

Assignment 14: Advanced Exercises in Molecular Dynamics

1. Calculate the ‘natural’ time unit for molecular dynamics simulations of biomolecules from the relation: energy = mass * (length/time)², to obtain the time unit τ corresponding to the following units:

$$\begin{array}{lll} \text{length} & (\text{l}): & 1 \text{ \AA} = 10^{-10} \text{ m} \\ \text{mass} & (\text{m}): & 1 \text{ amu} = 1 \text{ g/mol} \\ \text{energy} & (\text{v}): & 1 \text{ kcal/mol} = 4.184 \text{ kJ/mol.} \end{array}$$

Estimate the “quantum mechanical cutoff frequency”, $\omega_c = kT/\hbar$ at room temperature ($\sim 300^\circ \text{ K}$).

2. Derive the amplitude decay rate of $\gamma/2$ for an underdamped harmonic oscillator due to *friction* by solving the equations of motion:

$$m \frac{d^2 x}{dt^2} = -kx - m\gamma \frac{dx}{dt} \quad (\text{D.18})$$

and examining time behavior of the solution.

3. Derive the amplitude decay rate of $\omega^2(\Delta t)/2$ *intrinsic* to the *implicit-Euler* scheme by solving the discretized form of eq. (D.18).
4. Compare your answer in problem 2 above with behavior of the *explicit-Euler* solution of eq. (D.18).
5. Compare molecular and Langevin dynamics simulations of two water molecules by the Verlet discretization of the equation of motion and its Langevin analog. Use the “SPC” *intermolecular* potential, given by:

$$E = \sum_{\substack{(i,j) \equiv (\text{O},\text{O}) \text{ pairs} \\ i < j}} \left[\frac{-A}{r_{ij}^6} + \frac{B}{r_{ij}^{12}} \right] + \sum_{\substack{(k,\ell) \equiv \text{intermolecular} \\ (\text{O},\text{O}), (\text{O},\text{H}), (\text{H},\text{H}) \text{ pairs} \\ k < \ell}} \left[\frac{Q_k Q_\ell}{r_{k\ell}} \right]$$

where

$$\begin{aligned} A &= 626 \text{ (kcal \AA}^6\text{)}/\text{mol} \\ B &= 629 \times 10^3 \text{ (kcal \AA}^{12}\text{)}/\text{mol} \\ Q_{\text{H}} &= 0.41 e \\ Q_{\text{O}} &= -0.82 e . \end{aligned}$$

A numerical factor of 332 is needed in the electrostatic potential to obtain energies in kcal/mol with the coefficients above. For simplicity, assume that *intramolecular* geometries are rigid: $r_{\text{OH}} = 1 \text{ \AA}$, $\cos \theta_{\text{HOH}} = -1/3$. (You can use harmonic soft constraints). Begin by first minimizing the energy

of the water dimer and examining the hydrogen bond geometry (hydrogen-bond distance and angle θ between the hydrogen-bond vector and bisector of the acceptor molecule). Then study numerical behavior of the two models/schemes as a function of Δt , and examine the hydrogen bond geometry. Experiment with $\Delta t = 1, 2, 5,$ and 10 fs and use γ values in the range of 1 to 50 ps^{-1} . If you are more ambitious, continue to study energy-minimized structures of water clusters of larger sizes and their dynamics. Analyze the hydrogen bonding networks of these clusters.

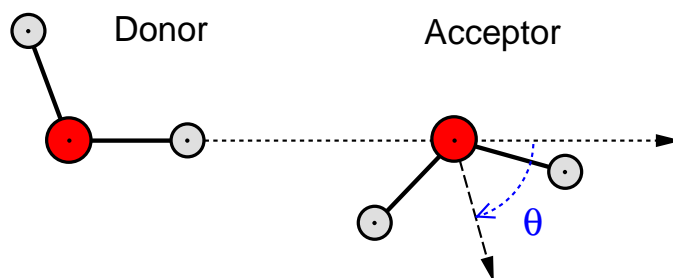


Figure D.4. Hydrogen bond geometry: The angle θ is defined between the Hydrogen-bond vector and the bisector of the acceptor molecule.

Some Useful Constants and Conversion Factors

Avogadro's Number	$N_A = 6.0221 \times 10^{23} \text{ mol}^{-1}$
Planck's Constant	$h = 6.6261 \times 10^{-34} \text{ Jsec}$
	$\hbar = h/2\pi = 1.055 \times 10^{-34} \text{ Jsec}$
Boltzmann's Constant	$k_B = 1.38066 \times 10^{-23} \text{ JK}^{-1}$
Gas Constant	$R = k_B N_A = 8.3145 \text{ JK}^{-1} \text{ mol}^{-1}$
Atomic Mass Unit, amu	$(1/N_A) = 1 \text{ g/mol} = 1.6605 \times 10^{-27} \text{ kg}$
	$\pi = 3.14159$
	$1 \text{ kcal} = 4.184 \text{ kJ}$