Chemistry 410B **Exam 3** **Spring 2008**

Solutions

1. Consider a molecular dynamics simulation using a square well potential where

$$u_{\rm sq}(R) = \begin{cases} \infty & \text{if } R \leq R_1 \\ -\epsilon & \text{if } R_1 < R \leq R_2 \\ 0 & \text{if } R > R_2 \end{cases} .$$

   (a) What is this force when A and B are separated by a distance $2R_2$? **Solution:** This is in the flat region where $u_{\rm sq}(R) = 0$, so the force $F = -du(R)/dR$ equals $\boxed{0}$.

   (b) What is this force when A and B are separated by a distance $(R_1 + R_2)/2$? **Solution:** This is in another flat region, where $u_{\rm sq}(R) = -\epsilon$, but the force is still $\boxed{0}$ because $u(R)$ is still a constant.

   (c) Use the change in potential energy to find an approximate expression for this force when the distance between A and B changes from $R_2 + (\Delta R/2)$ to $R_2 - (\Delta R/2)$, where $\Delta R \ll R_2 - R_1$. **Solution:** In this case, we can estimate the derivative numerically:

$$F = -\frac{du(R)}{dR} \approx -\frac{\Delta u(R)}{\Delta R} = -\frac{-\epsilon}{\Delta R} = \frac{\epsilon}{\Delta R}.$$

2. What will be the average speed (*not* relative speed) of $^{19}F_2$ molecules in a sample where the average collision energy is 15.0 kJ mol^{-1}? **Solution:** The average collision energy depends only on the temperature, so we use that to get T. Then we can calculate $\langle v \rangle$ from T and the molecular mass. Because the energy is given as a *molar* energy, we can use this to calculate the mass in molar units as well:

$$\langle E_{\rm AA} \rangle = \frac{3k_BT\mathcal{N}_A}{2} = \frac{3RT}{2}$$

$$T = \frac{2\langle E_{\rm AA} \rangle}{3R}$$

$$\langle v \rangle = \sqrt{\frac{8k_BT}{\pi m}} = \sqrt{\frac{8RT}{\pi \mathcal{M}}} = \left[\frac{8R(2\langle E_{\rm AA} \rangle/3R)}{\pi \mathcal{M}}\right]^{1/2}$$

$$= \left[\frac{16\langle E_{\rm AA} \rangle)}{3\pi \mathcal{M}}\right]^{1/2} = \left[\frac{16(15.0 \cdot 10^3 \text{ J mol}^{-1}}{3\pi(0.038 \text{ kg mol}^{-1})}\right]^{1/2} = \boxed{819 \text{ m s}^{-1}}.$$

3. If we flip a coin an even number of times N, there's a chance that we will get an equal number of heads and tails.

   (a) Find a general expression for this probability in terms of N. **Solution:** This is solving for $\mathcal{P}(k)$ when $k = 0$ (same number of steps in each direction):

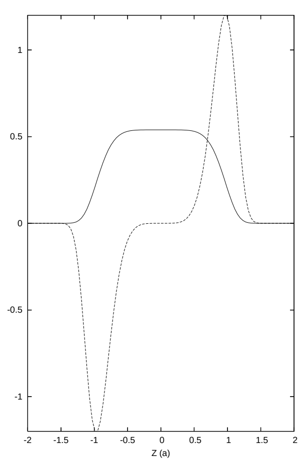
$$\mathcal{P}(k = 0) = \frac{N!}{2^N \frac{N+k}{2}! \frac{N-k}{2}!} = \frac{N!}{2^N \frac{N}{2}! \frac{N}{2}!} = \frac{N!}{2^N \left(\frac{N}{2}!\right)^2}$$

(b) Find the minimum number of flips so that this probability is less than 1/3. **Solution:** This equation gives 1/2 for $N = 2$, 3/8 for $N = 4$, and 5/16 for $\boxed{N = 6}$ flips.

4. A liquid is added to solvent with an initial (normalized) distribution at $t = 0$ of $\mathcal{P}(()Z) = Ae^{-(Z/a)^6}$, where $A = 0.53896$. This is a nearly constant value from $Z = 0$ to $Z = \pm a$, where it rapidly drops to zero. Find an expression for the flux as a function of Z, and sketch that function on the graph below. **Solution:** The number density will be proportional to the probability $\mathcal{P}(Z)$, so $\rho = \rho_0 A e^{-(Z/a)^6}$, where ρ_0 is the number density over the whole sample. Then use Fick's first law to get the flux:

$$J(Z) = -D\left(\frac{d\rho}{dZ}\right) = -D\frac{d}{dZ}\left(\rho_0 A e^{-(Z/a)^6}\right) = D\rho_0 A\left(\frac{Z^5}{a^6}\right)e^{-(Z/a)^6}.$$

Even without the math, we know the result – the flow will be where the concentration changes fastest, along the walls of the distribution. Where the density is roughly constant, the flow will be close to zero. The flux at $-Z$ is negative because it is in the $-Z$ direction.



5. Find the value of the absorption coefficient (including units) of a 0.100 M solution of pyrene that absorbs 12% of the radiation intensity when the pathlength is 1.00 cm. **Solution:** We use Beer's law and solve for ϵ. If 12% of the intensity is absorbed, then $I/I_0 = 0.88$:

$$\log_{10}\frac{I}{I_0} = -\epsilon c l$$

$$\epsilon = -\frac{1}{cl}\log_{10}\frac{I}{I_0} = -\frac{1}{(0.100\ M)(1.00\ \text{cm})}\log_{10}(0.88) = \boxed{0.56\ \text{L mol}^{-1}\ \text{cm}^{-1}}.$$