Physics 170:
Statistical Mechanics and Thermodynamics

Lecture 8B

Finishing Ex. 8A

Ideal gas with internal degrees of freedom

$$\mathfrak{z} = 1 + e^{\beta(\mu - \varepsilon_{\mathbf{n}})} Z_{\text{int}}$$

$$N(\mu)$$

$$\boxed{\begin{aligned} \mu(N) &= \mu_0 - \tau \ln(Z_{\text{int}}) \\ F(N,\tau,V) &= F_0 - N\tau \ln(Z_{\text{int}}) \\ &= F_0 + F_{\text{int}} \end{aligned}}$$

…where μ_0, F_0 are for monatomic gas.

I will collect 1 problem from today via Gradescope.

Names:

EXERCISE 8B: HEAT AND WORK IN AN IDEAL GAS

Objectives:

- Calculate the form of **adiabats** relating p and V in an ideal gas at constant entropy
- Understand the basic operating principle of a heat engine
- Calculate the Carnot Limit on the efficiency of a heat engine

References: Kittel & Kroemer, Ch. 6

Useful result from Ex. 8A:

- Free energy of an ideal gas: $F = F_0 + F_{\text{int}}$,

  where $F_{\text{int}} = -N\tau \ln Z_{\text{int}}$ and F_0 is the free energy of the monatomic ideal gas.

1. Which of the following properties of the ideal gas are modified by the internal degrees of freedom, and how? Explain.

   a. The equation of state $p(N, \tau, V)$
   b. The entropy $\sigma(N, \tau, V)$
   c. The heat capacity $C_V = \tau(\partial\sigma/\partial\tau)_V$ at constant volume.
   d. The heat capacity $C_p = \tau(\partial\sigma/\partial\tau)_p$ at constant pressure.
   e. The isothermal compressibility $\kappa_\tau = -V^{-1}(\partial V/\partial p)_\tau$
   f. The adiabatic compressibility $\kappa_\sigma = -V^{-1}(\partial V/\partial p)_\sigma$

$dF = -\sigma d\tau - p dV + \mu dN$ // $dE = \tau d\sigma - p dV + \mu dN$

a) $p = -\left(\frac{\partial F}{\partial V}\right)_{N,\tau}$ unchanged, since F_{int} is independent of volume V

b) $\sigma = -\left(\frac{\partial F}{\partial \tau}\right)_{V,N} = \sigma_0 + \sigma_{int}$ increased by entropy of internal degrees of freedom.

c) $C_V = \tau\left(\frac{\partial \sigma}{\partial \tau}\right)_V = C_{V,0} + C_{int}$ (modified)

For example, for f quadratic degrees of freedom from vibrational/rotational internal motion, $C_{int} = (f/2)N\tau \Rightarrow C_V = \left(\frac{3+f}{2}\right)N$

d) $C_p = \tau\left(\frac{\partial \sigma}{\partial \tau}\right)_{p,N} = \left(\frac{\partial E}{\partial \tau}\right)_{p,N} + p\left(\frac{\partial V}{\partial \tau}\right)_{p,N} = \left(\frac{3+f}{2}\right)N + p\cdot\frac{N}{p} = \left(\frac{5+f}{2}\right)N$

$E = \left(\frac{3+f}{2}\right)N\tau$, independent of p, V

$\therefore$ both heat capacities increased by fN for rotational/vibrational degrees of freedom, C_{int} depends on temperature (which d.o.f. accessible) and may also include a contribution from spin.

(cont'd)

Compressibilities:

e) Isothermal: $\kappa_\tau = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_\tau$ depends only on equation of state $\Rightarrow$ unchanged

f) Adiabatic: $\kappa_\sigma = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_\sigma$

For a monatomic gas, decreasing volume at fixed entropy requires putting the entropy lost by real-space compression into momentum space $\Rightarrow$ higher τ and p. If there are internal degrees of freedom, these can also help take up entropy, so less pressure is required to achieve the same decrease in $V \Rightarrow$ gas with internal degrees of freedom has higher adiabatic compressibility.

2. *Adiabatic expansion or compression of an ideal gas.* Show that for any ideal gas, the adiabats are of the form pV^γ = constant, where $\gamma = C_p/C_V$ is the **heat capacity ratio**.

   a. Write down the fundamental thermodynamic relation and simplify it for the case of constant entropy and constant particle number.

$$dE = \cancel{\tau d\sigma} - pdV + \cancel{\mu dN}$$

   b. Explain why the following relations hold for any ideal gas at fixed N:

$$Nd\tau = pdV + Vdp. \quad (1)$$

$$dE = C_V d\tau \quad (2)$$

(1) $pV = N\tau \Rightarrow pdV + Vdp = Nd\tau + \cancel{\tau dN}$

$\therefore$ @ const N, $pdV + Vdp = Nd\tau$

(2) $C_V = \tau\left(\frac{\partial\sigma}{\partial\tau}\right)_{V,N} = \left(\frac{\partial E}{\partial\tau}\right)_{V,N} \Rightarrow dE = C_V d\tau$

   c. Use the above results to derive a relation of the form

$$Vdp = -\gamma pdV. \quad (3)$$

What is the value of γ in terms of C_V?

$$Vdp = Nd\tau - pdV = N \cdot \frac{dE}{C_V} - pdV = -\left(\frac{N}{C_V} + 1\right) pdV$$
$$= -\gamma pdV$$

$$\Rightarrow \gamma = \frac{C_V + N}{C_V}$$

d. Show that in an adiabatic expansion or compression of an ideal gas, pV^γ is constant.

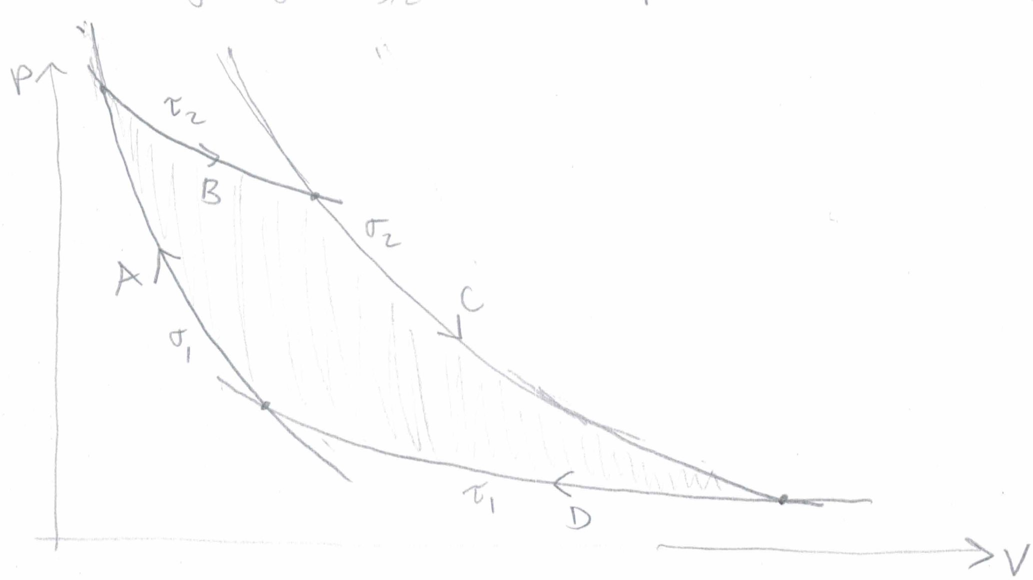
$$V dp = -\gamma p\, dV \Rightarrow \frac{dp}{p} = -\gamma \frac{dV}{V} \Rightarrow \int \frac{dp}{p} = -\gamma \int \frac{dV}{V}$$

$$\Rightarrow \ln p = -\gamma \ln V + \text{const}$$

$$\Rightarrow p \propto V^{-\gamma} \Rightarrow \boxed{pV^\gamma = \text{const}}$$

e. The relation pV^γ = constant defines a family of curves called **adiabats**. Sketch adiabats (showing p as a function of V) for a monatomic ideal gas at two different entropies $\sigma_1 < \sigma_2$.

Monatomic gas: $\gamma = \frac{5/2}{3/2} = 5/3 \Rightarrow p \propto V^{-5/3}$



f. Add to your sketch two **isotherms**, i.e., curves of p vs V at two different constant temperatures $\tau_1 < \tau_2$. What is their functional form?

$pV = N\tau \Rightarrow p \propto \tau/V$

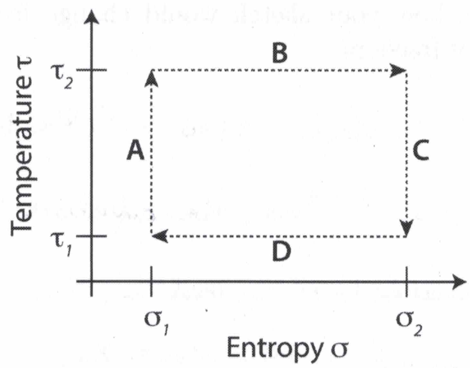


FIG. 1. Carnot cycle composed of adiabatic and isothermal quasi-static processes.

g. Consider a cycle of alternating isothermal and adiabatic processes that traces out the loop in the σ-τ plane shown in Fig. 1.
   i. In your plot in e., label the curves in the p-V plane corresponding to the trajectories A, B, C, and D, and shade in a region representing the amount of work done by the gas in one such cycle.
   ii. Is the net work done by the gas positive or negative?
   iii. How much heat is absorbed by the gas in the same cycle?

ii) Net work is positive, since volume increases @ high pressure & decreases @ low pressure. (Work done by gas is $-đW = +p\,dV$)

iii) $\Delta Q = (\tau_2 - \tau_1)(\sigma_2 - \sigma_1)$
[Area of rectangle in Fig. 1]

h. Show that the exponent γ is equal to the **heat capacity ratio**: $\gamma = C_p/C_V$. You will need the fundamental thermodynamic relation and ~~Eq. 2.~~ part (c).

$dE = \tau d\sigma - p dV + \mu dN \Rightarrow C_p = \tau\left(\frac{\partial \sigma}{\partial \tau}\right)_p = \left(\frac{\partial E}{\partial \tau}\right)_p + p\left(\frac{\partial V}{\partial \tau}\right)_p = C_v + N$
(as shown already on pg. 1).

$\Rightarrow \gamma \equiv \frac{C_v + N}{C_v} = \frac{C_p}{C_v}$ ✓

i. Explain in words how your sketch would change for a gas of molecules with internal degrees of freedom.

$\gamma = \frac{C_p}{C_v} = 1 + \frac{N}{C_v}$ is lower (closer to 1) the more internal degrees of freedom. Thus, the adiabats become less steep, i.e. smaller $|\Delta p|$ required for fixed $|\Delta V|$, consistent with the argument in 1(f) about x_σ.

* This means that adiabats become more similar to isotherms, so larger change in volume is needed for same amount of work.

I find this hard to draw, so I will show a Wolfram Demonstration:
http://demonstrations.wolfram.com/CarnotCycleOnIdealGas

3. **Carnot efficiency.** *How efficiently can we generate work from heat?* should say $\mathcal{M}$
Figure 2(a) illustrates a generic process wherein a system $\mathcal{A}$ absorbs heat q_2 from a reservoir at temperature τ_2 and outputs work w, dumping heat into a reservoir at temperature $\tau_1 < \tau_2$. Assume that the process is cyclic, so that it can be repeated indefinitely.

   a. Express the **second law of thermodynamics** in terms of the quantities labelled in Fig. 2(a).

   $$\Delta\sigma_1 + \Delta\sigma_2 > 0$$

   $$\Rightarrow \quad -\frac{q_2}{\tau_2} + \frac{q_1}{\tau_1} > 0$$

   b. Express the **first law of thermodynamics** in terms of the quantities labelled in Fig. 2(a).

   $q_2 - q_1 - w = 0$ (since energy is same after 1 cycle).

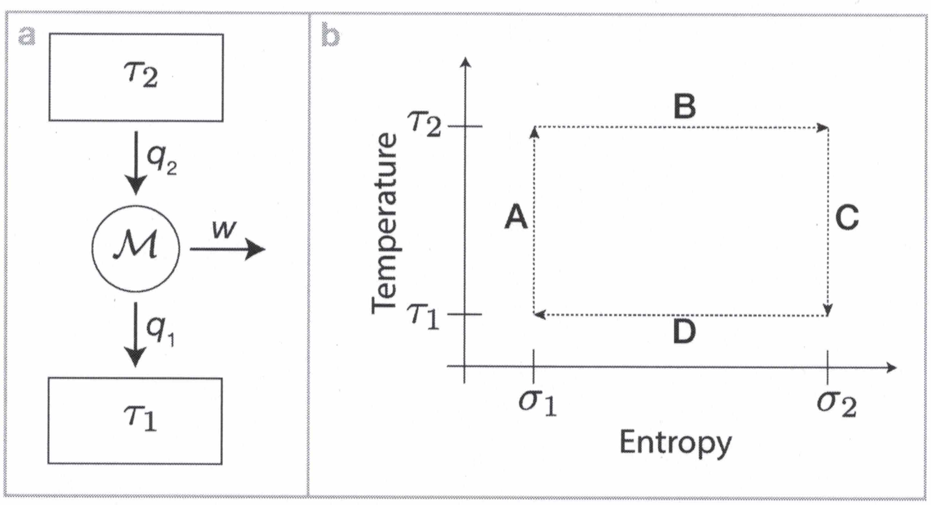


FIG. 2. **(a)** Schematic diagram of a heat engine. **(b)** Carnot cycle composed of adiabatic and isothermal quasi-static processes.

c. The **efficiency** of the heat engine is defined as the ratio $\eta \equiv w/q_2$ of work output by the system to heat input from the high-temperature reservoir. Calculate a fundamental limit on the efficiency of a heat engine operating between the two reservoirs at temperatures $\tau_2 > \tau_1$.

$\eta \equiv \frac{w}{q_2}$, where $w = q_2 - q_1$

$= 1 - \frac{q_1}{q_2}$

From 2nd law, we have $\frac{q_1}{\tau_1} > \frac{q_2}{\tau_2} \Rightarrow \frac{q_1}{q_2} > \frac{\tau_1}{\tau_2}$

$\therefore \boxed{\eta < 1 - \frac{\tau_1}{\tau_2} = \frac{\tau_2 - \tau_1}{\tau_2}}$

Perfect efficiency would require a zero-temperature reservoir.

$\therefore$ It is impossible to construct a perfect heat engine.

(Kelvin's formulation of the 2nd Law.)