Thermal Physics Appendix

Dr. Salwa Al Saleh
salwams@ksu.edu.sa

Partial Derivatives

- For functions of several variables
- $z=z(x,y)$, z is continuous function of independent variables x and y. Here z is called an explicit function.
- This function can be represented as a surface in Cartesian coordinates.

Partial Derivatives

- Imagine the surface intersects a planar surface parallel to the z-x plane which cuts the y-axis at y.
- The gradient of the line of intersection is given by the partial derivative of z with respect to x, and is defined as:-

$$\frac{\partial z}{\partial x} = \left[\frac{\partial z}{\partial x}\right]_y = \lim_{\delta x \to 0}\left[\frac{z(x+\delta x, y) - z(x, y)}{\delta x}\right]$$

Partial Derivatives

- This is the same expression as for normal differentials but with y considered as a constant.
- It effectively gives the gradient in the x direction. A similar expression can be written for the y direction.

$$\frac{\partial z}{\partial x} = \left[\frac{\partial z}{\partial x}\right]_y = \lim_{\delta x \to 0}\left[\frac{z(x+\delta x, y) - z(x, y)}{\delta x}\right]$$

Partial Derivatives - example

- Let $z = x^2 + 3xy + y^3$

$$z(x+\delta x, y) = (x+\delta x)^2 + 3y(x+\delta x) + y^3$$

$$z(x+\delta x, y) = x^2 + 2x\delta x + \delta x^2 + 3y(x+\delta x) + y^3$$

$$\frac{\partial z}{\partial x} = \left[\frac{\partial z}{\partial x}\right]_y = \lim_{\delta x \to 0}\left[\frac{z(x+\delta x, y) - z(x, y)}{\delta x}\right]$$

Partial Derivatives - example

- Ignoring terms second order in the limit $\delta x \to 0$

$$z(x+\delta x, y) \cong x^2 + 2x\delta x + 3y(x+\delta x) + y^3$$

$$z(x, y) = x^2 + 3xy + y^3$$

$$\frac{\partial z}{\partial x} = \left[\frac{\partial z}{\partial x}\right]_y = \lim_{\delta x \to 0}\left[\frac{2x\delta x + 3y\delta x}{\delta x}\right] = 2x + 3y$$

Partial Derivatives

- Differential form take the implicit function $f(x, y, z) = 0$, means x, y,and z are related and only two variables are independent so $x = x(y,z)$

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

- Similarly we can write $y = y(x,z)$ and

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

Partial Derivatives

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

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

- Substituting for *dy*

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

Partial Derivatives

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- We can choose x and z to be independent variables so choosing dz = 0 is valid, dx can then be non-zero.

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

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

Reciprocal relation

Partial Derivatives

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

- We can choose x and z to be independent variables so choosing dx = 0 is valid, dz can then be non-zero.

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

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

Cyclical relation

Partial Derivatives – Chain rule

- Supposing variables x, y, z, are not independent (so any two variables define the third) we can define the function $\phi = \phi(x, y)$ and re-arrange to $x = x(\phi, y)$.

$$dx = \left(\frac{\partial x}{\partial \phi}\right)_y d\phi + \left(\frac{\partial x}{\partial y}\right)_\phi dy$$

- Dividing by dz and hold ϕ constant.

$$\left(\frac{\partial x}{\partial z}\right)_\phi = \left(\frac{\partial x}{\partial y}\right)_\phi \left(\frac{\partial y}{\partial z}\right)_\phi$$

Chain Rule

Higher Partial Derivatives

- Repeated application allows the definition of higher derivatives.

$$\frac{\partial^2 z}{\partial x^2} = \frac{\partial}{\partial x}\left[\frac{\partial z}{\partial x}\right]_y$$

$$\frac{\partial^2 z}{\partial y \partial x} = \frac{\partial}{\partial y}\left[\frac{\partial z}{\partial x}\right]_y \qquad \frac{\partial^2 z}{\partial x \partial y} = \frac{\partial}{\partial x}\left[\frac{\partial z}{\partial y}\right]_x$$

Higher Partial Derivatives

- The order of differentiation does not matter as long as the derivatives are continuous.

$$\frac{\partial^2 z}{\partial y \partial x} = \frac{\partial}{\partial y}\left[\frac{\partial z}{\partial x}\right]_y = \frac{\partial}{\partial x}\left[\frac{\partial z}{\partial y}\right]_x = \frac{\partial^2 z}{\partial x \partial y}$$

Pfaffian forms

- The differential equation

$$df = Xdx + Ydy + Zdz$$

- In general the integral $\int_1^2 df$ depends on the path of integration. In this case this is called an inexact differential.
- But the integral is path independent if it can be expressed as a single valued function f(x,y,z).
- *df* is then an exact differential.

Pfaffian forms – exact differentials

- If we write

$$X = \left(\frac{\partial f}{\partial x}\right)_{y,z} \qquad Y = \left(\frac{\partial f}{\partial y}\right)_{x,z} \qquad Z = \left(\frac{\partial f}{\partial z}\right)_{x,y}$$

- It follows from the double differentials that

$$\left(\frac{\partial X}{\partial y}\right)_{x,z} = \left(\frac{\partial Y}{\partial x}\right)_{y,z} \qquad \left(\frac{\partial Y}{\partial z}\right)_{y,x} = \left(\frac{\partial Z}{\partial y}\right)_{z,x} \qquad \left(\frac{\partial Z}{\partial x}\right)_{z,y} = \left(\frac{\partial X}{\partial z}\right)_{x,y}$$

- These are necessary and sufficient for the Pfaffian form to be an exact differential.

Processes – functions of state

- The internal energy U of a system is a function of state. For a fluid (ideal gas) we could write $U=U(P,T)$ or $U=U(V,T)$.

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- We cannot make the same argument for Work or Heat as you cannot define a quantity of either to be associated with a state. They are only defined during changes.
- Work and heat flow are different forms of energy transfer.

Heat and Work

- The physical distinction between these two modes of energy transfer is:
  - Work deals with macroscopically observable degrees of freedom.
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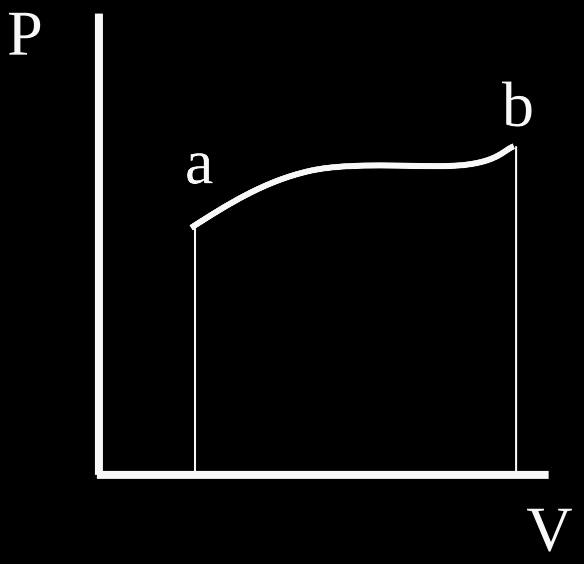
Work

- First Law of Thermodynamics $dU = đW + đQ$ is always true as it is just conservation of energy – you just have to account for all possible heat and work processes.
  - Stretching a wire (spring) $đW = Fdx$
  - Surface tension – bubble $đW = \Gamma dA$
  - Charging a capacitor $đW = EdZ$ where E is the emf and Z stored charge.

Analysis of processes

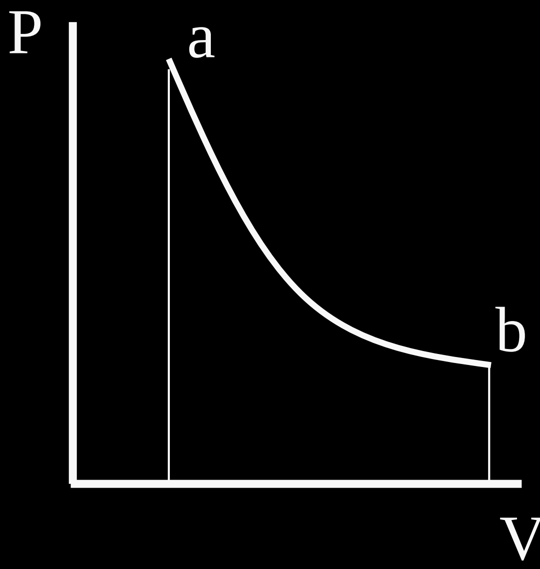
- Quasistatic work
  - $đW = -PdV$

$$(W_{ab})_{quasistatic} = -\int_a^b PdV$$



Analysis of processes

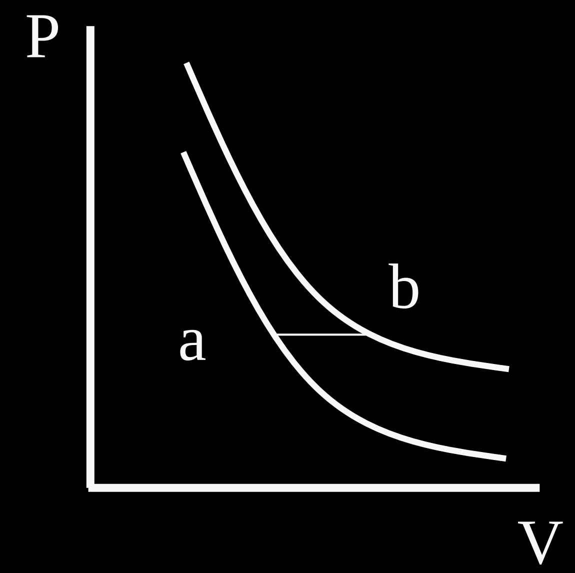
- Isothermal Work (ideal gas)



$$(W_{ab})_{Isothermal,quasistatic} = -\int_a^b PdV = -nkT\int_a^b \frac{dV}{V}$$

$$(W_{ab})_{isothermal,quasistatic} = -nkT\ln\left(\frac{V_b}{V_a}\right)$$

Heat Transfer



- Constant pressure heating
  - *đQ = dU - đW*
  - *đQ = dU + PdV*

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

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

$$C_p = \left(\frac{\partial U}{\partial T}\right)_V + \left(P + \left(\frac{\partial U}{\partial V}\right)_T\right)\left(\frac{\partial V}{\partial T}\right)_P$$

- $(đQ/\partial T)_P = C_P$ *specific heat capacity at constant pressure.*

Heat Transfer Ideal Gas Only

- $C_v = (đQ/\partial T)_v = (dU/\partial T)_v$
- $C_p = (đQ/\partial T)_p$

$$C_p = \left(\frac{\partial U}{\partial T}\right)_V + \left(P + \left(\frac{\partial U}{\partial V}\right)_T\right)\left(\frac{\partial V}{\partial T}\right)_P$$

- For ideal gas $PV = (\gamma\text{-}1)U = NRT$

$$\left(\frac{\partial U}{\partial V}\right)_T = 0 \quad \left(\frac{\partial V}{\partial T}\right)_P = \frac{NR}{P}$$

$$C_p = C_V + R \qquad C_p - C_V = R$$

Heat Transfer Ideal Gas Only

- $C_v = (đQ/\partial T)_v = (dU/\partial T)_v = 3/2\ R$
- $C_p = (đQ/\partial T)_p$

$$C_p = C_V + R \qquad C_p = {}^{5}\!/_{2}\, R$$