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Theoretical study of the laser-induced femtosecond dynamics of small Si_n clusters

K. Zickfeld
Institut für Theoretische Physik der Freien Universität Berlin, Arnimallee 14, 14195 Berlin, Germany

M. E. Garcia*
Departament de Física, Universitat de les Illes Balears, E-07071 Palma de Mallorca, Spain

K. H. Bennemann
Institut für Theoretische Physik der Freien Universität Berlin, Arnimallee 14, 14195 Berlin, Germany

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The ultrafast relaxation of Si_n clusters following laser excitation is studied as a function of energy and duration of the laser pulse. We perform molecular-dynamics simulations based on a tight-binding Hamiltonian and take the form and duration of the laser pulse explicitly into account. We show that the occurrence of the different relaxation channels is strongly dependent on the duration τ of the exciting pulse. Very short pulses ($\tau < 50$ fs) may induce melting or fragmentation of the cluster, depending on whether the intensity of the laser pulse is low or high, respectively. On the other hand, long pulses favor structural changes and an expansion of the cluster structure. By studying the response of the cluster as a function of the laser parameters we determine generalized ''phase diagrams'' for the occurrence of solidlike, liquidlike, and fragmented clusters as a product of the laser excitation. For certain values of τ and energy of the laser pulse structures are produced, which show a small energy gap. The laser induced ''metallization'' of small silicon clusters is also discussed. [S0163-1829(99)07919-9]

I. INTRODUCTION

Since the development of the femtosecond spectroscopy[1] much attention has been payed to the investigation of ultrafast processes in microscopic systems.[2] The availability of commercial lasers with pulse durations down to 10 fs together with the instrument of Pump & Probe spectroscopy make possible the investigation of an abundance of microscopic phenomena, like, for instance, the nonequilibrium dynamics of highly excited systems. The high power that can be reached by ultrashort laser pulses permits to create extreme nonequilibrium states in solids, clusters, and molecules. The subsequent relaxation of the atomic and electronic degrees of freedom towards equilibrium is a fundamental problem that has become a major research subject. In particular, the phenomenon of laser-induced phase transitions in semiconductors has attracted considerable attention.[3–5] In most studies, a very fast melting of the crystalline structure is observed,[3,4] with a time scale of a few hundreds femtoseconds. The question, whether other kind of laser-induced transitions, like structural transformations and changes in the bond character, are possible to achieve by suitable adjustment of the laser parameters, still remains open.

Different theoretical approaches have been used to describe the ultrafast melting of silicon.[6–8] These methods are, however, not suitable for studying arbitrary ultrafast structural changes due to the following reasons. First, the volume is assumed to remain constant during the relaxation. Due to this constraint, the silicon lattice is not allowed to expand and therefore it is not surprising that the system melts after absorbing the laser energy.

In laser ablation experiments, however, not the volume but rather external pressure is kept fixed and the system is allowed to expand in one or more directions. As a matter of fact, the system will tend to expand as a consequence of the laser-excitation process, in which binding electrons are excited into antibonding (repulsive) orbitals.

In the above mentioned theoretical investigations, the duration τ of the exciting pulse is not explicitly taken into account. A sudden excitation of the system is assumed (zero duration). Finite pulse durations are of fundamental importance, since they induce interesting physical processes that are different from those involved in the limiting cases $\tau \to 0$ (sudden excitation) and $\tau \to \infty$ (adiabatic excitation). The role of the pulse duration on the laser induced dynamics has been shown to be essential for optical control of microscopic processes (Pump & Control). On the field of atomic and molecular physics already first coherent control scenarios have been investigated.[9]

The goal of the present paper is to perform a theoretical study of the laser-induced ultrashort-time dynamics of small Si_n as a model example for the study of laser-induced phase transitions in solids. Clusters, having a few degrees of freedom can be used as model systems to understand the relaxation mechanisms after excitation. We take explicitly into account the duration of the exciting pulse. In the study of the relaxation dynamics we deal with the question, under which conditions the clusters undergo a transition to a liquidlike phase, as it was observed in crystalline semiconductors. Furthermore, we perform a study of the induced dynamics as a function of the laser parameters (energy and duration of the pulse) to find out if other kind of transitions, like structural changes (isomerization) can take place. For this study, we perform molecular-dynamics simulations based on a tight-binding Hamiltonian.

Some experimental groups[5] gained evidence, that in bulk silicon the laser-induced liquid phase has metallic character. We discuss, to which extent this applies to small systems. We also show that the laser excitation can lead to multiple bond breaking in the clusters and study the fragmentation dynamics as a function of the laser parameters.

Small Si_n clusters are not only interesting as model systems to understand bulk properties, but also due to their potential applications to micro- and nanoelectronics. Recently, the relaxation dynamics of Si_n clusters following femtosecond laser excitation has been experimentally investigated by Gerber *et al.*[10] They studied the photoionization and photofragmentation of Si clusters with pulses of 100-200 fs duration and intensities between 10^{11} W/cm^2 and 10^{13} W/cm^2, for which multiple ionization occur. The resulting mass spectrum of the ionized clusters was compared to a spectrum taken under identical source conditions but using nanosecond pulses. The spectra differ dramatically. These experimental results show that Si_n clusters undergo a much stronger fragmentation if they are excited using fs laser pulses. So far there is no theoretical description of this behavior. The same group[10] has performed time-resolved experiments, in which the concentration of Si^+ clusters excited by the pump pulse was recorded as a function of time after excitation. The resulting curves show an exponential decrease for all cluster sizes with time constants between 2 and 9 ps. The decay times are shown to be dependent on laser intensity.

In this paper, we also address the problem of laser-induced fragmentation of neutral Si_n clusters. Although a comparison with the experimental results is not possible because the intensities of the pulses and the relaxation products we study are different from those investigated in experiment, we give a qualitative theoretical explanation of why short pulses may lead to more fragmentation than long pulses.

The paper is organized as follows. In Sec. II, we present our model Hamiltonian, our approach for the calculation of the coupling between the laser pulse and the cluster. We also describe the method used to determine the forces on the atoms and to study the relaxation dynamics of the clusters. In Sec. III, we show our results and their connection to the experimental observations on bulk-silicon and Si_n clusters. Finally, in Sec. IV we summarize our results and present the conclusions.

II. THEORY

For the theoretical description of the laser-induced ultrashort-time dynamics of Si_n clusters we perform molecular dynamics (MD) simulations based on a tight-binding Hamiltonian. The femtosecond pulse is described by a time dependent field acting on the electrons. In the following, we assume that the time scales for the electron and atomic motion can be separated. This assumption is justified by experimental results on bulk-materials,[11,12] which indicate that the relaxation-time for the electrons is extremely small (10 fs) compared with the time scale for the motion of the atoms. Since we are interested in structural changes with time scales that are larger than 10 fs, the even-if drastic assumption of separated time scales should work reasonably. As a consequence of this separation of time scales we can study the dynamics of the cluster in the adiabatic limit and consider that electrons thermalize immediately after excitation. On this basis, we can then treat the atomic motion in the Born-Oppenheimer approximation.

Note that the approximation of separable time scales for atoms and electrons was also used by C. A. Ullrich *et al.* to treat the ultrafast dynamics of electrons in highly excited metallic clusters.[13]

In a first step we calculate the electronic energy of the ground-state configuration by diagonalization of a tight-binding Hamiltonian. The action of the laser is then considered by inducing electronic transitions from occupied to unoccupied tight-binding states. Since we assume an instantaneous thermalization of the electrons, the occupation of the excited states is given by a Fermi-Dirac distribution determined by the laser-induced temperature T_{el}.

The total energy of the excited electronic system is a function of atomic coordinates. Thus, it provides the potential energy surface to perform molecular-dynamics simulations. The forces governing the atomic motion are obtained using the Hellmann-Feynman theorem.

A. Hamiltonian

For the microscopic description of Si_n clusters we use a Hamiltonian built up by an attractive term, derived in the tight-binding approximation, and a potential accounting for the core-core repulsion

$$H_{el}=H_{TB}+\sum_{i<j}^{N}\Phi_{rep}(R_{ij}) \qquad (1)$$

The tight-binding part is given by

$$H_{TB}=\sum_{i\alpha\sigma}\varepsilon_{i\alpha}c_{i\alpha\sigma}^{\dagger}c_{i\alpha\sigma}+\sum_{\substack{i\alpha j\gamma\\ i\neq j,\sigma}}t_{ij}^{\alpha\gamma}c_{i\alpha\sigma}^{\dagger}c_{j\gamma\sigma}, \qquad (2)$$

where $c_{i\alpha}^{\dagger}$ $(c_{i\alpha})$ refers to the creation (annihilation) operator for an electron with spin σ at the orbital α of atom i. The quantities $\varepsilon_{i\alpha}$ are the on-site energies and the $t_{ij}^{\alpha\gamma}$ the hopping integrals between orbitals $i\alpha$ and $j\gamma$. These integrals are functions of the distance vector $\mathbf{R_{ij}}$ between atoms i and j. The angular dependence of the $t_{ij}^{\alpha\gamma}$ is taken into account following Slater and Coster.[14] For the distance dependence of the hopping elements and the repulsive potential we used the scaling form proposed by Ho *et al.*[15]

$$t_{\alpha}(R_{ij})=t_{\alpha}(r_0)\left(\frac{r_0}{R_{ij}}\right)^{n}\exp\left\{n\left[-\left(\frac{R_{ij}}{r_{c\alpha}}\right)^{n_{c\alpha}}+\left(\frac{r_0}{r_{c\alpha}}\right)^{n_{c\alpha}}\right]\right\}, \qquad (3)$$

where α denotes the four tight-binding matrix elements $ss\sigma$, $sp\sigma$, $pp\sigma$, and $pp\pi$. $r_{c\alpha}$ determines the range of the interaction, $n_{c\alpha}$ the decay of the scaling forms. n is the hopping exponent, and r_0 the nearest-neighbor separation in the equilibrium diamond structure of silicon. The repulsive potential is a sum of a functional f of the repulsive pair potential $\phi(R_{ij})$ (Ref. 15)

$$E_{rep}=\sum_{i} f\left[\sum_{j} \phi(R_{ij})\right],$$

$$f(x)=C_1x+C_2x^2+C_3x^3+C_4x^4,$$

$$\phi(R_{ij})=\left(\frac{r_0}{R_{ij}}\right)^m \exp\left\{m\left[-\left(\frac{R_{ij}}{r_c}\right)^{m_c}+\left(\frac{r_0}{r_c}\right)^{m_c}\right]\right\}. \quad (4)$$

B. Electronic energy

The total electronic energy of the Si_n clusters for a given electronic configuration described by the set of occupations $\{n_k\}$ of the tight-binding eigenstates is obtained by diagonalizing the tight-binding Hamiltonian and evaluating the expression

$$E(\{R_j\})=\sum_{k} 2n_k\langle\Phi_k|H_{TB}|\Phi_k\rangle+E_{rep}+E_0N_{at}. \quad (5)$$

The attractive term is a sum over the eigenvalues ε_k of filled tight-binding states, E_{rep} the potential energy due to the core-core repulsion, and E_0N_{at} is the energy of N_{at}-isolated Si atoms. The factor 2 arises, because each state is occupied by two electrons with opposite spin. The total electronic energy depends through the Hamiltonian H_{TB} and the energy E_{rep} on the atomic coordinates ($\{R_j\}$), thus providing the potential energy surface that determines the atomic motion.

We assume that the cluster is initially in its ground-state, i.e., at zero temperature. The action of the laser pulse consists in producing electron-hole excitations. In our model, the electronic system is always in equilibrium at the laser-induced temperature T_{el}, i.e., the laser produces thermalized electron-hole pairs. The occupation number of the tight-binding state ε_k is then given by a Fermi-Dirac-distribution

$$n_k(T_{el})=\frac{1}{e^{\beta(\varepsilon_k-\mu)}+1}, \quad (6)$$

where $\beta=1/k_BT_{el}$. The chemical potential μ can be determined by the constraint, that the number of electrons in the system is constant

$$N_{el}=\sum_{k} \frac{1}{e^{\beta(\varepsilon_k-\mu)}+1}=4N_{at}. \quad (7)$$

To get a better comparison with experimental parameters, it is convenient to characterize the laser by the energy it transfers to the electrons, which are assumed to be initially at $T_{el}=0$. This energy is referred to as the total absorbed energy E_{abs}.[16] The energy absorbed by the cluster until the time t can be written as

$$\Delta_{abs}(t)=E[T_{el}(t)]-E(T_{el}=0). \quad (8)$$

$E(T_{el}=0)$ is the electronic ground-state-energy of the cluster, i.e., the energy before the action of the laser pulse ($t\rightarrow-\infty$). Given a fixed amount of energy that the system absorbs, we get the electronic temperature T_{el} and the chemical potential μ by solving simultaneously Eqs. (7) and (8). From the definition of the total absorbed energy E_{abs} and Eq. (8) it is clear that $E_{abs}=\Delta_{abs}(t\rightarrow+\infty)$.

In order to illustrate the determination of $\Delta_{abs}(t)$, we first consider a laser pulse modeled by a temporal delta function (laser pulse duration $\tau=0$). In contrast to pulses with a finite width, the positions of the ions now are fixed during the laser excitation process. Since the energies ε_k and the potential E_{rep} are functions of the atomic coordinates ($\{R_j\}$) only, Eq. (8) reduces to

$$\Delta_{abs}(t)=\sum_{k} [n_k(T_{el})-n_k(T_{el}=0)]\varepsilon_k\theta(t), \quad (9)$$

where the step function $\theta(t)$ arises from the time integration of the delta pulse.

Now, we take form and duration of the laser pulse explicitly into account, by assuming that laser energy flows into the system following a Gauss profile. Thus, the energy absorbed by the electrons at time t is given by the integral

$$\Delta_{abs}(t)=I_0\int_0^t dt'\,\exp\left[\frac{-(t'-t_0)^2 4\ln 2}{\tau^2}\right], \quad (10)$$

where τ is the pulse duration. The intensity of the laser pulse I_0 is related to the total absorbed energy $\Delta_{abs}(t\rightarrow\infty)$ by $I_0=4\Delta_{abs}(t\rightarrow\infty)\sqrt{\ln 2/\pi}/\tau$.

Since the atoms are allowed to displace from their equilibrium positions during excitation, Eq. (8) now reads

$$\begin{aligned}\Delta_{abs}(t)&=E[T_{el},\{R_j(t)\}]-E(T_{el}=0,t=0)\\&=\sum_{k} n_k[T_{el},\{R_j(t)\}]\varepsilon_k[\{R_j(t)\}]+E_{rep}[\{R_j(t)\}]\\&\quad-E(T_{el}=0,t=0),\end{aligned} \quad (11)$$

where $E(T_{el}=0,t=0)=E[T_{el}=0,\{R_j(t=0)\}]$ is the total energy of the electronic subsystem before the action of the laser pulse, with initial conditions $T_{el}(t=0)=0$.

For times t smaller than the duration τ of the pulse electronic temperature, chemical potential and occupation of the electronic states have to be computed again at each timestep. After irradiation we keep the electrons in their excited state and continue the molecular-dynamics simulation in the microcanonical ensemble. Once $T_{el}(t)$ has been determined, it is possible to calculate the concentration of excited electrons (holes) as

$$\xi=\sum_{k>k_F} n_k/N_{el}. \quad (12)$$

C. Short-time dynamics

In a Born-Oppenheimer molecular-dynamics like scheme the trajectories $\{R_j(t)\}$ of the atoms are determined by the potential energy surface $E[\{R_j(t)\}]$ corresponding to the total energy of the electronic system. The force acting on atom i is thus given by

$$\begin{aligned}\mathbf{F}_i&=-\nabla_{R_i}E(\{R_j\})\\&=-\nabla_{R_i}\left(\sum_{k} 2n_k\langle\Phi_k|H_{TB}|\Phi_k\rangle+E_{rep}+E_0N_{At}\right).\end{aligned} \quad (13)$$

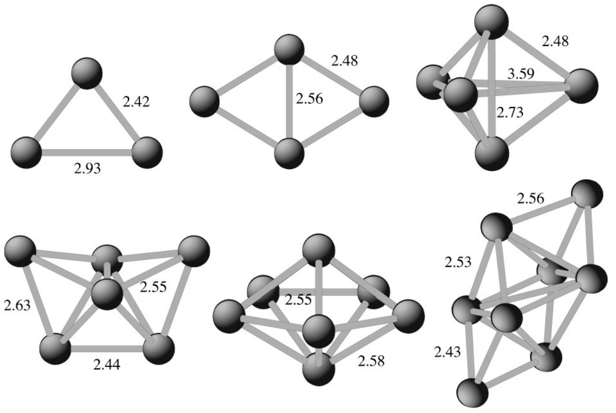

FIG. 1. Ground-state geometries of Si_n $(n=3-8)$ calculated as the global minima of the PES [Eq. (5)] at $T_{el}=0$. The bond lengths are given in Å . Note that these structures are in good agreement with *ab initio* calculations (Refs. 17 and 18) and experimental results (Ref. 19).

This equation can be further simplified by making use of the Hellmann Feynman theorem

$$\mathbf{F}_i=-\sum_k n_k\langle\Phi_k|\nabla_{R_i}H_{TB}|\Phi_k\rangle-\nabla_{R_i}E_{rep}. \qquad (14)$$

We treat the dynamics of the atoms classically and solve the equations of motion by using the Verlet integrator.

III. RESULTS

We have studied the relaxation dynamics of laser excited Si_n-clusters using the theory outlined in Sec. II. The parameterization of the hopping integrals and the repulsive potential is taken from the work of Ho *et al.*[15] The time step used for the molecular dynamics simulation was $\Delta t=0.05$ fs. We followed the time evolution of the clusters over a time interval $[0{:}t_s]$ of 5 ps.

A. Ground-state structures

The ground-state geometries of the Si_n clusters $(n=2-8)$ were determined by simulated-annealing as follows. Initially, the clusters were given random coordinates and velocities and then MD simulations were performed on the ground-state potential energy surface (PES) given by Eq. (5) at $T_{el}=0$. At fixed time intervals the cluster velocities were scaled to zero, removing the kinetic energy from the system and forcing it to relax towards a minimum of the PES. This procedure was repeated for several sets of initial coordinates and velocities, in order to find the global minimum of the PES. The resulting ground-state configurations are illustrated in Fig. 1. Note that our calculated structures and their bondlengths are in good agreement with those proposed by Ragavachari et al.[17] (all-electron *ab initio* molecular-orbital approach) and Fournier *et al.*[18] (local-density approximation approach).

B. Dynamics of Si_4 as a function of laser pulse duration

In previous theoretical works[6,8] about the laser-induced phase transition in crystalline silicon, it was assumed, that the action of the pulse is instantaneous $(\tau=0)$. In the following we show, that the relaxation dynamics resulting from excitation by pulses with a finite width differs dramatically from the behavior obtained assuming $\tau=0$. Delta pulselike excitations are simulated by determining the Fermi-Dirac distribution of the electrons at the laser induced temperature T_{el} and keeping the occupation of the tight-binding states constant during the MD-simulation interval [see Eq. (11)]. The relaxation dynamics of Si_4 for a pulse duration $\tau=0$ and absorbed energies of 4 and 14 eV is displayed in Figs. 2(a) and 2(c). After absorbing 4 eV, which corresponds to an initial electronic temperature of 10 200 K and an electron-hole concentration $\xi=10\%$, the system performs harmonic oscillations around the equilibrium structure [Fig. 2(a)]. New features appear for larger absorbed energies. For instance, if $E_{abs}=14$ eV $(T_{el}=23000$ K, $\xi=20\%)$, the cluster oscillates harmonically during the first few hundreds of fs after excitation. Then, the oscillations become anharmonic and the system shows a melting like behavior after 900 fs [Fig. 2(c)].

For excitations with pulses of finite duration we use Eq. 10. The fundamental difference to delta functionlike excitations is that atoms move while the excitation process takes place. Since in both cases investigated above, the kinetic energy increased strongly within 20 fs, we expect a change in the response of the clusters for durations larger than 20 fs. Figures 2(b) and 2(d) show the time evolution of the kinetic energy during and after excitation by a 100 fs pulse for the same absorbed energies as above. At a pulse energy of 4 eV, the kinetic energy shows a sharp peak and then performs small oscillations. The peak corresponds to a cluster expansion, as will be discussed below. By keeping the pulse duration constant and increasing the pulse energy up to 14 eV the

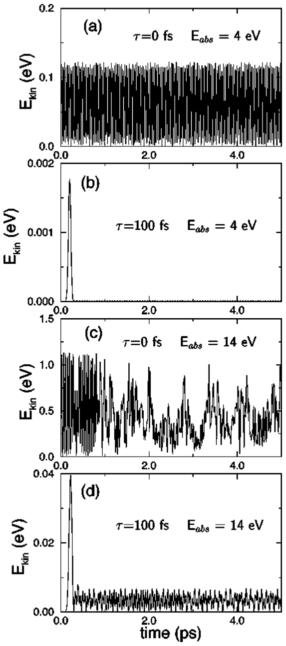

FIG. 2. Time evolution of the kinetic energy of Si_4 during and after the action of laser pulse for increasing pulse energies E_{abs} and pulse durations $\tau=0$ and $\tau=100$ fs. For constant E_{abs} the response of the cluster shows a qualitatively different behavior for both pulse durations. (a) The cluster oscillates. (b) The cluster expands. (c) Meltinglike behavior. (d) Expansion and oscillations around the new equilibrium.

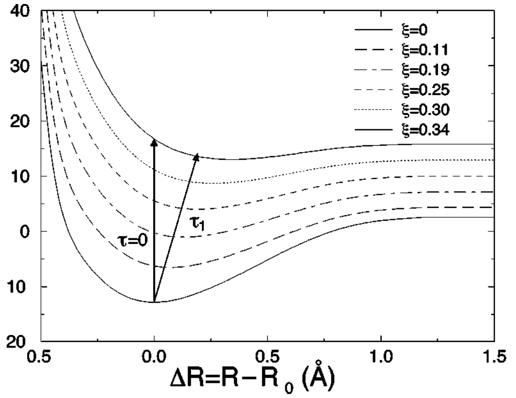

FIG. 3. Potential energy of Si_4 as a function of the changes in the interatomic distance (ΔR) when the cluster is expanded (contracted) homogeneously and isotropically. The different curves refer to increasing concentration of electron-hole excitations ξ induced by the laser pulse. Arrows indicate the evolution of the system for different pulse durations.

main feature is conserved: the system expands (more than for $E_{abs}=4$ eV) and performs small oscillations around the new equilibrium structure.

In order to give an intuitive illustration of the results shown in Fig. 2, we plot in Fig. 3 the potential energy of Si_4 as a function of the changes in the interatomic distances ΔR when the cluster is expanded (contracted) homogeneously and isotropically. Increasing the concentration of electron-hole excitations ξ, the minimum of the potential energy curves is shifted towards larger distances between the atoms. When the pulse energy flows into the system instantaneously ($\tau=0$), the cluster is vertically excited from the ground state ($\xi=0$) to an excited PES and relaxes towards the minimum, corresponding to an isomer of the cluster in its excited state. If the kinetic energy achieved by the cluster is lower then the potential energy barrier, the cluster remains trapped in the potential minimum and oscillates around the new geometry. Increasing the energy absorbed by the system, the gained kinetic energy may be large enough to overcome the potential barrier, permitting to the system to explore several minima of the excited PES. This continuous isomerization is what we define as meltinglike behavior. When we again increase the strength of the laser pulse, a considerable part of the electrons may be excited from the bonding to the antibonding states, leading to a repulsive PES and thus, to fragmentation of the cluster.

If the excitation pulse has a finite duration, the cluster is allowed to relax during the excitation process and therefore an adiabatic transition becomes favored. The evolution of the system along the potential energy curves is now indicated in Fig. 3 by τ_1. As the laser energy flows into the system, the cluster is transported from minimum to minimum of the PES corresponding to the respective degree of excitation. Since for increasing ξ the minimum is shifted towards larger distances between the atoms, this path results in an adiabatic expansion of the cluster.

C. Generalized phase diagrams

The fact that Si_n clusters show a different behavior when varying the laser parameters suggests the construction for each cluster size of a generalized ‘‘phase diagram,’’ where the relaxation products (‘‘phases’’) are plotted as a function of pulse duration and absorbed energy. If the relaxation process takes place in form of structural changes (isomerization), then we consider the final state as belonging to the ‘‘solid phase.’’ If meltinglike behavior occurs as a consequence of the laser excitation, the final state is considered to be in the ‘‘liquid phase.’’ Finally, if the relaxation process leads to a fragmentation of the cluster, we consider the final state as belonging to the fragmented (gas) ‘‘phase.’’ Since we investigate systems under extreme nonequilibrium conditions, the observed phases are not stationary but undergo an evolution in time. The Si_4 cluster, for example, may for certain laser parameters melt and at later time fragment. Thus, the MD-simulation interval plays a decisive role in the characterization of the points in the phase diagrams. We used a time interval $[0{:}t_s]$ of 5 ps. Test calculations for selected values of the laser parameters show that no dramatic energy redistributions occur beyond this time. This means that after 5 ps a considerable thermalization of the cluster has taken place and we expect the coexistence lines between the solid-liquid and solid-gas phases to remain almost unchanged if the simulation interval is increased. However, the liquid-gas transition line should further depend on t_s due to the occurrence of statistical fragmentation.

For the set-up of the diagrams we have to define criteria suitable for classifying the cluster behavior and marking the transition from one phase to another.

As described in Sec. III B the liquidlike phase is characterized by a continuous change of cluster geometry. A quantity that seems appropriate to describe this behavior is the mean square bonding length fluctuation δ

$$\delta=\frac{2}{N(N-1)}\sum_{\substack{i,j\\ i>j}}\frac{\sqrt{\langle r_{ij}^2\rangle-\langle r_{ij}\rangle^2}}{\langle r_{ij}\rangle}.$$

$\langle\rangle$ defines the mean value over a MD-simulation time interval $[0{:}t_s]$. The dependence of δ on the absorbed energy is illustrated in Fig. 4 for a delta pulse ($\tau=0$). The curve shows a rapid increase after $E_{abs}=8$ eV. We have observed that a good qualitative estimate of the solidlike to liquidlike transition can be obtained assuming the validity of the Lindemann-criterion[20] for nonequilibrium dynamics. This means, that the system may be considered to be molten when the bondlength fluctuations exceed 15%. For a delta pulse ($\tau=0$) this occurs for $E_{abs}=13$ eV.

As mentioned in Sec. III B, for high energetic laser pulses the system fragments. We define the system as fragmented when at least one atom has left the cluster, i.e., when the distance to the remaining atoms exceeds the cutoff radius of the attractive potential ($r_c=4.16$ Å), and the translational kinetic energy of the leaving atom becomes time independent. The fragmentation times t_{frag} are determined as a function of the laser parameters.

Using the discussed criteria we are now able to characterize the ‘‘phases’’ of the cluster dynamics resulting from excitation by pulses of different energy and duration. For the construction of the generalized phase diagrams we proceed as follows. First, we determine the separation line between the fragmented and the nonfragmented phase by monitoring the bond lengths. Then, and in order to distinguish between

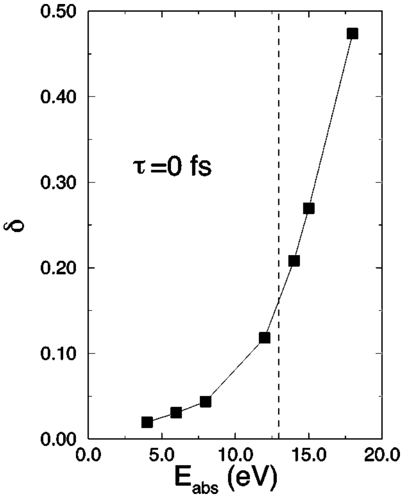

FIG. 4. Mean-square bonding length fluctuation δ of Si_4 as a function of absorbed energy for a delta pulse ($\tau=0$). The curve shows a rapid increase after $E_{abs}=8$ eV. The dashed line indicates the value of E_{abs} from which the Lindemann criterion is fulfilled.

liquidlike and solidlike, δ was calculated as a function of the laser parameters and separated into two regions corresponding to $\delta<0.15$ and $\delta>0.15$. The area lying between the line $\delta=0.15$ (Lindemann criterion) and the line delimiting the fragments characterizes the liquid phase. The remaining area belongs to the solid phase (expansions and structural changes).

Figure 5 displays the ''phase diagrams'' for Si_4 and Si_5 in a range of very short pulse durations. Both diagrams show the same feature: a liquid phase is only observed for pulse durations $\tau<30$ fs. For longer pulses, the transition occurs directly from the solid to the fragmented phase. This can be understood with the help of Fig. 3. For long durations and low values of E_{abs} the cluster evolves from minimum to minimum of the PES's along the path indicated by τ_1 and cannot become the kinetic energy needed to escape the potential minimum. This results in an expansion of the cluster. For a certain value of E_{abs} the minimum in the PES is so flat, that the the potential barrier can be easily overcome. This situation defines the onset of fragmentation. For higher absorbed energies, fragmentation occurs.

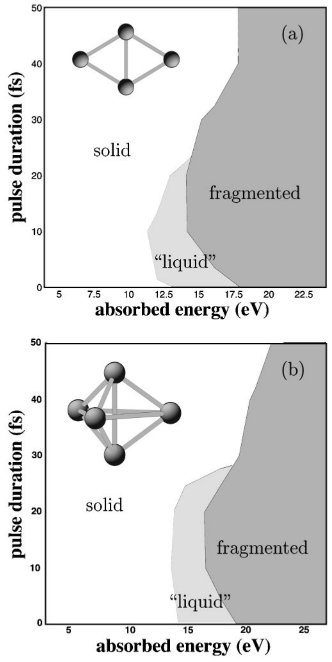

FIG. 5. Generalized ''phase diagrams'' (see text) for the products of the laser excitation (solidlike, liquidlike, and fragmented clusters) as a function of the pulse duration and absorbed energy. (a) and (b) refer to excitation of Si_4 and Si_5, respectively.

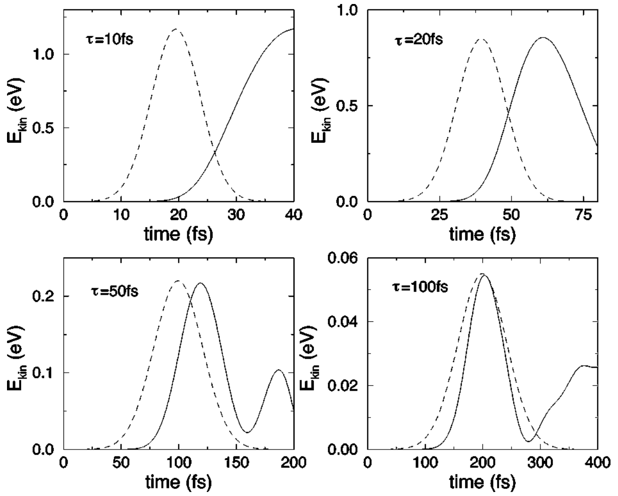

FIG. 6. Time evolution of the kinetic energy for Si_5 (solid line) upon excitation through the laser pulse (dashed line) for pulse durations τ of 10, 20, 50, and 100 fs and an absorbed energy of 15 eV. For very short pulses ($\tau=10,20$ fs) there is a large relative delay between the excitation and the response. For longer pulses ($\tau=50,100$ fs) the delay between the two curves is relatively small.

To give further insight into the mechanism, which prevents the cluster from melting at longer pulse durations, we introduce the response time t_{resp} of the cluster with respect to the laser pulse. The response of the clusters to the excitation manifests itself in an increase of the kinetic energy. t_{resp} may thus be defined as the time delay between the maximum of the laser pulse and the first increase in the kinetic energy.

In Fig. 6, we show the kinetic energy of the excited cluster and the time development of the laser pulse as a function of time for different pulse durations. For very short pulses ($\tau=10$ fs), t_{resp} is large. Atoms begin to move when almost the entire energy has flown into the system. This corresponds to an almost vertical excitation from one PES to another (see Fig. 3). The achieved kinetic energy is large enough to induce a meltinglike behavior. For increasing pulse duration, the relative delay between the pulse and the kinetic energy curve as well as the kinetic energy itself decrease. At a pulse duration $\tau=100$ fs, the overlap between the two curves is complete, the achieved kinetic energy very small. No melting is observed, the cluster expands adiabatically. As shown in Fig. 6, $t_{resp}\simeq 20$ fs for Si_5, independently of the pulse duration. We may qualitatively state, that a meltinglike behavior will be observed, if the pulse duration is shorter or comparable to the response time of the cluster.

Figure 7 illustrates the generalized phase diagram for Si_4 for pulse durations $\tau=50-350$ fs and absorbed energies in the range 12–30 eV. As discussed previously, the longer the

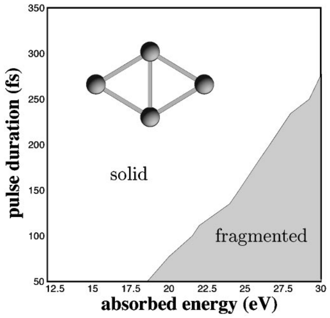

FIG. 7. Generalized ‘‘phase diagram’’ of Si_4 (see text) for the products of the laser excitation as a function of the absorbed energy and pulse durations larger than 50 fs. A liquidlike phase is not observed for pulse durations in the range 50–350 fs.

laser pulse, the lower the kinetic energy achieved by the cluster and thus the higher the energy, which the cluster must absorb to fragment.

At fixed pulse energies short pulses produce more fragmentation than long pulses. Such dependence of the fragmentation behavior on the pulse duration has also been observed in experiments using intensive laser pulses.[10]

Notice, however, that the source of fragmentation in our study and in the experiment are different. We describe fragmentation due to the excitation of electrons into antibonding states, whereas in experiment fragmentation is due to multiple ionization of the cluster (Coulomb explosion).

Our estimated fragmentation times are smaller than 10 ps and depend on the pulse duration and absorbed energy. For fixed pulse durations the fragmentation times decrease with increasing laser energy. A careful calculation of fragmentation times should involve a statistical averaging of the many different initial conditions, i.e., finite initial temperature (see Refs. 21 and 22 for more details). Such study is however, out of the scope of this paper.

For Si_6, Si_7, Si_8 we observe a similar behavior to that shown by Si_4 and Si_5: a liquid phase appears only for very short laser pulses. For longer pulses the clusters expand or undergo structural changes.

As is evidenced by the comparison of Figs. 5(a) and 5(b), the absorbed energies for which the phase transitions take place, are shifted towards larger values with increasing cluster size. This is not surprising, since the total number of electrons increases with cluster size and therefore the energy needed to achieve the degree of excitation inducing the phase transitions becomes larger. Note that the threshold absorbed energies of the different clusters are dependent also on the inter-level spacing near the Fermi energy.

Figure 8 illustrates as a function of cluster size the concentration of electron-hole pairs ξ_{melt} which must be excited to induce a transition to a liquid phase. The curves decrease with increasing cluster size, showing small odd-even oscillations. The bulk value lies around 8%.[6] The threshold values ξ_{melt} are shown to be dependent on laser pulse duration. This may be understood by the observation, that the pulse duration prescribes the path (Fig. 3) on which the system evolves along the PES’s. Since the potential energy well corresponding to the ground-state geometry is not necessarily symmetric, different paths mean different potential energy barriers that have to be overcome.

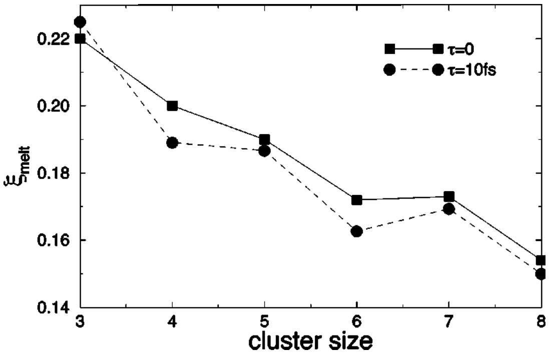

FIG. 8. Concentration of electron-hole pairs ξ_{melt}, which must be excited to induce a transition to a liquidlike phase, as a function of cluster size for a delta pulse ($\tau = 0$) and a pulse of 10 fs duration. The curves decrease with increasing cluster size and are shown to be lightly dependent on the pulse duration.

D. Laser-induced structural changes

We now investigate whether stable structural changes, i.e., without subsequent melting or fragmentation, going beyond a simple expansion of the ground-state geometry may be achieved by a suitable choice of the pulse parameters. Figure 9 shows the stable relaxation products of Si_5 in the range $E_{abs} = 3–18$ eV, $\tau = 100–900$ fs. All the geometries of the excited cluster, which can be reached by means of adiabatic structural changes, are distorted and/or expanded forms of the ground-state trigonal bipyramid. The angle a

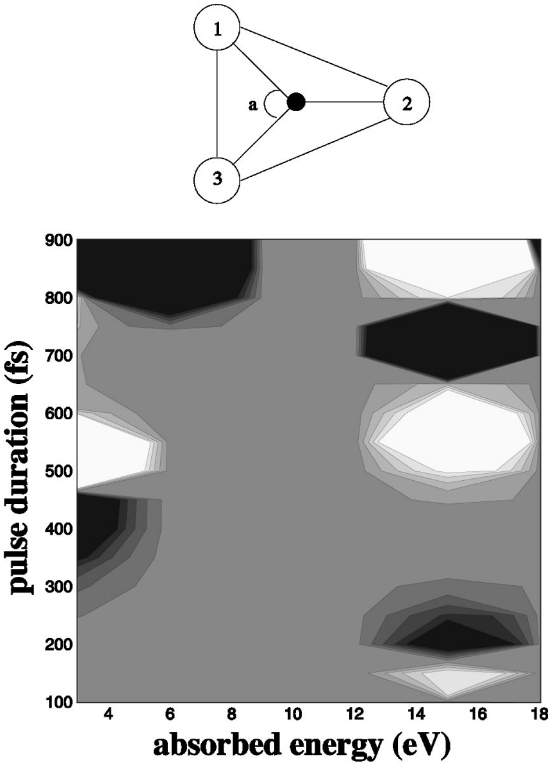

FIG. 9. The stable structures of Si_5 resulting from excitation by pulses in the range $E_{abs} = 3 - 18$ eV, $\tau = 100 - 900$ fs are distorted trigonal bipyramids. The angle a characterizing the structures is illustrated in the upper part of the figure. The grey area corresponds to $a = 120°$. The white and the black area indicate the resulting structures characterized by $a = 180°$ and $a = 72°$, respectively.

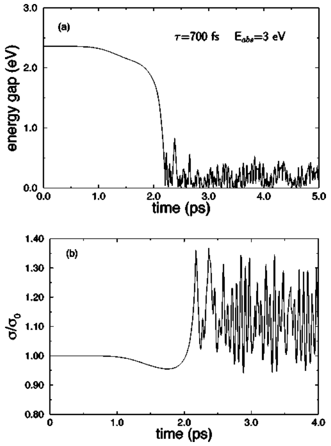

FIG. 10. (a) Time evolution of the energy gap of Si_5 for laser parameters ($E_{abs}=3$ eV, $\tau=700$ fs) inducing a stable structural change. When the transition to the new isomer occurs, the gap decreases strongly. (b) Relative Kubo conductivity σ of Si_5 as a function of time for the same pulse parameters as above. σ_0 is the conductivity of the cluster in the ground state. Since the isomerization is volume conserving, the decrease of the energy gap corresponds to a ''true'' increase in metallic character.

characterizing the structures in the diagram, is illustrated in the upper part of the figure. The extended gray area corresponds to the geometries that result by simply expanding the ground-state structure ($a=120°$). The white and the black areas indicate the structures characterized by an angle a of 180° and 72°, respectively. Structural changes, which are volume conserving, occur for $E_{abs}=3$ eV, $\tau=500-900$ fs and $E_{abs}=15$ eV, $\tau=800-900$ fs. The diagram shows, that at fixed absorbed energies the structural transitions are not necessarily the same for different pulse durations. We have already discussed (Sec. III B), that the duration of the excitation prescribes the path along which the system evolves on the PES. For different pulse durations, the cluster may thus be trapped in different minima, corresponding to different isomers of the excited PES. Note that, since the transition to the new geometry is almost adiabatic, the resulting isomer does not necessarily correspond to the global minimum of the PES of the excited state.

E. Laser-induced metallization

In the following we investigate, whether a transition to a metalliclike phase, like the observed in bulk semiconductors,[5] may be induced also in small systems. One could define as metallic the clusters that have a negligible energy gap between occupied and unoccupied states. However, since an expansion of the cluster structure always leads to a reduction of the interlevel spacing, this definition is suitable only for investigating transitions that are strictly volume conserving. Furthermore, since in the excited state certain levels lying above the Fermi energy ε_F are occupied and levels lying below ε_F are empty, one could argue, that the concept of energy gap between highest occupied and lowest unoccupied levels makes no sense. However, we show in Fig. 10 that, in spite of this problem, the energy gap may give, in certain cases, a good characterization of the metallic state.

Our approach yields for the ground-state geometries of the clusters Si_2-Si_8 energy gaps in the range 0.64 eV (Si_8) to 2.4 eV (Si_4, Si_5). The bulk value is 1.17 eV. Two scenarios may lead to a metallization: (i) the clusters undergo a continuous isomerization, such that the effective energy gap is given by the mean value over the isomers, or, (ii) a stable structural change to a geometry with a comparable small energy gap occurs. Figure 10(a) displays the time evolution of the energy gap of Si_5 for pulse parameters ($E_{abs}=3$ eV, $\tau=700$ fs) leading to a stable isomerization. When, after 2.1 ps, the transition to the new geometry occurs, the energy gap is strongly reduced. Note, that the transition is volume conserving.

When investigating structural changes involving a cluster expansion, a definition of the metallic character taking volume into account, is needed. A suitable way may be the calculation of the Kubo microscopic conductivity in the form proposed by Imry and Shiren[23]

$$\sigma=\frac{2e^2\hbar}{\Omega m^2}\eta\sum_{ij}\frac{(n_i-n_j)}{\varepsilon_j-\varepsilon_i}|\langle i|p_z|j\rangle|^2\frac{1}{(\varepsilon_j-\varepsilon_i)^2+\eta^2}. \tag{15}$$

ε_j is the energy and n_j the occupation number of the jth tight-binding sate, $\langle i|p_z|j\rangle$ the dipole matrix element in the z direction, Ω the cluster volume, and m the electronic mass. η characterizes the width of the energy levels, resulting from the assumption for small systems of an inelastic lifetime of the electrons. We have used $\eta=0.05$ eV. The time-dependence of σ is shown in Fig. 10. Note that, although Eq. (15) is actually applicable to a system coupled to a reservoir and not to a free cluster, it yields a qualitative picture of the time dependence of the electronic properties of the cluster after excitation.

IV. SUMMARY AND CONCLUSIONS

In this paper, the laser induced ultrafast relaxation of Si_n clusters ($n=5-8$) was studied, as a function of energy and duration of the laser pulse, by performing molecular-dynamics simulations based on a tight-binding Hamiltonian. We have shown, that the duration τ of the exciting pulse plays an important role in the relaxation dynamics. By varying τ it might be possible to control the relaxation path and the relaxation products. We have obtained that excitation by very short pulses ($\tau<30$ fs) may induce vibrations, melting or fragmentation of the cluster for increasing intensities of the laser pulse. On the other hand, longer pulses lead to an expansion of the cluster structure and, at high intensities, to fragmentation, while no melting of the cluster is observed.

By analyzing the relaxation products after a reasonably long simulation time as a function of the (external) laser parameters we were able to determine generalized ''phase diagrams'' for the occurrence of solidlike, liquidlike, and fragmented clusters. The liquidlike phase appears only for very short pulses. By defining a response time t_{resp} of the cluster with respect to the laser pulse, we observe, that for all investigated cluster sizes a liquidlike phase occurs if the pulse duration is shorter or comparable to t_{resp}. The threshold energies for the phase transitions are shifted towards larger values with increasing cluster size, while the number of excited electron-hole pairs leading to melting ξ_{melt} is shown to decrease, approximating the bulk value (8%).

For Si_5-Si_8, longer pulses favor stable structural changes going beyond a simple expansion of the ground-state geometry. For certain values of τ and energy of the laser pulse isomers are produced, which show a small an incipient metallic character.

Since the approach presented in this paper does not take into account multiple ionization of the cluster, it should break down for large absorbed energies. For low-absorbed energies it yields a well-defined theoretical model for the excitation, from which the time-dependent forces on the atoms can be determined in a transparent way.

A direct comparison of our results with the experimental results by Gerber *et al.* is not possible because in those experiments the intensity of the laser pulse is high enough to produce multiple ionization of the clusters, and only ionized clusters are detected. In order to achieve a quantitative description of the experimental results by Gerber *et al.*[10] both the multiple ionization and the atomic motion have to be taken into account. So far, there is no theory able to treat correctly and on equal footing laser-induced multiple ionization and atomic motion in clusters.

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*On leave from Institut für Theoretische Physik, Freie Universität Berlin, Arnimallee 14, 14195 Berlin, Germany.

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