Project III
Chemistry 5021/8021, Computational Chemistry, Spring, 2005
Assigned: March 2, 2005. Due: April 6, 2005

This project is to practice "free energy" simulation methods. In addition, this project will provide an introduction to solvation effects. Through these two problems, you will learn two useful modules in CHARMM, the umbrella sampling technique by the RXNCOR function, and FEP by the BLOCK approach. There are at least two other ways implemented in CHARMM to perform FEP calculations, but once you are familiar with rxncor and block, it will be convenient to learn other methods in the future when you need them. CHEM5021 needs to do only problem (1). CHEM8021 needs to do both.

1. "Gauche effect" describes the phenomenon that the gauche population of n-butane is enhanced in aqueous solution relative to that in the gas phase and in pure liquid butane. Use "RXNCOR" to define the dihedral angle (ϕ) about the C2 and C3 carbons of n-butane as the reaction coordinate. Then, calculate the potential of mean force as a function of ϕ by carrying out umbrella sampling simulations of one butane molecule in a cubic box containing 212 water molecules. Use periodic boundary conditions along with the NPT ensemble at 25 ^{o}C and 1 atm. Based on the computed potential of mean force, compute the total gauche population of butane in water. Compare your results with that of n-butane in the gas phase, determined from the Boltzmann distribution using the torsional potential energyE(ϕ). Explain the origin of the gauche effect.

   By symmetry, you only need to sample the conformational space from 0 to 180^{o}. Use $U_b(\phi) = -E(\phi)$ as the biasing potential, and divide the umbrella sampling into 3 to 5 "windows". Each window should consist of 5 ps of equilibration and 10 ps of data averaging. You should try to prepare your work carefully so that you do not waste a lot of computer time (*then, you might have to use your own laptop, and it will take more time that you really want…*).

2. Use the "BLOCK" function to determine the relative free energy of hydration between Cl^- and Br^- anions in water. Construct the simulation system similarly as in (1): one solute (actually two in the BLOCK-FEP calculation) in a cubic box consisting of 215 water. Perform all simulations using periodic boundary conditions along with the NPT ensemble at 25 ^{o}C and 1 atm. You only need to run one simulation to complete this problem as the perturbation is small. This simulation should also last 5 ps for equilibration, plus 10 ps for averaging. Compare your results with experimental data. Rationalize your findings by the Born model of solvation.