frac{\partial y}{\partial x}\right)_z dx + \left(\frac{\partial y}{\partial z}\right)_x dz \right] + \left(\frac{\partial x}{\partial z}\right)_y dz$$

Which we can multiply out to:

$$dx = \left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial x}\right)_z dx + \left[ \left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x + \left(\frac{\partial x}{\partial z}\right)_y \right] dz$$

And comparing coefficients, we must see that the right = 0 and the left = 1, giving:

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial x}\right)_z = 1$$

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1$$

□

**Example:** Total differential of an ideal gas.

If we consider 1 mole, we have:

$$pV = RT$$

To differentiate:

$$dV = \left( \frac{\partial V}{\partial T} \right)_p dt + \left( \frac{\partial V}{\partial p} \right)_T dp$$

We can now work out the components, and substitute in:

$$dV = \frac{RT}{p} \left[ \frac{dT}{T} - \frac{dp}{p} \right]$$

And finally:

$$\frac{dV}{V} = \frac{dT}{T} - \frac{dp}{p}$$

This tells us a small change in temperature or pressure leads to a small change in volume - which is what we would expect.

## 0.7 Exact and inexact differentials

With well behaved functions, the order of differentiation doesn't matter. These are called exact differentials.

**Exact differentials** include system properties, for example temperature or pressure.

**Inexact differentials** are things that aren't in the function of state, for example work - that are path dependent.

### 0.7.1 Changes in variables

We can say that an incremental volume change  $dV$  gives a total volume change between states 1 and 2:

$$\int_1^2 = V_2 - V_1 = \Delta V$$

This doesn't take into account anything that happens in the middle because it doesn't matter.

However, things like work;

$$W_{1 \rightarrow 2} = \int_1^2 \delta W \neq W_2 - W_1$$

This is because the work done is the area under the  $pV$  graph and as such depends on the path taken between two points.

## 0.8 Changes in notation

In the previous course, work in was negative and work out was positive. Here:

**WORK IN IS POSITIVE**

**WORK OUT IS NEGATIVE**

## 0.9 Work-energy

Work and energy are linked - work is equivalent to raising a weight (Joule). Energy contained in a system is its capacity to do work.

Two things not in thermal equilibrium connected via an engine get work out.

## 0.10 First Law of Thermodynamics

Internal energy ( $U$ ) is the sum of all of the internal degrees of freedom, which ties into the First Law.

The work done by adiabatic paths is the same for all paths. Experiments show that when a system changes between states by different adiabatic paths, as measured by a change in the level of a weight, the work done is always the same.

This law is based on empirical evidence and is a statement regarding the conservation of energy. Mathematically:

$$dU = \delta Q + \delta W$$

(here  $\delta$  is used to signify a non-exact differential).

### 0.10.1 Heat Capacity

Heat capacities describe how heat changes the internal energy of a gas. We have that:

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

$$C_p - C_V = R$$

*Proof.* Begin with:

$$U = U(V, T)$$

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

And we find by using the ideal gas law:

$$dU = \delta Q - p dV$$

Eliminate  $dU$ :

$$\delta Q = \left( \frac{\partial U}{\partial T} \right)_V dT + \left[ \left( \frac{\partial U}{\partial V} \right)_T + p \right] dV$$

Dividing through by  $dT$  and realising at constant volume  $dV = 0$ :

$$\left( \frac{\partial Q}{\partial T} \right)_V = C_V \text{ (def) } = \left( \frac{\partial U}{\partial T} \right)_V$$

We do a similar thing for  $C_p$ :

$$C_p = \left(\frac{\partial U}{\partial T}\right)_V + \left[\left(\frac{\partial U}{\partial V}\right)_T + p\right] \left(\frac{\partial V}{\partial T}\right)_p$$

Rearranging, we find that:

$$C_p - C_V = \left[\left(\frac{\partial U}{\partial V}\right)_T + p\right] \left(\frac{\partial V}{\partial T}\right)_p$$

And from the ideal gas law, we know that  $U = U(T)$  and as such:

$$C_p - C_V = R$$

□

Physical laws are reversible. Something is thermodynamically reversible if its direction can be changed by an infinitesimal change to a system property.

**Quasistatic** means that we have no shockwaves, not heat transfer etc. and this is the way that we study thermodynamics - in a ‘perfect’ environment.

In real processes energy will be converted to heat and dissipated.