Foundations of Physics 2B
Thermodynamics

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Lecture 1

1.1 Intro

This course will frame concepts in concrete maths from last year

Laws:

- Zeroth establishes the meaning of temperature
- First is a statement of energy conservation [we can only break even]
- Second defines entropy – why things do or do not happen
  - Entropy measures energy quality [you can only break even at 0 K]
- Third doesn't define thermodynamic property; tells us we can't get to 0 K

Thermodynamics developed by engineers wanting to develop machines that turn heat to work
Wanted most work for least effort
Subject developed had a number of under-ranging consequences
When it emerged, atoms were unknown – considered average properties of bulk material
There was no attention paid to what was inside
Macroscopic approach to look at 'black box':

- This approach is general and difficult to 'see the point'
  All good having relationships about heat capacities and expansicities but tells us nothing about the physics
- e.g. why a material has a certain temperature dependence for its heat capacity

Opening the black box gets microscopic picture (atomic) but this can be very detailed ($N_A \approx 6 \times 10^2 3$)
Statistical mechanics instead looks at average properties of all atoms in the thermodynamic limit

Example 1.1.1 Counting Molecules – simpler than recording position and motion as fewer DoFs

Lecture theatre has $10^2 9$ molecules (3×10^6 litres of air)
A 10GhZ processor can count $10^1 7$ molecules per year (each cycle counts one) $\approx 3 \times 10^1 1$ years to count all molecules
Thermodynamic limit – things tend to the average (to infinity)

Example 1.1.2 Rains drops hit small and large roof:

Fluctuations in force smooth out, even through force increasing
Consider pressure, $p = \frac{F}{A}$, same in both cases if you consider the average
Thermodynamic limit – $A \rightarrow \infty$

1.2 Thermo Systems and States

	Extensive – System Extent	Intensive – Independent
	Volume, V	Temp, T
	Energy, U	Pressure, P
	$V = V_A = V_B = \frac{V}{2}$	$T^* = T_A = T_B = T$
	$U = U_A = U_B = \frac{U}{2}$	$p^* = p_A = p_B = p$

Relate properties by equation of state, $f(p, V, T) = 0$
Most well known as the ideal gas law: $pV = nRT$

1.3 Thermal Equilibrium (TE), Heat, and Temperature

Can prepare sample of gas by suitable treatment to take a range of values of pressure and volume

$$p_1 V_1 = a > b = p_2 V_2 \text{ – Sample 1 is hotter than Sample 2}$$

Equation of state, $pV = f(T)$

Heat is thermal energy in transit, heat transferred from hot to cold (under its own action)
In transit is important – can't say object contains an amount of heat
Addition/subtraction of heat changes temperature
If two objects have the same temperature, they're in TE

Heat capacity – $\Delta Q = mc\Delta T$
More rigorously, a small change, dT, in a substance's temperature, requires the addition/subtraction of a differention and of heat, δQ:
$$\delta Q = mcdT$$

Capital C: Heat capacity of whole substance
Lower c: Specific heat capacity per unit mass/mole
$C = mc$

Total heat energy to change temperature, $T_1 \rightarrow T_2$:

$$\Delta Q = \int_{T_1}^{T_2} \delta Q = \int_{T_1}^{T_2} mcdT$$

Most changes take place whilst some other property is held constant:

$$C_V = \left(\frac{\partial Q}{\partial T}\right)_V; \quad C_p = \left(\frac{\partial Q}{\partial T}\right)_p \quad C_p > C_V$$

Work is needed to keep at constant pressure – work is a form of energy so requires more heat energy in to get to the same temperature at constant pressure

Lecture 2

2.1 Zeroth Law

"If two system are separately in TE with a third system, they must be in TE with each other"

If heat flows between two systems, they can't spontaneously turn back to initial states.
If two objects are at the same temperature, they're in TE
This defines the arrow of time

Thermometers have a low heat capacity relative to the object they're measuring

2.2 Relevant Maths

Thermodynamics is concerned with properties that change
Changing one (e.g. temp) will affect others (e.g. pressure) but might hold some more (e.g. volume) constant
Always denote what is held constant explicitly

$$C_p = \left(\frac{\partial Q}{\partial T}\right)_p \neq \left(\frac{\partial Q}{\partial T}\right)_V = C_V$$

Example 2.2.1

Kinetic energy in gases: $U = \frac{1}{2}m<v>^2 = \frac{3}{2}Nk_bT$
Look at ideal gases for simplification:

$$pV = nRT; \quad n = \frac{N}{N_A}; \quad R = N_A k_b$$

$$U = \frac{3}{2}Nk_bT = \frac{3}{2}pV$$

$$\left(\frac{\partial U}{\partial V}\right)_T = 0; \quad \left(\frac{\partial U}{\partial V}\right)_p = \frac{3}{2}p$$

Look at First Law:

$$dU = T\,ds - p\,dV$$

$$\left(\frac{\partial U}{\partial V}\right)_S = -p$$

Now consider the total differential of $z = f(x, y)$, $z = Z(x, y)$, or $f(x, y, z) = 0$
This has two independent variables

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

Infinitesimal change in z resulting from infinitesimal changes in x and y

Z represents a surface

Consider an intersection of the surface in the x-z plane at some y

Rather than consider the value of z, we look at the shape at any point of the lines of intersection with planes constant x or y
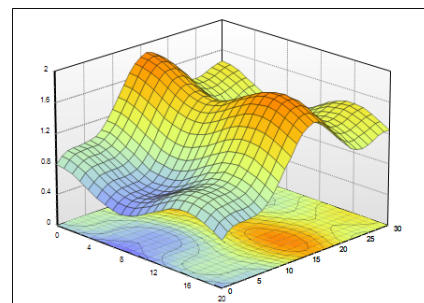
Example 2.2.2

For $p = p(V, T)$:

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

$$pV = nRT \implies$$

$$\left(\frac{\partial p}{\partial V}\right)_T = -\frac{RT}{V^2}; \quad \left(\frac{\partial p}{\partial T}\right)_V = \frac{R}{V}$$

$$dp = -\frac{RT}{V^2} dV + \frac{R}{V} dT$$

$$dp = \frac{RT}{V}\left(-\frac{dV}{V} + \frac{dT}{T}\right) \quad \left[p = \frac{RT}{V}\right]$$

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

$$d(\ln p) = -d(\ln V) + d(\ln T) \quad \left[\frac{d(\ln x)}{dx} = \frac{1}{x}\right]$$

Proof 2.2.2.1

x, y, and z related via $f(x, y, z)$

$$x = X(y, z) \; ; \; y = Y(x, z)$$

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

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

$$dx = M(x, y) dx + N(x, y) dz$$

For $M = 1$:

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial x}\right)_z = 1 \text{ – Reciprocal Theorem}$$

For $N = 0$:

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x + \left(\frac{\partial x}{\partial z}\right)_y = 0 \quad \left[\times \left(\frac{\partial z}{\partial y}\right)_y\right]$$

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial y}\right)_y + 1 = 0$$

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial y}\right)_y = -1 \text{ – Reciprocity Theorem (Cyclic)}$$

Well-behaved functions (as above) are exact differentials

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For $z = f(x, y)$ with two independent variables

$$dz = M(x, y)\,dx + N(x, y)\,dy$$

If exact:

$$\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y$$

$$\frac{\partial}{\partial y}\left[\left(\frac{\partial M}{\partial y}\right)_x\right]_y = \frac{\partial^2 z}{\partial x \partial y} \equiv \frac{\partial}{\partial x}\left[\left(\frac{\partial N}{\partial x}\right)_y\right]_x = \frac{\partial^2 z}{\partial x \partial y}$$

For exact functions, the order of the second derivatives doesn't matter.
These are *line integrals*.

$$I = \int_1^2 dz = \int M(x, y)\,dx + \int N(x, y)\,dy = Z_2 - Z_1$$

Parts can be integrated independently and the answer doesn't depend on the path
These correspond to functions of state in thermodynamics (p, V, T)

If $\frac{\partial^2 z}{\partial x \partial y} \neq \frac{\partial^2 z}{\partial y \partial x}$, this is inexact, and a *point function.*
The value of the integral depends on the path (W, Q)

dV - incremental volume change
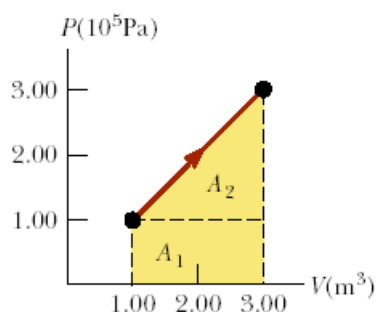Total volume change from state 1 to 2:

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

If we return to original state, the path is closed:

$$\oint dV = 0$$

The work between two states is path dependent:

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

Differential works along the path are added.

$$\left.\begin{array}{l} \Delta V_1 = V_2 - V_1 \\ \Delta V_2 = V_2 - V_1 \end{array}\right\} \quad \text{exact dV, path independent}$$

$W_1 \neq W_2$ – areas are different, so inexact δW

Example 2.2.3

Consider $\delta F = x\,dx + x\,dy$ (inexact) with two paths for $(0, 0) \rightarrow$
(X, Y)

Path A: $(0, 0) \rightarrow (X, 0) \rightarrow (X, Y)$
Path B: $(0, 0) \rightarrow (0, Y) \rightarrow (X, Y)$

$$A = \begin{cases} A_1 & \int_{A_1} \delta F = \int_0^X x\,dx + \int_0^0 x\,dy^{dy=0} = \frac{X^2}{2} \\ + \\ A_2 & \int_{A_2} \delta F = \int_X^X X\,dx^{dx=0} + \int_0^Y X\,dy = [Xy]_0^Y = XY \end{cases}$$

$$\int_A \delta F = \int_{A_1} + \int_{A_2} = \frac{X^2}{2} + XY \;\; ; \;\; \int_B \delta F = \frac{X^2}{2}$$