ENVIRONMENTAL PHYSICS COMPUTER LAB #5: Pollutant Diffusion

We simulate the diffusion of a pollutant in air. In this lab we will learn about the Einstein- Smoluchowsky law of diffusion. We will study the diffusion of CO_2 molecules in air. Throughout this worksheet I will use SI units (meters, seconds, kg) but I will not use Mathcad's units which will slow the computations.

Number of molecules: $N := 100$

i is the particle index: $i := 0 .. N-1$

j is the time index: $J := 1000$ $\quad j := 0 .. J-1$

Time is j*Δt.

Δt is time interval between collisions
I have estimated this value from the measured value of the diffusion constant and $D = (k_BT/m)(\Delta t/2)$ assuming room temperature.

$$\Delta t := 5.8\cdot10^{-10}$$

Start with the N molecules from a random configuration inside a small cube of side size 1 micron.

$$s := 10^{-6}$$

$$x_{i,0} := \left(\text{rnd}(1) - \frac{1}{2}\right)\cdot s \qquad y_{i,0} := \left(\text{rnd}(1) - \frac{1}{2}\right)\cdot s \qquad z_{i,0} := \left(\text{rnd}(1) - \frac{1}{2}\right)\cdot s$$

The new position of a molecule is $x_{new} = x_{old} + \Delta x$, $y_{new} = y_{old} + \Delta y$, and $z_{new} = z_{old} + \Delta z$, where $\Delta x = v_x\Delta t$, $\Delta y = v_y\Delta t$, and $\Delta z = v_z\Delta t$. The velocities v_x, v_y and v_z are random variables each normally distributed: v~N(meanv,σ). This is the Maxwell-Boltzmann distribution. The variance is $\sigma^2 = k_BT/m$ and in the absence of a driving force the mean of v is zero. First we input the Boltzmann constant (in j/K) the temperature (in K) and the molecular mass for CO_2 (in kg).

$$k_B := 1.381\cdot10^{-23} \qquad T := 300 \qquad m := 7.35\cdot10^{-26}$$

$meanvx := 0$ $\quad$ $meanvy := 0$ $\quad$ $meanvz := 0$

$$\sigma x := \sqrt{\frac{k_B \cdot T}{m}} \qquad \sigma y := \sqrt{\frac{k_B \cdot T}{m}} \qquad \sigma z := \sqrt{\frac{k_B \cdot T}{m}}$$

$$\sigma x = 237.418 \qquad \sigma y = 237.418 \qquad \sigma z = 237.418$$

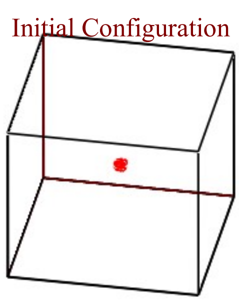
$$vx_{i,j} := rnorm(N, meanvx, \sigma x)_i$$

$$vy_{i,j} := rnorm(N, meanvy, \sigma y)_i$$

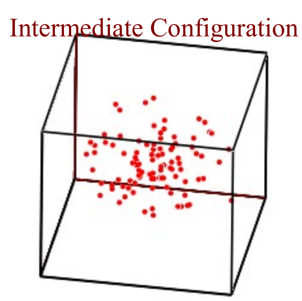
$$vz_{i,j} := rnorm(N, meanvz, \sigma z)_i$$

$$\begin{pmatrix} x_{i,j+1} \\ y_{i,j+1} \\ z_{i,j+1} \end{pmatrix} := \begin{pmatrix} x_{i,j} + vx_{i,j} \cdot \Delta t \\ y_{i,j} + vy_{i,j} \cdot \Delta t \\ z_{i,j} + vz_{i,j} \cdot \Delta t \end{pmatrix}$$

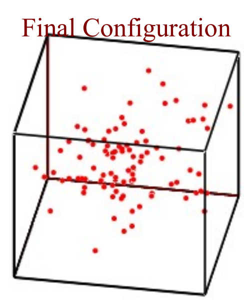
We approximate the time between collisions to be constant. In reality it is a random variable following the Poisson (exponential) distribution.
We represent the N molecules in space by using 3D Scatter Plot from the Graph Palette. From Format Graph 3D, Axes choose for x and y and z the range -10 to 10. We show below the initial configuration, an intermediate configuration and the final configuration:



$$\left(\frac{x^{\langle 0 \rangle}}{s}, \frac{y^{\langle 0 \rangle}}{s}, \frac{z^{\langle 0 \rangle}}{s}\right)$$



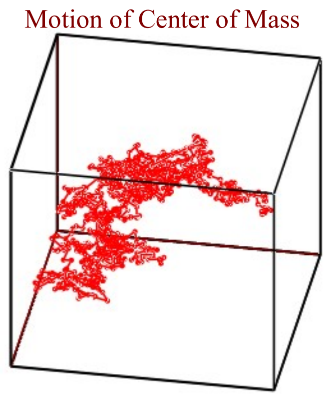
$$\left(\frac{x^{\langle \frac{J}{2} \rangle}}{s}, \frac{y^{\langle \frac{J}{2} \rangle}}{s}, \frac{z^{\langle \frac{J}{2} \rangle}}{s}\right)$$



$$\left(\frac{x^{\langle J \rangle}}{s}, \frac{y^{\langle J \rangle}}{s}, \frac{z^{\langle J \rangle}}{s}\right)$$

We look next at the motion of the center of mass of the gas.

$$xcm_j := \frac{1}{N}\cdot\sum_{i=0}^{N-1} x_{i,j} \qquad ycm_j := \frac{1}{N}\cdot\sum_{i=0}^{N-1} y_{i,j} \qquad zcm_j := \frac{1}{N}\cdot\sum_{i=0}^{N-1} z_{i,j}$$



$$\left(\frac{xcm}{s}, \frac{ycm}{s}, \frac{zcm}{s}\right)$$

Finally we compute the square of the distance between the initial position and the current position for each molecule:

$$rsqr_{i,j} := \left(x_{i,j} - x_{i,0}\right)^2 + \left(y_{i,j} - y_{i,0}\right)^2 + \left(z_{i,j} - z_{i,0}\right)^2$$

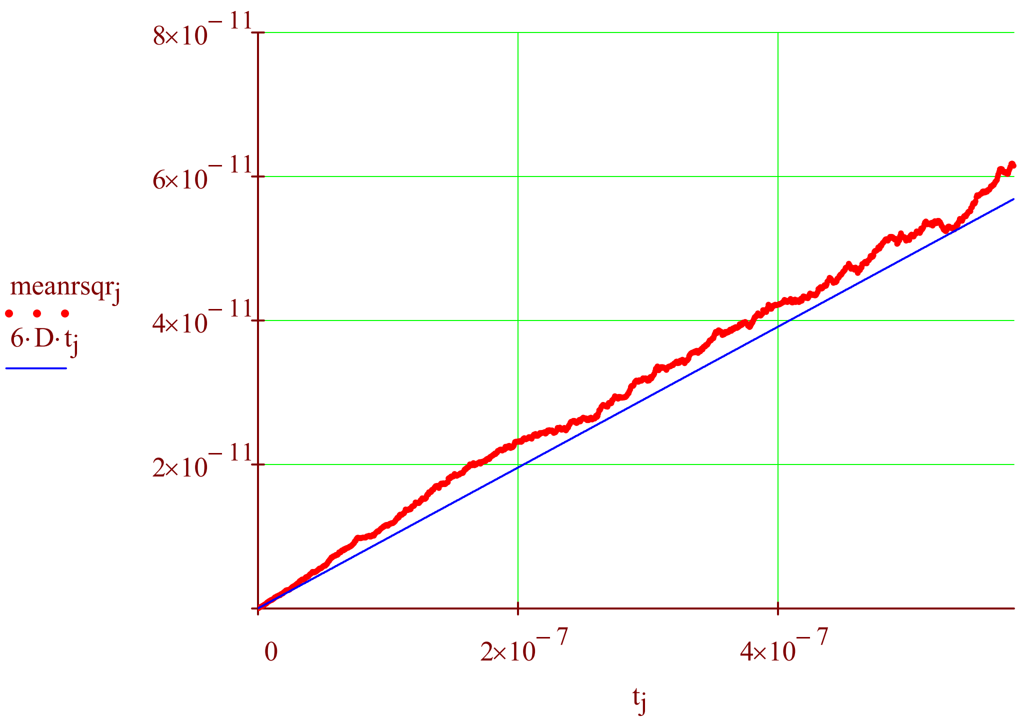
Then we calculate the mean of the squared distance for the N particles.

$$meanrsqr_j := \frac{1}{N}\cdot\sum_{i=0}^{N-1} rsqr_{i,j}$$

According to the diffusion law (discovered independently by Albert Einstein in 1905 and the Polish physicist Smoluchowski) the average of the square of the displacemnt $<r^2>$ increases linearly in time: $<r^2> = 6*D*t = 6(k_BT/m)*\tau*t$, where the diffusion constant is $D = (k_BT/m)*\tau$ and τ is the collision time.

To compare our numerical simulation to the Einstein-Smoluchowski diffusion law note that the time is: $t = j*\Delta t$ and $\Delta t = 2\tau$ is average time between last and next collision. For carbon dioxide diffusing in air $D = 16.4*10^{-6}\ m^2/s$. (Source: Environmental Physics by Boeker, Grondelle page 189).

$$\tau := \frac{1}{2}\cdot\Delta t \qquad D := \frac{k_B\cdot T}{m}\cdot\tau \qquad t_j := j\cdot\Delta t$$



Application: How long does it take for the CO_2 pollutant to diffuse for a distance of 1cm?

Answer: From $\langle r^2 \rangle = 6Dt$ we get $t = \langle r^2 \rangle/(6D) = \frac{0.01^2}{6\cdot 16.4\cdot 10^{-6}} = 1.016$ seconds.

The ideal gas has only kinetic energy:

$$E_j := \frac{m}{2}\cdot\sum_i \left[\left(vx_{i,j}\right)^2 + \left(vy_{i,j}\right)^2 + \left(vz_{i,j}\right)^2\right]$$

As you have learned in Thermal and Statistical Physics the mean energy of an ideal gas is: $U = 3Nk_BT/2$ and the variance of the energy (energy fluctuation) is given by the Einstein-Gibbs formula: $<\Delta U^2> = k_BT^2C_V$. For an ideal gas the isochoric heat capacity is $C_V = 3Nk_B/2$. So the standard deviation is $<\Delta U^2>^{1/2} = [k_BT^2 3Nk_B/2]^{1/2}$. In the graph below we graph the actual energy E vs time and on the same graph we plot the mean energy, and mean energy +/- standard deviation. Note that most points fall inside this confidence interval. In fact for a large system about 68% of the points should be inside this interval.