Homework 4

Reduced Lennard Jones Units

The units of temperature can be expressed as $[\epsilon/k_b] = $ Joules*Kelvin/(Joules) = Kelvin. So to convert to the real energy

$$T = T^* \frac{\epsilon}{k_B} = 300 \ K$$

Similarly we have that $[\rho] = [m * N_m/\sigma^3]$. Where N_m is the number of molecules (30) and m is the mass per molecule (which which is derived from the g/mol by multiplying by $1/N_A$). Then

$$\rho = \rho^*(30 \cdot 40/(N_A(3.3 \cdot 10^{-7})^3 \ cm^3) = 1407.83 \ g/cm^3$$

And $[\Delta t] = [\sigma\sqrt{m_{kg}/k_b\epsilon}]$, where m_{kg} is the mass in SI units:

$$\Delta t = \Delta t^* \sigma\sqrt{m/\epsilon} = (0.005) \cdot 3.3 \cdot 10^{-10} \cdot \sqrt{0.04/k_b300} = 4.0 \cdot 10^{-14} \ s$$

Fokker-Planck Equation Derivation

We assume that the hopping process is Markovian, therefore $\mathbb{P}(x, t + \Delta t)$ depends only on the probability of being in the current state times the probability of transition.

   We further assume that the transition probability of moving a distance greater than a is zero. Then there are only three transition probabilities

$$\begin{cases} \text{Right} & k_+\Delta t \\ \text{Left} & k_-\Delta t \\ \text{Stay} & 1 - (k_+\Delta t + k_-\Delta t) \end{cases}$$

The total probability is the sum of the probability of each state times its above transition. Now consider the Taylor Expansions:

$$\mathbb{P}(x, t + \Delta t) = \mathbb{P}(x, t) + \Delta t \frac{\partial \mathbb{P}}{\partial x}$$

$$\mathbb{P}(x \pm a, t) = \mathbb{P}(x, t) \pm a\frac{\partial \mathbb{P}}{\partial x} + \frac{a^2}{2}\frac{\partial^2 \mathbb{P}}{\partial x^2}$$

If we rewrite the change in the probability using the transition probabilities from a above as

$$\frac{\mathbb{P}(x, t + \Delta t) - \mathbb{P}(x, t)}{\Delta t} = \mathbb{P}(x, t)(x, t)(-k_+ - k_-) + \mathbb{P}(x \pm a, t)k_\pm$$

$$\frac{\partial \mathbb{P}(x, t)}{\partial t} = \mathbb{P}(x, t)(x, t)(-k_+ - k_-) + \left(\mathbb{P}(x, t) \pm a\frac{\partial \mathbb{P}}{\partial x} + \frac{a^2}{2}\frac{\partial^2 \mathbb{P}}{\partial x^2}\right)k_\pm$$

Where take the continuum limit in the second line and apply the second Taylor Expansion. Rearranging we get that

$$\frac{\partial \mathbb{P}(x,t)}{\partial t} = a(k_+ - k_-)\frac{\partial \mathbb{P}}{\partial x} + \frac{a^2}{2}(k_+ + k_-)\frac{\partial^2 \mathbb{P}}{\partial x^2}$$

Now define $D \equiv a^2(k_+ + k_-)/2$ and $v \equiv a(k_- - k_+)$.

These define the diffusion term (the changing standard deviation of the final probability distribution) and the mean shift term/velocity respectivly, in terms of these the final Fokker-Planck Equation is

$$\boxed{\frac{\partial \mathbb{P}(x,t)}{\partial t} = -v\frac{\partial \mathbb{P}}{\partial x} + D\frac{\partial^2 \mathbb{P}}{\partial x^2}}$$

Which reduces to the simple diffusion equation if the movement is unbiased ie $k_- = k_+$:

$$\frac{\partial \mathbb{P}(x,t)}{\partial t} = D\frac{\partial^2 \mathbb{P}}{\partial x^2}$$