Mutual and self diffusion

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This exercise sheds light on mixing by diffusion (mutual diffusion), self diffusion and random walk. The extract from a text by Anders Malthe-Sørenssen "virrevandrer_diffusjon.pdf" may also be useful background for this exercise.

I. DIFFUSION AS A MIXING PROCESS

Diffusion equation:

$$J = -D_{12}\frac{\partial \rho}{\partial y} \tag{1}$$

Divergence theorem (continuity equation)

$$\frac{\partial \rho}{\partial t} + \nabla J = 0 \tag{2}$$

Combine the two to get the partial differential equation for diffusion:

$$\frac{\partial \rho}{\partial t} + D_{12}\frac{\partial^2 \rho}{\partial y^2} = 0 \tag{3}$$

Starting with particles in $y = 0$ at time $t = 0$: $\rho(t = 0, y) = \delta(y)$, where δ is the Kroeneker delta function the diffusion equation has solution (you may easily verify this):

$$\rho(t, y) = \frac{1}{\sqrt{4\pi D_{12}t}}\exp(-\frac{y^2}{4D_{12}t}) \tag{4}$$

This is a Gaussian distribution with mean $y = 0$ and standard deviation $\sqrt{4Dt}$. Thus the width of the distribution is proportional to the square root of the diffusion coefficient. When data is sparse and noisy one always obtains a more precise estimate of the width by integrating over all the data. The second moment of the distribution is:

$$\int_{-\infty}^{\infty} y^2 \rho(t, y) dt = 2D_{12}t \tag{5}$$

where I have used that

$$\int_{-\infty}^{\infty} y^2 e^{-y^2/a} dt = \frac{\sqrt{\pi}}{2}a^{3/2} \tag{6}$$

II. RANDOM WALK AND SELF DIFFUSION

The Matlab program random_walk.m simulates N_{walk} random walkers moving N_{step} steps. They are all released at $y = 0$ at time $t = 0$ and are an approximation to a delta function. The distribution of positions is at all times Gaussian (when enough walkers are used) and the width and second moment are related to the diffusion coefficient as above. Put labels on the axes of the plots and calculate the diffusion coefficient of the random walker. In addition to the macroscopic picture of the diffusion equation we have information of the position of every single walker at all times. From this we may calculate the mean square dsplacement (MSD), $< y^2 >$, the slope of which equals $2D$. Does this definition of the diffusion coefficient match the macroscopic? How does all this relate to the random walker in exercise 6.1 (p. 191)?

III. SELF AND MUTUAL DIFFUSION IN MD

We have slightly modified the introductory example of atomify. In addition to measuring the MSD and self diffusion coefficients of the ligh and heavy atoms it now also counts the number of light and heavy atoms in 20 bins along the cell.

Start atomify, open the input file in.diffusion_mut_self and start the execution. By holding your mouse over chunkID in the analysis pane to the right the measurement bins (chunks) will be highlighted in the rendering. By clicking msd_light and msd_heavy you may view and save plots of the two MSDs. The program will write chinkID, number of light, number of heavy to the file count.txt every 1000 timesteps. Open the file count.txt and copy the data into Matlab or python to analyze the distributions. These distributions may be analyzed in the same manner as the random walk distributions were analyzed. The main difference is that now the distribution of light particles measures the mutual diffusion, D_{12} of light and heavy particles.

Can you find a relation between the mutual diffusion D_{12} and the two self diffusion coefficients D_1 and D_2?