

Dammak *et al.* Reply: In their Comment, Barrozo and de Koning [1] make two remarks about the quantum thermal bath (QTB) introduced in our Letter [2]: QTB is (i) an approximate method when dealing with anharmonic potentials, (ii) inconsistent with the second fluctuation-dissipation theorem. We fully agree with the first comment but we disagree with the second assertion.

Let us first clarify the issue regarding the consistency of the QTB with the second fluctuation-dissipation theorem. The spectrum of the correlation function of the force fluctuation [3] is the product of two terms which can both depend on frequency producing a colored spectrum: the friction coefficient $\gamma(\omega)$ and the energy $E(\omega, T)$. To include the statistical quantum effects that appear when the condition $\hbar\omega \ll k_B T$ is not fulfilled, we use the colored form $E(\omega, T) = \frac{\hbar\omega}{2} \coth(\frac{\hbar\omega}{2k_B T})$ instead of its classical limit $k_B T$. As explained in the Letter [2], we use a nondispersive friction coefficient γ as a technical parameter of the QTB-molecular dynamics (MD). This is fully consistent with the fluctuation-dissipation theorem. In the QTB-MD, the dynamics and the associated relaxation processes are produced by the interaction between nuclei.

Regarding the comment on the role of anharmonicity, we note that one should clearly separate quantum effects associated with the dynamics of the system (Newton's equations or Schrödinger equation) and quantum effects associated with the statistical average ($k_B T$ or $E(\omega, T)$). Ehrenfest theorem shows the equivalence of classical and quantum dynamic equations for harmonic potentials. This is no longer valid for anharmonic potentials so that it is not surprising to observe differences when introducing anharmonicity. The question is how important is their impact on the results for realistic potentials.

The QTB accounts for quantum dispersion effects of nuclei while using standard molecular dynamics (MD). This approach is, in particular, applied to systems described by anharmonic potentials, like MgO crystal or nonsuperfluid liquid ^4He . The good agreement of the results of our computations with experiments shows the efficiency of the method also in the case of anharmonic models.

We have compared QTB-MD, path integral molecular dynamics (PIMD) [4] and the exact solution for two types of nonlinear oscillators. The exact results were derived by solving numerically the Schrödinger equation and occupying the resulting eigenstates with the proper Boltzmann factor. The exact solution for both oscillators is well reproduced by PIMD simulations, whereas the QTB-MD exhibits some inconsistency, that is to say an incorrect sampling near the minimum of the potential [Fig. 1(a)]. The quartic potential is an interesting case to test the influence of anharmonicity because it is an example in which the harmonic term is lacking. However, this model is very far from standard potentials. For the Morse potential [Fig. 1(b)], the discrepancy between the predic-

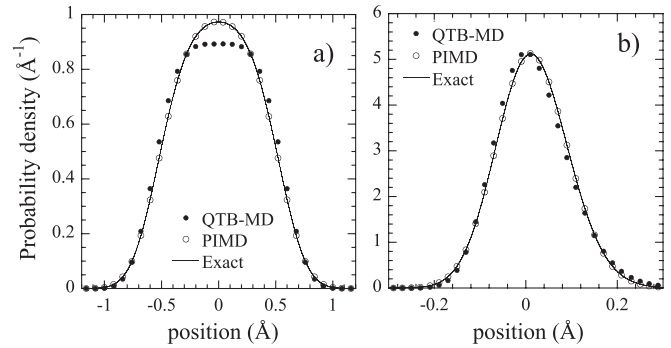


FIG. 1. Position probability density at 300 K of one-dimensional oscillators obtained by QTB-MD and PIMD simulations and compared to the exact solution. (a) quartic oscillator: $V(x) = Ax^4$, $m = 0.98 \text{ g mol}^{-1}$, $A = 0.2 \text{ eV } \text{Å}^{-4}$. (b) Morse potential of HCl molecule [5]: $V(x) = D(e^{-\beta x} - 1)^2$, $m = 0.98 \text{ g mol}^{-1}$, $D = 4.6141 \text{ eV}$, $\beta = 1.81 \text{ Å}^{-1}$.

tion by the QTB-MD and the exact solution is much weaker than for the quartic oscillator. This disagreement does not clearly impact the quantum effect on physical quantities such as average position and linear expansion, total energy and heat capacity, etc. For instance, the average position and the vibrational amplitude are equal to 0.0162 Å and 0.078 Å for the PIMD computation, whereas the QTB-MD yields 0.0163 Å and 0.079 Å , respectively.

In summary, the PIMD method can provide the exact position distribution even for anharmonic systems. This method is very time consuming and therefore the range of its applicability is reduced. The QTB-MD technique is an approximate approach that yields accurate results and saves at least 2 orders of magnitude of computation time compared to the PIMD method.

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- [1] A. H. Barrozo and M. de Koning, preceding Comment, *Phys. Rev. Lett.* **107**, 198901.
- [2] H. Dammak, Y. Chalopin, M. Laroche, M. Hayoun, and J. J. Greffet, *Phys. Rev. Lett.* **103**, 190601 (2009).
- [3] H. B. Callen, T. A. Welton, *Phys. Rev.* **83**, 34 (1951).
- [4] D. Marx, M. E. Tuckerman, J. Hutter, and M Parrinello, *Nature (London)* **397**, 601 (1999).
- [5] P. M. Morse, *Phys. Rev.* **34**, 57 (1929).