(HW 2008 7.1) (2009 3.2)

A17 N hard spheres, single sphere vol w, total Volume V only h.c. interactions. $a = V^{\frac{1}{3}}$

a) $$Z = \frac{1}{N!}\underbrace{\left(\frac{1}{2\pi\hbar}\right)^{3N}\int_{-\infty}^{\infty}\prod_i d\bar{p}_i\, e^{-\frac{\beta \bar{p}_i^2}{2m}}}\ \underbrace{\int_{\forall_{ij} |x_i - x_j| > a}\prod_i d\bar{x}_i}$$

$$\approx \frac{1}{N!}\lambda_T^{3N}\, V(V-w)(V-2w)\cdots(V-(N-1)w)$$

validity of approx: the physical meaning: 1st ball has available volume V, 2nd ball available volume $(V-w)$ ... N^{th} ball has available vol $(V-(N-1)w)$.

Ignores excluded volume between neighbours - "packing" which is a 3-body effect.

b) $F = -k_B T \ln Z$

Notice that $V(V-w)\cdots(V-(N-1)w) = V\cdot\left[(V-w)(V-(N-1)w)\right] \times \left[(V-2w)(V-(N-2)w)\right]$

Giving $$Z \approx \frac{\lambda_T^{3N}}{N!}\left(V - \frac{Nw}{2}\right)^{N-1} V = \frac{1}{N!}\underbrace{(\lambda_T^3 V)^N}_{\text{free gas}}\underbrace{\left(1 - \frac{Nw}{2V}\right)^{N-1}}_{\text{h.c. interaction}}$$

$$F = F_{free} - k_B T (N-1)\ln\left(1 - \frac{Nw}{2V}\right)$$

$$S = -\left(\frac{\partial F}{\partial T}\right)_{V,N} = S_{free} + k_B (N-1)\ln\left(1 - \frac{Nw}{2V}\right)$$

The approximation used is valid when $(V-aw)(V-(N-a)w) \approx \left(V - \frac{Nw}{2}\right)^2$ which can be expanded such that

$$V^2 - VNw + w^2 a(N-a) \approx V^2 - VNw + \frac{N^2 w^2}{4} \rightarrow a(N-a) \approx \frac{N^2}{4} \rightarrow N \approx 2a$$

c) Equation of state:

$$P = -\left(\frac{\partial F}{\partial V}\right)_{N,T} = -\left(\frac{\partial F_{free}}{\partial V}\right)_{N,T} + k_B T(N-1)\cdot\frac{\frac{Nw}{2V^2}}{1-\frac{Nw}{2V}}$$

$$\approx \frac{k_B T N}{V} + \frac{k_B T N}{V}\left(\frac{1}{\frac{2V}{Nw}-1}\right)$$

$$PV = k_B T N\left(1+\frac{1}{\frac{2V}{Nw}-1}\right) = k_B T N\left(\frac{2V/Nw}{\frac{2V}{Nw}-1}\right)$$

$$\boxed{PV = k_B T N \cdot \frac{1}{1-\frac{Nw}{2V}}} \longleftrightarrow P\left(V-\frac{Nw}{2}\right) \approx N k_B T$$

for $V >> Nw$ we have $PV \approx k_B T N$

for $V \approx Nw$ we have $PV \approx \frac{1}{2} k_B T N$

d) Isothermal compressibility: $-\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_{T,N}$

we have $\left(V-\frac{Nw}{2}\right) \approx \frac{N k_B T}{P}$

$$-\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_{T,N} = -\frac{1}{V}\left(\frac{\partial\left(V-\frac{Nw}{2}\right)}{\partial P}\right)_{T,N} = \frac{N k_B T}{V P^2} > 0$$

as required.