Universität Freiburg – Institut für Physik
Applied Theoretical Physics
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Exercise 5 for '*Computational Physics - Material Science*', SoSe 2021
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Please provide a well documented submission of your solution. Your submission should include

- A pdf file containing the solution to the questions with the corresponding equations that are implemented in your codes. Figures must contain axis titles with corresponding units and a caption.
- The source code should be commented, and the equations given in the pdf file have to be referenced in the source code.
- There is no need to provide the trajectory files.
- In case your code is not working properly, please provide a description of the debugging attempts you did.

Exercise 5.1: Nose-Hoover thermostat

From a statistical mechanics perspective, the temperature of an ensemble of atoms is imposed by coupling the system with a large heat bath of temperature T_d. The velocities of the atoms in the system are then following a Maxwell-Boltzmann distribution corresponding to T_d. The temperature T_d then is not constant but fluctuates around a mean value. In atomistic modeling, the temperature is controlled by applying a thermostat. The objective of this exercise is to enrich the NVE-MD engine implemented in the previous exercises with a thermostat to simulate a LJ fluid in the canonical ensemble (NVT). Once implemented and validated, the heat capacity of the LJ fluid is calculated as an application of the thermostat.

Although there exist different thermostatting schemes, our focus is on the Nose-Hoover (NH) thermostat. The basic idea of the NH thermostat is to introduce a new variable, s, that can exchange heat with the system. Since the equations of motion derived from the Lagrangian of the system conserve the total energy of the system, an extended Lagrangian is considered by adding fictitious degrees of freedom such as s. The equations of motion derived from the NH thermostat can be implemented using a half-step Velocity-Verlet algorithm according to:

$$
\begin{aligned}
\mathbf{v}_i(t+\frac{\Delta t}{2}) &= \left(\mathbf{v}_i(t) + \frac{\mathbf{f}_i(t)}{m_i}\frac{\Delta t}{2}\right) / \left(1+\xi(t)\frac{\Delta t}{2}\right) \\
\mathbf{r}_i(t+\Delta t) &= \mathbf{r}_i(t) + \mathbf{v}_i(t+\frac{\Delta t}{2})\Delta t \\
\ln s(t+\Delta t) &= \ln s(t) + \xi(t)\Delta t + \frac{1}{2}G(t+\frac{\Delta t}{2})\Delta t^2 \\
\xi(t+\Delta t) &= \xi(t) + G(t+\frac{\Delta t}{2})\Delta t \\
\mathbf{v}_i(t+\Delta t) &= \mathbf{v}_i(t+\frac{\Delta t}{2}) + \frac{1}{2}\Delta t\left(\frac{\mathbf{f}_i(t+\Delta t)}{m_i} - \xi(t+\Delta t)\mathbf{v}_i(t+\frac{\Delta t}{2})\right)
\end{aligned}
$$

with

$$G(t) \equiv \frac{1}{Q}\left(2K(t) - 3Nk_BT_d\right)$$

where $K(t)$ is the kinetic energy at time t, N is the number of particles in the system, k_B is the Boltzmann constant, T_d is the desired temperature, and Q is the *thermal mass* associated to s. Assuming t_c as the characteristic time for the instant temperature to converge and fluctuate around the desired temperature ($t_c \approx m\delta t$ where δt is the simulation timestep), an educated guess of Q is $Q \approx gk_BT_d\delta t_c^2$. The variable ξ results from a change of variable, e.g. $\xi = \frac{d(\ln s)}{dt}$

a) Enrich the 3D MD implementation of Exercise sheet #3 with a function that updates the positions, $\mathbf{r_i}$, and the velocities, $\mathbf{v_i}$, according to the equations of motion derived from the NH thermostat. Simulate, during 4000 time steps, the trajectory of a system containing $N = 6^3$ atoms included in a simulation box of volume V such that the number density $\rho = N/V = 0.5\sigma^{-3}$. The desired temperature of the first half of the trajectory is $T_d = 300K$, while $T_d = 100K$ in the remaining time of the trajectory. Plot the result $T(t)$ versus t for $m = 50$. How does the temperature behave? Plot $\xi(t)$ versus t. Interpret your results using $\dot{\xi} = \frac{3Nk_B}{Q}(T - T_d)$.

b) Simulate the trajectory of a system containing $N = 10^3$ atoms included in a simulation box of volume V such that the number density $\rho = N/V = 0.5\sigma^{-3}$ during 20000 time steps using the NH thermostat. The desired temperature is $T_d = 300K$, and $m = 50$. The first 4000 time steps are used for the equilibration of the system, and the last 16000 time steps are for the production run. Plot $T(t)$ versus t obtained during the production run. What is the mean and the variance of T during the production run? Calculate and plot as a function of the time the total energy, E_{NH}, defined as

$$E_{NH} = \sum_i \frac{\mathbf{p}_i^2}{2m_i} + U\left(\mathbf{r}^N\right) + \frac{\xi^2 Q}{2} + 3Nk_BT_d \ln s$$

Is the total energy of your system, E_{NH}, conserved? What is the mean, the variance and the standard deviation of E_{NH}?

c) The heat capacity at constant volume, C_V, can be written in the NVT ensemble as:

$$C_V = \left(\frac{\partial \langle E\rangle}{\partial T}\right)_V = \frac{\sigma_E^2}{k_BT^2} = \frac{1}{k_BT^2}\left[\sigma_U^2 + \frac{3}{2}N(k_bT)^2\right].$$

where $\sigma_E^2 = \langle E^2\rangle - \langle E\rangle^2$ is the variance of the total energy fluctuations, and $\sigma_U^2 = \langle U^2\rangle - \langle U\rangle^2$ is the variance of the potential energy fluctuations.

i) Starting with the definition of the heat capacity written in terms of σ_E^2, recover the definition of the heat capacity as a function of σ_U^2.

ii) Using the simulation setup of (b) with $m = 50$, calculate and plot the running averages for C_V calculated with σ_E^2 and σ_U^2. The running average, $\bar{x}(t)$, of an observable x, is defined as

$$\bar{x}(t) = \frac{1}{t}\int_0^t x(t')\mathrm{d}t'$$

iii) Perform similar simulations as in (ii) but now with $T = 250K$ and $T = 350$. Plot the radial distribution function obtained for the three temperatures ($T \in (250K, 300K, 350K)$) obtained during the production run. Calculate the C_V as in (ii) for $T = 250$ K and $T = 350$ K. How do you observe C_V changing with T? Calculate $C_V = \partial\langle E\rangle/\partial T$, and compare the result at $T = 300$ K from the variance calculation. Conclude.

Numerical values of quantities to be used:

quantity	value (units)
k_B	1.38×10^{-23} (m^2 kg s^{-2} K^{-1})
ϵ	0.5 k_BT
σ	2.55×10^{-10} (m)
T_d	300 (K) or see text
mass	105.52×10^{-27} (kg)
Δt	10^{-15} (s)