extra problems for chapter 3 of Statistical Thermodynamics by Iwao Teraoka

6. The Buckingham potential combines exponential repulsion and r⁻⁶ attraction.

\[ \Phi(r) = -\frac{\epsilon}{\alpha - 6} \left[ 6e^{\alpha \left(1 - \frac{r}{r_0}\right)} - \alpha \left(\frac{r_0}{r}\right)^6 \right] \]

The constant  \( \epsilon \) is the depth of the attractive energy well and  \( r_0 \) is the minimum-\( \Phi \) distance. The unitless constant  \( \alpha \) affects the steepness of repulsion.

(1) The force constant,  \( k \), is given in equation 3.15 in terms of the interatomic potential. Derive a formula for the force constant of the Buckingham potential.

(2) Consider interaction of two nitrogen molecules. From Table 3.7, use  \( \epsilon = 92K \) and  \( r_0 = 4.40 \times 10^{-10} \text{m} \). Let  \( \alpha = 12 \). Calculate the force constant,  \( k \), and the vibration frequency,  \( \nu = \frac{1}{2\pi \sqrt{\mu}} \).

(3) An equivalent expression for the Buckingham potential is

\[ \Phi(r) = Ae^{-Br} - \frac{C}{r^6} \]

Use the values of  \( \epsilon \),  \( \alpha \), and  \( r_0 \) from part 2. Calculate  \( A \),  \( B \), and  \( C \).

7. Two molecules made of nitrogen and hydrogen are imidogen, NH, and ammonia, NH₃. This problem is about their rotational energies. (Rotation only is considered, not rotation coupled to other angular momenta or to vibration.)

(1) NH is a linear rotor. Its moment of inertia is  \( 1.70 \times 10^{-47} \text{kg} \cdot \text{m}^2 \).

Formulas for energy and degeneracy are given in Table 3.9. Calculate the energy and degeneracy for  \( J = 0, 1, \text{ and } 2 \).

(2) NH₃ is an "oblate symmetric" rotor. Its moments of inertia are

\( I_C = 4.50 \times 10^{-47} \text{kg} \cdot \text{m}^2 \) (parallel to the symmetry axis) and \( I_B = 2.80 \times 10^{-47} \text{kg} \cdot \text{m}^2 \) (perpendicular to the symmetry axis). The formula for energy is

\[ \frac{\hbar^2}{8\pi^2 I_C}(J + 1) + \frac{\hbar^2}{8\pi^2 I_B} \left( \frac{1}{I_B} - \frac{1}{I_C} \right) K^2 \]

where  \( J = 0, 1, 2, \ldots \) and  \( K = 0, \pm 1, \pm 2, \ldots \pm J \). Degeneracy comes from the energy's dependence on the square of  \( K \). Calculate the energies and degeneracies of all states for which  \( J = 0, 1, \text{ or } 2 \).

(3) Compare qualitatively the number and spacing of the rotational levels of the two molecules.
8. The Lennard-Jones potential is
\[ V_{LJ}(r) = \epsilon_0 \left( \frac{r_0}{r} \right)^{12} - 2 \left( \frac{r_0}{r} \right)^6. \]
At \( r = r_0 \), \( V_{LJ} = -\epsilon_0 \) and \( \frac{dV_{LJ}}{dr} = 0 \).
A difficulty with using \( V_{LJ} \) for simulations is that it goes to zero only slowly as \( r \) increases. A solution is the "shifted-force" potential.
\[ V_{SF}(r) = V_{LJ}(r) - V_{LJ}(r_c) - (r - r_c) \left( \frac{dV_{LJ}}{dr} \right)_{r=r_c} \]
for \( r \leq r_c \), zero for \( r \geq r_c \). The cut-off distance \( r_c \) marks the end of the shifted-force potential's range.
An advantage to the shifted-force potential is that it and its derivative are continuous and are zero beyond \( r_c \). A disadvantage is that \( V_{SF} \) and \( V_{LJ} \) differ slightly in shape and depth.
Let \( r_c = 6r_0 \).
Calculate \( \frac{1}{\epsilon_0} V_{SF}(r_0) \) and \( \frac{r_0}{\epsilon_0} \frac{dV_{SF}}{dr} \) at \( r = r_0 \). Note that both answers are unitless numbers.

9. Here is a potential-energy function for anharmonic vibration:
\[ \Phi(r) = -\epsilon_0 + \frac{1}{2} \kappa (r - r_0)^2 - \frac{\kappa a}{2r_0} (r - r_0)^3 \]
where \( a \) is a small unitless constant that represents anharmonicity. The probability distribution is
\[ f(r) = N_a \exp \left( -\frac{\kappa (r - r_0)^2}{2k_B T} + \frac{\kappa a (r - r_0)^3}{2r_0 k_B T} \right) \]
The normalization constant, \( N_a \approx \left( \frac{\kappa}{2\pi k_B T} \right)^{1/2} \); equal if \( a = 0 \).
The Taylor series for \( \langle r - r_0 \rangle \), expanded in \( a \) and truncated to the first-order term, is
\[ \langle r - r_0 \rangle = \left( \frac{d \langle r - r_0 \rangle}{da} \right)_{a=0} a \]
(1) Write the integral that equals \( \langle r - r_0 \rangle \).
(2) Write the expression for the derivative of \( \langle r - r_0 \rangle \), the integral, with respect to \( a \). Simplify the derivative for the case \( a = 0 \).
(3) Use the Taylor-series expression given above to write a simple expression for \( \langle r - r_0 \rangle \). Based on your result, what is the effect of temperature on \( \langle r - r_0 \rangle \)?