

***Ab Initio* Molecular Dynamics with a Classical Pressure Reservoir: Simulation of Pressure-Induced Amorphization in a Si₃₅H₃₆ Cluster**

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We present a new constant-pressure *ab initio* molecular dynamics method suitable for studying, e.g., pressure-induced structural transformations in finite nonperiodic systems such as clusters. We immerse an *ab initio* treated cluster into a model classical liquid, described by a soft-sphere potential, which acts as a pressure reservoir. The pressure is varied by tuning the parameter of the liquid potential. We apply the method to a Si₃₅H₃₆ cluster, which undergoes a pressure-induced amorphization at ~35 GPa, and remains in a disordered state even upon pressure release.

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Very recently pressure has been used as a valuable tool for the investigation of molecular, low-dimensional, and biological systems [1,2]. In particular, the study of clusters and nanocrystals in solution under applied pressure has revealed a wealth of interesting new phenomena that sheds light on important issues such as crystal structure transformation and nucleation phenomena in systems such as CdSe, CdS, and Si [3]. Here, computer simulations could substantially complement the experimental information, allowing, in principle, the observation of the full transition path from one structure to another, which is not directly accessible in an experiment. Many of the transformations studied involve a rearrangement of the electronic structure. A realistic description of these phenomena requires the use of *ab initio* molecular dynamics. However, the complete simulation of the cluster plus the pressure-transmitting liquid is beyond the limit of what can presently be handled. For this reason it is important to develop new computational tools that can allow these important classes of phenomena to be studied in a realistic way. Constant-pressure *ab initio* molecular dynamics for periodic systems has already been developed and has proved its usefulness in a large variety of cases, leading to the prediction and discovery of new phenomena [4–6]. The aim of this paper is to extend this approach to finite nonperiodic systems of arbitrary shape. While we shall focus mostly on the application to clusters, the method is fairly general and can find widespread applications. We shall demonstrate its usefulness with an application to a small cluster of silicon Si₃₅H₃₆. We find here that pressure can induce a nonmetal metal transformation accompanied by a massive structural change. The transformation is irreversible and when the pressure is released a structure

different from the initial one is created, thus offering a way to generate new cluster structures.

Since the main role of the liquid in the above experiments is to transmit the hydrostatic pressure, it is actually not necessary to model specific properties of a real liquid in the simulation. It is known that basic properties of a real simple liquid are captured by a classical short-range repulsive pair potential [7]. Thus, for the liquid to act as a pressure reservoir in the simulation, even such a simplified and computationally cheap description can be expected to be sufficient, provided the potential parameters as well as the liquid density are appropriately chosen. We now show how to couple such classical liquid with a quantum mechanical treatment of the system of interest (cluster) within the Car-Parrinello molecular dynamics method (CPMD) [5].

In order to have a well-defined isotropic constant pressure on the cluster, the number of particles N_L and the volume Ω_L of the liquid should be much larger than that of the cluster. At the same time, however, it is desirable to minimize the number of plane waves used as the basis set in the *ab initio* calculation, limiting them to the region of space where the wave functions of the cluster are significant. To meet both requirements, we used a smaller “quantum” simulation box without periodic boundary conditions [8] for the *ab initio* treatment of the cluster, and a larger “classical” box, containing the quantum box, with periodic boundary conditions applied for the liquid. We chose the liquid-liquid and cluster-liquid interactions as pairwise additive potentials, $V_{L-L}(r)$ and $V_{C-L}(r)$, respectively. Adding both interactions as well as the kinetic energy of the liquid particles to the Car-Parrinello Lagrangian [5], we obtain a new Lagrangian for the extended system, consisting of electrons and ions of the cluster and the liquid particles,

$$L = \frac{1}{2} \sum_i \mu \int d\mathbf{r} |\dot{\psi}_i(\mathbf{r})|^2 + \frac{1}{2} \sum_I M_I \dot{\mathbf{R}}_I^2 - E[\{\psi_i\}, \{\mathbf{R}_I\}] + \sum_{i,j} \Lambda_{ij} (\langle \psi_i | \psi_j \rangle - \delta_{ij}) + \frac{1}{2} \sum_I m \dot{\mathbf{X}}_I^2 - \sum_{I,J} V_{C-L}(|\mathbf{R}_I - \mathbf{X}_J|) - \sum_{I<J} V_{L-L}(|\mathbf{X}_I - \mathbf{X}_J|). \quad (1)$$

Here, \mathbf{X}_I and m are the coordinates and masses of the liquid particles, \mathbf{R}_I and M_I are those of the cluster atoms, and ψ_i and μ are the electronic wave functions and the associated electronic fictitious mass. From this Lagrangian, equations of motion corresponding to the coupled Car-Parrinello/classical MD can be derived.

Since the pressure might induce a macroscopic shape change in the cluster, the liquid should be able to flow fast enough to accommodate such a change, without developing appreciable pressure gradients or shear components which might hinder the transformation. Under high enough pressure, however, any liquid would crystallize, or, in the short time scale of the simulation, undergo a glass transition, marked by a dramatic slowing down of the liquid dynamics. To avoid this, we have to choose the potential $V_{L-L}(r)$ in such a way that our region of interest stays sufficiently far away from the freezing point of the liquid. Since an attractive component in the potential would favor freezing, we chose the purely repulsive soft-sphere potential $V_{L-L}(r) = \epsilon(\frac{\sigma_{L-L}}{r})^{12}$. We set $\epsilon = 1$ a.u.; the potential is then fully specified by the single parameter σ_{L-L} . The corresponding equation of state has the form

$$p = \frac{N_L k_B T}{\Omega_L} \xi(x), \quad (2)$$

where p is pressure, T is temperature, and

$$x = \frac{N_L \sigma_{L-L}^3}{\sqrt{2} \Omega_L} \left(\frac{\epsilon}{k_B T} \right)^{1/4} \quad (3)$$

is the reduced density; the function $\xi(x)$ is known from simulations [9]. The liquid crystallizes at $x = x_c \sim 0.8$, where $\xi(x_c) \sim 20$ [9]. For a given p and T , once the density, $n_L = N_L/\Omega_L$ is chosen, σ_{L-L} is uniquely determined. This parameter can thus be conveniently used to tune the pressure in the system, keeping N_L and Ω_L constant, with no need to change the size of the classical box when changing the pressure. There are two essentially different routes to achieve a high pressure p . The first is to work in the dilute regime (nearly ideal gas), where $x \rightarrow 0$ and $\xi \rightarrow 1$; the repulsion between the liquid particles is very low and a high value of p is achieved due to a high density n_L , or high number of particles N_L . The other extreme possibility is to use a liquid close to its crystallization point $x \rightarrow x_c$, and reach a given pressure with the lowest possible n_L due to a strong repulsion (dense liquid regime). Here $\xi(x_c) \sim 20$, so the same pressure could be reached with N_L reduced by a factor of 20; however, the danger is that the dynamics of the liquid close to its freezing point might already be too slow. A suitable compromise between the extremes has therefore to be found.

We now demonstrate in detail the application of the method to an example of a silicon cluster $\text{Si}_{35}\text{H}_{36}$, and provide some guidelines for the design of the liquid. The initial structure of the cluster is derived from the diamond structure of bulk Si and consists of an atom surrounded by four shells of atoms; the dangling bonds at the surface are saturated with hydrogen atoms. The cluster has

an octahedral shape with a diameter of 12.5 Å, and is relatively small. Even small clusters, however, can undergo a well-defined structural transformation under pressure, as shown experimentally for a $\text{Cd}_{32}\text{S}_{14}(\text{SC}_6\text{H}_5)_{36} \cdot \text{DMF}_4$ cluster [10]. We used a cubic quantum box of size 18.5 Å and a cubic classical box of size 36.5 Å. For the density functional theory calculations, we used norm-conserving pseudopotentials, a plane-wave basis set, a kinetic energy cutoff of 15 Ry, and the local density approximation.

Since bulk Si undergoes a transition from diamond to β tin at 11 GPa, in a small Si cluster we may expect to need a considerably larger pressure to observe fast structural changes. A suitable pressure-transmitting liquid should therefore withstand at least a pressure $p \sim 50$ GPa at temperatures $T \sim 600$ K, at which we choose to work. To reach $p \sim 50$ GPa at $T \sim 600$ K and $\Omega_L = (36.5 \text{ Å})^3$ in a nearly ideal gas regime, one would need $N_L \sim 3 \times 10^5$, which is too large for the method to be practical. We compromised between the two extreme choices of N_L , requiring $\xi(x) \sim 10$ at $p \sim 50$ GPa (i.e., the liquid would crystallize at $p \sim 100$ GPa). This results in $N_L \sim 30\,000$, still a reasonable number for particles interacting via a simple classical potential. In the actual simulation, we used $N_L = 31^3 = 29\,791$; at 600 K we can reach $p = 50$ GPa for $\sigma_{L-L} = 0.66$ Å. Under these conditions, the soft-sphere liquid is still well diffusive, as checked by monitoring the mean-square displacements of the liquid particles during a test MD run.

In the experiments [3], the surfaces of the nanocrystals were either covered by organic surfactants (CdSe and CdS) or passivated with an oxide layer (Si). These, apart from saturating the dangling bonds at the surface and making the clusters soluble in the liquid, also protect the clusters from possible penetration of liquid particles inside. In principle, it is possible to include a surfactant in the simulation, either at a classical or at an *ab initio* level. Here we used the simplest possible arrangement, where the dangling bonds were saturated with hydrogen atoms. These are not allowed to interact with the liquid and simply follow the Si atoms to which they are bonded; only the Si atoms interact with the liquid. Also for the cluster-liquid interaction we chose a purely repulsive soft-sphere potential $V_{C-L}(r) = \epsilon(\frac{\sigma_{C-L}}{r})^{12}$ with a suitable parameter σ_{C-L} . This must be sufficiently large to prevent the penetration of liquid particles inside the cluster up to the highest pressure used. At the same time, however, σ_{C-L} determines the interface tension between cluster and liquid. Therefore σ_{C-L} should not be too large, since the interface tension energy should not become dominant. In our example, we chose $\sigma_{C-L} = 1.75$ Å, which has proved sufficient to prevent the penetration of the liquid into the cluster for pressures up to $p = 50$ GPa.

The last liquid parameter to fix is the mass m , which was set to 20 u, a value low enough not to slow down the liquid excessively, but large enough to allow a reasonable MD time step. We used a fictitious electron mass $\mu = 400$ a.u., a time step $\Delta t = 0.121$ fs, and the atomic mass

of deuterium for hydrogen atoms. A cutoff of 3σ was used for both classical potentials and no long-range corrections were applied.

To prepare an initial configuration, we first equilibrated the liquid at $T \sim 600$ K and $p \sim 10$ GPa. We also equilibrated the cluster in vacuum at the same temperature by standard CPMD. The cluster was immersed into the liquid, and those liquid particles which were closer than 2.5 \AA to any Si atom were removed. The liquid was then equilibrated for a further 1.2 ps while the cluster was kept frozen; the liquid could thus approach the cluster and fill the empty layer around it. Starting from this initial configuration, we quickly increased the pressure by running the combined Car-Parrinello/classical MD for 0.24 ps at 10 GPa, 0.24 ps at 15 GPa, and 1.48 ps at 25 GPa. In all runs described in this paper, the temperature of both liquid and cluster was close to 600 K. Whenever the pressure was changed, we again froze the cluster, changed the interaction parameter σ_{L-L} , and reequilibrated the liquid for 1.2 ps, and also re-optimized the electronic wave functions. This time turned out to be sufficient to produce a liquid with equilibrated temperature and pressure. At 25 GPa, the cluster structure exhibited some thermal and pressure-induced fluctuations, but the tetrahedral coordination was preserved [Fig. 1(a)].

We then increased the pressure to 35 GPa and ran the simulation for 3.37 ps. During this time, the cluster quickly underwent a transformation to a disordered structure, changing shape from an octahedron to a roughly spherical object, where tetrahedral coordination was no longer dominant and amorphous features appeared [Fig. 1(b)]. An analysis of the time evolution of the Kohn-Sham energy gap of the cluster shows that the transition starts about 0.3 ps after the pressure increase to 35 GPa, and proceeds very fast, with the gap decreasing from 1.9 to 0.6 eV in 0.12 ps. In order to see what happens with the high-pressure structure upon release of pressure, we performed the latter in three steps, simulating the system further for 2.35 ps at 25 GPa, 4.17 ps at 15 GPa, and 2.73 ps at 5 GPa. The cluster locally relaxed and appeared to be again predominantly tetrahedrally coordinated, but

did not recover its original global structure. Instead, a new form, clearly elongated along one direction and containing empty space inside, appeared [Fig. 1(c)]. The Kohn-Sham gap also gradually increased, but recovered only half of its original low-pressure value.

In order to obtain some insight into the bonding properties of the cluster at different pressures, we used the maximally localized Wannier function method [11] which for a finite system is actually equivalent to the application of Boys' criterion [12]. In an ideal diamond structure, the Wannier function centers (WFC), which represent points where the electronic charge is maximally concentrated, are localized in the middle of the Si-Si bonds. When the structure deviates from the ideal (e.g., in amorphous Si [13]) and from perfect covalency, the WFC move away from their central positions, providing an indication of the disorder and of the presence of defects [see Figs. 1(a)–1(c)]. To characterize quantitatively the local bonding in the final configurations at 25, 35, and 5 GPa, we show in Fig. 2 the distribution of WFC–Si atom–WFC “bond angles” Θ for centers closer to a Si atom than 1.75 \AA (position of the first minimum in the pair-correlation function $g_{\text{Si-WFC}}$). While at 25 GPa the distribution is clearly centered at the tetrahedral angle, at 35 GPa it becomes considerably broader, with structures at lower angles. Upon the release of pressure to 5 GPa, the distribution becomes narrower again and resembles that at 25 GPa, reflecting the almost complete recovery of local tetrahedral coordination. In the inset of Fig. 2, we plot for the final configurations at 25, 35, and 5 GPa the histogram of the spread $\sigma_n = \sqrt{\langle r^2 \rangle_n - \langle \vec{r} \rangle_n^2}$ of Wannier functions in real space, which provides a measure of the degree of localization of the electronic charge. The left and right peaks correspond to Si-H and Si-Si bonds, respectively. By comparing the position of the Si-Si bond peak in the low- and high-pressure structures, we observe a substantial increase of electronic delocalization in the latter. This, together with the band gap reduction, suggests that the high-pressure structural transition in the cluster is accompanied by a profound change in its electronic properties. Analogies

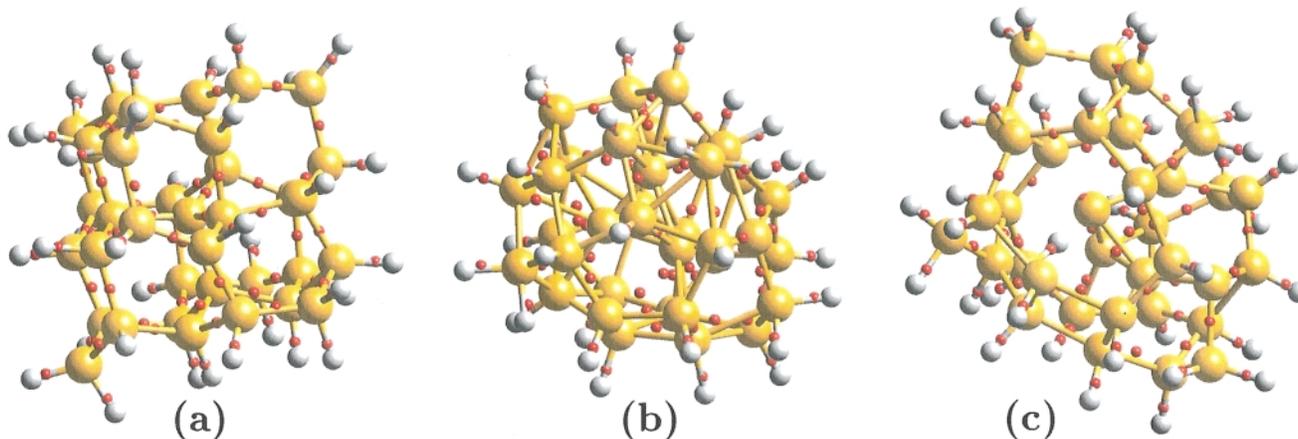


FIG. 1 (color). Final configurations of the cluster at 25 GPa (a), 35 GPa (b), and 5 GPa (c). The red balls represent the centers of Wannier functions. To allow a comparison of size and shape, all three figures have the same scale and orientation.

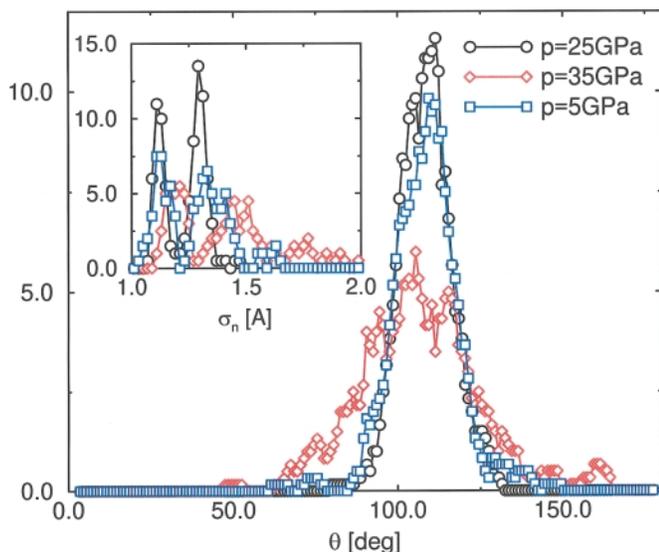


FIG. 2 (color). Distribution of the WFC-Si atom-WFC “bond angle” Θ in the final configurations at 25, 35, and 5 GPa. Inset: histogram of the spread σ_n of Wannier functions in the final configurations at 25, 35, and 5 GPa. All curves have been smoothed.

can be found with the metallization occurring in bulk Si upon transition from diamond to β -tin structure.

We are not aware of any high-pressure experiments on small Si clusters of a size comparable to the one we studied here that we could use for direct comparison. Si nanocrystals studied in Ref. [3] were several hundred Å large in diameter and exhibited a transition from a diamond to a simple hexagonal structure at $p \sim 22$ GPa. We believe that the transition to a disordered state in the simulation is likely to be associated with the small size of the system; to see a transition to an ordered crystalline structure, the cluster would probably have to be larger. Si nanocrystals are of obvious intrinsic basic and technological importance and it is likely that, in the future, progress in experimental techniques will allow the creation of very small clusters, of a size similar to those studied here. Also the short time scale accessible to the simulation poses a limitation. In first-order transitions, a crossing of a barrier is usually involved and therefore the associated time scale might be very long. While by sufficient overheating and overpressurizing of the clusters it should be possible to observe the relevant structural changes on a fast time scale and obtain qualitative information, the possibility of quantitative comparison to experiment is limited. An alternative might be the use of specific techniques designed for accelerating the crossing of high barriers [14,15].

In conclusion, we have shown how to set up an *ab initio* molecular dynamics with a classical pressure reservoir suitable for constant-pressure simulations of finite nonperiodic objects, and demonstrated its applicability to the study of pressure-induced structural phase transformations in clusters. The idea itself is quite general: depending on the desired accuracy, the finite system can be described

with various techniques, from quantum-mechanical methods, e.g., density functional theory or tight binding [16], to classical force fields. The method can also be applied to studies of general molecular systems under pressure, including systems of chemical and biochemical relevance. Applications to systems more realistic than $\text{Si}_{35}\text{H}_{36}$ cluster are presently underway.

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