1. For an idea gas in *two dimensions* confined to an area A, determine the multiplicity $\Omega(E)$: For a 2D particle in a box,

$$E = \frac{p}{2m} = \frac{\hbar^2 k^2}{2m}$$

$$\implies k = \sqrt{\frac{2mE}{\hbar^2}}, \quad dE = \frac{\hbar^2 k dk}{m} \quad \text{or} \quad dk = \frac{m}{\hbar^2 k} dE$$

In $k-$space, the area of a microstate is

$$k_x k_y = \frac{\pi^2}{L^2} = \frac{\pi^2}{A}$$

In the range $k \to k + dk$ the area of the peel is a quarter of the circles circumference times the width of the peel dk:

$$\frac{1}{4}(2\pi k)dk = \frac{\pi k dk}{2}$$

So the multiplicity is

$$\Omega(k)dk = \frac{1}{2}\frac{\pi k dk}{\pi^2/A} = \frac{A}{2\pi}k dk$$

$$\Omega(E)dE = \frac{A}{2\pi}(k)\frac{m}{\hbar^2 k}dE = A\frac{m}{2\pi\hbar^2}dE$$

$$\implies \Omega(E) = A\frac{m}{2\pi\hbar^2}$$

so for N particles we have to care for $N!$ permutations:

$$\boxed{\Omega(E) = \frac{A^N}{N!}\left(\frac{m}{2\pi\hbar^2}\right)^N}$$

2. van der Waals gas

$$\left(p + \frac{a}{v^2}\right)(v - b) = RT \tag{1}$$

where $v \equiv V/n$ is the molar volume.

(a) The constant a as units pressure times molar volume squared which captures the long range attractions, or the positive pressure that keep the molecules together. The constant b has units V/n, or molar volume, which expressess the occupied volume of the molecules.

(b) Molar energy (energy of one mol of gas) dependent on volume: To find the dependence of molar energy to volume we start from the first law of thermodynamics

$$dE = TdS - pdV \rightarrow \frac{dE}{dV} = T\frac{dS}{dV} - p$$

where we can apply the Maxwell relation

$$\frac{\partial S}{\partial V} = \frac{\partial p}{\partial T}$$

so

$$\frac{dE}{dV} = T\frac{\partial p}{\partial T} - p$$

We can differentiate (1) by $\frac{d}{dT}$:

$$(v - b)\frac{dp}{dT} = R \implies \frac{\partial p}{\partial T} = \frac{R}{v - b}$$

Thus

$$\frac{dE}{dV} = T\frac{R}{v - b} - p$$

solving (1) for p

$$p = \frac{RT}{v - b} - \frac{a}{v^2}$$

and substituting back into the energy equation

$$\frac{dE}{dV} = T\frac{R}{v - b} - \left(\frac{RT}{v - b} - \frac{a}{v^2}\right)$$

$$= \boxed{\frac{a}{v^2}}$$

(c) Show that molar heat capacity is independent of volume: Starting with the relation

$$c_V = \left(\frac{dQ}{dT}\right)_V = T\left(\frac{\partial S}{\partial T}\right)_V$$

and differentiating with respect to volume (with T constant)

$$\left(\frac{\partial c_V}{\partial V}\right)_T = T\left[\frac{\partial}{\partial V}\left(\frac{\partial S}{\partial T}\right)\right]$$

$$= T\left[\frac{\partial}{\partial T}\frac{\partial S}{\partial V}\right]_V \quad \text{using} \quad \frac{\partial S}{\partial V} = \frac{\partial p}{\partial T}$$

$$= T\frac{\partial^2 p}{\partial T^2} = 0$$

using what we found for p in part (b), So c_V is independent of volume.

(d) Taking temp T and volume v as independent parameters, determine dS in terms of dv and dT:

$$s = s(v, T)$$

so the differential is

$$ds = \left(\frac{\partial s}{\partial T}\right)_V dT + \left(\frac{\partial s}{\partial v}\right)_T dv$$

So using the Maxwell relation and molar heat capacity equations

$$\frac{\partial s}{\partial T} = \frac{c_V}{T} \quad \text{and} \quad \frac{\partial s}{\partial v} = \left(\frac{\partial p}{\partial T}\right)_V = \frac{R}{v - b}$$

We get

$$\boxed{ds = \frac{c_V}{T} dT + \frac{R}{v - b} dv}$$

3.

(a) Using the ideal gas law for the molar volume $pV = vRT$

$$p_i V_i^\gamma = p_f V_f^\gamma$$
$$\frac{vRT_i}{V_i} V_i^\gamma = \frac{vRT_f}{V_f} V_f^\gamma$$
$$T_i V_i^{\gamma-1} = T_f V_f^{\gamma-1}$$

so

$$\boxed{T_f = T_i \left(\frac{V_i}{V_f}\right)^{\gamma-1}}$$

(b) With constant entropy $\Delta S = 0$:

$$\Delta S(T, V; v) = v\left(\int_{T_i}^{T_f} \frac{dQ}{T}\right) = v\left(\int_{T_i}^{T_f} c_V \frac{dT}{T} + \int_{V_i}^{V_f} \frac{R}{V} dV\right) = 0$$
$$= vc_V \ln\left(\frac{T_f}{T_i}\right) + vR \ln\left(\frac{V_f}{V_i}\right) = 0$$
$$\implies 0 = \ln\left[\frac{T_f}{T_i}\left(\frac{V_f}{V_i}\right)^{R/c_V}\right]$$

where $R = c_P - c_V$ so

$$\frac{R}{c_V} = \frac{c_P - c_V}{c_V} = \gamma - 1$$

Exponentiating both sides and using the result above:

$$e^0 = \frac{T_f}{T_i}\left(\frac{V_f}{V_i}\right)^{\gamma-1} \implies \boxed{T_f = T_i \left(\frac{V_i}{V_f}\right)^{\gamma-1}}$$

4.   Molar specifc heat at constant volume for a monoatomic ideal gas $c_V = \frac{3}{2}R$. One mole $n = 1$ of gas is subjected to a cyclic quasi-static process:
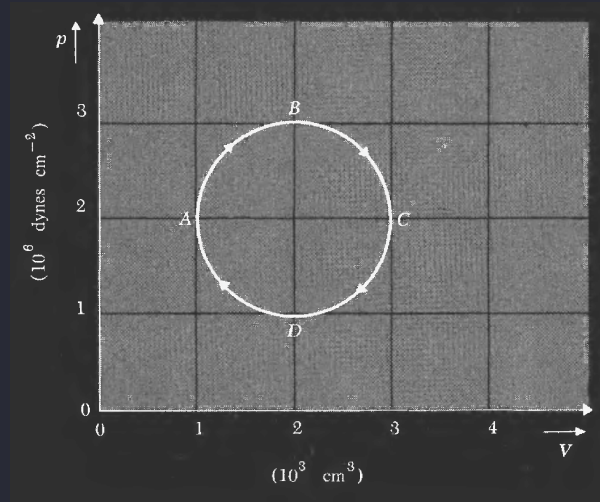

Figure 3.1: Cyclic process pV diagram

(a) The net work in one cycle is the area enclosed by the cycle in the pV diagram i.e. the area of the ellipse $A = \pi pV$:

$$W = \int pdV = \pi \cdot 10^6 \,\text{dynes cm}^{-2} \times 10^3 \,\text{cm}^3$$

$$= \pi \cdot 10^9 \,\text{dyne cm} \times \frac{10^{-7}\,\text{J}}{\text{dyne cm}}$$

$$\approx \boxed{314\,\text{J}}$$

(b) The internal energy difference between state C and A:

$$\Delta U = c_V \delta T \quad \text{using} \quad PV = nRT \implies T = \frac{PV}{R}$$

$$= \frac{3}{2}R\left(\frac{P_C V_C}{R} - \frac{P_A V_A}{R}\right)$$

$$= \frac{3}{2}(P_C V_C - P_A V_A) \quad P_C = P_A = 2 \times 10^6 \,\text{dynes cm}^{-2}$$

$$= \frac{3}{2}(3 - 1) \times 10^9 \,\text{dyne cm}$$

$$= 6 \times 10^9 \,\text{dyne cm} \times \frac{10^{-7}\,\text{J}}{\text{dyne cm}}$$

$$\approx \boxed{600\,\text{J}}$$

(c) The heat absorbed by gas going from A to C via path ABC:

The change in internal energy is the same as (b) and the work done is the area under the curve i.e. semicircle + rectangle area:

$$Q = \Delta U + W$$

$$= 600\,\text{J} + \left[A_{\text{rect}} + A_{\text{semicircle}}\right]$$

$$= 600\,\text{J} + (2 \cdot 210^9 \,\text{dynes cm}) + \frac{1}{2}314\,\text{J}$$

$$= 600\,\text{J} + 400\,\text{J} + 157\,\text{J}$$

$$= \boxed{1157\,\text{J}}$$

5. The piston is in equilibrium with the force of gravity + the force due to the atmosphere:

$$F = pA - p_0 A - mg = 0 \implies p = p_0 + \frac{mg}{A}$$

and at equilibrium we can use the adiabatic equation of state $pV^\gamma = \text{constant}$:

$$pV^\gamma = \left(p_0 + \frac{mg}{A}\right) V_0^\gamma = \text{constant}$$

where $V = Ax$ for the piston moving in the x direction. So we can rewrite Newton's 2nd law as

$$m\ddot{x} = \frac{1}{x^\gamma}\left(p_0 + \frac{mg}{A}\right)\left(\frac{V_0}{A}\right)^\gamma A - mg - p_0 A$$

$$= \frac{1}{x^\gamma}\left(p_0 + \frac{mg}{A}\right)\left(\frac{V_0}{A}\right)^\gamma A - \left(p_0 + \frac{mg}{A}\right) A$$

$$= \left(p_0 + \frac{mg}{A}\right) A \left[\frac{1}{x^\gamma}\left(\frac{V_0}{A}\right)^\gamma - 1\right]$$

and approximating small $x = x_0 + \delta x = x_0 + \epsilon$ near equilibrium:

$$x = \frac{V_0}{A} + \epsilon$$

We can taylor expand about x_0:

$$\frac{1}{x^\gamma} \approx \frac{1}{\left(\frac{V_0}{A}\right)^\gamma} - \gamma \frac{\epsilon}{\left(\frac{V_0}{A}\right)^{\gamma+1}}$$

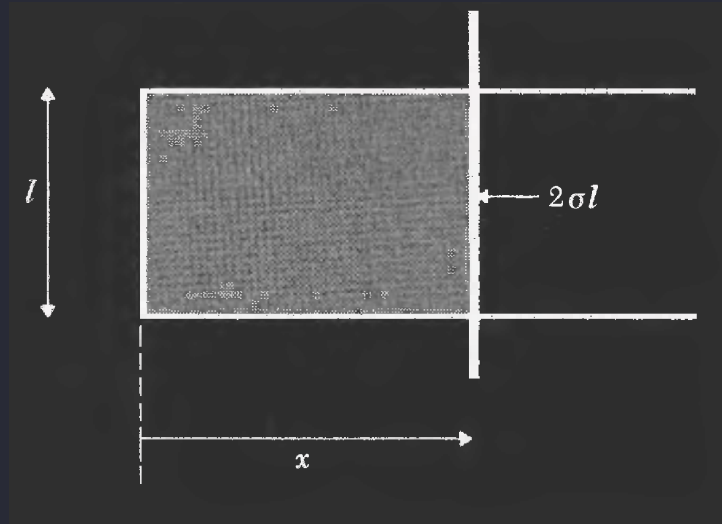Substituting back into the equation of motion we now have a function of ϵ:

$$m\ddot{\epsilon} = \left(p_0 + \frac{mg}{A}\right) A \left[\frac{\left(\frac{V_0}{A}\right)^\gamma}{\left(\frac{V_0}{A}\right)^\gamma} - \gamma\frac{\epsilon\left(\frac{V_0}{A}\right)^\gamma}{\left(\frac{V_0}{A}\right)^{\gamma+1}} - 1\right]$$

$$= \left(p_0 + \frac{mg}{A}\right) A \left[1 - \gamma\epsilon\frac{A}{V_0} - 1\right]$$

$$= -\left(p_0 + \frac{mg}{A}\right)\frac{A^2\gamma}{V_0}\epsilon = -k\epsilon$$

The solution to the differential equation $m\ddot{\epsilon} = -k\epsilon$ is a simple harmonic oscillator:

$$\epsilon = A\cos(\omega t + \phi)$$

where we know the angular frequency:

$$\omega = 2\pi\nu = \sqrt{\frac{k}{m}} = \sqrt{\frac{(p_0 + \frac{mg}{A})\gamma A^2}{mV_0}}$$

$$\implies \boxed{\gamma = \frac{4\pi^2 m V_0 \nu^2}{p_0 A^2 + mgA}}$$

6. From Reif, the relation between c_p and c_V is

$$c_p - c_V = VT\frac{\alpha^2}{\kappa} \tag{5.7.13}$$

So the quantity on the right is

$$VT\frac{\alpha^2}{\kappa} = 14.72\,\text{cm}^3/\text{mol} \times 273\,\text{K} \times \frac{\left(1.81 \times 10^{-4}\,\text{deg}^{-1}\right)^2}{3.88 \times 10^{-12}\,\text{cm}^2/\text{dyne}} \times \frac{1 \times 10^{-7}\,\text{J}}{\text{dyne\,cm}}$$

$$= 3.39\,\text{J}/\text{mol\,deg}$$

and the specific heat at constant volume is

$$c_V = c_p - VT\frac{\alpha^2}{\kappa} = 28\,\text{J}/\text{mol\,deg} - 3.39\,\text{J}/\text{mol\,deg} = \boxed{24.6\,\text{J}/\text{mol\,deg}}$$

Furthermore, the ratio is

$$\gamma = \frac{c_p}{c_V} = \frac{28}{24.6} = \boxed{1.14}$$

Figure 3.2: Soap film supported by wire frame with force $2\sigma l$.

7. For a soap film in Fig. 3.2, the temperature dependence of the surface tension σ is given by

$$\sigma = \sigma_0 - \alpha T$$

(a) With x as the only external parameter the change dE in terms of heat $đQ$ absorbed and the work done by it dx:

$$đQ = dE + đW, \quad đW = -Fdx = -2\sigma l dx$$
$$\implies \boxed{dE = đQ + 2\sigma l\ dx}$$

(b) Calculate the change in mean energy $\Delta E = E(x) - E(0)$ when it is stretched at constant T_0 from $x = 0 \to x$:

$$đQ = TdS = dE + đW = dE - Fdx$$
$$\implies dS = \frac{dE}{T} - \frac{Fdx}{T} = \frac{dE}{T} - \frac{2\sigma l dx}{T}$$

Using the differential for $S = S(x, T)$ and $E = E(x, T)$:

$$dS = \left(\frac{\partial S}{\partial T}\right)_x dT + \left(\frac{\partial S}{\partial x}\right)_T dx, \quad \text{and} \quad dE = \left(\frac{\partial E}{\partial T}\right)_x dT + \left(\frac{\partial E}{\partial x}\right)_T dx$$

Since the film is stretched at constant T_0

$$\frac{\partial S}{\partial T} = 0, \quad \frac{\partial E}{\partial T} = 0$$

so

$$\left(\frac{\partial S}{\partial x}\right)_T dx = \frac{1}{T}\left(\frac{\partial E}{\partial x}\right)_T dx - \frac{2\sigma l}{T}dx$$
$$\implies \left(\frac{\partial E}{\partial x}\right)_T = T\left(\frac{\partial S}{\partial x}\right)_T + 2\sigma l$$

From $TdS = dE - Fdx$ we can get the Maxwell relation

$$\frac{\partial S}{\partial x} = -\frac{\partial F}{\partial T} = -2l\frac{\partial \sigma}{\partial T} \quad \text{using} \quad \sigma = \sigma_0 - \alpha T$$
$$\implies \frac{\partial S}{\partial x} = 2l\alpha$$

Finally

$$\left(\frac{\partial E}{\partial x}\right)_T = T\left(\frac{\partial S}{\partial x}\right)_T + 2\sigma l = 2l\alpha T + 2l(\sigma_0 - \alpha T) = 2l\sigma_0$$

so the change in mean energy is

$$\Delta E = \int_0^x \left(\frac{\partial E}{\partial x}\right)_T dx = \boxed{2l\sigma_0 x}$$

(c) Calculate the work $W(0 \to x)$ done in order to stretch the film at constant temp from $x = 0 \to x$:

$$W = -\int_0^x F dx = -\int_0^x 2\sigma l dx = \boxed{-2l\sigma x}$$