Statistical physics

lecture 9

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14-12-2009

X

1. Lets consider a movement of the particle in gas. Kinetic energy of a particle (in a given moment):

$$E_k = \frac{mv^2}{2}$$

2. Colisions change the kinetic energy. How often the molecules colide (e.g. what is the avg. number of colisions of a single H_2O particle during 1s)?

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1. avg. number of colisions of a single H_2O particle during 1s $= 60 * 10^{12}$
2. This is the reason to introduce a "mean kinetic energy". Termodynamics helps in this idea, the absolute temperature of a molecule, T is defined:

$$T \equiv \frac{\overline{mv^2}}{3k}$$

,where k is a Boltzmann constant ($1.38 * 10^{-23} \frac{J}{K}$).

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We will try to use this relation to describe the diffusion process. To simplyfy the process lets consider the movement of a molecule along only one axis (e.g. x). Then:

avg. kin. energy along x-axis $= \frac{\overline{mv_x^2}}{2} = \frac{1}{3}\frac{3kT}{2}$

Since the mass does not change: $m\frac{\overline{v_x^2}}{2} = \frac{kT}{2} \Rightarrow \overline{v_x^2} = \frac{kT}{m}$

$$v_{x,rms} = \sqrt{\overline{v_x^2}} = \sqrt{\frac{kT}{m}}$$

Example: movement of the sucrose..

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Movement of the sucrose

$$m_{suc} = 342u$$

$$\Rightarrow m_p = 0.342kg/6.02 * 10^{-23} mol^{-1} = 5.7 * 10^{-25} kg$$

$$1J = N * m = (\frac{kg * m}{s^2}) * m = \frac{kg * m^2}{s^2}$$

$$v_{x,rms} = \sqrt{\frac{kT}{m_p}} = \sqrt{\left(1.38 * 10^{-23} \frac{J}{K}\right) * 273K/(5.7 * 10^{-25} kg)}$$

$$= \sqrt{0.66 * 10^4 m^2 s^{-2}} = 81m/s$$

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Random walk

1. We start at $t = 0$ with $x = 0$.
2. The particle moves a fixed distance at every τ seconds.
3. The particle moves with the velocity $\pm u_x$. Effective step length is then $\delta = \pm\tau u_x$.
4. The probability of choosing the $\pm$ direction is $1/2$.
5. The $\pm$ direction of each step is independent from previous steps.
6. If we place N molecules in the same time, they are not interfering each other.

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According to these rules, we know that the position of ith particle after n steps differs from its position after $n-1$ steps is δ:

$$x_i(n) = x_i(n-1) + \delta$$

For N particles, the average displacement after n steps:

$$\overline{X}(n) = \frac{1}{N}\sum x_i(n),$$

$$= \frac{1}{N}\sum x_i(n-1) + \frac{1}{N}\sum \delta$$

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Random walk - expectation

Now the last term can be viewed as an expectation of Bernoulli process. $E\left(step\ dist\right) = p\delta + q(-\delta) = 0$

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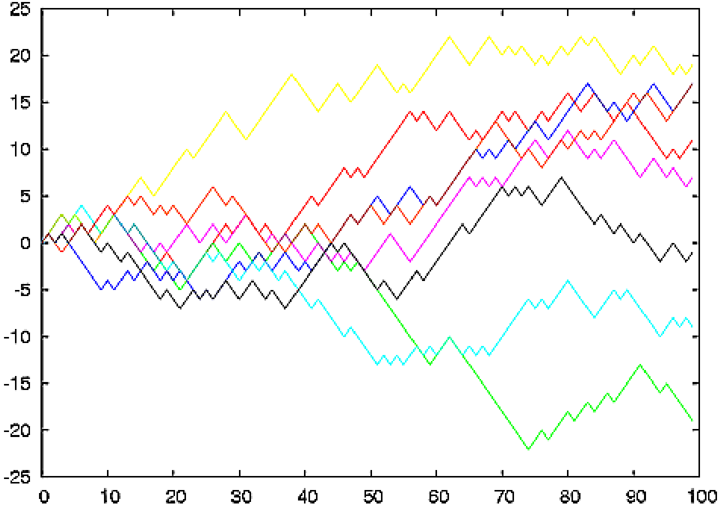

Random walk - variance

Where exactly are we going to find a given particle after a number of steps? The diference of the particle position from the expectation is given by variance. Since the mean was 0, the difference of the ith particle after nth step from the expected position is: $x_i^2(n) = [x_i(n-1) + \delta]^2$

$$\sigma_X^2(n) = \overline{X^2}(n) = \frac{1}{N}\sum [x_i(n-1) + \delta]^2$$

$$= \frac{1}{N}\sum \left[x_i^2(n-1) + 2x_i(n-1)\delta + \delta^2\right]$$

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Random walk - variance

Lets consider the spread of the particles after time t. We know that $n = t/\tau$. Then $X_{rms}(n) = \sqrt{n}\delta = \sqrt{\frac{t}{\tau}}\delta$. Now if we would like to calculate the average velocity of walking particle: $v = x/t \Rightarrow v_{rms} = \sqrt{\frac{1}{t\tau}}\delta$. This means that the "average velocity of diffusion decreases" with time.

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Diffusion coefficient

Diffusion coef. is equal to half of the rate at which the variance of particle location changes through time i.e.

$$D \equiv \frac{1}{2}\frac{d\sigma}{dt}$$

For the one dimensional case $X(n) = \frac{t}{\tau}\delta^2$ so $D = \frac{\delta^2}{2\tau}$. Now we can rewrite: $X_{rms}(n) = \sqrt{\frac{t}{\tau}}\delta = \sqrt{2t\frac{\delta^2}{2\tau}} = \sqrt{2tD}$

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Sucrose

The diffusion coefficient of sucrose in water is: $10^{-9} m^2/s$. So how far a particle of sucrose can move at average during a one second?

$$X_{rms}(1s) = \sqrt{2 * 10^{-9} * 1} m/s < 10^{-4} m/s \ll 81 m/s$$

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Link with Binomial distribution

Lets see the random walk as an istance of Binomial distribution. Then the probability of finding particle at the starting point is:

$$P(x=0) = \binom{n}{n/2} p^{n/2} q^{n/2} = \binom{n}{n/2} (1/2)^n$$

This is coherent with our previous reasoning about the variance.For large n the Binomial distribution can be approximated by the Normal distribution. We have calculated that $\mu = 0, \sigma^2 = \sqrt{2tD}$. From this we can write a PDF:

$$g(x) = f_X(x) = \frac{1}{\sigma\sqrt{2\pi}} e^{-\frac{1}{2}\left(\frac{x-\mu}{\sigma}\right)^2}$$

$$= \frac{1}{\sqrt{4\pi Dt}} e^{-\frac{x^2}{4Dt}}$$

Now, to compute the probability that for a given time t, the particle is between $a < x < b$ we only need to compute the integral of $g(x)$.

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