

★ Week 3 reading: Blundell+Blundell, chapters 11, 12, 13.

- Last time: $dU = \delta Q + \delta W$, with $\delta W_{rev} = -pdV$. Heat capacity. $C_V \equiv \left(\frac{\partial Q}{\partial T}\right)_V$ and $C_P \equiv \left(\frac{\partial Q}{\partial T}\right)_P$. Note that both are extensive, and it is convenient to define the specific heats $c_V = C_V/M$ and $c_P = C_P/M$, which just depend on the material (and in general T), independent of the size of the sample.

- Define $\gamma \equiv C_P/C_V$. Always the case that $\gamma \equiv C_P/C_V > 1$: more heat required, for fixed ΔT , in case of $P = \text{constant}$, because some goes into doing a positive amount of work, whereas at constant V no work is done, so all added heat goes toward increasing the internal energy, and thus the temperature.

- Plot c_p and c_V as a function of temperature, with $T \in [0, 1000K]$ and e.g. $c \in [0, 30 \times 10^3 J/kmoleK]$. Classical physics dilemma: why does $c(T \rightarrow 0) \rightarrow 0$? We'll see why later, e.g. for small T , $c(T)T^{-2}e^{-\alpha/T}$ with $\alpha \propto \hbar$. For T large, $C_V \rightarrow \frac{f}{2}Nk_B$.

- Write $U = U(T, V)$. Exact differential means

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

$\delta Q = dU + pdV$ so $C_V = \left(\frac{\partial U}{\partial T}\right)_V$ and $C_P = C_V + \left[\left(\frac{\partial U}{\partial V}\right)_T + p\right]\left(\frac{\partial V}{\partial T}\right)_P$. Note that $C_P - C_V = \left(\frac{\delta Q}{\delta V}\right)_T \frac{\partial V}{\partial T}_P$. We will later discuss Maxwell's relations and see that this can be rewritten in a way to show that it is always positive.

- For an ideal gas, $U = \frac{f}{2}Nk_B T$ and thus $C_V = \frac{f}{2}Nk_B$ and $C_P = C_V + Nk_B$.

Note that $\gamma = 1 + (Nk_B/C_V)$. For an ideal gas, $U = C_V T = Nk_B T/(\gamma - 1)$, with $\gamma = 1 + \frac{2}{f}$. Emphasize that γ is a macroscopic observable, it is an easily measured property of a gas. Isn't it amazing that it tells us something about f ?! That is a microscopic property of molecules. In fact, this observable gave, in hindsight, amazing clues about quantum mechanics already in the 1800s! Plots of f as a function of temperature showed for some gasses it increasing as T increases, first $f = 3$, then $f = 5$, then $f = 7$. This is as rotational and vibrational degrees of freedom were activated (which requires non-zero energy because angular momentum and vibrational energy levels are quantized).

- Adiabatic means $\delta Q = 0$ and reversible. For an ideal gas, $dU = C_V dT$ and then the first law for an adiabatic process gives $C_V dT = -pdV$. Plug in $dT = d(pV)/Nk_B$ to get $C_V(p dV + V dp) = -Nk_B p dV$ so $V dp + \gamma p dV = 0$. This integrates to $pV^\gamma = \text{constant}$.

- Adiabatic atmosphere is a better approximation than $T = \text{constant}$, which we discussed last time. Eliminate V to write $p(Nk_B T/p)^\gamma = \text{constant}$. So $(1 - \gamma)(dp/p) + \gamma(dT/T) = 0$. Also $\frac{dp}{dz} = -m g p / k_B T$ (last time), so $\frac{dT}{dz} = -(\frac{\gamma-1}{\gamma})(m g / k_B)$.

- Examples of ΔW for ideal gas

1. isothermal: $\Delta U = 0$. $\Delta Q = -\Delta W = Nk_B T \ln(V_f/V_i) = Nk_B T \ln(P_i/P_f)$.

2. isochoric: $\Delta W = 0$. $\Delta Q = \Delta U = C_V \Delta T$

3. isobaric: $\Delta W = -P\Delta V = -Nk_B \Delta T$. $\Delta Q = C_P \Delta T = (C_V + Nk_B) \Delta T$

4. adiabatic: $\Delta Q = 0$. $\Delta W = \Delta U = C_V \Delta T = \frac{1}{\gamma-1} \Delta(PV)$.

- Engines. Efficiency $\eta \equiv |W|/|Q_H|$. E.g. isothermal expansion of ideal gas: $|W| = |Q| = nRT \ln(P_i/P_f)$ has $\eta = 1$, but this is a one-shot process. Final state differs from initial.

- For an engine, want cyclic process, coming back to starting state, i.e. closed loop in P/V diagram. For complete cycle, $\Delta U = 0$ (state variable). Total work of process = $|W|$ = area enclosed by cycle in P/V diagram. In process, some heat $|Q_H|$ is taken out of some hot working substance (e.g. boiler), and then some heat is ejected into cold area (e.g. the smoke going out into the atmosphere). $|W| = |Q_H| - |Q_C|$, so $\eta = 1 - |Q_C|/|Q_H| \leq 1$. Perfect engine would have $\eta = 1$, but this is impossible.