

## RESEARCH ARTICLE

### Dynamical consequences of a constraint on the Langevin thermostat in molecular cluster simulation

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We investigate some unusual behaviour observed while performing molecular dynamics simulations of small molecular clusters using a constrained Langevin thermostat. Atoms appear to be thermalised to different temperatures that depend on their mass and on the total number of particles in the system. The deviation from the zeroth law of thermodynamics can be considerable for small systems of heavy and light particles. We trace this behaviour to the absence of thermal noise acting on the centre of mass of the system. This is demonstrated by solving the stochastic dynamics for the constrained thermostat and comparing the results with simulation data. By removing the constraint, the Langevin thermostat may be restored to its intended behaviour. We also investigate a Langevin thermostat constrained to have zero total force acting on its centre of mass, and find similar deficiencies.

#### 1. Introduction

Molecular dynamics (MD) is a powerful technique for studying various phenomena at an atomistic level and a number of leading simulation codes with many features and options have been developed. Nevertheless, it is necessary to check that modelling schemes operate as intended. In this note we describe, and resolve, some strange behaviour encountered during thermostated MD simulations of small clusters of sulphuric acid molecules. The temperature control imposed by a particular 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 expressions to the velocity distributions of atoms, grouped by mass, extracted from ‘equilibrated’ system trajectories. Further investigation revealed that this discrepancy was also a function of the total number of particles,  $N$ , in the system as shown in Figure 1. Clearly this is not the desired outcome.

The Langevin thermostat was implemented in such a way that no thermal noise was allowed to act upon the centre of mass of the molecular system. This might be considered to be a natural constraint to employ since the objective of thermalisation is to control the internal dynamical degrees of freedom, leaving the centre of mass of the system unaffected, and indeed maintained at a fixed position, if so desired.

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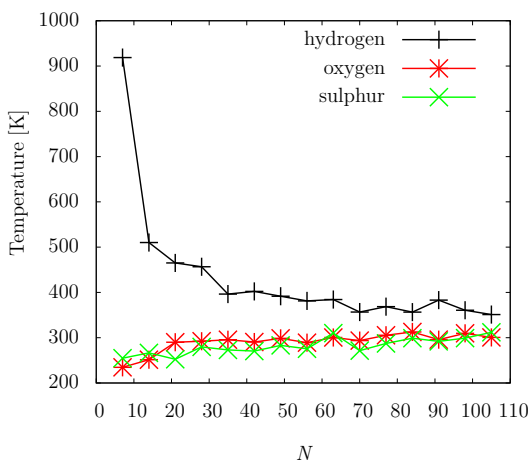


Figure 1. Dependence of the temperature of each atomic species on the total number of particles,  $N$ , in a study of up to 15 sulphuric acid molecules in an MD simulation using DL\_POLY\_4.03 [3] with a target temperature of 300 K imposed by a constrained Langevin thermostat. The heavier atoms (oxygen and sulphur) are seen to be cooler than desired and the lighter atoms (hydrogen) are hotter, though the effect decreases as  $N$  increases.

However, in Section 2 we derive the temperatures of atomic species thermalised by such a constrained Langevin thermostat and show that they do not evolve as required. We demonstrate that the strange observed behaviour is a direct result of the imposed constraint and we perform various numerical tests to validate the analysis.

Elaborations of the simple Langevin thermostat have been studied previously, for example by Ermak and McCammon [1] where additional friction and noise terms were incorporated and found to affect the dynamics of diffusion, and by Warren and Espanol [2] in the context of dissipative particle dynamics, but to our knowledge no similar undesirable effects on the thermalisation of particles have previously been noted. To explore this further, we examine a second constrained Langevin scheme where both the thermal noise and frictional forces acting on the system centre of mass are eliminated using Gauss' principle of least constraint, and find that a different, but equally undesirable, distortion of the thermalisation emerges. In Section 3 we discuss the implications of our study.

## 2. Constrained stochastic dynamics

### 2.1. Langevin derivation of thermalisation temperature

The most simple 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  $i$ ,  $\gamma$  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 particle interactions could be added to these equations, but this should not affect the thermalisation and we consider non-interacting particles for simplicity.

Such dynamical equations inevitably affect the total momentum of a system and disturb the position of its centre of mass (CoM). If this is judged to be undesirable,

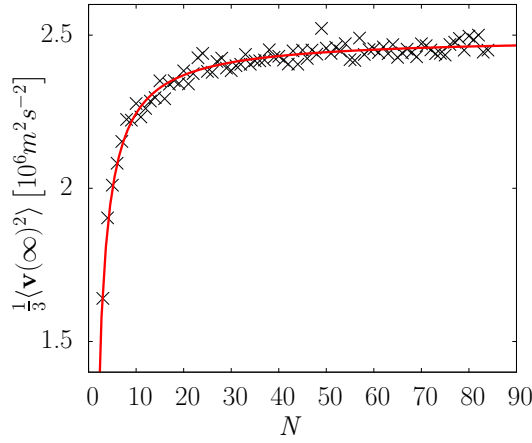


Figure 2. Plot of  $\frac{1}{3} \langle \mathbf{v}(\infty)^2 \rangle$  in a simulation against the number of non-interacting identical particles  $N$ . The points are found from ‘equilibrated’ DL\_POLY\_4.03 trajectories with parameters  $m = 1$  a.u.,  $\gamma = 100 \text{ ps}^{-1}$ , and total simulation time 0.1 ns, and the solid line corresponds to Equation (6).

one way to proceed is to demand that the sum of all the Langevin noise terms, weighted appropriately, is constrained to be zero. This is indeed the way in which the Langevin thermostat has been implemented in version 4.03 of the DL\_POLY MD code [3]. Under such dynamics, the CoM momentum is obliged to relax deterministically towards zero. However, we now show that such a constraint distorts the operation of the thermostat and leads to undesirable dynamical behaviour.

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

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

which has the feature that each particle is influenced by a set of noise terms. A standard solution to such a Langevin equation [4] 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 this we can obtain  $\langle v_i(t)^2 \rangle$  using the properties of  $\xi_i(t)$ . Taking the limit  $t \rightarrow \infty$  we find that

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

where  $\mathcal{M} = \sum_i m_i$  is the total mass of the system. We can then define a temperature of the particle,  $T_{\text{eff}}^i$ , according to  $\frac{1}{2} m_i \langle v_i(\infty)^2 \rangle = \frac{1}{2} k_B T_{\text{eff}}^i$ , such that

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

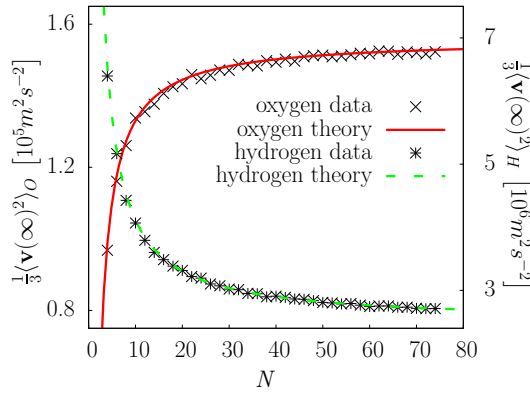


Figure 3. Plot of  $\frac{1}{3} \langle \mathbf{v}(\infty)^2 \rangle_\alpha$  against the number of non-interacting particles  $N$  in a DL\_POLY\_4.03 simulation, half of which are oxygen and the other half hydrogen. Results for the oxygen and hydrogen groups refer to the left and right hand axes, respectively. 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 Equation (7).

which depends on both species mass and the 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 temperature. The average kinetic energy in three dimensions is then  $\langle K \rangle = 3 \sum_i m_i \langle v_i(\infty)^2 \rangle / 2 = \frac{3}{2} k_B T (N - 2 + \sum_i \mathcal{M} / (N^2 m_i))$ .

We now compare this analysis with simulation data. First we study a system of identical non-interacting particles of mass  $m = 1$  a.u. held within a three dimensional non-periodic box. Equation (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 Equation (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 a more detailed testing of Equation (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.), with no mutual interactions. It is again possible to simplify Equation (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 temperatures of the hydrogen, oxygen and sulphur species according to Equation (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 entirely consistent with the unexpected thermalisation

behaviour illustrated in Figure 1.

## 2.2. Fokker-Planck derivation of temperature

For completeness, we consider the Fokker-Planck equation (FPE) equivalent to Equation (2), namely

$$\frac{\partial p}{\partial t} = \gamma \frac{\partial (v_i p)}{\partial v_i} + \frac{1}{2} \left( \left( \frac{N-1}{N} \right)^2 b_i^2 + \frac{1}{N^2} \sum_{j=1, j \neq i}^N b_j^2 \left( \frac{m_j}{m_i} \right)^2 \right) \frac{\partial^2 p}{\partial v_i^2}, \quad (8)$$

for the probability distribution  $p(v_i, t)$ . The stationary solution to this equation satisfies

$$\gamma v_i p_{\text{st}} = -\frac{1}{2} \left( \left( \frac{N-1}{N} \right)^2 b_i^2 + \frac{1}{N^2} \sum_{j=1, j \neq i}^N b_j^2 \left( \frac{m_j}{m_i} \right)^2 \right) \frac{\partial p_{\text{st}}}{\partial v_i}, \quad (9)$$

and after some algebra it may be shown that  $p_{\text{st}}$  is given by

$$p_{\text{st}}(v_i) \propto \exp \left( -\frac{m_i v_i^2}{2kT_{\text{eff}}} \right), \quad (10)$$

with  $T_{\text{eff}}^i$  given by Equation (5). The thermalisation arising in the FPE is in agreement with the analysis in Section 2.1.

## 2.3. Gauss' principle of least constraint

Another method for maintaining a condition during the evolution of a system makes use of Gauss' principle of least constraint [4]. In contrast to the analysis presented up to now, however, it is a method for the elimination of the total force on the centre of mass, rather than just the thermal noise force. It may be shown that a constraint whereby the net momentum of the system,  $\mathcal{P}$ , is conserved

$$\sum_i p_i - \mathcal{P} = 0, \quad (11)$$

modifies the equations of motion to give

$$m_i \dot{v}_i = -\gamma m_i (v_i - \mathcal{V}) + b_i m_i (1 - w_i) \xi_i(t) - \sum_j b_j m_i w_j \xi_j, \quad (12)$$

where  $\mathcal{V} = \mathcal{P}/\mathcal{M}$  and  $w_i = m_i/\mathcal{M}$ . As in Equation (2), we see several noise terms acting on each particle. We set  $\mathcal{V} = 0$  and derive a temperature as in Section 2.1 resulting in

$$T_{\text{eff,G}}^i = T \left( 1 - \frac{m_i}{\mathcal{M}} \right). \quad (13)$$

It is interesting to compare Equations (13) and (5). Both approaches thermalise particles to temperatures that depend on system size (or total mass) and species mass. However, the Gauss approach thermalises all species to a temperature below the target, while the approach based on the elimination of thermal noise acting on the CoM typically gives elevated temperatures to the lighter particles while depressing the temperatures of the heavier species. There is one advantage to the Gauss scheme, however, which is that the average kinetic energy of the whole system, with fixed CoM, is reproduced correctly, namely  $\langle K \rangle = 3 \sum_i k_B T_{\text{eff},G}^i / 2 = 3(N-1)k_B T / 2$  [5]. In this respect, eliminating CoM motion through Gauss' principle of least constraint is a better constraint than one that merely eliminates the total thermal noise.

### 3. Discussion

This investigation was motivated by an observation of strange behaviour arising from a Langevin thermostat implementation in a particular molecular dynamics model. Clearly, a modification of a mathematical scheme, however intuitively reasonable, can spoil its intended operation. It is of some interest to note that the modification under consideration has the rather remarkable effect of thermalising different atomic species to mass- and system size-dependent temperatures. This curious behaviour is a direct consequence of removing the thermostat noise that would normally act on the centre of mass (CoM). An analysis of the stochastic dynamics associated with such a scheme leads to mean square velocities and effective temperatures given by Equations (4) and (5), and we have shown that the results of simulations with the DL\_POLY\_4.03 MD code are consistent with these expressions.

An alternative method for preserving the total momentum is to employ Gauss' principle of least constraint, whereby the entire force on the CoM is eliminated. This results in the correct total average kinetic energy of the system, but the thermalisation of each species is incorrect.

We conclude by noting that in version 4.05 of the DL\_POLY code the CoM constraint responsible for the strange behaviour has been removed, such that it thermalises small molecular systems correctly, in line with the zeroth law of thermodynamics [6].

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