1 January 2004, Thermodynamics, Problem 3

1.1 (a)

The partition function represents the number of accessible states, which is proportional to the probability of that state. Therefore:

$$P(\boldsymbol{R}) = \frac{3^{3/2}}{(2\pi N)^{3/2} 2b^3} e^{-3R^2/2Nb^2}$$

with the proportionality constant determined by the requirement that $\int_0^\infty P(\boldsymbol{R})\, d^3R$=1. Then we can calculate:

$$< R^2 > \int_0^\infty R^2 \frac{3^{3/2}}{(2\pi N)^{3/2} 2b^3} e^{-3R^2/2Nb^2} 4\pi R^2\, dR = Nb^2 \tag{1}$$

1.2 (b)

$$P(\boldsymbol{R})\, d^3R = P(\boldsymbol{R}) 4\pi R^2 = P(R) dR$$
$$P(R) = 4\pi R^2 P(\boldsymbol{R})$$

The most probable end-to-end distance will be the one that maximizes P(R):

$$\frac{dP(R)}{dR} = \frac{-3R}{Nb^2} e^{-3R^2/2Nb^2} + 8\pi R e^{-3R^2/2Nb^2} = 0$$
$$R = \sqrt{\frac{2Nb^2}{3}} \tag{2}$$

1.3 (c)

The dimensions of U must be the dimensions of pressure. The introduction of the excluded volume leads to a new "effective radius":

$$\frac{4\pi R_{eff}^3}{3} = \frac{4\pi R^3}{3} - Nv$$
$$R_{eff} = \left(\frac{3(\frac{4\pi R^3}{3} - Nv)}{4\pi} \right)^{1/3}$$
$$F(\boldsymbol{R}, N) = C + kT \frac{3R_{eff}^2}{2Nb^2} \approx C + \frac{3kTR^2}{2Nb^2} - \frac{v3kT}{4\pi b^2 R}$$
$$U = -\frac{3kT}{4\pi b^2 R} \tag{3}$$

1.4 (d)

We make the same calculation as in part (b), but now with the full free energy. We get a polynomial of order 5, set equal to 0. It's quite hard to find the roots of that polynomial exactly. However, we can assume that if v is small, the result should not be far from the one we obtained in part (b). So we assume that and linearize the equation in the small difference between the new answer and the old answer. We get the result:

$$R \approx \sqrt{\frac{2N}{3}}b - \frac{3v}{16\pi b^2} \tag{4}$$

What I don't like about these results is that the problem says "you should get a different N-dependence than in part (b)", while here, in the leading order, we have the same dependence.