Self-Learning Method for Construction of Analytical Interatomic Potentials to Describe Laser-Excited Materials

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Large-scale simulations using interatomic potentials provide deep insight into the processes occurring in solids subject to external perturbations. The atomistic description of laser-induced ultrafast nonthermal phenomena, however, constitutes a particularly difficult case and has so far not been possible on experimentally accessible length scales and timescales because of two main reasons: (i) *ab initio* simulations are restricted to a very small number of atoms and ultrashort times and (ii) simulations relying on electronic temperature- (T_e) dependent interatomic potentials do not reach the necessary *ab initio* accuracy. Here we develop a self-learning method for constructing T_e -dependent interatomic potentials which permit ultralarge-scale atomistic simulations of systems suddenly brought to extreme nonthermal states with density-functional theory (DFT) accuracy. The method always finds the global minimum in the parameter space. We derive a highly accurate analytical T_e -dependent interatomic potential $\Phi(T_e)$ for silicon that yields a remarkably good description of laser-excited and -unexcited Si bulk and Si films. Using $\Phi(T_e)$ we simulate the laser excitation of Si nanoparticles and find strong damping of their breathing modes due to nonthermal melting.

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Intense femtosecond-laser pulses can induce dramatic changes in the potential energy surface (PES) of materials due to the excitation of a large amount of electron-hole pairs [1]. These changes manifest themselves in the form of bond hardening, bond softening, and lattice instabilities, for example [2–4]. It is known that these light-induced effects lead to measurable ultrafast nonthermal phenomena such as structural solid-solid and solid-liquid phase transitions [5–7], phonon squeezing [8,9], and coherent phonons [10,11]. However, the impact of short-lived changes in the PES, occurring within the first picosecond after an ultrashort excitation [12], on the further dynamics of the material at longer timescales (nanoseconds) and on larger length scales (hundreds of nanometers) still remains unknown. As an example, it has been proposed that bond softening and instabilities occurring immediately after the action of a femtosecond-laser pulse followed by a relaxation involving self-organization processes might play a role in the spontaneous formation of surface patterns like laser-induced periodic surface structures [13–15]. However, this hypothesis could not be theoretically tested so far because of the lack of an *ab initio* description of laser-induced nonthermal material transformations on macroscopic length scales and long timescales, which constitutes a still-unresolved problem in the theory of ultrafast phenomena. This is due to the fact that *ab initio* molecular dynamics (MD) simulations are typically restricted to, at most, 1000 atoms [9,16,17] whereas, on the other

hand, large-scale MD simulations based on interatomic potentials depending on the electronic temperature T_e , i.e., taking laser-induced changes of the PES into account [18–23], have not been so far able to achieve *ab initio* accuracy.

In this Letter, we develop a self-learning method for deriving analytical T_e -dependent interatomic potentials that have a physically intuitive form and reproduce the results of *ab initio* MD simulations with minimal error and computational effort. As an example, we applied this method to Si due to its technological importance. Another motivation to derive $\Phi(T_e)$ for Si is that it can be directly compared with other available T_e -dependent Si potentials [19,23], which permits us to appreciate the high accuracy of our derived potential. Moreover, laser-excited Si has been intensively studied by means of *ab initio* calculations [2,9,16,17, 24–27]. As a first application of $\Phi(T_e)$, we predict, by means of atomistic simulations, a strongly damped breathing mode in laser-excited spherical Si nanoparticles.

To derive $\Phi(T_e)$, we must take into account that, ideally, it should reproduce forces and energies over any pathway on the *ab initio* PES. In practice, we perform reference *ab initio* simulations on a treatable small cell and require that $\Phi(T_e)$ matches forces and energies at every simulation step t . The reference simulations were performed on a cell consisting of 320 Si atoms forming a thin film of 5.3 nm thickness to take both bulk and surface effects into account. The construction of a reliable interatomic potential needs a

very good sampling of the available phase space. In case of laser excitation, it should include extreme fluctuations of local atomic configurations. For this reason, we performed various sets of reference *ab initio* simulations (labeled as s_k) as follows [28]. (s_1) We simulated the laser-induced dynamics of a thin film—initially thermalized at an ionic temperature, $T_i = T_e = 1$ mHa (316 K)—by suddenly increasing T_e to a constant value. We considered 11 different T_e 's in the range 1 mHa (316 K)–100 mHa (31 577 K) [28]. (s_2) Since the laser excitation of solids can lead to high local positive pressures with high atomic local densities, we compressed the thin film initialized at 1 mHa (316 K) stepwise and calculated the related forces and energies. (s_3) Since the laser excitation of solids can also lead to high local negative pressures with low local atomic densities, the *ab initio* calculations must also contain a mechanical expansion of the thin film for each studied T_e . Note that expansion occurs naturally for high T_e 's in simulation set s_1 . For low T_e 's we manually simulated expansion [28]. In total, we obtained around 10^6 *ab initio* data points for low T_e 's and 5×10^5 for high T_e 's.

The *ab initio* simulations were performed using our in-house density-functional theory (DFT) program CHIVES (Code for Highly excited Valence Electron Systems) [3,9,17] within the local density approximation (LDA). CHIVES reproduces results of established DFT codes, including Wien2k and ABINIT [33], yields a very good agreement with experiment [34], and is up to 200 times faster than ABINIT with the same degree of accuracy [33].

To obtain a reliable and appealing analytical form of $\Phi(T_e)$, we construct it as a sum of different local interaction terms with a clear physical interpretation. We use two- and three-body interaction terms (Φ_2 and Φ_3 , respectively) to account for covalent bonding. Note that two- and three-body terms were already successfully applied to describe the Si crystal in the electronic ground state [35], where covalent bonds are responsible for the tetragonal bonding geometry. In addition, we account for metallic bonding, which dominates in Si under pressure [36] or in the molten phase [16], by using an embedding function Φ_ρ . Here, the local potential energy at an atomic site is calculated as a function of the surrounding atomic density ρ . Embedding functions were already successfully applied for describing metals [37,38]. $\Phi(T_e)$ reads

$$\Phi = \sum_{\substack{i < j \\ r_{ij} < r_2^{(c)}}} \Phi_2(T_e, r_{ij}) + \sum'_{\substack{ijk \\ r_{ij}, r_{ik} < r_3^{(c)}}} \Phi_3(T_e, r_{ij}, r_{ik}, \theta_{ijk}) + \sum_i \Phi_\rho(T_e, \rho_i^{(2)}, \rho_i^{(3)}, \dots, \rho_i^{(N_\rho^{(r)})}) + \sum_i \Phi_0(T_e). \quad (1)$$

Here r_{ij} denotes the distance between atoms i and j , θ_{ijk} is the angle between $\mathbf{r}_{ij}$ and $\mathbf{r}_{ik}$, the prime indicates that all summation indices are distinct, and $\rho_i^{(2)}, \rho_i^{(3)}, \dots$ are

different measures for the atomic density surrounding atom i (see below). $\Phi_0(T_e)$ is the Helmholtz free energy of an isolated atom, which is needed to reproduce correctly the derivatives of $\Phi(T_e)$ with respect to T_e .

In Eq. (1), $r_2^{(c)}$, $r_3^{(c)}$, and $r_\rho^{(c)}$ (see below) denote the individual cutoff radii for Φ_2 , Φ_3 , and Φ_ρ , respectively. The cutoff radius is defined as the distance beyond which the interaction between atoms is set equal to zero and, therefore, it controls the interaction range of the corresponding term. For covalent and metallic bonding, the interatomic interactions become negligible at relatively short interatomic distances, as can be seen for Si from the *ab initio* data in the bottom inset of Fig. 2. Therefore, a physical upper limit exists for the cutoff radii in such systems. By discretely testing all values of the cutoff radii starting from the nearest neighbor distance occurring in the equilibrium crystal structure up to the previously mentioned upper limit, we surely find the optimal cutoff radii for $\Phi(T_e)$ [28]. For ionic systems with long-ranged Coulomb interaction, this procedure must be modified.

Our goal is to construct an expression for $\Phi(T_e)$ that is very flexible and simple enough to allow the optimization procedure to find the global minimum in the parameter space. Therefore, we expand the terms Φ_2 , Φ_3 , and Φ_ρ into *polynomials*, which can, in principle, reproduce any physically reasonable function. Φ_2 , Φ_3 , and Φ_ρ are constructed as

$$\Phi_2 = \sum_{q=2}^{N_2^{(r)}} c_2^{(q)} \left(1 - \frac{r_{ij}}{r_2^{(c)}} \right)^q, \quad (2)$$

$$\Phi_3 = \sum_{q_1=2}^{N_3^{(r)}} \sum_{q_2=q_1}^{N_3^{(r)}} \sum_{q_3=0}^{N_3^{(\theta)}} c_3^{(q_1 q_2 q_3)} \times \left(1 - \frac{r_{ij}}{r_3^{(c)}} \right)^{q_1} \left(1 - \frac{r_{ik}}{r_3^{(c)}} \right)^{q_2} [\cos(\theta_{ijk})]^{q_3}, \quad (3)$$

$$\Phi_\rho = \sum_{q_1=2}^{N_\rho^{(r)}} \sum_{q_2=1}^{N_\rho^{(\rho)}} c_\rho^{(q_1 q_2)} \left(\frac{\rho_i^{(q_1)}}{1 + \rho_i^{(q_1)}} \right)^{q_2}, \quad (4)$$

and, for $q_1 = 2, 3, \dots, N_\rho^{(r)}$, the measures for the atomic density surrounding atom i are constructed as

$$\rho_i^{(q_1)} = \sum_{\substack{j \neq i \\ r_{ij} < r_\rho^{(c)}}} \left(1 - \frac{r_{ij}}{r_\rho^{(c)}} \right)^{q_1}. \quad (5)$$

The expansions (2)–(4) guarantee high numerical stability and that the interatomic potential and its first derivatives decrease continuously to zero as distances reach the cutoff radii [28].

To determine the accuracy of $\Phi(T_e)$ in reproducing the *ab initio* reference simulations $\{s_k\}$ at a given T_e , we defined the following error function $W(T_e)$ (cf. Ref. [39]), which is the weighted sum of the mean square relative errors in the $\Phi(T_e)$ description of Helmholtz free cohesive energies and atomic forces of the different simulations $\{s_k\}$ with weights $w_E^{(s_k)}$, $w_f^{(s_k)}$, respectively, obeying the sum rule $\sum_{s_k} w_E^{(s_k)} + \sum_{s_k} w_f^{(s_k)} = 1$:

$$W = \sum_{s_k} w_E^{(s_k)} \frac{\sum_t [\Phi(\{\mathbf{r}_j^{(s_k)}(t)\}) - \sum_i \Phi_0 - E^{(s_k)}(t)]^2}{\sum_t [E^{(s_k)}(t)]^2} + \sum_{s_k} w_f^{(s_k)} \frac{\sum_{ti} |-\nabla_{\mathbf{r}_i^{(s_k)}} \Phi(\{\mathbf{r}_j^{(s_k)}(t)\}) - \mathbf{f}_i^{(s_k)}(t)|^2}{\sum_{ti} |\mathbf{f}_i^{(s_k)}(t)|^2}. \quad (6)$$

Here, $\mathbf{r}_i^{(s_k)}$ denotes the position of atom i , $E^{(s_k)}(t)$ the total *ab initio* Helmholtz free cohesive energy of the system, and $\mathbf{f}_i^{(s_k)}(t)$ the *ab initio* force acting on atom i . Since we aim at describing all considered T_e 's with a minimal error, we finally use the average of $W(T_e)$ over $T_e = 316$ K and $T_e = 18946$ K as a measure of the fitting error, which we denote as $\langle W \rangle$.

The polynomial degrees $N_2^{(r)}$, $N_3^{(r)}$, $N_3^{(\theta)}$, $N_\rho^{(r)}$, and $N_\rho^{(\rho)}$ control the complexity of the different local interaction terms Φ_2 , Φ_3 , and Φ_ρ . By adjusting the polynomial degrees, we can adapt the analytical form of the interatomic potential to reproduce the *ab initio* data most accurately and efficiently. For this, we require minimal error $\langle W \rangle$, and, at the same time, reasonably low computational cost, i.e., a small total number of coefficients N_c . In principle, for an optimal selection of the final polynomial-degree combination, we would have to consider an infinite number of possible degree combinations. Fortunately, the polynomial expansion of Eqs. (2)–(4) converges to the *ab initio* determined PES relatively quickly, so that the inclusion of high degrees does not bring significant improvement in accuracy, as can be seen in Fig. 1. Consequently, high degrees can be excluded. Therefore, we initially set arbitrary upper degree limits and determined the minimal error $\langle W \rangle$ for all polynomial-degree combinations up to these limits. From the corresponding calculations, we can check whether the initially chosen upper degree limits were high enough (see Fig. 1) and can eventually increase them. In this way, we perform a complete search over all “reasonable” interatomic potentials of the form of Eq. (1). Moreover, due to the construction of the interatomic potential, one can reliably calculate the global minimum of $\langle W \rangle$ and the corresponding optimal parameters (N_c coefficients and 3 cutoff radii) for all considered polynomial-degree combinations, since all coefficients $\{c_2^{(q)}\}$,

FIG. 1. Error $\langle W \rangle$ averaged over $T_e = 316$ K and $T_e = 18946$ K as a function of N_c for all polynomial-degree combinations up to the upper degree limits (see text). Each red dot represents an interatomic potential which is, for the corresponding polynomial-degree combination, a global minimum in parameter space. $\langle W \rangle$ decreases insignificantly for large values of N_c , indicating that the chosen upper degree limits are high enough. The subset S_{best} is highlighted in light blue (see text), the series $\Phi^{(k)}$ is highlighted in black (see text), and the final choice, $\Phi(T_e)$, is highlighted in green and marked by an arrow.

$\{c_3^{(q_1 q_2 q_3)}\}$, and $\{c_\rho^{(q_1 q_2)}\}$ are independent from each other and enter linearly into the potential [see Eqs. (2)–(4)] [28]. The ability to determine the global minimum of $\langle W \rangle$ allows us to find, for any polynomial-degree combination (i.e., for any analytical form of the interatomic potential) the related parameters that describe the *ab initio* data most accurately.

Figure 1 presents the global minimum of $\langle W \rangle$ (red points) as a function of the total number of coefficients N_c for 165 344 polynomial-degree combinations, which we obtained by taking all polynomial degrees into account up to the upper degree limits $N_2^{(r, \max)} = 15$ for the two-body term and $N^{(\max)} = 9$ for all other terms.

To select the polynomial-degree combination of the final interatomic potential showing physical behavior and having minimal $\langle W \rangle$ and reasonably low computational cost, we first extracted a relatively small subset S_{best} of reliable polynomial-degree combinations that exhibit low $\langle W \rangle$ combined with a relatively small N_c (see blue points in Fig. 1). To construct S_{best} , we applied an iterative procedure that selects a series $\Phi^{(1)}, \Phi^{(2)}, \dots$ of polynomial-degree combinations with $N_c^{(1)} < N_c^{(2)} < \dots$ and $\langle W \rangle^{(1)} > \langle W \rangle^{(2)} > \dots$ (see black points in Fig. 1). We start by setting $\Phi^{(0)} = \sum_i \Phi_0(T_e)$ as the constant potential with $\langle W \rangle^{(0)} = 1$ and $N_c^{(0)} = 0$. On each step $k = 1, 2, \dots$, we select $\Phi^{(k)}$ such that it maximizes the error reduction per added coefficients,

$$\frac{\Delta \langle W \rangle}{\Delta N_c} = \frac{\langle W \rangle^{(k-1)} - \langle W \rangle}{N_c - N_c^{(k-1)}}, \quad (7)$$

among all polynomial-degree combinations with $N_c > N_c^{(k-1)}$. We continue the iterations until step k for which $\Phi^{(k)}$ reaches the upper degree limits. S_{best} contains not only the elements of the series $\Phi^{(1)}, \Phi^{(2)}, \dots$ but also all polynomial-degree combinations that exhibit a 10% lower value of $\Delta\langle W \rangle / \Delta N_c$ than $\Phi^{(k)}$ (see light blue points in Fig. 1). In this way, we developed a self-learning method that constructs the small subset S_{best} containing optimally adjusted polynomial-degree combinations for the following detailed analysis to select the final interatomic potential.

Within the members of S_{best} , a further decrease of $\langle W \rangle$ is quite low for $N_c > 50$ (see Fig. 1). Thus, we analyzed only the members with $N_c \leq 50$. For those polynomial-degree combinations of S_{best} , we constructed the corresponding interatomic potential at each of the 11 studied T_e 's by determining the related optimal coefficients and cutoff radii that minimize $W(T_e)$. Using these interatomic potentials, we checked the description of the following physical properties at all studied T_e 's: (i) the phonon band structure of the bulk diamondlike crystal structure, (ii) the cohesive energy curves of the diamondlike, fcc, bcc, and simple cubic (Sc) bulk crystal structures, and (iii) the time evolution of the atomic root-mean-square displacements (RMSDs) in the MD simulation of bulk Si. The finally selected polynomial-degree combination with $N_c = 23$ is the one for which the corresponding interatomic potential best describes the abovementioned physical properties with a minimal possible N_c . Note that the performance of the studied members of S_{best} varies considerably; i.e., not all members of S_{best} represent reliable interatomic potentials. In addition, the analysis and selection, which we performed manually, can also be done fully automated.

Since the resulting optimal cutoff radii vary insignificantly around $r_c^{(2)} = 0.63$ nm, $r_c^{(3)} = 0.42$ nm, and $r_c^{(p)} = 0.48$ nm at

the 11 studied T_e 's, we chose these values and kept them constant for all T_e 's. Thus, as a result of the optimization procedure, now only the coefficients depend on T_e . These coefficients, up to now found for 11 T_e 's, were approximated by polynomials of degree 5 in T_e to obtain a continuous dependence on T_e . This allows us to calculate the internal energy U_e and the specific heat C_e of the electrons using the thermodynamic relations

$$U_e = \Phi - T_e \frac{\partial \Phi}{\partial T_e}, \quad C_e = -T_e \frac{\partial^2 \Phi}{\partial T_e^2}. \quad (8)$$

Note that for the resulting final $\Phi(T_e)$, which is provided as a table and a FORTRAN subroutine in the Supplemental Material [28], both U_e and C_e are in very good agreement with the corresponding *ab initio* results for bulk Si (see Fig. 2 for C_e and Supplemental Material [28] for U_e). Only at T_e 's above 27 000 K, C_e of $\Phi(T_e)$ starts to deviate from the *ab initio* values. It is remarkable that $\Phi(T_e)$ does not only reproduce lattice properties but also electronic properties. As expected, $\Phi(T_e)$ describes well the physical properties (i)–(iii) used for selecting the final polynomial-degree combination (see exemplary Fig. 3 and the insets of Fig. 2). The relative error of $\Phi(T_e)$ in the forces [second term of Eq. (6)] decreases from 26% to 6% when T_e increases from 316 to 31 577 K. This indicates that the PES becomes less complex for higher T_e 's. The relative error in the Helmholtz free cohesive energies [first term of Eq. (6)] always lies below 1.7%. It is important to stress here that $\Phi(T_e)$ also reproduces forces in independent *ab initio* MD simulations, which were not used for its development, with the same accuracy [28]. Furthermore, the atomic RMSD perpendicular to the surface of the thin film after laser excitation is well reproduced by $\Phi(T_e)$ at all T_e 's, indicating that $\Phi(T_e)$ accounts for surface effects [28]. The selected potential $\Phi(T_e)$ also reproduces properties that were not used in the fitting procedure, like the elastic

FIG. 2. Specific heat of the electrons C_e as a function of T_e for diamondlike bulk Si. The upper inset indicates the phonon band structure of diamondlike bulk Si at $T_e = 18315$ K. The lower inset shows the Helmholtz free cohesive energy E of the diamondlike (red diamonds), fcc (magenta crosses), bcc (green circles), and Sc (blue squares) structures as a function of the lattice parameter at $T_e = 18315$ K. Black dashed curves represent *ab initio* data obtained using the code CHIVES and colored solid curves represent the values obtained from $\Phi(T_e)$.

FIG. 3. Atomic root-mean-square displacements (RMSDs) during nonthermal melting [17] for bulk Si at $T_e = 22\,104$ K from MD simulations with 288 atoms performed *ab initio* (black dashed curve) and using $\Phi(T_e)$ (red solid line) averaged over 40 runs. The inset shows the RMSD during thermal phonon squeezing [9] at $T_e = 15\,789$ K averaged over 10 runs with 640 bulk Si atoms.

constants, pair-correlation function, and bond-angle distribution for finite T_e 's in diamondlike bulk Si [28].

By performing liquid-crystal coexistence MD simulations for 65 536 Si atoms with $\Phi(T_e)$, we determined the melting temperature $T_m(p) = (1199 \pm 2) \text{ K} - (40 \pm 3) \text{ K GPa}^{-1}(p)$ near zero pressure p . It agrees with $T_m(p) = (1300 \pm 50) \text{ K} - 58 \text{ K GPa}^{-1}(p)$ from LDA DFT [40] and differs from the experimental value, $T_m = (1687 \pm 5) \text{ K} - 58 \text{ K GPa}^{-1}(p)$ [41,42]. However, and thanks to the simple physical analytical form of $\Phi(T_e)$, one can adjust the coefficients to reproduce the experimental T_m without significant influences on the other properties [43]. Note that such adjustment would be impossible in machine-learning potentials [44–47], since they do not use a physically motivated and easily controllable analytical form and which, so far, do not take T_e into account.

Notice also that previously developed potentials for Si at high T_e 's [19,23,48] exhibit a very inaccurate description of the atomic RMSD during thermal phonon squeezing and nonthermal melting in bulk Si and of the atomic RMSD perpendicular to the surface of the thin film [49]. It is important to point out that interatomic potentials fitted to data in the film geometry can describe bulk properties, whereas the opposite is not true. We have confirmed this by using our method.

To provide an application of $\Phi(T_e)$, we used it to perform MD simulations of a laser-excited Si nanosphere with a radius of 4.75 nm containing 23 976 atoms, which cannot be done with *ab initio* methods. Our simulations show that at high T_e nonthermal melting occurs, which strongly damps the laser-excited breathing mode of the nanosphere (see Fig. S13 and Fig. S14 in the Supplemental Material [28]).

In summary, we presented an automatized method for developing highly accurate analytical T_e -dependent interatomic potentials from *ab initio* MD simulations. We applied the method to Si and obtained an interatomic potential $\Phi(T_e)$ that can describe the material for a wide range of T_e 's. $\Phi(T_e)$ is able to accurately describe laser-driven effects caused by bond softening, including non-thermal melting and thermal phonon squeezing. It is remarkable that $\Phi(T_e)$ does not only reproduce bulk lattice properties but also takes into account surface effects and describes electronic properties. $\Phi(T_e)$ can be used to describe laser processing of Si in the framework of the combined two temperature model MD [50] and Si subject to ion bombardment at moderate energies, for example.

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