Hw #5

1) for an ideal gas of point particles, we argued that the number of microstates available to the 1st particle is proportional to the volume V, and the number of microstates available to the 2nd particle is V, etc...

so that $\Omega \sim V^N$ for the whole gas.

In this case, we take into account the volume occupied by each particle, so that

$$\Omega \sim V(V-v_0)(V-2v_0)\cdots(V-[N-1]v_0).$$

$$= V^N\left(1-\frac{v_0}{V}\right)\left(1-2\frac{v_0}{V}\right)\cdots\left(1-\frac{N-1}{V}v_0\right)$$

and

$$\ln\Omega \sim N\ln V + \sum_{k=1}^{N-1}\ln\left(1-k\frac{v_0}{V}\right)$$

Now since $Nv_0 \ll N$, $\ln\left(1-k\frac{v_0}{V}\right) \approx -k\frac{v_0}{V}$

So

$$\ln\Omega \sim N\ln V - \frac{v_0}{V}\sum_{k=1}^{N-1}k = N\ln V - \frac{v_0}{V}\left(\frac{N(N-1)}{2}\right),$$ but $N(N-1)\sim N^2$ for large N

$$S = k\ln\Omega \approx k\left[N\ln V - \frac{N^2 v_0}{2V}\right]$$

Now form $\displaystyle \frac{P}{T} = \left.\frac{\partial S}{\partial V}\right|_{N,E}$

$$\frac{P}{T} = k\left(\frac{N}{V} + \frac{N^2 v_0}{2V^2}\right) = \frac{kN}{V}\left(1+\frac{Nv_0}{2V}\right)$$

using $\frac{1}{1-x} = 1+x+x^2+\cdots$, and since $\frac{Nv_0}{2V}$ is small,

$$\frac{P}{T} \approx \frac{kN}{V\left(1-\frac{Nv_0}{2V}\right)}$$

which gives

$$PV\left(1-\frac{NV_0}{2V}\right) = NkT$$

$$P\left(V-\frac{NV_0}{2}\right) = NkT.$$

This is the ideal gas law with V replaced by $(V-b)$

where

$$b = \frac{NV_0}{2}.$$

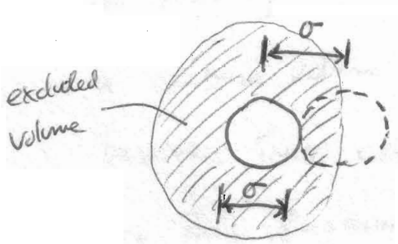
Now, how does b compare to the actual space occupied by the particles?

Call that s, for space.

$$s = N\left(\frac{4}{3}\pi\left(\frac{\sigma}{2}\right)^3\right) = \frac{N}{8}\left(\frac{4}{3}\pi\sigma^3\right)$$

Now lets interpret V_0. The presence of a particle excludes a certain volume from being occupied by another particle. Assuming that only binary collisions occur (classical gas), the closest two particles can come is s.t. their centers are a distance σ apart.

See the diagram:



So, neglecting the approximately-half-sphere piece of the other particle, the excluded volume is $\frac{4}{3}\pi\sigma^3 = V_0$.

Then $$b = \frac{N}{2}V_0 = \frac{N}{2}\left(\frac{4}{3}\pi\sigma^3\right) = 4\left[\frac{N}{8}\left(\frac{4}{3}\pi\sigma^3\right)\right]$$

i.e. $\underline{\underline{b = 4s.}}$