

Thermal boundary conditions for the computation of dynamical properties with molecular dynamics

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Abstract

We present a method to enforce thermal boundary conditions in molecular dynamics (MD) simulations. This method consists in considering a stochastic forcing that acts only on particles located near the boundary of the simulated box, with decreasing magnitude as the distance to the boundary increases. This allows to preserve the physical Newtonian dynamics in the core region of the system, while still conserving some NVT forcing. This approach gives rise to an efficient way to compute dynamical properties such as thermal conductivities.

Most molecular dynamics simulations are performed at fixed temperature. For this purpose, the Newton equations associated with the microcanonical NVE ensemble are modified in such a way that they (hopefully) generate an ergodic dynamics with respect to the canonical NVT distribution. This is the case both for the Langevin approach, where the modification is of stochastic nature, and for the Nosé-like thermostating methods [5], where the modification is of deterministic nature. Quite often, constant temperature MD simulations aim at computing, using the ergodicity of the dynamics, some phase-space average providing the value of some time-independent physical variable at thermal equilibrium. However, it is also common to compute dynamical properties at constant temperature by integrating some correlation function along the non-physical Langevin or Nosé-like trajectories. This approach is not rigorous from a statistical physics point of view, and can even lead to wrong results. It is for example well-known that the results may depend on the type of the NVT trajectories used for the simulation. Some examples are the diffusion coefficient of a tracer particle, or the response of a system to an increase of the heat bath temperature [5], that depend on the magnitude of the random force when computed with the Langevin dynamics.

We present here a very simple way to perform constant temperature dynamics without perturbing the “physical” Newton equations in a large part of the simulation box. The method consists in coupling NVT dynamics, performed near the boundary of the system, and NVE dynamics, performed in the core region. The coupling can be done in a smooth way by considering a random forcing whose magnitude depends on the position of the thermostated particle. It can be assumed for instance that the magnitude of the random forcing is a decreasing function of the distance to the boundary, that vanishes beyond some prescribed cut-off. This allows for a seamless coupling between NVT and NVE dynamics.

From a more general viewpoint, this paper is a first step toward an alternative to periodic boundary conditions for MD in the condensed phase. The random forcing with decreasing magnitude may indeed be seen as a convenient way to take into account the particles that lay outside the simulation box. It is then natural that the noise vanishes beyond a cut-off distance corresponding to the cut-off radius of the potential. The next step would be to get rid of the periodic boundary conditions (which are almost universally used in condensed phase MD), and replace them by stochastic boundary conditions allowing fluctuations of the number of particles in the simulation box. Such an approach will be carried out in [3].

This article is organized as follows. In section 1, we set the model we consider here, and establish some of its properties. We then turn to some applications, concerning the heating (or cooling) of a Lennard-Jones fluid (section 2), and show how the thermal conductivity can be computed through a (short) transient non-equilibrium simulation.

1 Description of the model

We consider a simulation box $\Omega \subset \mathbb{R}^d$ ($d = 2$ or 3) with periodic boundary conditions (the configuration space therefore has the geometry of a torus). The particles are indexed by $i = 1, \dots, N$. The mass matrix is $M = \text{Diag}(m_1, \dots, m_N)$, the configuration variable is $q = (q_1, \dots, q_N) \in \Omega^N$, and the momentum variable $p = (p_1, \dots, p_N) \in \mathbb{R}^{dN}$. Assuming that the particles interact via the potential $V(q)$, the Hamiltonian associated with the system reads

$$H(q, p) = \frac{1}{2} p^T M^{-1} p + V(q), \quad (1)$$

and the corresponding Hamiltonian dynamics is defined by

$$\begin{cases} \frac{dq}{dt} = M^{-1} p, \\ \frac{dp}{dt} = -\nabla V(q). \end{cases} \quad (2)$$

We then decompose the simulation box Ω into two non-overlapping domains Ω_i and Ω_e (see Figure 1), the outer region Ω_e being for example the set

$$\Omega_e = \{x \in \Omega \mid d(x, \partial\Omega) < r_c\},$$

where $d(x, \partial\Omega)$ is the distance from $x \in \Omega$ to the boundary $\partial\Omega$, and r_c some positive cut-off radius.

The dynamics we propose is as follows. The particles that are located in Ω_i are only subjected to the forces that derive from the interaction potential V , whereas the particles that are located in Ω_e also experience some random forcing. More precisely, we consider the dynamics

$$\begin{cases} dq_t = M^{-1} p_t dt, \\ dp_t = -\nabla V(q_t) dt - \Gamma(q_t) M^{-1} p_t dt + \Sigma(q_t) dW_t, \end{cases} \quad (3)$$

where $(W_t)_{t \geq 0}$ is a dN -dimensional Wiener process, and where the matrices Σ and Γ represent the magnitude of the fluctuations and of the dissipation respectively. They are linked by the fluctuation-dissipation relation:

$$\Sigma(q_t) \Sigma(q_t)^T = \frac{2}{\beta} \Gamma(q_t). \quad (4)$$

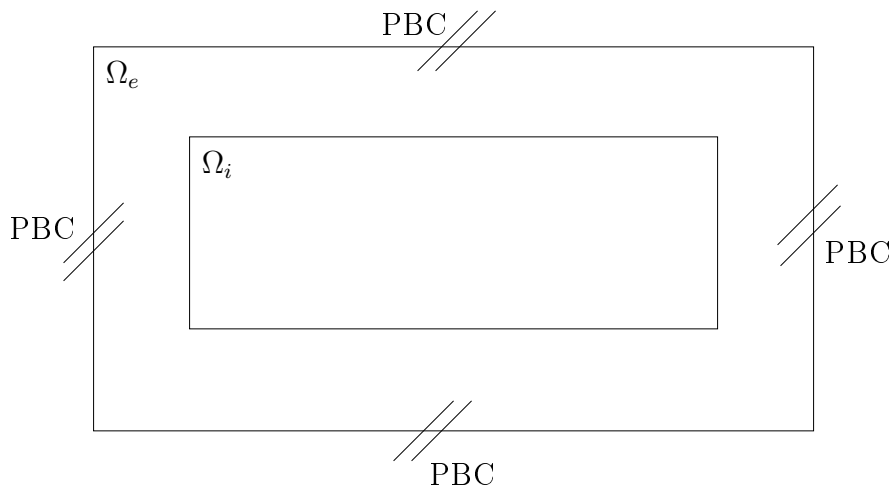


Figure 1: Decomposition of the simulation box Ω into two non-overlapping domains Ω_i and Ω_e .

In this expression, $\beta = (k_B T)^{-1}$ is the inverse temperature of the bath. In the sequel, we choose a diagonal matrix for $\Gamma(q)$:

$$\Gamma(q) = \text{Diag}(\gamma(q_1), \dots, \gamma(q_N)),$$

where the function γ is taken to be a smooth decreasing function of $d(x, \partial\Omega)$ such that $\gamma(x) = 0$ in Ω_i and $\gamma(x) > 0$ in Ω_e . We also consider

$$\Sigma(q) = \text{Diag}(\sigma(q_1), \dots, \sigma(q_N))$$

with

$$\sigma(\cdot) = \sqrt{\frac{2\gamma(\cdot)}{\beta}}. \quad (5)$$

It is easy to check that the canonical probability measure

$$d\mu(q, p) = Z^{-1} \exp(-\beta H(q, p)) dq dp \quad (6)$$

with

$$Z = \int_{\Omega^N \times \mathbb{R}^{dN}} \exp(-\beta H(q, p)) dq dp,$$

is an invariant probability measure for (3). Indeed, the infinitesimal generator \mathcal{A} associated with (3) is

$$\mathcal{A}f(q, p) = M^{-1}p \cdot \nabla_q f - (\nabla V(q) + \Gamma(q)M^{-1}p) \cdot \nabla_p f + \frac{1}{2}\Sigma(q)\Sigma(q)^T \Delta_p f,$$

and the corresponding Fokker-Planck equation therefore reads

$$\partial_t f + \mathcal{A}^* f = 0,$$

where \mathcal{A}^* is the adjoint of \mathcal{A} . A straightforward computation shows that

$$f(q, p) = \exp(-\beta H(q, p)) \quad (7)$$

is an invariant density when (4) holds, since $\mathcal{A}^* f = 0$ in this case.

It is not clear whether the stochastic differential equation (3) is ergodic since $\Sigma = 0$ in Ω_i . However, we have observed in numerical simulations that, whatever the starting distribution, the correct kinetic temperature is quickly attained.

In the numerical examples presented in section 2 we have used the following numerical implementation of (3), inspired from the classical BBK scheme used to integrate the Langevin equation [1]:

$$\begin{cases} p_i^{n+1/2} = p_i^n + \frac{\Delta t}{2} \left(-\nabla_{q_i} V(q^n) - \frac{\gamma(q_i^n)}{m_i} p_i^n + \frac{\sigma(q_i^n)}{\sqrt{\Delta t}} Z_i^n \right) \\ q_i^{n+1} = q_i^n + \frac{\Delta t}{m_i} p_i^{n+1/2} \\ p_i^{n+1} = p_i^{n+1/2} + \frac{\Delta t}{2} \left(-\nabla_{q_i} V(q^{n+1}) - \frac{\gamma(q_i^{n+1})}{m_i} p_i^{n+1} + \frac{\sigma(q_i^{n+1})}{\sqrt{\Delta t}} Z_i^{n+1} \right) \end{cases} \quad (8)$$

where σ is still given by (5), and $\{Z_i^n\}_{1 \leq i \leq N, n \in \mathbb{N}}$ are identical and independently distributed (i.i.d.) standard gaussian random variables.

2 Thermal conductivity of Lennard-Jones systems

In section 2.1, we describe the Lennard-Jones system and the thermalization procedure we have considered. The NVE-NVT heating and cooling processes are then dealt with in section 2.2, and alternative approaches to determine the thermal conductivity are briefly reviewed. Some simulation results are finally provided in section 2.3.

2.1 Description of the system

We consider a three-dimensional ($d = 3$) Lennard-Jones system, with standard periodic boundary conditions (we refer to [3] for a more general approach of the stochastic forcing at the boundaries). The potential energy is given by

$$V(q) = \sum_{1 \leq i < j \leq N} V_{\text{LJ}}(|q_i - q_j|) + \frac{1}{2} \sum_{i,j=1}^N \sum_{k \in \mathcal{R} \setminus \{0\}} V_{\text{LJ}}(|q_i - q_j + k|), \quad (9)$$

where \mathcal{R} is the Bravais lattice and V_{LJ} the usual Lennard-Jones potential

$$V_{\text{LJ}}(r) = 4\epsilon \left(\left(\frac{a}{r} \right)^{12} - \left(\frac{a}{r} \right)^6 \right), \quad (10)$$

with $\epsilon > 0$ and $a > 0$.

The system is first thermalized at an inverse temperature β as follows. Starting from an equilibrium position such as a FCC lattice for solid state simulations, or a square lattice for

liquid phase simulations¹, the momenta of the particles are generated from the kinetic part of the canonical measure, that is according to the probability density

$$d\kappa(p) = \left(\frac{\beta}{2\pi}\right)^{3N/2} |\text{Det } M|^{-1/2} \exp(-\beta p^T M^{-1} p/2) dp.$$

The system is then simulated until the time t_{init} using the *full* Langevin dynamics, which amounts to taking $\Gamma(q) = \gamma_0 \mathbf{I}_{3N}$ in (3), where \mathbf{I}_{3N} is the identity matrix on \mathbb{R}^{3N} . In this thermalization process, $\gamma_0 > 0$ is a given positive constant, and all the particles in Ω experience stochastic forcing. The numerical implementation makes use of (8) with $\gamma(\cdot) = \gamma_0$ and

$$\sigma(q_i) = \sqrt{\frac{2\gamma_0}{\beta} \left(1 + \frac{\gamma_0 \Delta t}{2m_i}\right)}.$$

The correction term $\frac{\gamma_0 \Delta t}{2m_i}$ in the above formula ensures that the kinetic temperature is correct, even for large frictions. A theoretical justification in a simplified case, together with numerical arguments in more general cases, can be read in [2]. Notice that such a correction term cannot be derived theoretically for the NVE-NVT model (3), and that numerical simulations show that considering a correction to the random forcing magnitude in (5) leads to a bias in the kinetic temperature in the inner region Ω_i .

Under suitable conditions (see [2] for a short introduction to the subject), it can be shown that the Langevin stochastic process converges in law toward the canonical measure (6). For t_{init} large enough, the configuration of the system can therefore be taken as an initial configuration with inverse temperature β .

2.2 Computation of the thermal conductivity

The thermal conductivity λ of a system can be computed either at equilibrium, using a Green-Kubo formula [5], or in a non-equilibrium setting. The former method relies on the integration of the heat flux correlation function, and often requires long simulation times for the time integral to converge. Non-equilibrium molecular dynamics (NEMD) approaches assume a linear response regime, so that the heat flux depends linearly on the temperature gradient. To specify this linear relation, external fictitious mechanical forces can be added [4, 6] to the NVE dynamics, or a temperature gradient can be specified, while the heat flux is then measured. Since these methods also suffer from slow convergence, a different approach has been proposed, where the heat flux is specified, and the temperature field is measured [8].

A recent interesting alternative method [7] relies on transient simulations. A small fraction of the system is instantaneously heated, and the kinetic temperature relaxation is monitored. The thermal conductivity can then be computed by comparison with the Fourier law. However, the approach of [7] is based on NVE simulations of relatively small systems, so that complete relaxation toward the canonical ensemble cannot be observed.

We will now show that the NVE-NVT model (3) is fairly suited for thermal conductivity computations. Let us consider a Lennard-Jones system modeled by (3) initially at thermal equilibrium with temperature T_1 (such an equilibrium state is obtained as described in section 2.1) and let us suddenly change the temperature of the thermostat to T_2 . The inner

¹This initial configuration is much less stable than a FCC lattice, and thermalization is therefore expected to occur faster.

system Ω_i is then heated or cooled down through energy exchanges with Ω_e , itself thermostated by the environing heat-bath, and the kinetic temperature of Ω_i as a function of time can be monitored. To reduce statistical errors, several independent relaxations must be performed, starting from initial configurations sampled independently from the canonical measure.

The thermal conductivity can then be recovered as follows. Assuming that the Fourier law holds in the domain $\Omega_i =]0, L[^3$, the local temperature obeys the heat equation

$$\rho C_v \partial_t T = \lambda \Delta T,$$

where ρ denotes the density of the system (expressed in mol/m³), C_v the specific heat capacity (in J/K/mol), and λ the thermal conductivity (in W/m/K). For variations in a small temperature range, it can indeed be assumed that C_v and λ remain constant in space and time. The specific heat capacity can be found in thermodynamic tables, or computed as a time-independent canonical average according to

$$C_v = \frac{\mathcal{N}_a}{N k_B T^2} (\langle H^2 \rangle - \langle H \rangle^2),$$

where \mathcal{N}_a is the Avogadro number and $\langle \cdot \rangle$ denotes a canonical average.

Setting $\sigma = \frac{\lambda}{\rho C_v}$, it follows

$$\partial_t T = \sigma \Delta T.$$

Consider the heating or cooling of the sytem from T_1 to $T_2 = T_1 + \delta T$ with $|\delta T| \ll T_1, T_2$. Setting $u = (T_2 - T)/\delta T$, the evolution of u is governed by the Cauchy problem

$$\begin{cases} \partial_t u = \sigma \Delta u & \text{in } \Omega_i, \\ u|_{t=0} = u_0 \equiv 1 & \text{in } \Omega_i, \\ u = 0 & \text{on } \partial\Omega_i. \end{cases} \quad (11)$$

The initial condition u_0 can be expanded on the Fourier modes

$$\phi_{klm}(x, y, z) = \left(\frac{2}{L}\right)^{3/2} \sin\left(\frac{k\pi x}{L}\right) \sin\left(\frac{l\pi y}{L}\right) \sin\left(\frac{m\pi z}{L}\right)$$

as

$$u_0(x, y, z) = \frac{16\sqrt{2}L^{3/2}}{\pi^3} \sum_{k,l,m \geq 0} \frac{1}{(2k+1)(2l+1)(2m+1)} \phi_{2k+1, 2l+1, 2m+1}(x, y, z).$$

Let us denote by

$$h(t, x) = \sum_{k \geq 0} \frac{1}{(2k+1)} \exp\left(-\sigma \frac{(2k+1)^2 \pi^2}{L^2} t\right) \sin\left(\frac{(2k+1)\pi x}{L}\right).$$

Since $\Delta \phi_{klm} = -\frac{(k^2 + l^2 + m^2)\pi^2}{L^2} \phi_{klm}$, it follows,

$$u(t, x, y, z) = \frac{64}{\pi^3} h(t, x) h(t, y) h(t, z).$$

The deviation to the target temperature T_2 is therefore, on average on the domain Ω_i ,

$$\bar{u}(t) = \frac{1}{L^3} \int_{]0, L[^3} u(t, x, y, z) dx dy dz = \frac{512}{\pi^6} k(t)^3,$$

where, setting $A = \sigma\pi^2 L^{-2}$,

$$k(t) = \sum_{k \geq 0} \frac{1}{(2k+1)^2} \exp\left(-\sigma \frac{(2k+1)^2 \pi^2}{L^2} t\right) = e^{-At} \left(1 + \frac{1}{9} e^{-8At} + \frac{1}{25} e^{-24At} + \dots\right). \quad (12)$$

It then holds

$$\frac{\bar{u}(t)}{\bar{u}(t_0)} = \left(\frac{k(t)}{k(t_0)}\right)^3 \sim e^{-3A(t-t_0)}$$

for $t \geq t_0$ and t_0 large enough. Therefore, the value of A (and thus of λ provided C_v is known) can be computed by fitting $\bar{u}(t)/\bar{u}(t_0)$ to an exponential function.

2.3 Numerical results

The kinetic temperature for a given number N_i of particles is defined as

$$T_{\text{kin}} = \frac{2}{3N_i k_B} \sum_{n=1}^{N_i} \frac{p_n^2}{2m_n}.$$

We also define, in analogy with the previous section, $u_{\text{kin}} = (T_2 - T_{\text{kin}})/\delta T$.

Figure 2 shows a plot of the instantaneous kinetic temperature in Ω_i in the case of a heating process for fluid Argon from T_1 to T_2 , and the corresponding plot of $\bar{u}(t)/\bar{u}(t_0)$ (with $t_0 = 5$ ps), averaged over 30 realizations of the heating process conducted from independent initial conditions. The parameters of the model are $N = 64000$, $\epsilon/k_B = 119.8$ K, $a = 3.405 \times 10^{-10}$ m, $T_1 = 400$ K, $T_2 = 420$ K, $\Delta t = 2.5 \times 10^{-15}$ s. We use a truncated Lennard-Jones potential with a cut-off radius $r_c = 2.5a$. The molar mass is $M = 39.95 \times 10^{-3}$ kg/mol, and the density is $\rho = 35044$ mol/m³. The simulation cell Ω is then a cubic box of edge length $L = 37.51a$. The parameters used for the thermalization are $\gamma_0/m = 10^{12}$ s⁻¹ and $t_{\text{init}} = 20$ ps. Then, the independent initial configurations are obtained from this thermalized configuration by running an additional Langevin dynamics for 15 ps before each realization of the heating process.

For the coupled NVE/NVT dynamics, we have used

$$\gamma(\cdot) = \gamma_1 \cos\left(\frac{\pi \cdot}{2r_c}\right) \quad (13)$$

with $\gamma_1/m = 5 \times 10^{12}$ s⁻¹. We have checked that the thermal response is not sensitive to the specific shape of the friction function nor to the value of γ_1 in a broad range.

As can be seen from Figure 2 (Left), the kinetic temperature in the inner region of the system converges toward the target value determined by the temperature of the thermostat. The function $\bar{u}(t)/\bar{u}(t_0)$ is plotted on the time interval $[t_0, t_1]$ with $t_0 = 5$ ps and $t_1 = 75$ ps. Notice that, as we discard the initial relaxation, the higher order exponential terms in (12) can be neglected, so that we can indeed approximate $\bar{u}(t)/\bar{u}(t_0)$ by $e^{-3A(t-t_0)}$. A least-square fit gives $A = 0.01438$ s⁻¹. A numerical computation of C_v at $T = 400$ K (using a Langevin NVT sampling with 6×10^5 time-step as described in [2]) gives $C_v = 18.01$ J/K/mol, in good agreement with the experimental value $C_v = 18.12$ J/K/mol [9]. Therefore, the computed value of λ is $\lambda = 0.1509$ W/m/K, which is in good agreement with the experimental value [9] $\lambda = 0.1557$ W/m/K at $T = 400$ K.

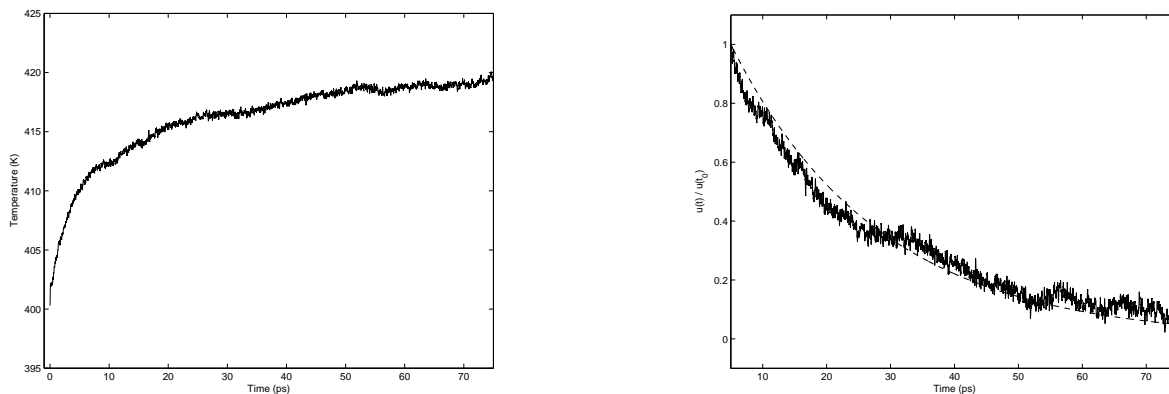


Figure 2: Left: Kinetic temperature in Ω_i as a function of time. Right: Plot of $\bar{u}_{\text{kin}}/\bar{u}_{\text{kin}}(t_0)$ as a function of time with $t_0 = 5$ ps (solid line), as well as its exponential fitting function (dashed line). Notice that the exponential approximation seems to be justified.

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