Homework 3 (due Sept. 26, 2019)

(1) More on the *Keesom* energy **(15 pts)**

Two molecules with permanent dipole moment $\boldsymbol{\mu}_i = q_i \boldsymbol{d}_i$ (bold symbols indicate vectors) are fixed in their center positions with $\boldsymbol{r}_{12} = \boldsymbol{r}_1 - \boldsymbol{r}_2 \equiv \boldsymbol{r}$. If the dipole orientations are also fixed, their interaction potential is

$$U_{dipole} = -\frac{\mu_1 \mu_2}{2\pi\varepsilon\varepsilon_0} \cdot \frac{1}{r^3} .$$

However, if they rotate freely due to thermal energy, the interaction potential is

$$U_{Keesom} = -\frac{\mu_1^2 \mu_2^2}{3k_B T \left(4\pi\varepsilon\varepsilon_0\right)^2} \cdot \frac{1}{r^6} .$$

Apparently, the equations for these interaction potentials break down for $r \to 0$, where they predict singularities. But already at small, yet finite (non-zero) r values, they lead to unphysical results. For example, because U_{Keesom} increases more rapidly than U_{dipole} for $r \to 0$, a cross-over in r is expected, below which the rotating dipoles would attract more strongly than the two static, aligned dipoles with $\boldsymbol{\mu}_1 \parallel \boldsymbol{\mu}_2 \parallel \boldsymbol{r}$ (*i.e.*, the highest possible interaction energy between two dipoles)—clearly an unphysical result.

a) From this analysis, develop a criterion for the critical distance r_{crit} between two identical dipoles, below which the formula for the Keesom interaction must break down. Write this result in terms of the Bjerrum length, l_B.

b) Using the criterion derived in (a), estimate whether the attraction between H_2O molecules in fluid water ($\mu_w = 1.85$ D where 1 D(ebye) = 3.335×10^{-30} Cm, $\varepsilon_w = 80$) can be approximated by the Keesom term. For this estimate, derive the average distance r between H_2O molecules from the water density and the molecular weight of H_2O. (Avogadro's number is $N_A = 6.022\times10^{-23}$)

(2) Lenard-Jones potential **(15 pts)**

A common form used for the interaction potential between neutral molecules is the Lennard-Jones potential $U(r) = 4\varepsilon[(r_0/r)^{12} - (r_0/r)^6]$, depicted below, where r is the distance between the molecules, ε is the depth of the potential well and r_0 is the distance at which U crosses zero.

a) What is the force $\boldsymbol{F}$ between two molecules at a distance r? Show that the expression you obtained has the correct physical dimensions of a force.

b) What is the distance r_m between the molecules at which $U(r)$ obtains its minimum?