1. $$S = 2cn\sqrt{\frac{U}{n}}\; g(\ell/\ell_0) \qquad c>0$$

$$|\ell/\ell_0| \le 1$$

$$g(x) = (1-x^2)^r \qquad |x| \le 1$$

(a) $U(T, L/n)$

$$\boxed{\left.\frac{\partial S}{\partial U}\right)_{L,n} = \frac{1}{T} = \frac{2cn}{\sqrt{n}}\,\frac{1}{2}\,\frac{1}{\sqrt{U}}\,g(\ell/\ell_0).} \rightarrow 1$$

$$\Rightarrow \boxed{\begin{aligned} \frac{1}{T} &= c\sqrt{\frac{n}{U}}\,g(\ell/\ell_0). \\ \sqrt{U} &= cT\sqrt{n}\,g(\ell/\ell_0) \end{aligned}} \rightarrow 1$$

$$\boxed{U = c^2T^2 n\, g^2(\ell/\ell_0) = nc^2g^2T^2} \rightarrow 1$$

(b) Specific heat $\left. C_L = T\frac{\partial S}{\partial T}\right)_L$

$$dU = T\,dS + f\,dL$$

$$\boxed{\left. C_L = T\frac{\partial S}{\partial T}\right)_L = \left.\frac{\partial U}{\partial T}\right)_L} \rightarrow 1$$

$$\boxed{\left. C_L = \frac{\partial U}{\partial T}\right)_L = 2n g^2 T c^2} \rightarrow 1$$

$$\boxed{\frac{C_L}{n} = 2nc^2g^2T} \rightarrow 1$$

(c) $\left.\dfrac{\partial S}{\partial L}\right)_{U,n} = -\dfrac{f}{T}$

$\left.\dfrac{\partial S}{\partial \ell n}\right)_{U,n} = -\dfrac{f}{T}$

$\boxed{\left.\dfrac{\partial S}{\partial \ell}\right)_{U,n} = -\dfrac{nf}{T}} \rightarrow 1$

$$\frac{\partial S}{\partial \ell} = 2cn\sqrt{\frac{U}{n}}\,\frac{\partial g(\ell/\ell_0)}{\partial \ell}$$

$$= 2cn\sqrt{\frac{U}{n}}\,\frac{\partial g}{\partial x}\frac{\partial x}{\partial \ell}$$

$x = \dfrac{\ell}{\ell_0}$

$\dfrac{\partial x}{\partial \ell} = \dfrac{1}{\ell_0}$

$$= \frac{2cn}{\ell_0}\sqrt{\frac{U}{n}}\,\frac{\partial g}{\partial x} \quad - 1$$

$\dfrac{\partial g}{\partial x} = \gamma(1-x^2)^{\gamma-1}(-2x)$

$$\boxed{\frac{\partial g}{\partial x} = \gamma(1-x^2)^{\gamma-1}(-2x) = \frac{-2x\gamma}{(1-x^2)}\,g(x)} \quad - 1$$

For small $\ell/\ell_0 = x$ $\quad (1-x^2)^{\gamma} \simeq 1 \quad (1-x^2) \simeq 1$

$$-\frac{nf}{T} = -\frac{4cn\gamma}{\ell_0}\sqrt{\frac{U}{n}}\,\frac{\ell}{\ell_0}$$

$$\frac{f}{T} = \frac{4c\gamma}{\ell_0}\frac{\ell}{\ell_0}\sqrt{\frac{U}{n}}$$

$$\sqrt{\frac{U}{n}} = Tc\,g(\ell/\ell_0) \simeq Tc$$

$$\frac{f}{T} = \frac{4c^2 r}{l_0^2} T l$$

$$\boxed{\boxed{f = bT^2 l} \quad \boxed{b = \frac{4c^2 r}{r_0}}} \text{ — } 1$$

(d) $$\boxed{\Delta Q = T\int_{f_1}^{f_2} dS = T\int_{f_1}^{f_2} \left.\frac{\partial S}{\partial f}\right)_{T,n} df} \text{ — } 1$$

Look at the Gibb's Free Energy

$$dG = -S\,dT - L\,df$$

$$\boxed{\left.\frac{\partial S}{\partial f}\right)_{T,n} = \left.\frac{\partial L}{\partial T}\right)_{f,n}} \text{ — } 1$$

$$f = bT^2 \frac{L}{n}$$

$$L = \frac{nf}{bT^2} \qquad \left.\frac{\partial L}{\partial T}\right)_{f,n} = -\frac{2nf}{bT^3}$$

$$\Delta Q = T\int_{f_1}^{f_2}\left(-\frac{2nf}{bT^3}\right) df = -\frac{2n}{bT^2}\int_{f_1}^{f_2} f\,df$$

$$= -\frac{2n}{bT^2}\frac{1}{2}\left(f_2^2 - f_1^2\right)$$

$$\boxed{\Delta Q = -\frac{n}{bT^2}\left(f_2^2 - f_1^2\right)} \text{ — } 1$$

If $f_2 > f_1$ Heat flows out and vice versa.

2 (a) $$F = -Nk_BT\left[1 + \ln\frac{(V-nb)}{N\Lambda_T}\right] - a\frac{N^2}{V}$$

$$\Lambda_T = \left(\frac{h}{\sqrt{2\pi m k_B T}}\right)^3$$

$$\left.\frac{\partial F}{\partial V}\right)_{TN} = -P$$

$$\frac{\partial F}{\partial V} = -Nk_BT\left[\frac{N\Lambda_T}{(V-nb)}\right]\frac{1}{N\Lambda_T} + a\frac{N^2}{V^2} \quad \text{— } 1$$

$$-P = -Nk_BT\left[\frac{N\Lambda_T}{(V-nb)}\right]\frac{1}{N\Lambda_T} + a\frac{N^2}{V^2} \quad \text{— } 1$$

$$P = \frac{Nk_BT}{(V-nb)} + a\frac{N^2}{V^2}$$

$$\boxed{\left(P - a\frac{N^2}{V^2}\right)(V-nb) = Nk_BT} \quad \text{— } 1$$

Set $a=0$, $b=0$ and we recover the ideal gas equation $PV = Nk_BT$.

(b) $$-S = \left.\frac{\partial F}{\partial T}\right)_{V,N}$$

$$F = -Nk_BT\left[1 + \ln(V-nb) - \ln N - \ln\Lambda_T\right] - a\frac{N^2}{V}$$

$$\boxed{\begin{aligned}\frac{\partial F}{\partial T} &= -Nk_B\left[1 + \ln\frac{(V-nb)}{N\Lambda_T}\right] - Nk_BT\left[-\frac{1}{\Lambda_T}\frac{\partial \Lambda_T}{\partial T}\right] \\ &= -Nk_B\left[1 + \ln\left(\frac{V-nb}{N\Lambda_T}\right)\right] + Nk_BT\,\frac{\partial \ln\Lambda_T}{\partial T}\end{aligned}}$$ — 1

$$\Lambda_T = \left[\frac{h}{(2\pi m k_B T)^{1/2}}\right]^3 = \left(\frac{h}{\sqrt{2\pi m k_B}}\right)^3 \frac{1}{T^{3/2}} = \frac{C}{T^{3/2}}$$

$$\ln\Lambda_T = \cancel{3}\ln C - \frac{3}{2}\ln T$$

$$\frac{\partial \ln\Lambda_T}{\partial T} = -\frac{3}{2T}$$

$$-S = -Nk_B\left[1 + \ln\left(\frac{V-nb}{N\Lambda_T}\right)\right] - \frac{3}{2}Nk_B$$

$$\boxed{S = +Nk_B\left[\frac{5}{2} + \ln\left(\frac{V-nb}{N\Lambda_T}\right)\right]}$$ — 1

Set $b=0$ then

$$S = Nk_B\left[\frac{5}{2} + \ln\frac{V\,T^{3/2}}{N\,C}\right]$$ and use $U = \frac{3}{2}Nk_BT$

$$U^{3/2} = \left(\frac{3}{2}k_B\right)^{3/2} N^{3/2}T^{3/2}$$

$$= Nk_B\left[\frac{5}{2} + \ln\frac{kVU^{3/2}}{N^{5/2}}\right]$$ (Expression derived in class).

(b) $F = U - TS$

$$\boxed{\begin{aligned} U &= F + TS = F - T \left.\frac{\partial F}{\partial T}\right)_{V,N} \\ &= -T^2 \left.\frac{\partial (F/T)}{\partial T}\right)_{V,N} \\ \frac{F}{T} &= -Nk_B \left[1 + \ln \frac{V - nb}{N \Lambda_T} \right] - \frac{aN^2}{VT} \end{aligned}}$$ — (1)

$$\frac{\partial}{\partial T}(F/T) = -Nk_B \left[-\frac{\partial}{\partial T} \ln \Lambda_T \right] + \frac{aN^2}{VT^2}$$

$$= -Nk_B \left[+ \frac{3}{2T} \right] + \frac{aN^2}{VT^2}$$

$$\boxed{U = -T^2 \left.\frac{\partial (F/T)}{\partial T}\right)_{V,N} = \frac{3}{2} N k_B T - \frac{aN^2}{V}}$$ — (1)

Set $a = 0$ and you recover the classical ideal gas.

3 (a) Since there is one particle and there is no potential in the box it follows that the probability density must be uniform.

If this was not the case then there would be an external force in the system.

$$\rho_1(x) = \alpha$$

Normalization: $$\int_0^L \rho_1(x)\, dx = 1$$

$$\alpha = \frac{1}{L}$$

$$\rho_1(x) = \frac{1}{L} \qquad 0 \leq x \leq L$$ — 1

(b) If I have two particles then

$$\rho_2(x_1, x_2) = \alpha'$$

$$\int dx_1\, dx_2\ \rho_2(x_1, x_2) = 1$$

$$\alpha' L(L-a) = 1$$ — 1

$$\alpha' = \frac{1}{L(L-a)}$$

$$\rho_2(x_1, x_2) = \frac{1}{L}\frac{1}{(L-a)}$$ — 1

(c) The generalization ~~would~~ to N particles would mean

$$\rho_N(x_1, x_2, \ldots x_N) = \frac{1}{L}\frac{1}{(L-a)}\frac{1}{(L-2a)}\cdots\frac{1}{[L-(N-1)a]} \quad — 2$$

$$\frac{1}{(L-a)}\frac{1}{L-(N-1)a} \simeq \left(L-\frac{Na}{2}\right)^2$$

$$\frac{1}{(L-2a)}\frac{1}{L-(N-2)a} \simeq \left(L-\frac{Na}{2}\right)^2$$

$$\therefore \rho_N(x_1, x_2, \ldots x_N) = \frac{1}{L}\frac{1}{\left(L-\frac{Na}{2}\right)^{N-1}} \quad — 1$$

$$\simeq \frac{1}{L^N}\frac{1}{\left(1-\frac{Na}{2L}\right)^N} \quad — 1$$

Can we use this to get some more information. Let's start with the entropy. For discrete events

$$S = -\sum_j p_j \ln p_j$$

and this becomes

$$S = -k_B \int dx_1\, dx_2 \ldots dx_N \; \rho_N \ln \rho_N$$

$$= -k_B \rho_N \ln \rho_N \int dx_1\, dx_2 \ldots dx_N$$

But $\int dx_1\, dx_2 \ldots dx_N = L(L-a)\ldots[L-(N-1)a]$

$$= L^N\left(1-\frac{Na}{2L}\right)^N$$

So that $S = -\ln e_N$

$$S = Nk_B \ln\left(L - \frac{Na}{2}\right)$$

This however is not the complete entropy. It is only the configurational part of the entropy.

$$\frac{\partial S}{\partial L} = +\frac{P}{T}$$

$$\left.\frac{\partial S}{\partial L}\right) = \frac{Nk_B}{\left(L - \frac{Na}{2}\right)}$$

$$P\left(L - \frac{Na}{2}\right) = Nk_BT \rightarrow \text{Equation of state.}$$

If you replace one dimensional box by volume V, then you have

$$\boxed{P\left(V - \frac{Na}{2}\right) = Nk_BT}$$

4 (a) $$p(n, N, p) = \frac{N!}{n!\,(N-n)!}\, p^n q^{N-n} \quad \text{with } p+q = 1$$

Normalization: $$\sum_{n=0}^{N} \frac{N!}{n!\,(N-n)!}\, p^n q^{N-n} = (p+q)^N = 1 \quad \text{— 1}$$

(b) Mean of the distribution:

$$\bar{n} = \sum_{n=0}^{N} n \frac{N!}{n!\,(N-n)!}\, p^n q^{N-n}$$

$$= \sum_{n=0}^{N} \frac{N!}{n!\,(N-n)!} \left(p\frac{\partial}{\partial p} p^n\right) q^{N-n} = p\frac{\partial}{\partial p} \sum_n \frac{N!}{n!\,(N-n)!}\, p^n q^{N-n} \quad \text{— 1}$$

$$\bar{n} = p\frac{\partial}{\partial p}(p+q)^N$$

$$= Np\,(p+q)^{N-1} = Np$$ 1

(c) $$\overline{n^2} = \sum_n n^2 \frac{N!}{n!\,(N-n)!}\, p^n q^{N-n}$$

$$= \sum_n \frac{N!}{n!\,(N-n)!}\left(p\frac{\partial}{\partial p}\right)^2 p^n q^{N-n}$$

$$= \left(p\frac{\partial}{\partial p}\right)^2 (p+q)^N$$ 1

$$= p\frac{\partial}{\partial p}\left[p\frac{\partial}{\partial p}(p+q)^N\right]$$

$$= p\frac{\partial}{\partial p}\left[pN\,(p+q)^{N-1}\right]$$

$$= Np\,(p+q)^{N-1} + p^2 N(N-1)(p+q)^{N-2}$$

$$= Np + p^2N(N-1)$$

$$\overline{n^2} = N^2p^2 + Np(1-p)$$

$$\overline{n^2} = \bar{n}^2 + Npq$$ 1

$$\sigma_N^2 = \overline{n^2} - \bar{n}^2 = Npq$$

$$\frac{\sigma_N}{\bar{n}} = \frac{\sqrt{Npq}}{Np} = \sqrt{\frac{q}{p}}\,\frac{1}{\sqrt{N}}$$ 1

Hence for $N \gg 1$ the width of the distribution becomes small and the distribution is peaked around the mean $\bar{n}$. This is our second connection to thermodynamics.

5) $$\psi(x_1,x_2) = \frac{1}{\sqrt{\pi x_0}} \left(\frac{x_2 - x_1}{x_0}\right) e^{-\frac{(x_1^2+x_2^2)}{x_0^2}}$$

$$p(x_1,x_2) = \frac{1}{\pi x_0} \left(\frac{x_2 - x_1}{x_0}\right)^2 e^{-2x_1^2/x_0^2} e^{-2x_2^2/x_0^2} \quad \text{—— } 1$$

$$p(x_1) = \int_{-\infty}^{+\infty} dx_2 \; p(x_1,x_2)$$

$$= \frac{1}{\pi x_0^3} \int_{-\infty}^{+\infty} (x_2^2 - 2x_2x_1 + x_1^2)\, e^{-2x_1^2/x_0^2} e^{-2x_2^2/x_0^2} dx_2 \quad \text{—— } 1$$

$$= \frac{e^{-2x_1^2/x_0^2}}{\pi x_0^3} \left[\int_{-\infty}^{+\infty} x_2^2 e^{-2x_2^2/x_0^2} dx_2 + x_1^2 \int_{-\infty}^{+\infty} dx_2\, e^{-2x_2^2/x_0^2} \right] \text{—— } 1$$

$$= \frac{1}{\pi x_0^3} e^{-2x_1^2/x_0^2} \left[\frac{1}{4}\sqrt{\frac{\pi}{2}}\, x_0^3 + x_1^2 \sqrt{\frac{\pi}{2}} x_0 \right]$$

$$= \frac{1}{\pi x_0^3} x_0 e^{-2x_1^2/x_0^2} \sqrt{\frac{\pi}{2}} \left[x_1^2 + x_0^2 \right]$$

$$= \frac{1}{\sqrt{2\pi}} e^{-2x_1^2/x_0^2} \left[\frac{1}{4} + \frac{x_1^2}{x_0^2} \right] \text{—— } 1$$

Similarly, $$p(x_2) = \frac{1}{\sqrt{2\pi}} \, e^{-2x_2^2/x_0^2} \left[\frac{1}{4} + \frac{x_2^2}{x_0^2} \right] \quad \text{— } 1$$

There is however a dimensional in consistency with the result. $p(x_1)$ & $p(x_2)$ should have the dimension of $[x]^{-1}$! The reason it is not so is that the normalization is not correct.

$$\int_{-\infty}^{+\infty} dx_1 \, dx_2 \; N^2 \left(\frac{x_2 - x_1}{x_0} \right)^2 e^{-2\left(\frac{x_1^2 + x_2^2}{x_0^2}\right)} = 1$$

$$N^2 \cdot \frac{\pi x_0^2}{4} = 1$$

$$N^2 = \frac{4}{\pi x_0^2}$$