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Problem set 1: Computational Molecular Physics and Methods of Molecular Simulations

Published: 29th April 2014, 4pm *Please hand in by: 6th May 2014, 4pm*

1. Random walker (Computational, 25 points)
Write a small programme (choosing your favourite programming language) to generate a N-step random walk in 1-D, with each step uniformly distributed on the interval [-0.5,0.5].

(a) Plot the position of the walker over time for three trajectories of different lengths. Looking at single trajectories of N-steps one cannot gather any useful information about the process as each realisation will look differently due to its randomness.

(b) Let's instead look at the emergent properties of an ensemble of these trajectories. Generate 5000 random walks of length N=1, 3, 5 and 10 with the programme you wrote in (a). From these 4 different ensembles of trajectories, compute and plot the histogram (using 50 bins) of the endpoints for all cases (N=1, 3, 5, 10). What can you say about the distribution of end points?

(c) We now turn to a random walk in two dimensions. Write a programme to calculate the endpoints of M random walkers each of N steps, where each step consists of moving in the x and y direction with a step size a uniformly chosen from the interval $[-0.5, 0.5]$. Plot a scatter plot of 10000 walkers of step size N=1 and N=10 in the same plot. What do you observe? Do you have an explanation for why this might happen?

2. Probability distributions (15 points)
In statistical physics one often encounters different probability distributions, three common examples are:
(i) the uniform distribution $\rho(x) = \frac{1}{b-a}$ for $x \leq x \leq b$.
(ii) binomial distribution $\rho(n|N) = \frac{N!}{n!(N-n)!}p^n(1-p)^{N-n}$, where N is the number of trials and n the number of successes.
(iii) the Gaussian distribution $\rho(x) = \frac{1}{\sqrt{2\pi\sigma^2}}\exp[\frac{-x^2}{2\sigma^2}]$.

(a) What are the mean and variance of the distributions (i)-(iii)? Plot an example for each of them.
(b) Suppose we have a particle in 3 dimensions, whose velocity vector has components in each dimension v_x, v_y and v_z that are independent and Gaussian distributed. The over all velocity distribution becomes a product of the three Gaussians:

$$\rho(v_x, v_y, v_z) = \sqrt{\frac{m}{2\pi k_B T}}\exp\left[\frac{-mv_x^2}{2k_BT}\right] \times \sqrt{\frac{m}{2\pi k_B T}}\exp\left[\frac{-mv_y^2}{2k_BT}\right] \times \sqrt{\frac{m}{2\pi k_B T}}\exp\left[\frac{-mv_z^2}{2k_BT}\right]$$

Show that the mean kinetic energy per dimension is $k_BT/2$. Here m is the mass of the particle, T the temperature and k_B the Boltzmann constant.

3. Energy minimization (10 points) (Optional for those who do not attend Thursday's lectures)

In C2v symmetry the water (H_2O) molecule can be defined by two internal coordinates: the bond lenght between an O and H-atom and the H-O-H angle, between the two O-H bonds. The O-H ond lengths are then defined to have equal length.

Given is the following energy function

$$V_{water} = \Sigma_{bonds} \frac{1}{2} k_{bond} \left(bond - bond_0\right)^2 + \Sigma_{angles} \frac{1}{2} k_{angle} \left(angle - angle_0\right)^2 \quad (1)$$

with

$$k_{bond} = 450.0 kcal/mol Angstrom^2$$
$$k_{angle} = 55.0\, kcal/rad^2$$
$$bond_0 = 0.9572 Angstrom$$
$$angle_0 = 104.52\, degree$$

(a) How many bonds and how many angles have to be summed up?

(b) Starting at a water molecule with i) 90 degree angle and ii)linear (180 degree), which angle will the optimised water geometry show after

a steepest descent optmisation?

a Newton optimisation?

(c) How many steps (iterations) does the Newton optimisation need?