

Thermodynamics 2

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This lecture

- ▶ Work
- ▶ Degrees of freedom
- ▶ Equipartition
- ▶ Entropy
- ▶ Thermodynamic processes
- ▶ Adiabatic processes
- ▶ P-V diagrams
- ▶ Cycles
- ▶ Efficiency

Work

- ▶ Consider a gas. What is the work done if we *compress* it?

$$W = \int \tilde{F} \cdot d\tilde{x} = \int p A dx = - \int p dV$$

- ▶ To do this we needed a well-behaved P : uniform throughout gas
- ▶ Gas is compressed so it has time to equilibrate
- ▶ For a process that is slow in this sense we say it is **quasistatic**
- ▶ Perfectly quasistatic process ideal, but good approximation
- ▶ Not well-behaved: piston moving at speed of sound in the gas

Degrees of freedom

- ▶ **Degrees of freedom** are independent ways for a particle to store energy. Such as?
- ▶ Number of degrees of freedom f
- ▶ Monatomic gases have $f = 3$ translational degrees of freedom
- ▶ Diatomic gases have $f = 3 + 2 = 5$ translational and rotational degrees of freedom
- ▶ Triatomic, non-linear gases have $f = 3 + 3$ translational and rotational degrees of freedom
- ▶ We can also have vibrational degrees of freedom, but these are 'frozen out' for 'normal' temperatures. At cold temperatures (< 150 K) only translational.
- ▶ What kinds of degrees of freedom do particles in a solid have?

Equipartition

- ▶ **Equipartition theorem:** Each quadratic degree of freedom has an energy $\frac{1}{2}kT$
- ▶ Important principle and again can be related to statistical averages
- ▶ **Heat capacity:** to increase temperature, every particle needs to be given $fk\Delta T/2$ extra energy.
- ▶ Macroscopically, if we keep volume constant, extra energy is heat flow ($\Delta U = Q$): $\Delta U = C_V\Delta T$
- ▶ For liquids, solids: heat capacity is, in general, determined experimentally

Heat capacity at constant pressure

- ▶ Heat capacity: heat flow / change in temperature
- ▶ $C_P = \left(\frac{\Delta Q}{\Delta T} \right)_P = \left(\frac{\Delta U - (-P\Delta V)}{\Delta T} \right)_P$
- ▶ $C_P = \left(\frac{\partial U}{\partial T} \right)_P + P \left(\frac{\partial V}{\partial T} \right)_P$
- ▶ For an ideal gas what is $\left(\frac{\partial U}{\partial T} \right)_P$? What is $\left(\frac{\partial V}{\partial T} \right)_P$?
- ▶ $C_P = C_V + Nk = \frac{Nkf}{2} + Nk$

Entropy

- ▶ Fixed volume: $\frac{1}{T} = \frac{\partial S}{\partial U}$
- ▶ No work so $U \rightarrow Q$

$$dS = \frac{\delta Q}{T}$$

- ▶ In fact this result holds for when the volume changes as well, so long as process is quasistatic
- ▶ In short, adding heat always increases entropy

Reversible and quasistatic processes

- ▶ Processes can be **reversible** if the total entropy change of the universe is zero. The system's entropy can increase, but the surroundings must decrease in entropy by the same amount.
- ▶ A reversible process requires that at all times the system is in thermal equilibrium.
- ▶ So the change you make must be able to be viewed as a series of very small steps: **quasistatic** (process is slow on timescale of internal thermal mixing in system).
- ▶ Not all quasistatic processes are reversible!
- ▶ Example?

Thermodynamic processes

- ▶ Discuss at your tables: what does the word mean? First law application?
- ▶ Isochoric
- ▶ Isobaric
- ▶ Isentropic
- ▶ Isothermal
- ▶ Adiabatic
- ▶ What's the difference between isentropic and adiabatic processes?

The mystery of the rubber band

- ▶ Stretch rubber band and hold it stretched for a bit
- ▶ Quickly allow rubber band to relax and touch it to your lip

Adiabatic processes

- ▶ $\delta Q = 0$, so $dU = dW = -PdV$ (1)
- ▶ Equipartition: $U = \frac{1}{2}fNkT$ so $dU = \frac{1}{2}fNkdT$ (2)
- ▶ Ideal gas: $P = NkT/V$
- ▶ $dP = \left(\frac{\partial P}{\partial V}\right)_{N,T} dV + \left(\frac{\partial P}{\partial T}\right)_{N,V} dT$
- ▶ $dP = \frac{-NkT}{V^2} dV + \frac{Nk}{V} dT$
- ▶ Find dT using (1) and (2)
- ▶ $dP = \frac{-P}{V} dV + \frac{-2P}{fV} dV = -\frac{P}{V} \left(\frac{f+2}{f}\right) dV$
- ▶ We let the **adiabatic constant** be $\gamma = C_P/C_V = (f+2)/f$

Adiabatic processes

$$\frac{-dP}{P} = \frac{\gamma}{V} dV$$

$$\int \frac{-1}{P} dP = \int \frac{\gamma}{V} dV$$

$$\ln P = -\gamma \ln V + \ln C = \ln (CV^{-\gamma})$$

$$PV^{\gamma} = C, \text{ a constant}$$

- ▶ We can also use these equations – (1) and (2) – to find a relationship between temperature and volume
- ▶ Have a go!

P-V diagrams

- ▶ Pressure vs. volume, your new best friend for quasistatic processes
- ▶ Area under the curve?
- ▶ Put arrows to show which way the process is going, very helpful!

Check!

Answer me these questions three

- ▶ What does the P-V diagram of an isothermal process look like?
- ▶ Is an adiabatic process more or less “steep” than an isotherm?
- ▶ If we want to compress something isothermally, should we compress it faster or slower than if we wanted to compress it adiabatically?

Closed cycles

- ▶ Change in state:
- ▶ Enclosed area:

Heat engines

- ▶ Motivation for study: use thermal energy to do work.
- ▶ Heat engine has a cycle allowing conversion of internal energy into useful work.
- ▶ Have some 'working substance' which has its state changed by various processes
- ▶ **Second law:** can't decrease the total entropy. Original formulations – can't have heat engine that does nothing but extract heat from a reservoir and produce work.
- ▶ How close can we get? For the best, we want no nett entropy change during any process - completely reversible.

Efficiency

- ▶ **Efficiency** of a cycle is the net work done over the heat put in.

$$\eta = \frac{W_{\text{out}}}{Q_{\text{in}}} = 1 - \frac{Q_{\text{out}}}{Q_{\text{in}}}$$

- ▶ No cycle is 100% efficient. No cycle is 100% efficient.

Refrigerators / Heat pumps

- ▶ Run a cycle backwards
- ▶ **Coefficient of performance** for a refrigerator is the heat taken out / net work done

$$\kappa = \frac{Q_{\text{out}}}{W_{\text{in}}}$$

- ▶ Not all heat engines refrigerate in reverse – some just pump heat.