

Chem 860. Homework 4 Due: Mar. 9th

Molecular Dynamics simulation in different ensembles, umbrella sampling

February 21, 2009

1 Pencil exercise

1. Using the definition of T.C.F., show that

$$C_{AA}(\tau) = \langle A(0)A(\tau) \rangle \leq \langle A^2 \rangle$$

Can you think of any simple system in which the equal sign holds from time to time?

Hint: The Schwartz's inequality is, in the general form,

$$|\sum_i A_i B_i|^2 \leq (\sum_i A_i^2)(\sum_i B_i^2)$$

2. Generalize the discussion in class on umbrella sampling from “unbiasing” probability distribution to “unbiasing” general observables. That is, show that for any observable \hat{A} , the true ensemble average can be obtained from biased simulations with an umbrella potential, U^{umb} ,

$$\langle \hat{A} \rangle = \langle \hat{A} e^{\beta U^{umb}} \rangle_b / \langle e^{\beta U^{umb}} \rangle_b$$

where the subscript “b” emphasizes that the average is taken over the biased ensemble.

3. **Bonus** Another widely used thermostat is the “temperature coupling” of Berendsen et al. (*J. Chem. Phys.* 81, 3684, 1984). This method, however, does NOT generate the canonical ensemble exactly. In this algorithm, the temperature of the system is controlled by scaling the velocities to every time step with a factor $\lambda = \sqrt{1 + \Delta t / \tau_T (T_0/T - 1)}$, in which T_0 is the desired temperature, T is the actual temperature, Δt is the time step and τ_T is an input constant.

- Show that this scaling is equivalent to a temperature coupling of the system with a heat bath at $T = T_0$, $J = \alpha(T_0 - T)$, in which J is the heat flux and α is the heat transfer coefficient.
- What is the relationship between α and τ_T ?

2 Computational exercise

Related CHARMM scripts are in: hw4.tar.

1. Radial distribution function and velocity auto correlation function of water.

Use `tip3_box_rdf_vac.inp` to run a set of short MD runs. Compute the radial distribution functions ($g_{OO}(r)$, $g_{OH}(r)$, $g_{HH}(r)$). Also estimate the self diffusion constant of water using two different approaches: (1). The Einstein relation, $\langle \Delta \mathbf{r}^2 \rangle = 6Dt$; (2) Integrate the velocity auto-correlation function. Compare the results to available experimental data that you can find in the literature, make some comments on what you found.

Comment: Note that we are using a simple non-bond cut-off scheme here instead of Ewald summation. We will compare to Ewald result later. In fact, what IS the non-bond cut-off scheme that we are using?

2. Repeat the simulation using canonical ensemble - i.e., use Nose-Hoover instead and observe the same set of quantities. Explore the effect of changing “ Q ”.
3. Umbrella sampling for the isomerization of cyclohexane in the “gas-phase” (we used Langevin dynamics with a finite friction constant to maintain the average T).

With this exercise, you’ll get some flavor of umbrella sampling. Look at the input file `umbrella.inp`, try to understand what’s going on. First figure out the range of the reaction coordinate between the chair and boat forms. Look at the data file after the calculation (`data:rxn2.stt`) and plot the PMF as a function of the reaction coordinate (the first column is the reaction coordinate, the second is the PMF, the third is the histogram); the single window simulation used here may not be sufficient to cover the entire range. Comment on the statistics and convergence. **Bonus:** perform multiple window simulations, and use a WHAM code to construct the PMF for the entire conversion process. *Hint: The instantaneous values of the reaction coordinate can be found in the “trace” file, e.g., `rxn2mean.trc`, which can be used for the WHAM calculations. An example of WHAM code can be found at: <http://dasher.wustl.edu/alan/wham.tgz>. For more info regarding the `rxncor` module in CHARMM, see `doc/umbrella.doc`.*