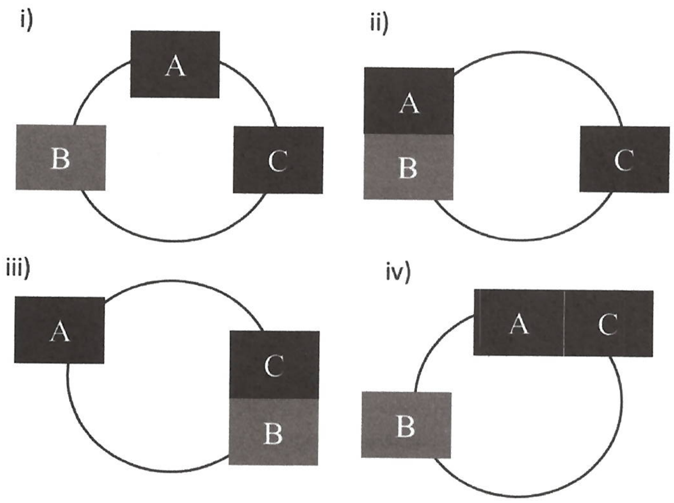
Foundations of Physics 2B/3C 2019-2020

Thermodynamics – Lecture 1 Recap

- Introduced the course – syllabus, books, contact etc.;
- Considered a motivation for studying the subject and appropriate terminology for describing thermodynamic systems;
- Looked at the concepts of:
  - Heat – thermal energy in transit;
  - Temperature – the system property which enables us to anticipate when two systems are in thermal equilibrium
- Considered the Zeroth law of thermodynamics – If two bodies are separately in thermal equilibrium with a third body, the original two bodies must be in thermal equilibrium with each other



Put A in contact with B, and B takes some value (ii)

Put C in contact with B, and see value of B doesn't change (iii)

A and C must therefore be in thermal equilibrium without doing the experiment.

B is thermometer

2nd Law give temperature scales

Lecture 2 Aims

- To look at the need to use and be careful with partial derivatives in thermodynamics.
- To look at the concepts and properties of exact and inexact differentials.
- To look at the meaning of work and internal energy.

5. Relevant Maths

System properties in thermo, we often vary one whilst holding another constant + seeing how a third changes $\rightarrow$ Partial derivatives

Thermo system is completely described by any two independent coordinates (functions of state), third (and any others) will depend on this. We can use equations of state

$f(p, V, T) = 0$ $\quad pV = RT$, that $U = U(T)$

instead write $f'(p, V, U) = 0$

Property held constant is important $\quad C_p = \left(\frac{\partial Q}{\partial T}\right)_p \neq \left(\frac{\partial Q}{\partial T}\right)_V = C_V$

<u>Example 5.1</u> $\quad$ Kinetic energy (molecular) $= \frac{1}{2} m \langle v \rangle^2 = \frac{3}{2} k_B T$

If molecules are ideal gas $pV = nRT$, $n = N/N_A$, $R = N_A k_B T$

$$U = \frac{3}{2} k_B T = \frac{3}{2} pV$$

$\left(\frac{\partial U}{\partial V}\right)_T = 0$ from 1st expression [T is constant]

$\left(\frac{\partial U}{\partial V}\right)_p = \frac{3}{2} p$ from 2nd expression

1st law $\Delta U = \Delta Q + \Delta W \Rightarrow TdS - pdV = dU$

$\div$ dU by dV whilst 'S' is constant $\quad S =$ entropy

Limit $dV \to 0$

$$\left(\frac{\partial U}{\partial V}\right)_S = 0 - p\left(\frac{\partial V}{\partial V}\right)_S = -p$$

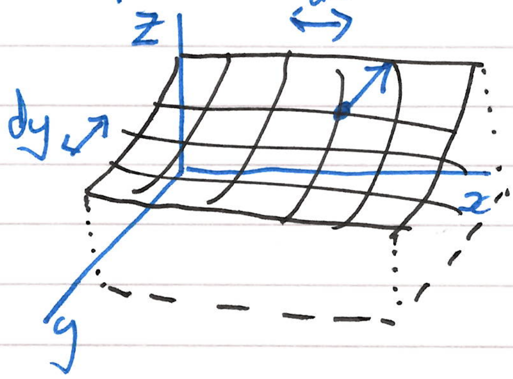
Three possible expressions for how U varies with V

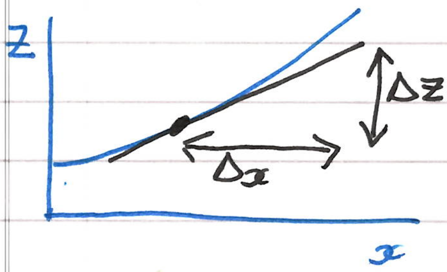
Consider $z = z(x, y)$ or $f(x, y, z) = 0$

x and y are independent, z is height of the surface

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

An infinitesimal change in surface height, as max small distance in the plane





x, z plane

Slope $\left(\frac{\partial x}{\partial z}\right)_y$ for infinitesimal changes

<u>Example 5.2</u> $p = p(V,T)$

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

Consider one mole of ideal gas $pV = RT$

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

$$dp = -\frac{RT}{V^2}dV + \frac{R}{V}dT = \underbrace{\frac{RT}{V}}_{=p}\left[-\frac{dV}{V} + \frac{dT}{T}\right]$$

$$\frac{dp}{p} = -\frac{dV}{V} + \frac{dT}{T} \quad \text{or} \quad d(\ln p) = -d(\ln V) + d(\ln T)$$

$$y = \ln x \qquad \frac{dy}{dx} = \frac{1}{x} \quad \text{or} \quad dy = \frac{dx}{x}; \; dy = d(\ln x)$$

<u>Proof 5.1</u> x, y, z related by an equation of state with any two independent $x = x(y,z)$, $y = y(x,z)$

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

Sub in

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

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

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

$M = 1$ and $N = 0$

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

Reciprocal therorm

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

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

X both sides $\left(\frac{\partial z}{\partial x}\right)_y$

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

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

Reciprocity theorem

Well behaved functions are represented by exact differentials.
Do not depend on a path $\oint dz = 0$

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

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

$N(x,y) = \left(\frac{\partial z}{\partial y}\right)_x$ $\qquad \frac{\partial}{\partial x}\left[\left(\frac{\partial z}{\partial y}\right)_x\right] = \frac{\partial^2 z}{\partial y \partial x}$ Identical

Order of derivatives doesn't matter

$$I = \int_1^2 dz = \int_{x_1}^{x_2} M(x,y)\,dx + \int_{y_1}^{y_2} N(x,y)\,dy = z_2 - z_1$$

Integrate parts separately. Value of I dosn't change (depend) on the path used.

If $\left(\frac{\partial^2 z}{\partial x \partial y}\right) \neq \left(\frac{\partial^2 z}{\partial y \partial x}\right)$ we have an inexact differential which is a point function. The integral between the states depends on the path

Use δz to describe inexact [$đz$ in books]

We must have $y = g(x)$ so $dz = M(x,y)dx + N(x,y)dy$

$$= M(x,g(x))dx + N(x,g(x))dy$$

$$dz = M(x,g(x))dx + N(x,g(x))\frac{dy}{dx}dx \qquad g' = \frac{dy}{dx}$$

$$dz = f(x)\,dx$$

$$I = \int_1^2 dz = \int_1^2 f(x)\,dx$$

On a different path $y = h(x)$ and $dz = \phi(x)dx$

In thermo functions of state $p, V, T, U \ldots$ are exact

Work, heat are inexact.

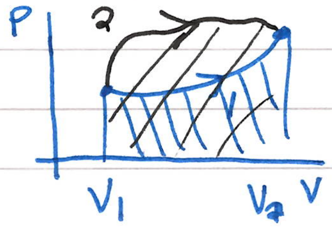
Change volume from state 1 to state 2, total volume chang

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

Same no matter how change undertaken

If I return to starting conditions $\oint dV = 0$

Work between two states $W_{12} = \int_1^2 \delta W \neq W_2 - W_1$



$$\Delta V = V_2 - V_1 \equiv \Delta V = V_2 - V_1$$

$$W_{12} \neq W_{12}$$

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Thermodynamics – Handout 2

Example 5.3

Consider the function $z = x^2\, y^3$.

We calculate $\left(\frac{\partial f}{\partial x}\right)_y = 2xy^3$ and $\left(\frac{\partial f}{\partial y}\right)_x = 3x^2\, y^2$. Thus

$$dz = 2xy^3\, dx + 3x^2\, y^2 dy \quad \Rightarrow$$

$$\frac{dz}{x^2y^3} = \frac{2xy^3dx}{x^2y^3} + \frac{3x^2y^2dy}{x^2y^3} \quad \Rightarrow \frac{dz}{z} = \frac{2dx}{x} + \frac{3dy}{y}.$$

Example 5.4 - Inexact differentials by integration

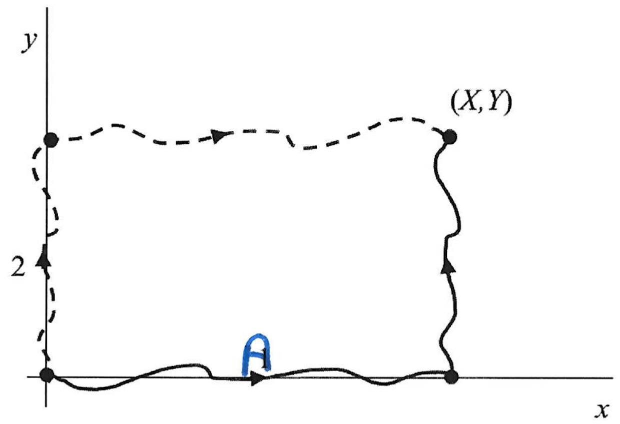

Figure 2: Integration paths considered in problem.

Consider the inexact differential represented by the infinitesimal change $\delta F = xdx + xdy$. If we compare this expression with total differential $dF = M(x,y)dx + N(x,y)dy,$ we have $M(x,y) = N(x,y) = x$. To be exact $\left({}^{\partial M}/_{\partial y}\right)_x = \left({}^{\partial N}/_{\partial x}\right)_y$, but we find $\left({}^{\partial M}/_{\partial y}\right)_x = 0$ and $\left({}^{\partial N}/_{\partial x}\right)_y = 1$.

second derivatives don't match

Path A: $(0,0)$ to $(X,0)$ to (X,Y) → ↑ **Path B: $(0,0)$ to $(0,Y)$ to (X,Y)**

Path A from $(0,0)$ to $(X,0)$: $\int \delta F = \int_0^X xdx + \int \cancelto{0}{xdy}|_{dy=0} = \frac{X^2}{2}.$

→ $dy = 0$

constant X

Path A from $(X,0)$ to (X,Y): $\int \delta F = \int \cancelto{0}{xdx}|_{dx=0} + \int_0^Y xdy = XY$

↑ $dx = 0$, $x = X$

Total Path A from $(0,0)$ to (X,Y): $\int_A \delta F = \frac{X^2}{2} + XY.$

Path B from $(0,0)$ to $(0,Y)$: $\int \delta F = \int_0^Y \cancelto{0}{0dx}|_{dx=0} + \int 0dy = 0.$ $x = 0$ on 1st part

↑ → ↑ $dx = 0$

Path B from $(0,Y)$ to (X,Y): $\int \delta F = \int_0^X xdx + \int \cancelto{0}{xdy}|_{dy=0} = \frac{X^2}{2}.$

→ $dy = 0$ $y = Y$

Total Path B from $(0,0)$ to (X,Y): $\int_B \delta F = 0 + \frac{X^2}{2}.$

$$\oint_A \delta F \neq \oint_B \delta F$$