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Comment on "Quantum Thermal Bath for Molecular Dynamics Simulation"

The recent Letter by Dammak *et al.* [1] proposes a Langevin-type quantum thermal bath (QTB) for sampling quantum fluctuations in classical molecular dynamics (MD) simulations. Although a comparison was made with exact data only in the case of the harmonic oscillator, the authors claim that the thermostat "is valid at any temperature and for any interatomic potential as well as for *ab initio* schemes." In this Comment we challenge this assertion by showing that the method fails for anharmonic models. Furthermore, the QTB is inconsistent with the second fluctuation-dissipation theorem [2].

The QTB is a stochastic thermostat based on the Langevin equation [2]

$$m\dot{v} = -\frac{\partial V}{\partial x} - \zeta_0 v + \eta(t), \tag{1}$$

where x is the position, v is the velocity, $V(x)$ is an interaction potential, ζ_0 is the friction coefficient, and $\eta(t)$ is a random noise. Usually, $\eta(t)$ is a Gaussian white noise satisfying $\langle \eta(0)\eta(t)\rangle = k_B T \zeta_0 \delta(t)$ by virtue of the second fluctuation-dissipation theorem [2] in the classical limit. To incorporate quantum fluctuations, Dammak *et al.* modify only the random noise, imposing its autocorrelation function to satisfy

$$\langle \eta(0)\eta(t)\rangle = \frac{\zeta_0}{\pi}\int_{-\infty}^{\infty} \frac{\hbar\omega}{2} \coth\left(\frac{\hbar\omega}{2k_B T}\right) e^{-i\omega t} d\omega. \tag{2}$$

Unfortunately, the resulting colored-noise Langevin equation produces incorrect results for anharmonic potentials. To illustrate this we apply the method to a quartic oscillator (with potential energy $V(x) = \frac{1}{2}x^4$ and a ground-state energy of 0.530 181 04 [3]), for $T = 0$. We use $m = \hbar = 1$, an integration time step $\Delta t = 0.01$ and a frictional constant $\zeta_0 = 0.001$. The random noise sequences obeying Eq. (2) were generated in bunches of 1×10^7 MD steps using the method of [4]. Equilibrium averages were obtained along a series of 2×10^9 integration steps for 100 independent oscillators.

While correct for the harmonic oscillator, the QTB results systematically overestimate the ground-state energy of the quartic oscillator by ~2%, giving 0.541 ± 0.002. Similar overestimates were also observed for other anharmonic potentials, with the magnitude of the deviation growing with increasing degree of anharmonicity.

The origin of the discrepancies lies in the incorrect sampling of the ground-state probability-density functions. This is clearly illustrated in Fig. 1, which shows a comparison between the quantum-mechanical ground-state probability densities of the quartic oscillator in the position and momentum representations, respectively, and the distributions generated by the QTB method.

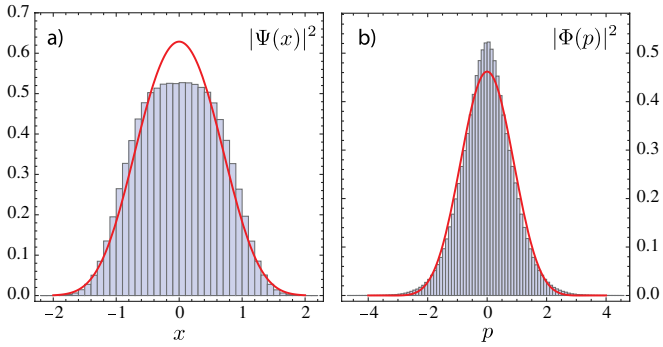

FIG. 1 (color online). Comparison between the position [panel (a)] and momentum [panel (b)] representations of the ground-state probability densities of the quartic oscillator (lines) and the distributions generated by QTB (histograms).

Finally, it is relevant to note that the QTB equations are inconsistent with the second fluctuation-dissipation theorem [2], by which the presence of a colored noise must be accompanied by a corresponding time-dependent retarded frictional kernel $\zeta(t)$ [2]. In the classical limit, for instance, the friction kernel is related to the colored-noise correlation function by $\langle \eta(0)\eta(t)\rangle = k_B T \zeta(t)$. Thus, in case of any colored noise, the Langevin equation based on a constant friction coefficient ζ_0 must be replaced by a generalized Langevin equation [2]

$$m\dot{v} = -\frac{\partial V}{\partial x} - \int_{-\infty}^{t} \zeta(t-t')v(t')dt' + \eta(t) \tag{3}$$

with a time-dependent friction kernel $\zeta(t)$.

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