

Langevin Equation with Colored Noise for Constant-Temperature Molecular Dynamics Simulations

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We discuss the use of a Langevin equation with a colored (correlated) noise to perform constant-temperature molecular dynamics. Since the equations of motion are linear in nature, it is easy to predict the response of a Hamiltonian system to such a thermostat and to tune at will the relaxation time of modes of different frequency. This allows one to optimize the time needed for equilibration and to generate independent configurations. We show how this frequency-dependent response can be exploited to control the temperature of Car-Parrinello-like dynamics without affecting the adiabatic separation of the electronic degrees of freedom from the vibrations of the ions.

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Solving Hamilton's equations leads to sampling of the microcanonical constant-energy distribution, but in real-life experiments, it is the temperature that is kept constant. Reproducing this condition in computer simulations is of great importance for the investigation of a large class of physical, chemical, and biological problems. Several approaches have been proposed to this aim [1–4]. Many of these [1,4] rely on stochastic methods, which are a natural choice for modeling the interactions with an external heat bath, and which display excellent ergodic behavior due to their random nature. A good thermostat should be able to rapidly enforce the correct probability distribution, and generate uncorrelated configurations. The efficiency is particularly important in *ab initio* simulations because of their high computational cost. The stochastic thermostats used so far are based on Markovian equations of motion and imply no memory.

Markovian processes are, however, only a subset of all possible stochastic processes. Furthermore, the Mori-Zwanzig theory ensures that whenever some degree of freedom is integrated out, the dynamics of the remaining degrees of freedom are described by a non-Markovian Langevin equation, with a finite-range memory function [5–7]. Hence, it is natural to explore the effect of using a non-Markovian Langevin equation to perform constant-temperature molecular dynamics (MD). We will show that, by using colored noise, it is possible to influence in a different manner the different vibrational modes of the system. Thus, the thermostat can be adjusted to the system under study so as to optimize its performance. This is, to our knowledge, the first time that a colored Langevin equation has been employed in atomistic simulations.

An area which would greatly benefit from an improved, tunable thermostat is that of Car-Parrinello (CP)-like, extended Lagrangian schemes [8]. The idea behind this approach is very general, as it applies to any system where the forces are the result of an expensive optimization proce-

dure. This is circumvented by extending the dynamical degrees of freedom (DOF) including the parameters to be optimized, and introducing an artificial dynamics which allows these extra variables to be maintained close to the ground state. In the prototypical example of CP molecular dynamics (CPMD), a fictitious mass is assigned to the electronic DOF so that they can be evolved at the same time as the ionic DOF. If the fictitious mass is small enough, the dynamics of the electrons are adiabatically separated from the dynamics of the ions. Hence, the electrons are kept close to the ground state, while the nuclei are evolved at the correct temperature. This same technique can be used in classical simulations that use polarizable force fields, where the electronic DOF describe the charge polarization of the system [9,10]. Similar approaches have also been suggested in the field of rare-events sampling [11].

Controlling the temperature in these CP-like techniques requires that one acts separately on the ionic degrees of freedom, which must sample the correct canonical ensemble, and on the variational parameters, which must always remain at low temperature to minimize the error in the forces [12]. Traditional stochastic thermostats allow for a highly ergodic sampling of all the degrees of freedom, irrespective of their frequency. This is beneficial for the ionic DOFs but causes the breakdown of adiabatic separation. For this reason, deterministic thermostats of the Nosé-Hoover (NH) type [2] have been adopted. However, the original NH thermostat has well-known ergodicity problems, and the extension to NH chains is normally used [3], at the price of introducing a large number of parameters, whose effect on the dynamics is not easy to predict. In the following, we show that by using correlated noise it is possible to tune the coupling of a stochastic thermostat with the various degrees of freedom. This allows one not only to use Langevin dynamics in CP-like methods, but also significantly improves the sampling because the ther-

mostat is tailored to the system under study, in a predictable and controlled fashion.

We consider here a system described by coordinates q_i , momenta p_i , and masses m_i , interacting via a potential $U(q)$, where q is the set of q_i 's. The colored Langevin equations [5,6] read

$$\begin{aligned}\dot{q}_i(t) &= p_i(t)/m_i \\ \dot{p}_i(t) &= f_i[q(t)] - \int_0^t dt' \mathcal{K}(t-t') p_i(t') + \zeta_i(t)\end{aligned}\quad (1)$$

where $f_i = -\partial U/\partial q_i$ are the forces, $\mathcal{K}(t)$ is the memory kernel, and $\zeta(t)$ is a vector of independent Gaussian noises. In order to set the temperature to a chosen value T , the noise term $\zeta(t)$ needs to be related to the memory kernel by the fluctuation-dissipation theorem $\langle \zeta_i(t) \zeta_j(t') \rangle = \delta_{ij} m_i T \mathcal{K}(t-t')$.

The non-Markovian Eqs. (1) might seem at first too complex to be used in practical applications. However, for a rather general form of the memory kernel, $\mathcal{K}(t) = \Re \sum_k c_k e^{-t(\gamma_k + i\omega_k)}$ with $\gamma_k > 0$, it is possible to rewrite Eq. (1) in an equivalent Markovian form by introducing a set of auxiliary momenta [13,14]:

$$\begin{aligned}\dot{q}_i(t) &= s_{0i}(t)/m \\ \dot{\mathbf{s}}_i(t) &= (f_i[q(t)], 0, \dots, 0)^T - \mathbf{A} \mathbf{s}_i(t) + \mathbf{B} \boldsymbol{\eta}_i(t).\end{aligned}\quad (2)$$

Here, $\mathbf{s}_i = (p_i, s_{i1}, \dots, s_{iN})^T$ is a $N+1$ dimensional vector, whose first component is the canonical momentum p_i associated to the i -th DOF, and $\boldsymbol{\eta}_i$ is a vector of Gaussian white noises, with $\langle \eta_{ik}(t) \eta_{jk}(t') \rangle = \delta_{ij} \delta(t-t') \delta_{kk'}$. The real-valued matrices \mathbf{A} and \mathbf{B} determine the dynamics of p_i , and can be related to $\mathcal{K}(t)$ by extending the arguments of Ref. [13], as will be discussed elsewhere.

In order to illustrate some of the effects of using a colored noise, we study the simple case in which

$$\mathbf{A} = \frac{1}{\tau_F} \begin{pmatrix} 0 & -\sqrt{\gamma \tau_F} \\ \sqrt{\gamma \tau_F} & 1 \end{pmatrix}, \quad \mathbf{B} = \sqrt{\frac{\gamma T m_i}{\tau_F}} \begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix}.\quad (3)$$

This choice leads to the stationary distribution

$$\bar{P}(q, p, s_1) \propto \exp \left[-\frac{1}{T} \left(\frac{p^2}{2m} + \frac{s_1^2}{2m} + U(q) \right) \right],$$

corresponding to the desired canonical ensemble for q and p . The memory kernel and its power spectrum are

$$\mathcal{K}(t) = \frac{\gamma}{\tau_F} e^{-|t|/\tau_F} \quad \text{and} \quad S(\omega) = \frac{\gamma}{\pi} \frac{1}{1 + \tau_F^2 \omega^2}, \quad (4)$$

respectively. Thus, the friction γ determines the kernel intensity and τ_F the autocorrelation time of the noise. One can consider $S(\omega)$ to be a low-pass filter for the noise, which has the cutoff frequency τ_F^{-1} . Clearly, when $\tau_F \rightarrow 0$, the white-noise limit is recovered.

We consider the dynamics of a set of harmonic oscillators. In this case, Eqs. (2) are fully linear, and the autocorrelation time for the total energy of an eigenmode of frequency ω can be explicitly evaluated [6,15]:

$$\tau_H(\omega) = \frac{\gamma}{4\omega^2} + \frac{1}{\gamma} + \frac{\omega^2 \tau_F^2}{\gamma}. \quad (5)$$

We take $\tau_H(\omega)$ as a measure of the time needed for the thermalization of each individual normal mode. For a white noise ($\tau_F = 0$), τ_H decreases with ω until it reaches a plateau at $\tau_H = 1/\gamma$, while for $\tau_F \neq 0$, the autocorrelation time has a minimum at $\omega = \sqrt{\gamma/(2\tau_F)}$ and grows quadratically thereafter. By properly adjusting τ_F , one can select which modes are going to be maximally coupled with the thermostat and thus reduce the coupling to the fastest modes (see also Fig. 1).

We next consider the application of the colored-noise thermostat [Eq. (3)] to classical MD simulation using a polarizable force field. Here, the electronic DOF are represented by charged shells, bound with harmonic potentials to the corresponding atomic cores. We couple a colored-noise thermostat to the ions, and choose the filtering time τ_F in such a way that the impact on the electronic DOF is minimal. At the same time, we apply a zero temperature, memory-less thermostat of friction γ_S to the electrons. This leads to a nonequilibrium dynamics, where heat is injected into the ionic DOF and subtracted from the electronic ones. In spite of the stochastic nature of these equations, it is still possible to introduce a conserved

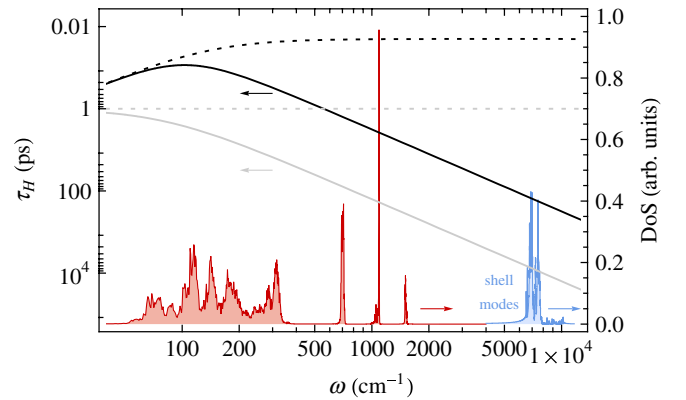


FIG. 1 (color online). The autocorrelation time of the total energy for harmonic oscillators of frequency ω [cf. Equation (5)] is plotted for different values of the thermostat parameters. Dark curves correspond to high friction ($\gamma^{-1} = 20$ fs) whereas light ones correspond to a more gentle thermostat ($\gamma^{-1} = 1$ ps). Dotted lines correspond to white noise ($\tau_F = 0$) and full ones to colored noise with $\tau_F = 2$ fs. The curves are superimposed on the vibrational density of states (DoS) for a polarizable force-field simulation of crystalline calcite, which was obtained from the Fourier transform of the velocity-velocity autocorrelation function. For reference, we report the shell vibrational modes as obtained from a run where we artificially heated the shells to 300 K.

quantity, which can be obtained by accumulating the change in kinetic energy due to the thermostat [4,16–18]. At variance with Refs. [4,16], the conservation of this quantity does not rigorously measure the sampling accuracy, but only the accuracy of the integration.

As an example, we consider the simulation of crystalline calcite, modeled by a polarizable force field [17]. The thermostats are applied to the nonpolarizable ions and to the centers of mass of the polarizable ion-shell pairs. The electronic temperature is controlled by the damping of the velocity of the shells relative to their partner ions. The vibrational density of states in the absence of any thermostat can be used to choose the thermostat parameters (see Fig. 1), without having to perform expensive tests. In real life, anharmonicity will introduce some coupling between the normal modes, so that deviations from the predictions of Eq. (5) are expected. However, at least in the case of quasiharmonic modes, they will most likely reduce $\tau_H(\omega)$.

We simulated [19] a box containing 96 CaCO_3 units, with a time step of 1 fs, performing *NVT* runs with target temperature $T = 300$ K. We performed systematic tests by varying τ_F , γ , and γ_S (Fig. 2). The averages have been computed from 1 ns-long runs, where we discarded the first 100 ps. Within a large range of parameters, the procedure performs as expected: the temperature of the shells remains below a few K, and the ions equilibrate to the desired temperature. Some care must be taken in choosing the friction γ_S because the shell thermostat can induce a small drag on the ions which results in an ionic temperature lower than desired. As τ_F is set to a value different from zero, the heat transferred to the electronic DOF is reduced. Since τ_H decays only quadratically for $\omega > \tau_F^{-1}$, one must make a tradeoff between heat transfer to the electrons and

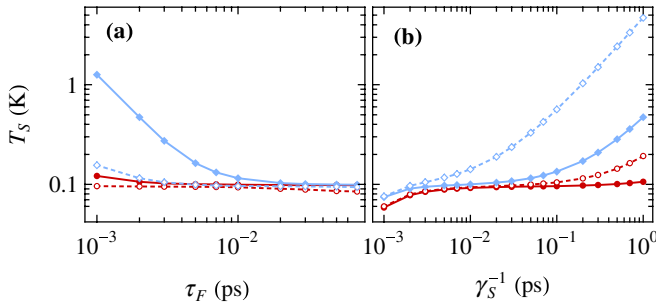


FIG. 2 (color online). Shell temperature (T_S) for calcite as a function of the thermostat parameters. The points are joined by continuous lines, for clarity sake. In both panels, we distinguish the strength of the ion thermostat by the line color. Lighter or darker (blue or red in the online version) curves correspond, respectively, to a strong ($\gamma^{-1} = 20$ fs) or mild ($\gamma^{-1} = 1$ ps) friction. In panel (a), we plot T_S against τ_F , and we choose two extreme values of the shell friction, $\gamma_S^{-1} = 1$ ps and $\gamma_S^{-1} = 50$ fs, which are represented, respectively, with full and dashed lines. In panel (b), we plot the dependence of T_S versus γ_S . Here, full and dashed lines correspond, respectively, to a physically meaningful filter ($\tau_F = 2$ fs) and to white noise ($\tau_F = 0$).

the efficiency of thermalization of the fastest ionic modes. This tradeoff can be avoided by introducing additional degrees of freedom to the thermostat, so as to obtain a more sharply defined filter as we will show below.

Thermostatting an *ab initio* CPMD is more challenging. Since wave functions are not atom centered, the coupling of the dynamics of the electronic DOF to the ions is stronger than in the shell-model case, and the presence of high-frequency components in the noise quickly heats up the electrons. Furthermore, because of the expense of *ab initio* CPMD, it is mandatory to have fast equilibration and sampling. We will show that both problems can be solved thanks to the tunability and predictability of our scheme. As a test example, we ran simulations of a single heavy water molecule in vacuum, using a standard literature setup (see Fig. 3 and Ref. [20]). We ran several independent trajectories for a total of 90 ps, starting from ionic configurations equilibrated at 300 K and from wave functions quenched to the Born-Oppenheimer surface [21].

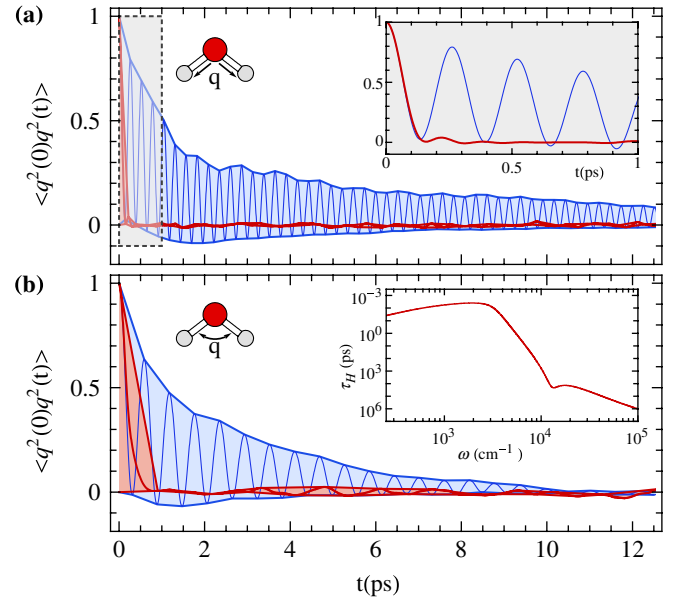


FIG. 3 (color online). Autocorrelation functions for the squares of (a) the symmetric stretching and (b) the bending modes of a heavy water molecule in vacuum, performed in the *NVT* ensemble at $T = 300$ K. We use a fictitious mass $\mu = 200$ a.u., and a time step of 4 a.u., in order to minimize the errors on the forces [24]. The Nosé-Hoover thermostat with chain length 4 has been used and its mass chosen so as to maximize the coupling to the stretching mode. The NH correlation functions (lighter lines, blue in the online version) are highly oscillating and decay very slowly. The shading highlights the curve's envelope. In contrast, using the new thermostat (darker lines, red in the online version), we find a much sharper decay, which in the case of the stretching requires an enlarged scale to be appreciated [inset of panel (a)]. In the inset of panel (b) we show the relation between τ_H and ω for our thermostat. The parameters have been optimized to obtain a sharp decay of the response for frequencies above the stretching mode.

We have used Eq. (4) with 5 extended momenta and fitted **A** and **B** in order to obtain a short, optimal response time over the ionic degrees of freedom, and an abrupt increase in the region corresponding to electronic modes [see inset of Fig. 3(b)]. We then compare this case with results from a massive NH chains simulation [3,22]. In both cases, the strength of the thermostat is such that the dynamics of the ions is severely altered, and the drift in electronic energy is negligible. In Fig. 3, we plot the autocorrelation function of the squares of the normal modes. The integral of these functions measures the time required to lose memory of the initial configuration. The dramatic reduction of the correlation time is evident.

The thermostat we have presented offers a number of advantages. It can be used in CP-like, extended-Lagrangian simulations, and it is also much faster in reaching equilibrium than the NH thermostat. This is relevant when performing expensive, *ab initio* simulations, but any problem which requires averaging over uncorrelated configurations of the system can benefit from the enhanced relaxation time. Here, in the difficult case of a molecule in vacuum, we have been able to reduce the correlation time down to a fraction of a picosecond, just by estimating the optimal parameters on the basis of analytical results. An additional advantage is that the exact propagator in the case of zero force is obtained easily [16], which makes the implementation simple and robust, at variance with NH chains [3] which require a high order integrator [23]. Finally, the introduction of highly tunable, non-Markovian thermostats in molecular dynamics simulations lays the foundations for the development of optimal sampling algorithms to be used in free-energy calculations, or in systems with a broad vibrational spectrum, such as path-integrals MD. We believe that this is only a first example and that colored noise will find many other applications in a variety of computational problems.

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- [1] T. Schneider and E. Stoll, Phys. Rev. B **17**, 1302 (1978); H.C. Andersen, J. Chem. Phys. **72**, 2384 (1980); D.M. Heyes, Chem. Phys. **82**, 285 (1983); C.P. Lowe, Europhys. Lett. **47**, 145 (1999); T. Soddemann, B. Dünweg, and K. Kremer, Phys. Rev. E **68**, 046702 (2003).
- [2] S. Nosé, J. Chem. Phys. **81**, 511 (1984); W.G. Hoover, Phys. Rev. A **31**, 1695 (1985).
- [3] G.J. Martyna, M.L. Klein, and M. Tuckerman, J. Chem. Phys. **97**, 2635 (1992).
- [4] G. Bussi, D. Donadio, and M. Parrinello, J. Chem. Phys. **126**, 014101 (2007).
- [5] R. Zwanzig, Phys. Rev. **124**, 983 (1961).
- [6] R. Zwanzig, *Nonequilibrium Statistical Mechanics* (Oxford University Press, New York, 2001).
- [7] H. Mori, Prog. Theor. Phys. **33**, 423 (1965).
- [8] R. Car and M. Parrinello, Phys. Rev. Lett. **55**, 2471 (1985).
- [9] M. Sprik, J. Phys. Chem. **95**, 2283 (1991).
- [10] S.W. Rick, S.J. Stuart, and B.J. Berne, J. Chem. Phys. **101**, 6141 (1994).
- [11] L. Rosso, P. Mináry, Z. Zhu, and M.E. Tuckerman, J. Chem. Phys. **116**, 4389 (2002); J. VandeVondele and U. Rothlisberger, J. Phys. Chem. B **106**, 203 (2002); L. Maragliano and E. Vanden-Eijnden, Chem. Phys. Lett. **426**, 168 (2006).
- [12] P.E. Blöchl and M. Parrinello, Phys. Rev. B **45**, 9413 (1992).
- [13] F. Marchesoni and P. Grigolini, J. Chem. Phys. **78**, 6287 (1983).
- [14] J. Łuczka, Chaos **15**, 026107 (2005).
- [15] C.W. Gardiner, *Handbook of Stochastic Methods* (Springer, Berlin, 2003), 3rd ed.
- [16] G. Bussi and M. Parrinello, Phys. Rev. E **75**, 056707 (2007).
- [17] F. Bruneval, D. Donadio, and M. Parrinello, J. Phys. Chem. B **111**, 12219 (2007).
- [18] B. Ensing, S.O. Nielsen, P.B. Moore, M.L. Klein, and M. Parrinello, J. Chem. Theory Comput. **3**, 1100 (2007).
- [19] W. Smith, T.R. Forester, I.T. Todorov, and M. Leslie, CCLRC Daresbury Laboratory, United Kingdom (2006).
- [20] P.H.L. Sit and N. Marzari, J. Chem. Phys. **122**, 204510 (2005).
- [21] CPMD, Copyright IBM Corp 1990-2006, Copyright MPI Stuttgart 1997-2001, <http://www.cpmc.org/>.
- [22] D.J. Tobias, G.J. Martyna, and M.L. Klein, J. Phys. Chem. **97**, 12959 (1993).
- [23] M.E. Tuckerman and M. Parrinello, J. Chem. Phys. **101**, 1302 (1994).
- [24] P. Tangney and S. Scandolo, J. Chem. Phys. **116**, 14 (2002).