Efficient Langevin dynamics for “noisy” forces

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Efficient Boltzmann-sampling using first-principles methods is challenging for extended systems due to the steep scaling of electronic structure methods with the system size. Stochastic approaches provide a gentler system-size dependency at the cost of introducing “noisy” forces, which serve to limit the efficiency of the sampling. In the first-order Langevin dynamics (FOLD), efficient sampling is achievable by combining a well-chosen preconditioning matrix S with a time-step-bias-mitigating propagator (Mazzola et al., Phys. Rev. Lett., 118, 015703 (2017)). However, when forces are noisy, S is set equal to the force-covariance matrix, a procedure which severely limits the efficiency and the stability of the sampling. Here, we develop a new, general, optimal, and stable sampling approach for FOLD under noisy forces. We apply it for silicon nanocrystals treated with stochastic density functional theory and show efficiency improvements by an order-of-magnitude.

Prediction of the equilibrium properties of extended systems using atomistic models often requires sampling from the Boltzmann distribution a series of configurations [1–6]. Most common sampling methods implicitly assume that either the potential energy surface [7] or the forces on the nuclei [8–12] are accessible, either through deterministic ab-initio methods such as density functional theory (DFT) or other quantum chemistry methods (for small-medium sized systems) [13] or through empirical force-fields. For extended systems, ab initio methods often rely on stochastic techniques such as Quantum Monte Carlo (QMC) [14–17] or stochastic DFT (sDFT) [18–23]. For example, in sDFT the forces are calculated using a relatively small number of stochastic orbitals instead of using the full set of deterministic Kohn-Sham eigenstates. Therefore, the forces calculated within sDFT are noisy with fluctuating values. Such noisy forces can also occur with partially-converged self-consistent field approaches to deterministic DFT [24,25].

Langevin dynamics (LD) often serves to generate a series of thermally-distributed nuclear configurations, based on the calculated forces on the nuclei. The balance between accuracy, which favors small time-steps, and efficiency, which requires large time-steps (to reduce the correlations between consecutive configurations in the series), determines the overall complexity and accuracy of this class of approaches. A common form of Langevin dynamics is the so-called second-order LD (SOLD) [15,17,19,20,28], in which the Newton equation of motion includes a friction term and a noisy force obeying the fluctuation-dissipation relation. An alternative is the first-order Langevin dynamics (FOLD) [15,29,30], which is conceptually simpler than SOLD because it does not have inertia and therefore only nuclear configurations are Boltzmann-sampled. FOLD is amenable to the introduction of a preconditioning matrix, which, by proper choice, dramatically increases the configurational sampling efficiency without affecting the accuracy [29]. Unfortunately, when the forces are noisy, this preconditioning matrix must be set equal to the force covariance matrix and, thus, cannot be used for obtaining optimal sampling efficiency. Therefore, it seems that noisy forces, used in conjunction with FOLD, are inherently less efficient than deterministic ones. An additional complication appears as numerical instabilities due to the singular nature of the force covariance matrix.

In this letter, we develop an approach that enables the use of noisy forces within FOLD lifting the constraints on the preconditioning matrix. Furthermore, we demonstrate the approach for silicon NCs within sDFT and show an order of magnitude increase in sampling efficiency compared to state of the art methods for noisy forces. The solution lies in adding random noise which combines with preconditioning matrix to complement the noise in the force coming from the stochastic electronic structure method.
In its simplest form, the time-discretized first-order Langevin dynamics produces a set of $M$ configurations $\mathbf{R}_\tau \equiv (R^1, \ldots, R^{3N})^\dagger$, $\tau = 1, \ldots, M$ for a $N$ nuclei system, through a random walk described by [10]:

$$\mathbf{R}_{\tau+1} = \mathbf{R}_\tau + \sqrt{2\kappa_B T \Delta_t} \mathbf{\xi}_\tau + \Delta_t S^{-1} \mathbf{f} (\mathbf{R}_\tau),$$

where $\mathbf{f} (\mathbf{R}) \equiv (f^1 (\mathbf{R}), \ldots, f^{3N} (\mathbf{R}))^\dagger = -\nabla V (\mathbf{R})$ is the force acting on the nuclear degrees of freedom $\mathbf{R}$, $\Delta_t$ is a unit-less time-step parameter and $S$ is an arbitrary $3N \times 3N$ symmetric positive-definite matrix. The random vector $\mathbf{\xi}_\tau = (\mathbf{\xi}_1, \ldots, \mathbf{\xi}_N)^\dagger$, with which thermal fluctuations are introduced, is distributed such that $\langle \mathbf{\xi}^\dagger \mathbf{\xi} \rangle = 0$ and

$$\langle \mathbf{\xi}_\tau \mathbf{\xi}^\dagger_{\tau'} \rangle = S^{-1} \delta_{\tau,\tau'}.$$  \hspace{1cm} (2)

For any choice of the preconditioning matrix $S$, the generated trajectory of $M$ samples the Boltzmann distribution at temperature $T$ in the $\Delta_t \to 0$ and $M \to \infty$ limits [30]. For finite values of $M$ and $\Delta_t$, the configurations can then be used to produce estimates of the thermal average of quantities $A$: $\langle A \rangle_T \approx (A_M) \equiv \langle 1/N \sum_{\tau=1}^M A (\mathbf{R}_\tau) \rangle$. One would expect that the variance of $A_M$ is $\sigma_{A,T}^2 = \frac{\sigma_A^2}{N}$, where $\sigma_A^2$ is the thermal variance in $A$ at temperature $T$. However, since configurations $\mathbf{R}_\tau$ and $\mathbf{R}_{\tau+\tau'}$ correlate, the actual variance is much larger: $\sigma_{A,T}^2 = \frac{\sigma_A^2}{M} \tau_c$, where $\tau_c$ is the number of correlated time-steps. The smaller $\tau_c$, the more efficient is the Langevin dynamics for sampling.

Consider now the efficiency of the method in the $T \to 0$ limit for the $3N$-dimensional harmonic oscillator $V (\mathbf{R}) = \frac{1}{2} \mathbf{R}^\dagger H \mathbf{R}$, where $H$ is the Hessian matrix ($H_{ij} = \frac{\partial^2 V (\mathbf{R})}{\partial R^i \partial R^j}$). In this limit, the trajectory generated by Eq. (1) with $\mathbf{f} (\mathbf{R}) = -H \mathbf{R}$ is given by $\mathbf{R}_\tau = (1 - \Delta_t U)^\tau \mathbf{R}_0$, where $U = S^{-1} H$ and $\tau = 0, 1, 2, \ldots$ enumerates the time steps. The correlation between displacements after many time-steps decays as $e^{-\Delta_t u_{\text{min}}}$, where $u_{\text{min}} > 0$ is the smallest eigenvalue of $U$, so $\tau_c \approx (\Delta_t u_{\text{min}})^{-1}$. Furthermore, the trajectory $\mathbf{R}_\tau$ remains stable as long as $u_{\text{max}} \Delta_t < 2$, where $u_{\text{max}}$ is the largest eigenvalue of $U$. Thus $\tau_c$ is limited from below by

$$\tau_c > \frac{1}{2} \frac{u_{\text{max}}}{u_{\text{min}}} \equiv \frac{1}{2} \text{cond} (U).$$  \hspace{1cm} (3)

It is now evident how preconditioning is important. Without it (say $S = I$) we find $\tau_c > \frac{1}{2} \text{cond} (U)$ which in typical problems can easily exceed $10^3$, making the random walk very inefficient. Optimal preconditioning involves taking $S = H$, enabling $\tau_c$ to be as low as 1. However, in this case one would have $\tau_c \approx \Delta_t^{-1}$, and since $\Delta_t$ has to be kept small to avoid bias, $\tau_c$ is often quite large even under preconditioning. This is where a method that reduce the time-step bias, thus allowing $\Delta_t$ to grow is required. Such a random walk was proposed in Ref. [30] based upon the exact solution for a harmonic potential. It involves the following process:

$$R_{\tau+1} = R_\tau + \sqrt{2\kappa_B T \Delta_t} \mathbf{\xi}_\tau + \Delta_t S^{-1} \mathbf{f} (\mathbf{R}_\tau),$$

employing two time-steps

$$\Delta_n = \frac{1}{n} (1 - e^{-n \Delta_t}), \, n = 1, 2$$

and was shown to lead to significantly lower time-step biases. We refer to this type of random walk as “reduced-bias FOLD” (RB-FOLD).

What happens when the forces are random? Can we still use RB-FOLD and have efficient sampling? The random forces $\mathbf{f} (\mathbf{R}_\tau) = \mathbf{f} (\mathbf{R}_\tau) + \mathbf{\eta}_\tau$ coming from sDFT or QMC will give the deterministic force $\mathbf{f} (\mathbf{R}_\tau) = \langle \mathbf{\phi} (\mathbf{R}_\tau) \rangle$ on the average but will also involve random inseparable fluctuations $\mathbf{\eta}_\tau = (\mathbf{\eta}_1, \ldots, \mathbf{\eta}_N)^\dagger$. Simply plugging the random force $\mathbf{\phi} (\mathbf{R})$ into the FOLD equation will give the wrong effective dynamics $R_{\tau+1} = R_\tau + \sqrt{2\kappa_B T \Delta_t} (\mathbf{\xi}_\tau + \sqrt{\Delta_t \tau} S^{-1} \mathbf{\eta}) + \Delta_t S^{-1} \mathbf{f} (\mathbf{R}_\tau)$ since the noise fluctuations $\mathbf{\eta}_\tau$ clearly cause additional heating, violating the fluctuation-dissipation relation. Hence, whenever one replaces $\mathbf{f} (\mathbf{R})$ by $\mathbf{\phi} (\mathbf{R})$ in Eq. (1), one also needs to replace $\mathbf{\xi}$ of Eq. (2) by a “smaller” fluctuation $\mathbf{\delta}$, so the FOLD is now

$$R_{\tau+1} = R_\tau + \frac{\sqrt{2\kappa_B T \Delta_t}}{S^{-1} \text{cov} \mathbf{\phi} (\mathbf{R}_\tau)} \delta_{\tau,\tau'}.$$  \hspace{1cm} (7)

where:

$$\langle \mathbf{\delta}_{\tau,\tau'} \rangle = \left[ S^{-1} - \frac{\Delta_t}{2\kappa_B T} S^{-1} \text{cov} \mathbf{\phi} (\mathbf{R}_\tau) S^{-1} \right] \delta_{\tau,\tau'}.$$

Here, $\text{cov} \mathbf{\phi} (\mathbf{R}_\tau) = \langle \mathbf{\eta} \mathbf{\eta}^\dagger \rangle$ is the force covariance matrix and it is proportional to $\frac{1}{\Delta_t}$, where $I$ is the number of stochastic iterations in the electronic structure calculation. Note however, that the term on the right-hand side must be positive-definite, a condition that can be achieved by sufficient reduction of either the time step $\Delta_t$ or the random force covariance. In both cases this requires additional computational work. In Ref. [10] the specific choice $S = \alpha \times \text{cov} \mathbf{\phi} (\mathbf{R}_\tau)$ (where $\alpha$ is a properly chosen constant) was made, which had the appeal that $\langle \mathbf{\delta} \mathbf{\delta}^\dagger \rangle$, like $\langle \mathbf{\xi} \mathbf{\xi}^\dagger \rangle$ of Eq. (2) was proportional to $S^{-1}$. But this choice has the follwing shortcomings: (a) $S$ is now time-dependent and requires special treatment in the equation of motion [16]; (b) it straddles $S$, leaving no room for using it as a preconditioning matrix for optimizing the efficiency and (c) it assumes implicitly that the covariance matrix is invertible, which is not always the case [31]. In light of these limitations, we advocate leaving $S$ in its original form as an optimal preconditioning matrix (e.g. $S \approx H$) and using Eq. (1) with $\mathbf{\phi} (\mathbf{R}_\tau)$
replacing $f(R_\tau)$ and with $\tilde{\zeta}$ of Eq. (7) replacing $\zeta$ of Eq. (2). We refer to this method as “noisy-FOLD”, since it is an extension of the FOLD method to noisy forces. A similar treatment in the case of the random force counterpart of RB-FOLD (Eq. 1), to which we refer henceforth as “noisy-RB-FOLD”, leads to the following FOLD

$$R_{\tau+1} = R_\tau + \sqrt{2k_B T \Delta t} \tilde{\zeta}_\tau + \Delta_1 S^{-1} \phi(R_\tau), \quad (8)$$

where:

$$\langle \tilde{\zeta}_\tau \tilde{\zeta}_{\tau'} \rangle = \left[ 1 - \frac{\Delta t^2}{2k_B T \Delta t} S^{-1} \text{cov}(R_\tau) \right] S^{-1} \delta_{\tau\tau'}. \quad (9)$$

These two equations form the main result of this letter, since this noisy-RB-FOLD preserves much of the flexibility in choosing the matrix $S$ as in the RB-FOLD solution while allowing for stochastic forces. As noted above for noisy FOLD, here too, the right-hand side of Eq. (9) must be positive-definite. To enforce this condition, additional numerical work is required, either by decreasing either the time-step or the force covariance. The first measure, decreasing the time-step, increases the sample correlation, so additional time-steps are needed as a compensation. The second measure, reducing $\text{cov}_\phi$, calls for a step up in the number of stochastic electronic-structure iterations.

We use the Harmonic potential discussed above to demonstrate the theory in Fig. 1. We plot the fluctuation $\sigma_V$ and the bias $\Delta V$ for various sampling procedures within FOLD, comparing the non-optimal preconditioning choice, $S = \alpha \text{cov}_\phi$ (with $\alpha = 1$ in the units of the Harmonic oscillator, triangles) discussed in Ref. 16 and the optimal preconditioning $S = H$ (squares) advocated here. It is evident from the figure, that whether one uses noisy-FOLD (blue symbols, Eqs. (6)-(7)) or noisy-RB-FOLD (red symbols, Eqs. (8)-(9)) the bias $\Delta V$ can be reduced only by decreasing the time steps $\Delta t$. However the above analysis of $\tau_c$ showed as $\Delta t$ decreases, the fluctuation $\sigma_V$ grows! Under optimal preconditioning $S = H$ (squares) we see that noisy-FOLD (blue symbols, Eqs. (6)-(7)) biases are reduced yet the error control is still unsatisfactory since any attempt to reduce the bias further (by decreasing $\Delta t$) increases once again the fluctuation $\sigma_V$. This problem does not arise for noisy-RB-FOLD results (red squares, Eqs. (8)-(9)) where $\Delta t$ can grow to lower $\sigma_V$ without a bias penalty. Note that to within small fluctuations the same results seen here for noisy forces also appear for deterministic ones (obtained by taking $\phi = f$ and $\text{cov}_\phi = 0$, not shown here).

We expect that noisy-RB-FOLD calculations to be highly efficient not only for the Harmonic model but also for more realistic systems. To demonstrate this, we apply the method to the problem of determining the structural properties of a realistic atomistic system such as the Si6-H8 nanocrystal at $T = 300K$ described with DFT at the the local density approximation level 32. Our purpose is to validate the noisy-RB-FOLD sampling approaches based on sDFT forces using calculations based on sampling methods which employ dDFT forces (RB-FOLD, FOLD and SOLD 19) and to compare the efficiencies of these methods. Note that all the FOLD methods in the figure are based on optimal sampling, with $S = H$. We could not show results for the choice $S = \alpha \text{cov}_\phi$ of Ref. 19 because of numerical problems stemming from the fact that the sDFT forces have a force-covariance matrix which is nearly singular (see supplementary material). In Fig. 2 (left panel) we show that indeed our new noisy-RB-FOLD method as well as the other methods predict the same first peak of the pair distribution function $g(r)$ (to within statistical fluctuations) 33. In order to study the efficiency, we plot in the right panel the the pair-distance correlation function in term of the distance $r_{ij}$ between a pair of Silicon atoms, numbered $i$ and $j$:

$$C_\tau = \frac{\sum_{t=1}^{N_\tau} r_{ij}(t) r_{ij}(t+\tau)}{\sum_{t=1}^{N_\tau} r_{ij}^2} \langle i,j \rangle, \quad (10)$$

where, $\langle \rangle_{i,j}$ represents an average over these pairs, and $N_\tau$ is the total number of steps in the Langevin trajectory. $C_\tau$ has the initial value of 1 at $\tau = 0$ and then it decays non-monotonically as it settles upon a steady
fluctuation around zero. We define the time scale $\tau_c$ for this decay as the earliest time for which $C_{\tau_c} = 0.1$. Consider first the correlation functions for the FOLD and the SOLD trajectories; both are seen to have a concave structure at small values of $\tau$ which delays decay and turns convex only at much longer times, and both trajectories exhibit a slow decay with $\tau_c \approx 100$. Next, consider the correlation functions for RB-FOLD: the deterministic RB-FOLD with $\Delta_1 = 1$ ($\Delta_2 = 10, \Delta_3 = 0.5$) and the noisy-RB-FOLD with $\Delta_1 = 0.5$ ($\Delta_2 = 0.375$) (having an identical form as that calculated within deterministic RB-FOLD with the same parameters, but not shown in the figure). In the figure, $\tau_c$ is twice as large when $\Delta_1 = 0.5$ than when $\Delta_1 = 1$, following our analysis above and both functions have a similar convex form. We have verified that the correlations of the noisy- and deterministic RB-FOLD trajectories for $\Delta_1 = 0.5$ are identical and we see that they represent an order of magnitude improvement on the previously used SOLD approach for sDFT.

Summarizing, in previous work [19], we used SOLD to address the problem of noisy forces in sDFT calculations but found that thousands of time steps were required to shake off the correlations. Here, we developed a radically more efficient method for sampling system configurations under stochastic forces. It capitalizes on a recently proposed method [10] but makes critical changes in the Langevin force sampling which restore optimal preconditioning. The final procedure is to perform a random walk following Eq. [5] while sampling the Langevin forces from Eq. [9]. Using a purely Harmonic model system we compared noisy-FOLD, and noisy-RB-FOLD and showed that the latter is much more efficient and insensitive to the time-step. We further showed that the noisy-RB-FOLD has similar characteristics also when applied to real atomistic system using sDFT forces. One notable difference between RB-DFT and noisy-RB-DFT concerns with increasing the time step. One must assure that the left-hand side of Eq. [9] is positive definite, hence at some point any increase of $\Delta_1^2/\Delta_2$ will necessitate a reduction of $\text{cov}\phi$. This is especially important at low temperatures. The results of this work provide a general recipe for efficient and stable Boltzmann sampling under the presence of stochastic forces. A good approximation to the Hessian which is required here can perhaps be obtained from a force-field calculation or from embedded fragment calculations used in the sDFT procedure [19, 22, 23, 34].

RB gratefully acknowledges the support of the Binational US-Israel Science Foundation under grant no. 2018368. D.N. acknowledges support from the National Science Foundation, grant CHE-1763176. E.R. acknowledges support from the Department of Energy, Photonics at Thermodynamic Limits Energy Frontier Research Center, under Grant No. de-sc0019140

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