9.2. For this problem, we integrate (9.2.3) by parts and write

$$a_2\lambda^3 = -\frac{2\pi}{3kT}\int_0^\infty e^{-u(r)/kT}\,\frac{\partial u(r)}{\partial r}\,r^3\,dr\ ;$$

cf. eqn. (3.7.17) and Problem 3.23. With given $u(r)$, we get

$$a_2\lambda^3 = \frac{2\pi}{3kT}\int_0^\infty e^{-A/kTr^m}\,e^{B/kTr^n}\left(\frac{mA}{r^{m-2}} - \frac{nB}{r^{n-2}}\right)dr$$

$$= \frac{2\pi}{3kT}\int_0^\infty e^{-A/kTr^m}\sum_{j=0}^\infty \frac{1}{j!}\left(\frac{B}{kT}\right)^j\left(\frac{mA}{r^{m-2+nj}} - \frac{nB}{r^{n-2+nj}}\right)dr$$

$$= \frac{2\pi}{3kT}\sum_{j=0}^\infty \frac{1}{j!}\left(\frac{B}{kT}\right)^j\left\{A\Gamma\left(\frac{m-3+nj}{m}\right)\left(\frac{kT}{A}\right)^{(m-3+nj)/m} - \frac{n}{m}B\Gamma\left(\frac{n-3+nj}{m}\right)\left(\frac{kT}{A}\right)^{(n-3+nj)/m}\right\}.$$

From the first sum we take the $(j=0)$-term out and combine the remaining terms with the second sum (in which the index j is changed to $j-1$); after considerable simplification, we get

$$a_2\lambda^3 = \frac{2\pi}{3}\left(\frac{A}{kT}\right)^{3/m}\left\{\Gamma\left(\frac{m-3}{m}\right) - \frac{3}{m}\sum_{j=1}^\infty \frac{1}{j!}\Gamma\left(\frac{nj-3}{m}\right)\left[\frac{B}{kT}\left(\frac{kT}{A}\right)^{n/m}\right]^j\right\}. \tag{1}$$

For comparison with other cases, we set $A = A'r_n^m$ and $B = B'r_0^n$ (so that A' and B' become direct measures of the energy of interaction). Expression (1) then becomes

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$$a_2\lambda^3 = \frac{2\pi}{3}r_0^3\left(\frac{A'}{kT}\right)^{3/m}\left\{\Gamma\left(\frac{m-3}{m}\right) - \frac{3}{m}\sum_{j=1}^\infty \frac{1}{j!}\Gamma\left(\frac{nj-3}{m}\right)\left[\frac{B'}{kT}\left(\frac{kT}{A'}\right)^{n/m}\right]^j\right\}. \tag{2}$$

Now, to simulate a *hard-core* repulsive interaction, we let $m \to \infty$, with the result that

$$a_2\lambda^3 = \frac{2\pi}{3}r_0^3\left\{1 - 3\sum_{j=1}^\infty \frac{1}{(nj-3)j!}\left(\frac{B'}{kT}\right)^j\right\}. \tag{2a}$$

With $n = 6$, expression (2a) reduces to the one derived in the preceding problem. Furthermore, if terms with $j > 1$ are neglected, we recover the van der Waals approximation (9.3.8).

For further comparison, we look at the behavior of the coefficient $B_2(\equiv a_2\lambda^3)$ at *high* temperatures. While the hard-core expression (2a) predicts a constant B_2 as $T \to \infty$, the soft-core expression (2) predicts a B_2 that ultimately vanishes, as $T^{-3/m}$, which agrees qualitatively with the data

[redacted]

$$a_2\lambda^3 = \frac{2\pi}{3}r_0^3\left(\frac{A'}{kT}\right)^{3/m}\left\{\Gamma\left(\frac{m-3}{m}\right)-\frac{3}{m}\sum_{j=1}^{\infty}\frac{1}{j!}\Gamma\left(\frac{nj-3}{m}\right)\left[\frac{B'}{kT}\left(\frac{kT}{A'}\right)^{n/m}\right]^j\right\}. \tag{2}$$

Now, to simulate a *hard-core* repulsive interaction, we let $m \to \infty$, with the result that

$$a_2\lambda^3 = \frac{2\pi}{3}r_0^3\left\{1-3\sum_{j=1}^{\infty}\frac{1}{(nj-3)j!}\left(\frac{B'}{kT}\right)^j\right\}, \tag{2a}$$

With $n = 6$, expression (2a) reduces to the one derived in the preceding problem. Furthermore, if terms with $j > 1$ are neglected, we recover the van der Waals approximation (9.3.8).

For further comparison, we look at the behavior of the coefficient $B_2(\equiv a_2\lambda^3)$ at *high* temperatures. While the hard-core expression (2a) predicts a constant B_2 as $T \to \infty$, the soft-core expression (2) predicts a B_2 that ultimately vanishes, as $T^{-3/m}$, which agrees qualitatively with the data shown in Fig. 9.2.

[redacted]

9.7. To the desired approximation,

$$\frac{P}{kT} \equiv \frac{1}{V} \ell n \mathcal{Q} = \frac{1}{\lambda^3}\left(z - a_2 z^2\right), \quad n = \frac{N}{V} = \frac{1}{\lambda^3}\left(z - 2a_2 z^2\right), \tag{1a,b}$$

where a_2 is the second virial coefficient of the gas. It follows that

$$z = n\lambda^3(1 + 2a_2 \cdot n\lambda^3), \text{ whence } P = nkT(1 + a_2 \cdot n\lambda^3) \; . \tag{2a,b}$$

Next

$$A = NkT \, \ell n \, z - PV = NkT\left\{\ell n\left(n\lambda^3\right) - 1 + a_2 \cdot n\lambda^3\right\} ,$$

$$G = NkT \, \ell n \, z = NkT\left\{\ell n(n\lambda^3) + 2a_2 \cdot n\lambda^3\right\} ,$$

$$S = -\left(\frac{\partial A}{\partial T}\right)_{N,V} = Nk\left\{\frac{5}{2} - \ell n(n\lambda^3) - n\frac{\partial}{\partial T}(Ta_2\lambda^3)\right\};$$

remember that the coefficient a_2 is a function of T. Furthermore,

$$U = A + TS = NkT\left\{\frac{3}{2} - nT\frac{\partial}{\partial T}(a_2\lambda^3)\right\} ,$$

$$H = U + PV = NkT\left\{\frac{5}{2} - nT^2\frac{\partial}{\partial T}\left(\frac{a_2\lambda^3}{T}\right)\right\} ,$$

$$C_V = \left(\frac{\partial U}{\partial T}\right)_{N,V} = Nk\left\{\frac{3}{2} - n\frac{\partial}{\partial T}\left(T^2\frac{\partial}{\partial T}\left(a_2\lambda^3\right)\right)\right\} , \text{ and}$$

$$C_P - C_V = -T\frac{(\partial P/\partial T)^2_{N,V}}{(\partial P/\partial V)_{N,T}} = Nk\left\{1 + 2nT\frac{\partial}{\partial T}(a_2\lambda^3)\right\} .$$

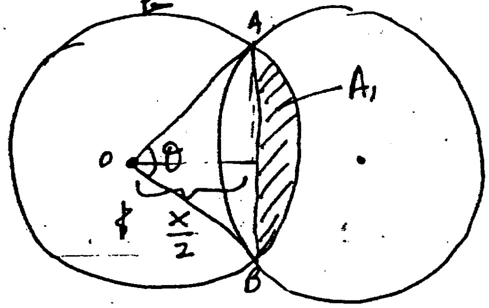
For the second part, use the expression for $a_2\lambda^3$ derived in Problem 9.5 and examine the temperature dependence of the various thermodynamic quantities.

3. Hard sphere : $u = \begin{cases} \infty & : r < a/2 \\ 0 & : r \geq a/2 \end{cases}$ (Let $a/2 = r_0$)

For 3 dimensions problem is solved in pathria ; $a_1 = 1$, $a_2 = \frac{2\pi r_0^3}{3\lambda^3}$, $a_3 = \frac{5}{18}\pi^2\left(\frac{r}{\lambda}\right)^6$

For 2 DIMENSIONS :

$$= \frac{1}{6\lambda^4}\int_0^{r_0} d^2 r_{12} \left[\text{Area of over lap of the two circles}\right]$$



Area of triangle OAB
$= 2\left(\frac{1}{2} r_0^2 \sin\frac{\theta}{2}\cos\frac{\theta}{2}\right)$
$= \frac{1}{2} r_0^2 \sin\theta$

Lets ~~call~~ $r_{12} \equiv x$

Shaded area $= A_1 = \left(\frac{1}{2} r_0^2\theta - \text{area of triangle}\right)$

$$= \frac{1}{2} r_0^2(\theta - \sin\theta)$$

$$\therefore a_3 = \frac{1}{6\lambda^4}\int_0^{2x} 2\pi x\, dx\, r_0^2(\theta - \sin\theta)$$

where ; $\cos\frac{\theta}{2} = x/2r_0$

$$a_3 = \frac{1}{6\lambda^4}\int_0^{\pi} 2\pi r_0^4\, d\theta \sin\theta(\theta - \sin\theta)$$

$$= \frac{\pi^2}{6}\left(\frac{r_0}{\lambda}\right)^4$$

a_2 is trivially calculated to be $\frac{\pi r_0^2}{2\lambda^2}$

1 DIM $a_2 = b = \frac{1}{4}\frac{r_0^2}{\ldots}$, $a_3 = \frac{a_0}{\ldots}$