Long-time convergence of an adaptive biasing force method: Variance reduction by Helmholtz projection

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Free energy computation techniques are very important in molecular dynamics computations, in order to obtain a coarse-grained description of a high-dimensional complex physical system. We study an adaptive biasing method to compute the free energy associated to the *Boltzmann-Gibbs* measure $\mu(dx) = Z_\mu^{-1} e^{-\beta V(x)} dx$ and the *reaction coordinate function* $\xi : (x_1, \ldots, x_n) \in \mathbb{T}^n \mapsto (x_1, x_2) \in \mathbb{T}^2$. The free energy is defined by $A(x_1, x_2) = -\beta^{-1} \ln \int_{\mathbb{T}^{n-2}} e^{-\beta V(x)} dx_3 \ldots dx_n$. More precisely, we study the following projected adaptive biasing force (PABF) method:

$$\begin{cases} dX_t = -\nabla\big(V - A_t \circ \xi\big)(X_t)dt + \sqrt{2\beta^{-1}} dW_t, \\ \nabla_{x_1^2} A_t = \mathcal{P}_{\psi^\xi}(F_t), \\ F_t^i(x_1, x_2) = \mathbb{E}[\partial_i V(X_t) | \xi(X_t) = (x_1, x_2)],\ i = 1, 2, \end{cases} \tag{1}$$

where $\mathcal{P}_{\psi^\xi} : H_{\psi^\xi}(\mathrm{div}; \mathbb{T}^2) \to H^1(\mathbb{T}^2) \times H^1(\mathbb{T}^2)$ is a linear operator defined by the following Helmholtz decomposition:

$$F_t \psi^\xi = \nabla A_t \psi^\xi + R_t \quad \text{ on } \mathbb{T}^2, \tag{2}$$

with $\mathrm{div}(R_t) = 0$. Here, $\psi^\xi(t, \cdot)$ denotes the density of the random variables $\xi(X_t)$. In practice, A_t is obtained from F_t by solving the Poisson problem:

$$\mathrm{div}(\nabla A_t \psi^\xi(t, .)) = \mathrm{div}(F_t \psi^\xi(t, .)) \text{ on } \mathbb{T}^2 \tag{3}$$

which is the Euler equation associated to the minimization problem:

$$A_t = \underset{g \in H^1(\mathcal{M})/\mathbb{R}}{\mathrm{argmin}} \int_{\mathcal{M}} |\nabla g - F_t|^2. \tag{4}$$

The interest of this projected ABF method compared to the original ABF approach (see for example [**?**, **?**, **?**, **?**]) is that the variance of ∇A_t is typically smaller than the variance of F_t. Moreover, A_t yields an estimate of the free energy at all time t.
Using entropy techniques, we study the longtime behavior of the nonlinear Fokker-Planck equation which rules the evolution of the density of X_t solution to (**??**). We prove exponential convergence to equilibrium of A_t to A, with a precise rate of convergence in terms of the Logarithmic Sobolev inequality constants of the conditional measures $\mu(dx \,|\, \xi)$.

This is a joint work with Tony Lelièvre.

Références

[1] E. Darve and A. Pohorille, *Calculating free energy using average forces, J. Chem. Phys., 2001,* ***115****, 9169-83.*

[2] J. Hénin and C. Chipot, *Overcoming free energy barriers using unconstrained molecular dynamics simulations, J. Chem. Phys., 2004,* ***121****, 2904-14.*

[3] T. Lelièvre, M. Rousset and G. Stoltz, *Free energy computations: A mathematical perspective, Imperial College Press, 2010.*

[4] T. Lelièvre, M. Rousset and G. Stoltz, *Long-time convergence of an adaptive biasing force method, Nonlinearity, 2008,* ***21****, 1155-1181.*

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