Prof. Dr. Petra Imhof
Prof. Dr. Felix Höfling
Irtaza Hassan (irtaza06@zedat.fu-berlin.de)

Freie Universität Berlin
FB Mathematik und Informatik

Computational Molecular Physics **Winter 2017/18**

Problem set 2 **9 November 2017**

Problem 2.1 *Langevin equation: harmonic and FENE potentials*

Consider a colloidal particle of mass m in a solvent of temperature T and subject to either of the following potentials:

(i) harmonic potential: $V(r) = \frac{1}{2}kr^2$,

(ii) FENE potential: $V(r) = -\frac{1}{2}kr_0^2 \log(1 - r^2/r_0^2)$,

with spring constant k and maximum bond length r_0. The one-dimensional Langevin equations for the position $r(t)$ and the momentum $p(t)$ of the mass read

$$\dot{r}(t) = p(t)/m, \quad \dot{p}(t) = -V'(r(t)) - \gamma p(t) + F_R(t)\,,$$

where $\gamma > 0$ denotes a damping coefficient and $F_R(t)$ is a random force modelled as Gaussian white noise with $\langle F_R(t)\rangle = 0$ and $\langle F_R(t)\, F_R(s)\rangle = 2m\gamma k_B T\, \delta(t - s)$.

a) Solve the Langevin equations numerically using the Euler–Maruyama method:

$$\begin{aligned} r(t + \Delta t) &= r(t) + p(t)\Delta t/m, \\ p(t + \Delta t) &= p(t) - V'(r(t))\Delta t - \gamma p(t)\Delta t + \sqrt{2m\gamma k_B T\, \Delta t}\,\xi(t)\,, \end{aligned}$$

where $\xi(n\Delta t) =: \xi_n \sim \mathcal{N}(0, 1)$ are independent and normalised Gaussian variables, i.e., $\langle \xi_n\rangle = 0$ and $\langle \xi_m\, \xi_n\rangle = \delta_{mn}$. Use $\gamma^{-1} = 10\,\text{ns}$, $m = 10^{-17}\,\text{kg}$, and for the thermal velocity $v_{\text{th}} := \sqrt{k_B T/m} = 0.02\,\text{m/s}$. For the potential parameters, choose $\omega_0 := \sqrt{k/m} = 0.1\gamma$, and $r_0 = v_{\text{th}}/\omega_0$, and for the initial conditions $r(0) = 0$ and $p(0)/m = 1\,\text{m/s}$. For both potentials, integrate over a time span $10^{-4}\,\text{s}$ with a timestep $\Delta t = 10^{-2}\gamma^{-1}$.

b) Plot the obtained trajectories in phase space and as function of time. Compare with the deterministic case ($\gamma = 0$) and with the underdamped case, e.g., $\omega_0 = 5\gamma$, and discuss your results qualitatively. What can be said about the initial behaviour? Estimate the time T_{eq} the system needs to converge to its equilibrium state. Calculate the root mean-square displacement $\ell := \langle r(t)^2\rangle^{1/2}$ and the the kinetic energy, $E_{\text{kin}} = \langle p(t)^2\rangle/2m$ as long-time limits of time averages, i.e., $\langle A(t)\rangle := \lim_{T\to\infty} T^{-1} \int_{T_0}^{T_0+T} A(s)\mathrm{d}s$ for $T_0 \gg T_{\text{eq}}$.

c) From the paths $r(t)$ obtained for $\omega_0 = 0.1\gamma$, calculate the mean density $\rho(r) = \langle \delta(r - r(t))\rangle$ in equilibrium as a time average. Show the results on a semi-logarithmic representation [$\log(\rho(r)/r_0)$ vs. r/r_0] and compare with the expected Boltzmann distributions. Compare different integration time steps and find a suitable value for each of the two potentials.

d*) Perform a response experiment: instead of the confining potentials, apply a constant drag force, $V(r) = -F_0 r$, to the mass and determine the drag coefficient $\mu = v_\infty/F_0$ from the terminal velocity, $v_\infty = \langle p(t)\rangle/m$. Use three different values for F_0 and two different temperatures T. What do you observe for the dependence of μ on F_0 and T?

Note: The FENE potential together with Lennard-Jones repulsion is often used to model long polymer chains. The acronym FENE means *Finitely Extensible Non-linear Elastic* bond.

Due date: ***16 November, 12 p.m.***