Solution 10

Excluded Volume Dependence on Temperature[1]

1. If we assume the potential to be infinite in the hard-core repulsive part, we have $f(r) \simeq -1$ for $r < b$. Moreover, under the assumption $u(r) \ll k_B T$ in the attractive well, by Taylor-expanding the exponential we find

$$f(r) = e^{-\frac{u(r)}{k_B T}} - 1 \simeq 1 - \frac{u(r)}{k_B T} - 1 = -\frac{u(r)}{k_B T} \qquad \text{for } r > b \tag{1}$$

By substituting in the definition of the excluded volume, we find

$$v = -\int d\vec{r} f(r) \simeq 4\pi \int_0^b r^2 dr + 4\pi \int_b^\infty \frac{u(r)}{k_B T} r^2 dr \sim b^3 + \frac{1}{k_B T} \int_b^\infty u(r) r^2 dr \tag{2}$$

By defining

$$\theta = -\frac{1}{b^3 k_B} \int_b^\infty u(r) r^2 dr \tag{3}$$

we can rewrite the previous result as

$$v \sim \left(1 - \frac{\theta}{T}\right) b^3 \tag{4}$$

which is the formula reported in the text. Notice that, since $u(r) < 0$ in the attractive part of the potential, we have $\theta > 0$.

2. By substituting the Lennard-Jones (LJ) potential in eqn (3), we find

$$\theta = \frac{4\epsilon}{b^3 k_B} \int_b^\infty \left(\frac{b^6}{r^4} - \frac{b^{12}}{r^{10}}\right) dr = \frac{4\epsilon}{b^3 k_B} \left(\frac{b^6}{3b^3} - \frac{b^{12}}{9b^9}\right) = \frac{8\epsilon}{9k_B} \tag{5}$$

Notice that the in the minimum the LJ potential has value $-\epsilon$. Therefore, in order for the assumption $u(r) \ll k_B T$ to be justified, the condition $\epsilon \ll k_B T$ should hold, meaning that according to our calculation eqn (4) is valid only for temperatures much larger than θ. However, more accurate calculations as well as simulations and experimental results show that eqn (4) is valid for a wide range of temperatures, in particular for roughly all $T > \theta/2$.

[1] M. Rubinstein and R. H. Colby, *Polymer Physics*, Oxford University Press.