

Dynamical consequences of the application of a thermal noise constraint to the Langevin thermostat

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We investigate some unusual behaviour observed while performing molecular dynamics simulations with the DL_POLY_4.03 code. Under the standard Langevin thermostat, atoms appear to be thermalised to different temperatures, depending on their mass and on the total number of particles in the system. We find that an imposed constraint whereby no thermal noise acts on the centre of mass of the system is the cause of the unexpected behaviour. This is demonstrated by solving the stochastic dynamics for the constrained thermostat and comparing the results with simulation data. The effect of the constraint can be considerable for small systems with disparate masses. By removing the constraint the Langevin thermostat may be restored to its intended behaviour and this has been implemented as an option in DL_POLY_4.05.

I. INTRODUCTION

Molecular dynamics (MD) is a powerful method for studying various phenomena at an atomistic level and several leading codes with many features and options have been developed. Nevertheless, one should always check that codes operate as intended. In this note we describe, and resolve, some strange behaviour encountered when using the DL_POLY (version 4.03) code¹ to perform thermostated MD simulations of small clusters of sulphuric acid molecules. The temperature control imposed by the implementation of a Langevin thermostat was found to deviate from expectation: groups of atoms were brought to different temperatures depending on their mass. Such species-dependent temperatures were deduced by fitting Maxwell-Boltzmann distributions to velocity distributions of atoms, grouped by mass, extracted from ‘equilibrated’ system trajectories. Further investigation revealed that this discrepancy was a function of the number of particles, N , in the system as shown in Figure 1. Clearly this is not the desired outcome.

We show that this behaviour is a direct result of a constraint imposed in the code whereby no thermal noise acts upon the centre of mass. In Section II we derive the expected temperatures of atomic species generated by such a constrained Langevin thermostat. We perform various numerical tests to validate the analysis and in Section III we discuss the implications of our study.

II. THEORY

Langevin thermostating of a set of particles moving in one spatial dimension is implemented through the use of the equation of motion

$$m_i \dot{v}_i = -\gamma m_i v_i + b_i m_i \xi_i(t), \quad (1)$$

where m_i and v_i are the mass and velocity for particle i , γ is the friction coefficient and $b_i = \sqrt{2\gamma k_B T / m_i}$ where k_B is the Boltzmann constant and T is the target temperature. $\xi_i(t)$ is a noise term with the statistical properties $\langle \xi_i(t) \rangle = 0$, $\langle \xi_i(t) \xi_i(t') \rangle = \delta(t - t')$ and $\langle \xi_i(t) \xi_j(t') \rangle_{i \neq j} = 0$. Mutual interactions could be added to these equations, but this should not affect the thermalisation and we consider non-interacting particles for simplicity. However, in DL_POLY_4.03 the sum of all the Langevin noise terms is constrained to be zero.

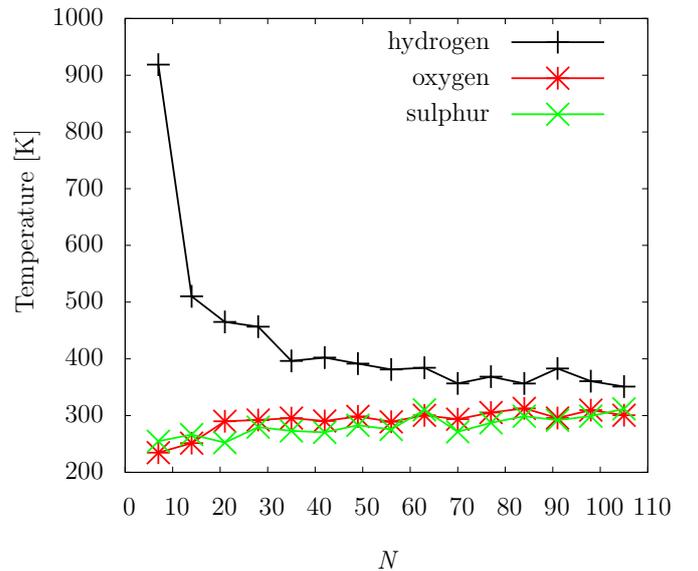


Figure 1. Dependence of the temperature of each atomic species against the number of particles, N , in a simulation of up to 15 sulphuric acid molecules in a Langevin thermostated DL_POLY_4.03 simulation with a target temperature of 300 K. The heavier atoms (oxygen and sulphur) are seen to be cooler than desired and the lighter atoms (hydrogen) are hotter.

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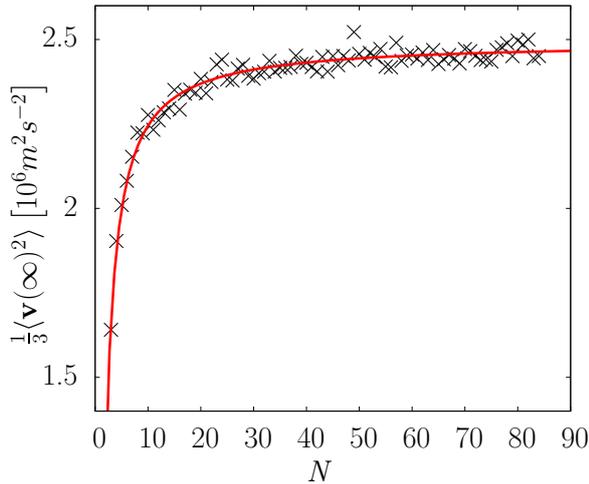


Figure 2. Plot of $\frac{1}{3}\langle \mathbf{v}(\infty)^2 \rangle$ against the number N of non-interacting identical particles. The points are found from ‘equilibrated’ DL_POLY_4.03 trajectories with parameters $m = 1$ a.u., $\gamma = 100 \text{ ps}^{-1}$, and total simulation time 0.1 ns, and the solid line corresponds to Eq. (6).

This is perhaps motivated by a desire not to allow the thermostat to disturb the centre of mass (CoM) motion of the system; in the scheme the CoM momentum is allowed to relax deterministically towards zero. However, this constraint affects the function of the thermostat and leads to undesirable dynamical behaviour as shown below.

We demonstrate this in detail. Defining C as the sum of the noise terms $\sum_1^N b_j m_j \xi_j(t)$, the random force on the CoM may be eliminated by subtracting C/N from the equation of motion (1) of each particle. After dividing by m_i we obtain

$$\dot{v}_i = -\gamma v_i + \frac{N-1}{N} b_i \xi_i(t) - \frac{1}{N} \sum_{j=1, j \neq i}^N b_j \frac{m_j}{m_i} \xi_j(t), \quad (2)$$

and a standard solution to such a Langevin equation with several independent noise terms² gives

$$v_i(t) = v_i(0)e^{-\gamma t} + \frac{N-1}{N} b_i \int_0^t e^{-\gamma(t-t')} \xi_i(t') dt' - \frac{1}{N} \sum_{j=1, j \neq i}^N b_j \frac{m_j}{m_i} \int_0^t e^{-\gamma(t-t')} \xi_j(t') dt', \quad (3)$$

from which we can obtain $\langle v_i(t)^2 \rangle$ using the properties of $\xi_i(t)$. Taking the limit $t \rightarrow \infty$ we find

$$\langle v_i(\infty)^2 \rangle = \frac{k_B T}{m_i N^2} \left[(N-1)^2 + \sum_{j=1}^N \frac{m_j}{m_i} - 1 \right], \quad (4)$$

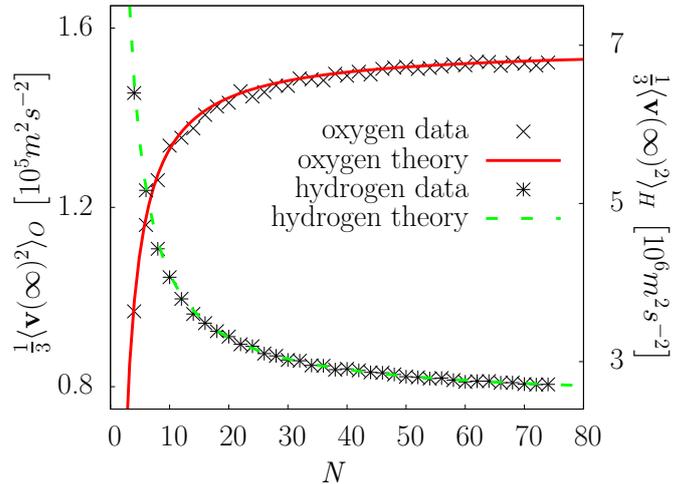


Figure 3. Plot of $\frac{1}{3}\langle \mathbf{v}(\infty)^2 \rangle$ against the number of non-interacting particles in a DL_POLY_4.03 simulation, half of which are oxygen and the remaining half hydrogen. Results for oxygen and hydrogen refer to the left and right hand axes, respectively. The points correspond to an average of five ‘equilibrated’ simulations ($\gamma = 100 \text{ ps}^{-1}$ with a simulation length of 0.1 ns) for each value of N and the curves are defined by Eq. (7).

and defining an effective temperature of the particle, T_{eff}^i , by $\frac{1}{2} m_i \langle v_i(\infty)^2 \rangle = \frac{1}{2} k_B T_{\text{eff}}^i$ we obtain

$$T_{\text{eff}}^i = \frac{T}{N^2} \left[(N-1)^2 + \sum_{j=1}^N \frac{m_j}{m_i} - 1 \right], \quad (5)$$

which depends on both mass and number of particles. The target temperature is returned only in the limit $N \rightarrow \infty$. A treatment of the motion in three dimensions gives the same expression for the effective temperature.

We now compare this analysis with simulation data. First we study a system of identical non-interacting particles of mass $m = 1$ a.u. in a 3-d non-periodic box. Eq. (4) for the asymptotic mean square of one velocity component of the particles leads to

$$\frac{1}{3} \langle \mathbf{v}(\infty)^2 \rangle = \langle v_x(\infty)^2 \rangle = \langle v_y(\infty)^2 \rangle = \langle v_z(\infty)^2 \rangle = a \left(1 - \frac{1}{N} \right), \quad (6)$$

where $a = k_B T/m$. Figure 2 shows $\frac{1}{3}\langle \mathbf{v}(\infty)^2 \rangle$ obtained from a set of NVT simulations with target temperature $T = 300 \text{ K}$, plotted against Eq. (6) with $a = 2.494 \times 10^6 \text{ m}^2 \text{ s}^{-2}$, showing that the dependence on N is consistent with the model.

A system containing particles with different masses was chosen for more detailed testing of Eq. (4). For simplicity the system of N particles was composed of equal numbers of light particles (hydrogen, $m_H = 1$ a.u.) and heavy particles (oxygen, $m_O = 16$ a.u.), again with no mutual interactions. It is again possible to simplify Eq. (4) to

give

$$\frac{1}{3} \langle \mathbf{v}(\infty)^2 \rangle_\alpha = a_\alpha \left(1 - \frac{\tilde{N}_\alpha}{N} \right), \quad (7)$$

where $\alpha = H$ or O , $a_\alpha = k_B T / m_\alpha$, $\tilde{N}_H = [3 - (m_O/m_H)]/2 = -13/2$ and $\tilde{N}_O = [3 - (m_H/m_O)]/2 = 47/32$. The results for $N \geq 4$ are summarised in Figure 3. As the system size increases, the average squared velocity component of the heavy atoms increases, while that of the light atoms decreases, in line with the trends observed.

Returning to our simulations of sulphuric acid, the effective temperatures of the hydrogen, oxygen and sulphur species according to Eq. (5) would be given by $T_{\text{eff}}^H = T[1 + 12/N]$, $T_{\text{eff}}^O = T[1 - 9/(8N)]$ and $T_{\text{eff}}^S = T[1 - 25/(16N)]$ using appropriate atomic masses. This behaviour is consistent with the unexpected thermalisation behaviour illustrated in Figure 1.

III. DISCUSSION

This investigation was motivated by the unintended effect of the Langevin thermostat implemented in DL_POLY_4.03; namely the peculiar thermalisation of different atomic species to mass- and system size-dependent temperatures. This behaviour is a direct con-

sequence of a constraint imposed in the code such that the CoM momentum is not influenced by the noise component of the thermostat. An analysis of the stochastic dynamics introduced by such a scheme leads to mean square velocities and effective temperatures given by Eqs. (4) and (5), and we have shown that the results of simulations with DL_POLY_4.03 are consistent with these expressions.

If an MD scheme is required where the CoM of a system is held fixed, uninfluenced by noise, an appropriate Galilean transformation of the velocity configuration after the implementation of the equations of motion for each timestep might be a workable alternative algorithm.

We conclude that it is advisable to check behaviour carefully when using MD codes for systems that are not the usual focus of attention, such as the small molecular clusters that are of interest to us. In version 4.05 of DL_POLY the CoM constraint that produced the strange behaviour we encountered has been removed, such that small systems can be thermalised correctly, in line with the zeroth law of thermodynamics³.

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