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Phys. Rev. B **99**, 066302 — Published 14 February 2019

DOI: [10.1103/PhysRevB.99.066302](https://doi.org/10.1103/PhysRevB.99.066302)

Electron Dynamics Matters—Reply to “Comment on ‘*Ab initio* evidence for nonthermal characteristics in ultrafast laser melting””

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(Dated: January 31, 2019)

In the Comment on our original publication [Phys. Rev. B 94, 184310(2016)], Zier *et al.* claimed that no melting is observed in real-time time-dependent density functional simulations and there are several inconsistencies in our paper. In this Reply, we demonstrate that, the “correct” melting behavior indicated in the comment by Zier *et al.*, which was adopted from empirical concept of thermal melting, is inappropriate and conflicts with ultrafast experiments on nonthermal laser melting. The barrier calculated from phonon spectra is a static barrier and different from the dynamic ones, causing no inconsistency. We confirm that nonthermal melting behaviors and interpretation in the original paper are credible.

The comment by Zier, Garcia, and Silvestrelli on our original article¹ reports a few disputes on the topic of ultrafast laser melting in Si crystal. The major criticisms seem to be concerned about some terminology that were adopted historically, the exact meaning of “*ab initio*” dynamics and two-temperature methods, as well as some obvious misunderstanding and apparent mistakes. The main message conveyed in¹, namely, the physical electronic excitation and the nonadiabatic quantum dynamics, stands against these disputes.

In the original paper¹, we freely admitted that there were “parameter-free *ab initio* molecular dynamics (MD)” simulations on “ultrafast melting” prior to the publication of our work. In fact, relevant papers on this topic^{2–4} were correctly cited and discussed. As emphasized in the original text, however, *ab initio* MD with the fixed electron temperature (T_e) cannot be considered fully “*ab initio*”, since T_e is predetermined as an empirical parameter and is not allowed to evolve, at variance with what time-dependent Schrödinger equation predicts. The authors of the comment also admit this and name their method as *electronic-temperature dependent* DFT. However, this approach relies on Born-Oppenheimer (BO) adiabatic approximation, with neither nonadiabatic effects nor quantum dynamics of excited electrons can be considered. Furthermore, the studies in Ref.^{2,5–9} adopted unphysical ensembles (see Supplementary Materials of¹) and a fixed electronic temperature T_e , which is not directly related to practical initial conditions of materials under a real laser setup. Since the results depend on the artificial choice of T_e , which could be out-of-question in the non-equilibrium regime, these studies are not *parameter-free* *ab initio* studies in terms of electron dynamics. In fact, the choice of T_e in Ref.² leads to unphysical excitations different from experiment (Table I of¹).

Zier *et al.* claim that, in the electronic-temperature dependent simulations, the major melting mechanism is

not laser heating effect but instead laser-induced modification of the interatomic potential. In contrast, in Ref.², Silvestrelli *et al.* clearly denied the nonthermal character of ultrafast melting: “*Several conclusions can be drawn from this observation. The system disorders; however, the hypothesis that this happens while the lattice remains relatively cold can be rejected.*”. In the simulations of Ref.², silicon always melts at high laser-induced lattice temperatures (~ 1700 K), with or without the change in the interatomic potential. The origin for their conclusion that “the lattice remains relatively cold can be rejected” comes from the unphysical ensemble adopted in the two-temperature model (TTM) based BOMD (as clearly illustrated in¹, Supplementary Materials). We correctly discussed the results obtained by Silvestrelli *et al.*² in our original paper¹.

Zier *et al.* prefer their method to be named as electronic-temperature dependent DFT instead of two-temperature method. We would like to point out two important notations:

i) The term “two-temperature” exactly expresses the major approximations used in the method of Zier *et al.* The two-temperature in the TTM means that, the electronic subsystem has a well-defined equilibrium temperature T_e , which is different from the ionic temperature T_i , therefore two different temperatures instead of an equilibrium one are used. This is exactly the scenario used in Ref.^{2,5–9}, in which the authors combined two-temperature assumption with *ab initio* Born-Oppenheimer MD simulations. Note that, T_e is arbitrary chosen to be 10000 K and 25000 K during the TTM-BOMD simulations.

ii) The electronic-temperature dependent approach used in Ref.² is indeed different from the commonly used empirical TTM (e.g.¹⁰). Empirical TTM intrinsically includes the evolution of T_e based on rate equations, which describe energy transfer from the electronic sub-

system to ionic subsystem. In contrast, T_e is not allowed to evolve in TTM-BOMD used in Ref.^{2,5-9}, which breaks energy conservation law and causes fictitious energy input as illustrated in the Supplementary Material of the original paper¹. Obviously, TTM in¹⁰ is more realistic and yields more consistent results with experiment. To give an unbiased review on TTM-BOMD, we note that the energy transfer described by the rate equations has been included in recent improvements¹¹. We agree with Zier et al. about referring their method as electronic-temperature dependent method to distinguish itself from this latest implementation.

Zier et al. claim that no “melting” is observed in our original simulations. They pointed out that: i) root-mean-square displacement (RMSD) of atoms crosses Lindemann criterion R_c is inadequate to mark melting. The RMSD should increase continuously after it crosses R_c . ii) The radial distribution function (RDF) does not catch any characteristic of a molten state, such as the appearance of the liquid peak, and uniform background after the liquid peak. We note that, all these arguments were built upon a simple baseline that, ultrafast laser melting has the same features as regular thermal melting. However, these two scenarios have very different origins and behaviors (see Table I), as revealed in experimental observations¹²⁻¹⁴.

TABLE I. Comparison between ultrafast nonthermal melting and regular thermal melting¹²⁻¹⁴.

	Nonthermal	Thermal
Timescale	$10^{-15} \sim 10^{-12}$ s	$1 \sim 10^2$ s
Lattice temperature	room temperature	melting point (~ 1700 K)
Final state	recrystallize	liquid

Strictly speaking, laser-induced ultrafast melting corresponds to a reversible amorphization process, namely, the photoexcited solid turns into an amorphous structure upon laser irradiation, then recrystallizes shortly after laser pulses went away. In such a circumstance, ultrafast structural disordering upon laser illumination was constantly observed and the process does not necessarily involve diffusive liquid structure in many experiments¹²⁻¹⁴. For example, the authors of¹² stated that “*Finally, a nonrastered diffraction image (Fig. 1E) taken several seconds after irradiation on a vertical sequence of single-shot damage spots shows nearly complete recovery of the diffraction signal on a semi-infinite time scale.*” However, for historical reasons and being consistent with the vast literature, the term nonthermal “melting” is often used in many papers including the original paper¹. In these papers it is freely admitted that lattice disordering rather than regular thermal melting into a liquid state is what are indeed observed. Instead, the so-called “melting” or “molten state” within 1 ps of laser excitation indicated by the authors of the comment, is not observed in experiments. Although “ultrafast disordering” might be a more precise terminology, the “ultrafast melting”

was used to keep up with the consistency established in a large body of literature studies. The major criticism on the absence of “molten state” right after laser excitation is thus out of question.

Zier et al. also commented on some technical details, which we organize from their redundant statements as follows: i) Instead of the Debye-Waller formula, time-dependent diffraction intensity should be calculated. ii) If the system is molten, then the RMSD keeps monotonically increasing in accordance to a diffusive behavior. iii) Even at thermal equilibrium conditions below the melting threshold, the RMSD of a solid could exceed the Lindemann criterion. iv) The theoretically computed decay time differs by a factor of 5 instead of 3 with the experimental data. v) We only show 5 branches in phonon spectra, which should contain 6 branches. (vi) The melting barrier calculated from phonon spectra is different from that from the RMSD.

We reply to these comments point-by-point below.

- (i) We note that the Lindemann criterion and the correspondence between RMSD and diffraction intensity through the Debye-Waller formula are widely used for nonthermal melting experimental studies¹⁴⁻¹⁸. To demonstrate that the results from the simulation are consistent with experimental observations, in Ref.¹ the same criterion was adopted to give a direct comparison to experimental data. Nevertheless, we have also calculated the time-dependent diffraction intensity directly from the atomic positions as

$$I(t) = I_0 \left| \sum_j \exp[-i\mathbf{q} \cdot \mathbf{R}_j(t)] \right|^2 \quad (1)$$

where \mathbf{q} is the scattering vector of (220) plane. As shown in Fig. 1, the time-dependent intensity shows similar trends with the results calculated by the Debye-Waller formula.

- (ii) The monotonically increases in RMSD, although in accord with a diffusive behavior in regular melting, were not observed in experiments on nonthermal melting. Instead, the experimental observation demonstrated that the RMSD stops at a certain value after a rapid initial increase^{13,14,17}. Therefore, the “imaginary” diffusive behaviors in ultrafast nonthermal melting are at variance with these experiments. The simulations which are “consistent” with such behaviors could be an indication of drawbacks in physical models and failure to capture the right physics.
- (iii) On the Fig. 1 in the comment: It is not a sufficient justification against the Lindemann criterion. At high temperatures (1000-1500 K), the simulation cell should be sufficiently large to avoid fictitious large fluctuations, which are unphysical in thermal equilibrium states. Only for silicon under low temperatures (300-500 K), a 64-atom cell may be sufficient, where the RMSD only oscillates at ~ 0.1 Å.

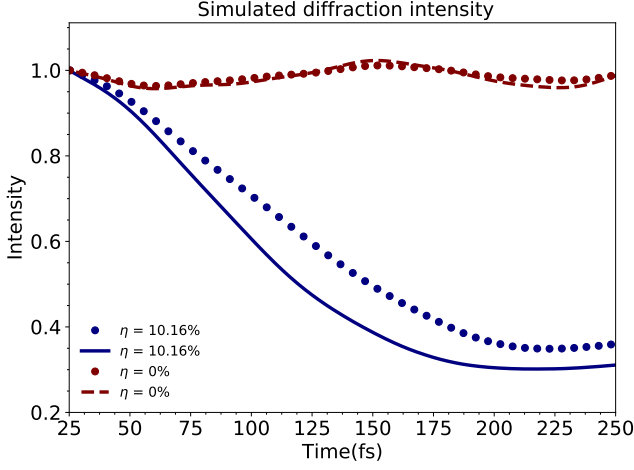


FIG. 1. The diffraction intensities calculated by the Debye-Waller formula (solid lines) and Eq. 1 (filled circles).

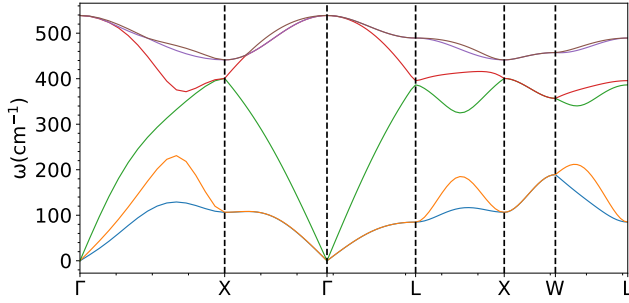


FIG. 2. The phonon spectrum calculated for bulk Si crystal.

- (iv) The time delay of experimental measurements starts from the peak time of the pulse, which is different from the simulations starting from the end of the pulse. To compare the timescales directly with the experiment, the pulse width (usually on the scale of 200-300 fs) should be taken into account. The difference in timescale between experiment and simulation can originate from the limited penetration depth of pump laser too. In Ref.¹⁹, which is on a different material other than Si, the maximum decrease in RMSD is 0.12, much smaller than that discussed in the original paper¹. Within this regime, the penetration problem is not obvious.
- (v) There are six phonon branches in silicon phonon calculations, as shown in Fig. 2. The highest two are almost degenerate, which are overlapped in¹. The authors of the comment erroneously state "Amazingly, although silicon has six phonon branches ... Lian et al. only show five of them..."
- (vi) Figure 7 and Figure 5(b) in the original paper¹ indicates two different kinds of melting barriers. Firstly, different from the statement in the com-

ment, only some of acoustic mode is unstable near X point. Secondly, Fig. 5(b) displays the dynamic barrier obtained from dynamics simulations whose atomic geometry is far away from ideal ground-state geometry, while Fig. 7 describes the barrier for the ground-state symmetric crystal structure. It is natural that the two barriers are not the same.

Finally, we would like to clarify that the different RMSD for $\eta = 10.16\%$ in Fig. 4 and Fig. 5(a) in Ref. 1 originate from different initial ionic temperatures. The initial temperatures are 300 K and 150 K in Fig. 4 and Fig. 5(a), respectively. Therefore the RMSD are slightly different for the two cases, even though both are under the same excitation condition ($\eta = 10.16\%$).

In conclusion, we believe that the original paper¹ correctly discussed the results from previous TTM-BOMD simulations, which are not parameter-free but electronic-temperature-dependent. The TTM-BOMD simulations yield thermal melting behaviors, as summarized in the original article. The "correct" melting behavior indicated by Zier et al. is inappropriately adopted from empirical concept of thermal melting, which conflicts with ultrafast nonthermal melting behaviors observed experimentally. Since the barriers calculated from phonon spectra and RMSD correspond to static and dynamical crystal geometries, respectively, the difference between them raises no inconsistency. We confirm that the nonthermal melting behaviors and the interpretation in the original article are credible.

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