Foundations of Physics 2B/3C 2019-2020

Thermodynamics – Lecture 2 Recap

- Considered why care needs to be taken when using and defining partial derivatives in thermodynamics.
- Looked at the concepts of exact and inexact differentials and how they relate to thermodynamic properties.
- Saw how to describe the total differential of a property, of two independent variables, $z = z(x, y)$

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

- Saw how to derive the reciprocal and reciprocity theorems:

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

Thermodynamics – Lecture 3 Aims

- To look at the meaning of work and internal energy and understand sign conventions for work and heat used in the course.
- To see how work and internal energy lead to the first law of thermodynamics.
- To investigate the first law of thermodynamics, mathematically,

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

- To consider the meaning of reversibility and quasi-static when applied to thermodynamics, including the equation of state for how an ideal gas behaves under adiabatic conditions.

6. Work + Internal Energy

Work is a form of energy (Work-energy theorem $\Delta KE = \int F dx$)
When motion happens against a force, work is done

Work is inexact $\delta W = F dx = -p dV$

Do work on a substance, change its internal energy. Our convention: when do work on a substance it is +ve.

Thermo: Interested in configuration. Change system's configuration (in terms of thermo coordinates) does/requires work. This is 'useful', work converted to motion

Dissipative work: Work in turned into intenal of a reservoir
If non-zero, work 'lost' as heat to the environment, and our process is irreversible - cannot be expressed in terms of changes to a system property.

Adibatic work - done on a system in isolation

Internal energy - sum of all systems internal degrees of freedom.
Doing work or adding heat can change it
Well defined for each equilibrium state

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Thermodynamics – Handout 3

Example 6.1

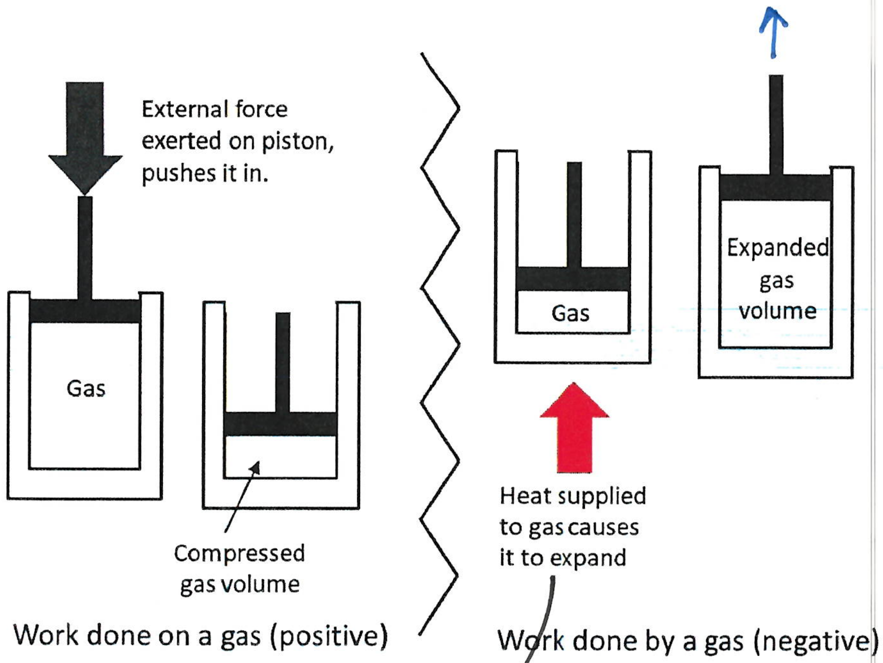


Figure 3: Sign conventions used during this course, adopted from Blundell and Blundell.

Adding heat is positive

Positive work if done on the system

$\delta W = -p\,dV$

Pressure constant, p_0

$$W_{12} = -\int_{V_1}^{V_2} p_0\, dV$$

$$= -p_0(V_2 - V_1)$$

V_2 is less than V_1 (compression)

$V_2 - V_1 < 0$

$\therefore W_{12} > 0$

Exercise 2: Find an expression relating C_p and C_V for an ideal gas.

Use $C_p = \left[p + \left(\frac{\partial U}{\partial V}\right)_T\right]\left(\frac{\partial V}{\partial T}\right)_p + C_V$ [From page 6]

Ideal gas has $pV = RT$ so $\left(\frac{\partial V}{\partial T}\right)_p = \frac{R}{p}$

Also $U = U(T)$ for ideal gas [see homework 2]

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

Hence $C_p = [p + 0]\frac{R}{p} + C_V$

$C_p = R + C_V$ [Meyer's equation]

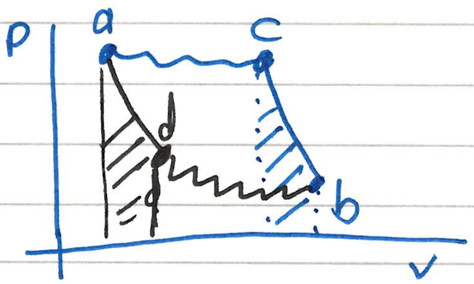
7. 1st Law of Thermodynamics

Statement of energy conservation - do work on a substance or add heat, it changes the internal energy
- Joule's mechanical equivalence of heat
- Two objects not in thermal equilibrium (different temps) can connect a heat engine to get work out.

$$\underset{\text{(Internal energy)}}{\Delta U} = \underset{\text{Heat}}{\Delta Q} + \underset{\text{Work}}{\Delta W} \implies \underset{\substack{\text{Exact} \\ \text{(Depends on the system state)}}}{dU} = \underbrace{\delta Q + \delta W}_{\text{inexact (depend on path)}}$$

For a system in a macrostate described by two of p, V, T (independent, related by equation of state), MUST assert that any given state has the same total energy, U

Consider a system enclosed by adiabatic walls (no heat flow)



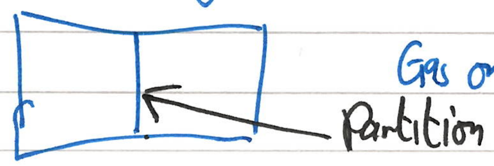
$a \to c$: adiabatic (free) expansion so no configuration work

$c \to b$: reversible adiabatic expansion and configuration work is blue

$a \to d$ (reversible) adiabatic expansion, with configuration work is the black area

$d \to b$: free (adiabatic) expansion [No configuration work]

Free expansion - system state (volume) changes without doing work



Gas on left, break the partition

Empirically found: for all adiabatic processes between states, the work is the the same

1st Law: For a system moving from state i to state f, via adiabatic paths, the work is the same for all adiabatic paths

Independence of adiabatic work suggests exact function of state. U, internal energy

$$\int_i^f dU = U_f - U_i = W_{i \to f}^{\text{adiabatic}}$$

If work done on the system (compression) $W_{i \to f} > 0$ we have $U_f > U_i$

U is fourth function of state, written as function of any other two $U = U(V,T)$ $U(p,V)$; $U(p,T)$

$$dU = \left(\frac{\partial U}{\partial V}\right)_T dV + \left(\frac{\partial U}{\partial T}\right)_V dT \quad \text{(using the 1st)}$$

Surround system by a diathermal wall (heat can be transferred) + system is not thermally isolated, work is not the same as the internal energy change

$$W_{i \to f} \neq U_f - U_i \quad \text{instead} \quad W_{i \to f} + Q_{i \to f} = U_f - U_i$$

$Q_{i \to f}$ is the heat supplied (removed) from the system

Internal energy change = Heat supplied/removed + Work done on/done by

$$\boxed{dU = \delta Q + \delta W} \qquad \boxed{dU = \delta Q - p\,dV}$$

Holds for all sign conventions

Heat capacity – energy required to change a systems temperature by dT

$$\delta Q = C\,dT \qquad C_V = \left(\frac{\partial Q}{\partial T}\right)_V ; \quad C_p = \left(\frac{\partial Q}{\partial T}\right)_p$$

Prob 7.1 How does adding heat change the internal energy of a gas?

$U = U(V, T)$

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

1st Law $dU = \delta Q - p\,dV$

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

Divide $(*)$ by dT when the volume is constant $dV = 0$

Take Limit $dT \to 0$

$$\frac{\delta Q}{dT} = \left[p + \left(\frac{\partial U}{\partial V}\right)_T\right] \cancel{dV}^{\,0} + \left(\frac{\partial U}{\partial T}\right)_V \cancel{\frac{dT}{dT}}^{\,1}$$

as $dT \to 0$ becomes a partial derivative

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

Now divide $(*)$ by dT at constant pressure $dT \to 0$

$$\underbrace{\frac{\delta Q}{dT}}_{\left(\frac{\partial Q}{\partial T}\right)_p} = \left[p + \left(\frac{\partial U}{\partial V}\right)_T\right] \underbrace{\frac{dV}{dT}}_{\left(\frac{\partial V}{\partial T}\right)_p} + \left(\frac{\partial U}{\partial T}\right)_V \cancel{\frac{dT}{dT}}^{\,1}$$

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

Exercise 2 [on handout]. (See scan page 3)

8. Quasi-static + Reversibility

All physical laws are reversible. Certain outcomes in the real world are more likely – find always more ways to convert energy to heat than anything else

A process is reversible if its direction can be changed by making some infinitesimal change to a system property.