

Simulation of Si Clusters via Langevin Molecular Dynamics with Quantum Forces

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We present a dynamical-stochastic scheme to determine from first principles the structure of low-symmetry atomic systems. The method is based on Langevin molecular dynamics and quantum-mechanical interactions derived from self-consistent local-density-functional calculations. It can be used for insulating as well as metallic and charged systems. Here we examine small neutral and charged Si clusters, and show that the ground-state structures can be efficiently obtained with this approach.

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In condensed matter physics, structural determination of complex nonperiodic systems, such as clusters or extended defects in solids, remains a serious challenge. Conventional theoretical methods are hindered by the large number of degrees of freedom and the lack of symmetry or periodicity in these systems. Computer experiments exploiting the simulated annealing strategy [1] can overcome such obstacles. The challenge with this type of extensive numerical investigation is to reconcile an accurate description of the potential-energy surface and an appropriate configuration-space sampling for global geometry optimization.

Different simulation schemes have been used in the past with empirical descriptions. Simulated annealing was originally proposed [1] with the Monte Carlo (MC) approach. This is a robust scheme well suited for complex energy surfaces, but in general the MC approach is not the most efficient. Traditional (Newtonian) molecular dynamics (MD) is more efficient than the MC approach when the potential-energy surface is smooth, but is also more likely to be affected by local minima in complex energy surfaces. Recently, Biswas and Hamann [2] proposed Langevin molecular dynamics (LMD) for simulated annealing. Within a force field description, this approach has been applied to clusters [2-4] and defects [5], and proved to be efficient even in difficult cases [4].

Here we combine for the first time LMD with realistic quantum-mechanical interactions obtained in the local-density-functional (LDF) framework. Car and Parrinello [6] coupled LDF and MD simulations using a fictitious dynamics for the electrons and classical dynamics for the ions, simultaneously minimizing the energy with respect to the electronic and ionic degrees of freedom. This approach has been exploited, in particular, to determine the ground-state structure of small clusters [7-13]. We present and test a different scheme to perform global geometry optimization based on first-principles LDF calculations. We exploit LMD for simulated annealing and determine the atomic interactions by means of efficient self-consistent pseudopotential plane-wave calculations. The method can be used for insulating as well as metallic and charged systems. We have applied this approach to

small neutral and negatively charged Si_n clusters ($n < 6$), and successfully reproduced their known geometry [14, 15]. In addition, we have examined Si_6 and Si_6^+ clusters, which are of special interest since they correspond to a magic number in the mass spectrum of Si clusters. Si_6 has been shown recently to be the major fragmentation product of large clusters [16]. The annealing runs for Si_6 lead to different isomers which are degenerate within the accuracy of LDA, and can be obtained by relatively small distortions from the same structure.

In the simulations, the ionic positions \mathbf{R}_I evolve according to the Langevin equation [2]

$$M_I \ddot{\mathbf{R}}_I = -\nabla_{\mathbf{R}_I} E(\{\mathbf{R}_J\}) - \gamma M_I \dot{\mathbf{R}}_I + \mathbf{G}_I, \quad (1)$$

where $E(\{\mathbf{R}_J\})$ is the total energy of the system and M_I is the ionic mass. The last two terms on the right-hand side of Eq. (1) are the Langevin dissipation and fluctuation forces defined, respectively, by the friction coefficient γ and the random Gaussian variables $\{\mathbf{G}_I\}$ with a white spectrum:

$$\begin{aligned} \langle G_I^\alpha(t) \rangle &= 0, \\ \langle G_I^\alpha(t) G_J^\beta(t') \rangle &= 2\gamma M_I k_B T \delta_{IJ} \delta(t - t'). \end{aligned} \quad (2)$$

The angular brackets denote ensemble or time averages, and α stands for the Cartesian coordinate. The coefficient on the right-hand side of Eq. (2) ensures that the formalism is consistent with the fluctuation-dissipation theorem [17].

We determine the force $-\nabla_{\mathbf{R}_I} E$ in Eq. (1) by efficient self-consistent pseudopotential plane-wave calculations. We use a fast iterative diagonalization procedure [18], and exploit the Broyden mixing scheme [19] to accelerate self-consistency. The self-consistent deformation charge density at each LMD step is also used to extrapolate the charge density at the next time step. Metallic systems are conveniently handled by means of the Gaussian broadening scheme [20,21]. In this way we can treat clusters which have occupied and empty orbitals that are degenerate or quasidegenerate, and properly include in the sampling metallic configurations which may occur in a cluster at $T > 0$. This scheme also accelerates the self-

consistency. The quantum-mechanical forces are easily evaluated with the Gaussian broadening scheme [22]. For charged clusters the broadening technique can be exploited to include a partially filled electronic level. The neutrality of the supercell is maintained in this case by introducing a compensating jellium background [23].

LMD offers several advantages as a general tool for simulated annealing, since the computer annealing simulation does not have to follow explicitly each time step of the natural evolution of the physical system. The annealing can be significantly faster if the artificial constraints in the simulation lead to acceptable shortcuts relative to the natural evolution. In LMD simulations, the particles are subjected to random and dissipative forces which are related and controlled by the temperature through the fluctuation-dissipation theorem. The temperature of the system can be changed without rescaling the velocities, as normally done in Newtonian MD. Energy is free to flow in and out of the system, as it should. For simulated annealing LMD combines some of the advantages of MD and MC simulations. As opposed to MC simulations, LMD and MD sample the configurational space by collectively moving the particles, and move faster to the minima by exploiting the gradient. The shaking due to random forces in LMD helps the system to escape from metastable states in a manner reminiscent of "uphill" moves in MC simulations. With empirical potentials, LMD has been used, for instance, to anneal silicon clusters with up to 32 atoms [2,3]. Recent work [4] has shown the efficiency of this method for carbon clusters for which MD with empirical approaches was found to be impractical [24], and the MC approach had been the only reasonable alternative [24,25].

In our simulations for Si clusters, we use a soft ionic pseudopotential generated with the method of Troullier and Martins [26] from the atomic $3s^23p^23d^0$ ground-state configuration, and cast into the Kleinman-Bylander separable form [27] with s and d nonlocality. This potential reproduced accurately the structural and elastic properties of bulk Si. Exchange and correlation effects are included with the Ceperley-Alder functional [28] in the parametrized form given by Perdew and Zunger [29]. The simulations have been carried out in a simple cubic supercell with an edge $a = 18$ a.u., and an energy cutoff of 7 Ry for the plane-wave basis set. Changes in the bond lengths using a larger cell ($a = 24$ a.u.) and a higher energy cutoff (12 Ry) were found to be less than 1%. Only the Γ point is considered for reciprocal space sampling, as is appropriate for a cluster simulation, and we use an electronic level Gaussian broadening of 0.01 Ry. As a Langevin friction parameter we use $\gamma = 5 \times 10^{-4}$ a.u., which is similar to the value employed in the previous studies [3]. The equation of motion, Eq. (1), is integrated with the algorithm given in Ref. [30] using a time step of 8×10^{-15} sec (~ 330 a.u.).

For the simulated ground-state search of Si_n ($n=4, 5, 6$) we heated the system up to 3000 K, and cooled it

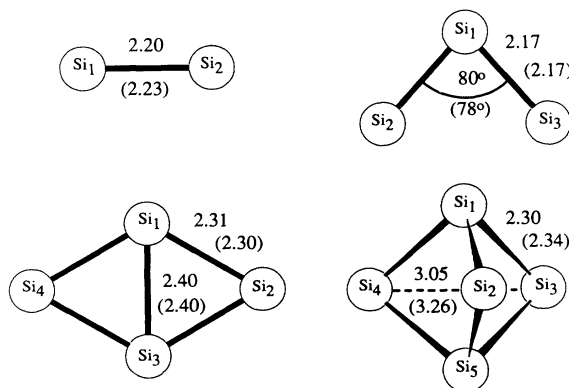


FIG. 1. LDA ground-state geometry of the neutral Si_2 - Si_5 clusters. The bond lengths are in Å. The results from the Hartree-Fock calculations [14] are also given in parentheses.

down to 300 K with six temperature steps, in an approximately linear annealing schedule, and using about 100 integrations per temperature step. The system was then quenched by a conjugate gradient minimization. The resulting geometries and bond lengths or angles for Si_4 and Si_5 together with those of the smaller Si aggregates obtained within the LDA are shown in Fig. 1. These results are in good agreement with the Hartree-Fock (HF) calculations including correlation effects by perturbation theory [14] and consistent with the LDA ground-state structures determined previously [8,31].

A typical annealing for Si_6 is shown in Fig. 2. The initial random geometry, the final structure, and a few

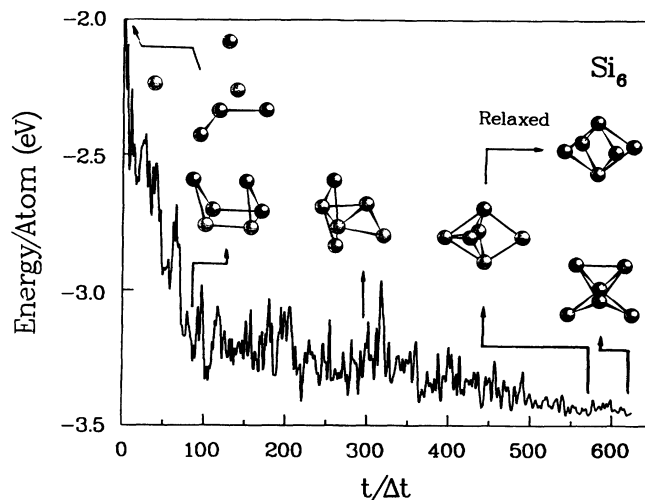


FIG. 2. Binding energy of Si_6 during a typical Langevin annealing run from 3000 to 300 K. The time step Δt is 8×10^{-15} sec. The initial, final, and some of the intermediate configurations of the cluster are also shown. Bonds are drawn for interatomic distances smaller than 2.60 Å.

representative examples of the structures occurring during the anneal are also shown in Fig. 2. We notice, in particular, that a triangular prism occurred in the early stage of the formation of the cluster. This structural unit has been found to be a basic element [8,32] for several clusters with $n > 8$. We find as lowest-energy structures two isomers which are degenerate within the accuracy of the LDA. These structures are a bicapped tetrahedron and an edge-capped trigonal bipyramid which subsequently relaxes to a distorted octahedron (see Fig. 2). HF calculations [32] yield binding energies for these two structures which are also within 0.01 eV/atom of each other. In Ref. [32] the distorted octahedron and the bicapped tetrahedron were found to relax to the edge-capped trigonal bipyramidal structure, predicted as the ground state.

The negatively charged Si_n^- clusters ($n < 6$) have structures similar to those of the neutral clusters shown in Fig. 1. The optimized structural parameters for the Si_n^- clusters are given in Table I together with those of the HF calculations [15]. The results obtained here with a fictitious neutralizing background in the supercell are in surprisingly good agreement with the HF results. We have also determined the structure of Si_6^+ using the same thermal treatment as for Si_6 . In this case, we find the edge-capped trigonal bipyramid as the final structure of the annealing, which is consistent with the result of the HF calculations [14].

There are different motivations for performing self-consistent calculations at each time step in LMD and not using a fictitious electron dynamics. The random forces introduced in the simulations are useful for shaking the ions out of metastable states. However, their effect on the evolution of the electronic states, if not decoupled from the ionic motion, is undesirable and could even be counterproductive. In Ref. [33], *ab initio* finite-temperature MD simulations were performed for the first time without using a fictitious molecular dynamics for the electronic degrees of freedom. The numerical effort in self-consistently solving the Kohn-Sham equations at each time step using an efficient iterative diagonalization scheme was found to be comparable to the effort involved in Car-Parrinello simulation, mainly because the time

step of the fictitious electron dynamics for adiabatic motion [34] is 1 to 2 orders of magnitude smaller than in simulations involving only ionic dynamics. More recently, another scheme has been proposed to perform *ab initio* MD without the fictitious electron dynamics [35].

The larger time step which can be used in simulations decoupling electronic and ionic dynamics essentially compensates for the number of operations necessary to achieve self-consistency at each time step. For the Si_6 and Si_6^+ simulations a total of about 80 matrix-vector multiplications were performed at each LMD time step for the diagonalization and self-consistency. Our time step is about 60 times larger than in the simulated annealing [8] for Si clusters using the Car-Parrinello method, in which a single matrix-vector multiplication is performed at each step. The computational burden for one LMD time period, as measured by the number of matrix-vector multiplications, is thus comparable in the two simulations. For systems with a vanishing gap the original Car-Parrinello method [6] cannot be applied straightforwardly. The time step has to be reduced and additional minimization of the electronic parameters has to be performed to remain close to the Born-Oppenheimer surface.

We would like to stress that the Langevin quantum molecular dynamics presented here can also be used to perform finite-temperature simulations and evaluate properties as a function of temperature. For instance, LMD is an ideal tool to study the properties of clusters in the buffer gas in which they are usually grown in practice, since the random and friction forces can simulate collision and dissipative effects with the gas molecules. The method can also be used in the simulation of surfaces, or deposition of atoms on surfaces. A temperature gradient perpendicular to the surface can be easily introduced by means of the Langevin forces. With this approach one can take into account the effect of the energy exchange between the adatoms or surface atoms and the bulk material in an approximate, but realistic way.

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TABLE I. LDA bond lengths (in Å) and angles for Si_2^- - Si_5^- . The bonds are labeled according to Fig. 1. The results of the Hartree-Fock (HF) calculations [15] are also given.

	Bond (angle)	LDA	HF
$\text{Si}_2^- (\Pi_u)$	$d_{1,2}$	2.15	2.20
$\text{Si}_3^- (B_2)$	$d_{1,2}$	2.29	2.32
	θ_{2-1-3}	59°	57°
Si_4^-	$d_{1,2}$	2.31	2.32
	$d_{1,3}$	2.35	2.37
Si_5^-	$d_{1,2}$	2.32	2.34
	$d_{2,3}$	2.70	2.75

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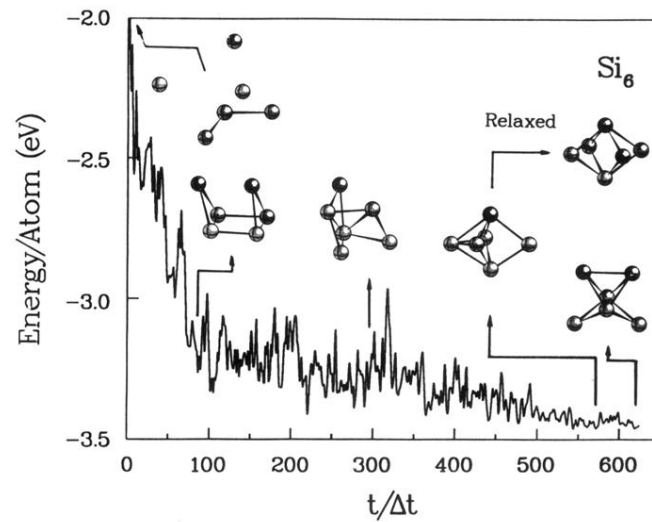


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