Universität of Göttingen
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Methods of Computational Physics
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Sheet 2: Molecular Dynamics Simulation

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- **Harmonic Oscillator in the microcanonical ensemble**

  Consider the one-dimensional harmonic oscillator with the Hamiltonian

  $$\mathcal{H}'(q', p') = \frac{p'^2}{2m} + \frac{1}{2} m\omega^2 q'^2 \tag{1}$$

  where q' and p' denote the position and linear momentum of the particle, respectively. m is the mass of the particle and ω characterizes the frequency of the oscillator.

  a) Define units of length, L, time, T, and energy, E, such that the Hamiltonian (measured in these units) takes the simple form

  $$\mathcal{H} \equiv \frac{\mathcal{H}'}{E} = \frac{1}{2}\left(p^2 + q^2\right) \qquad \text{with} \quad q = \frac{q'}{L} \quad \text{and} \quad p = \frac{p'}{ET/L} \tag{2}$$

  In the following use these dimensionless quantities.

  b) Solve the Hamiltonian equation of motions via the forward Euler scheme and plot the trajectory in phase space for three different values of the integration time step $\Delta t = 0.1$, 0.01, and 0.001.

  c) Do the same as task b for the backward/implicit Euler scheme.

  d) Do the same as task b for the Runge-Kutta algorithm of fourth order (RK4).

  e) Consider the first-order algorithm described by the time-step operator

  $$T(\Delta t) = e^{\Delta t \frac{\partial \mathcal{H}}{\partial p}\frac{\partial}{\partial q}} e^{-\Delta t \frac{\partial \mathcal{H}}{\partial q}\frac{\partial}{\partial p}} \tag{3}$$

  Explain the algorithm (i.e., write down the explicit equations for the changes of q and p) and do the same as task b for this algorithm. Why does it perform better than all previous algorithms (forward and backward Euler, as well as RK4 schemes).

  f) Do the same as task b for the velocity-Verlet algorithm.

  g) Calculate the shadow Hamiltonian, $\mathcal{H}_s$, for the velocity-Verlet algorithm of the harmonic oscillator. (hint: It corresponds to a harmonic oscillator with a different mass and frequency and converges for $\Delta t \to 0$ to Equation 2.) Verify explicitly that the velocity-Verlet algorithm *exactly* conserves $\mathcal{H}_s$.

- **Rouse polymer in the microcanonical and canonical ensemble**

  Consider a single, Gaussian polymer (in three spatial dimensions) that is described the coordinates and velocities, $\{\mathbf{r}_i, \mathbf{p}_i\}$ with $i = 1, \cdots, N$, of its N segments. Neighboring segments are bonded together by entropic, harmonic springs, and the Hamiltonian of the system takes the form

  $$\mathcal{H} = \frac{1}{2m}\sum_{i=1}^{N} \mathbf{p}_i^2 + \frac{3(N-1)k_B T}{2R_e^2} \sum_{i=1}^{N-1} \left[\mathbf{r}_{i+1} - \mathbf{r}_i\right]^2 \tag{4}$$

  For the numerics use $N = 64$ and set the length scale $R_e = 1$, energy scale $k_B T = 1$, and mass $m = 1$.

a) Create an initial configuration by drawing an equilibrium conformation $\{\mathbf{r}_i\}$ from the statistics of a Gaussian polymer (random walk with variance of step length $R_e^2/(N-1)$), and the velocities from the Maxwell-Boltzmann distribution.

b) Implement the velocity-Verlet algorithm and choose the time step, Δt, such that the Hamiltonian dynamics (reasonably well) conserves the total energy, $\mathcal{H}$ (see also task c).

c) Observe the time evolution of the first Rouse modes, $\mathbf{X}_p$, with $p = 1, 2$, and 3.

$$\mathbf{X}_p = \frac{1}{N}\sum_{i=1}^{N} \frac{\mathbf{r}_i}{R_e} \cos\left(\frac{\pi p}{N}[i-1/2]\right) \tag{5}$$

and calculate their distribution along a trajectory. Is the system ergodic? Explain your observation. Calculate the probability distribution of $\mathbf{X}_p$ for $p = 1$.

d) Calculate the mean-squared displacement (MSD) of the center of mass,

$$g_3(t) \equiv \left\langle [\mathbf{r}_{\text{cm}}(t_0+t) - \mathbf{r}_{\text{cm}}(t_0)]^2 \right\rangle_{t_0} \qquad \text{with} \quad \mathbf{r}_{\text{cm}}(t) = \frac{1}{N}\sum_{i=1}^{N} \mathbf{r}_i(t) \tag{6}$$

($\langle \cdots \rangle_{t_0}$ runs over times along a trajectory or multiple simulation runs), the MSD of all segments

$$g_1(t) \equiv \frac{1}{N}\sum_{i=1}^{N} \left\langle [\mathbf{r}_i(t_0+t) - \mathbf{r}_i(t_0)]^2 \right\rangle_{t_0} \tag{7}$$

and the MSD of all segments with respect to the center of mass

$$g_2(t) \equiv \frac{1}{N}\sum_{i=1}^{N} \left\langle [\mathbf{r}_i(t_0+t) - \mathbf{r}_i(t_0) - \mathbf{r}_{\text{cm}}(t_0+t) + \mathbf{r}_{\text{cm}}(t_0)]^2 \right\rangle_{t_0} \tag{8}$$

e) Implement the Andersen thermostat, i.e., every time interval, Δt_{AT}, all velocities are newly drawn from the Maxwell-Boltzmann distribution. Redo parts c and d of the exercise and explain the changes that you observe.

f) Replace the Andersen thermostat by the Lowe-Andersen thermostat, allowing a fraction, $\gamma \Delta t_{\text{LAT}} \leq 1$, of segment pairs with a distance of less than $r_c = R_e/\sqrt{3(N-1)}$ to "collide" (i.e., update their relative momentum) every time interval, Δt_{LAT}. Implement a box list and periodic boundary conditions with a minimum image convention to find segment pairs. Redo parts c and d of the exercise and explain the changes that you observe.

g) Add to the Hamiltonian, Equation 4, the additional, soft, pairwise interaction

$$H_{\text{nb}} = \sum_{i<j} V(|\mathbf{r}_i - \mathbf{r}_j|) \qquad \text{with} \qquad \frac{V}{k_B T} = \frac{\epsilon}{2}\left(1 - \frac{r}{r_c}\right)^2 \tag{9}$$

Use the value $\epsilon = 20$ in your simulation. Calculate the distribution of the mean-squared end-to-end distance $R^2 = (\mathbf{r}_N - \mathbf{r}_1)^2$. Verify your program by estimating the probability distribution of R^2 for $\epsilon = 0$ using single-histogram extrapolation.