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Predicting Crystal Structures: The Parrinello-Rahman Method Revisited

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By suitably adapting a recent approach [A. Laio and M. Parrinello, Proc. Natl. Acad. Sci. U.S.A. **99**, 12 562 (2002)] we develop a powerful molecular dynamics method for the study of pressure-induced structural transformations. We use the edges of the simulation cell as collective variables and define a metadynamics that drives the system away from the local minimum towards a new crystal structure. In contrast to the Parrinello-Rahman method, our approach shows no hysteresis, and crystal structure transformations can occur at the equilibrium pressure. We illustrate the power of the method by studying the pressure-induced diamond to simple hexagonal phase transition in a model of silicon.

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Predicting equilibrium crystal structures at a given pressure and temperature is an important problem in fields of science as different as solid-state physics, geophysics, planetary physics, materials science, polymer science, chemistry, etc. Upon increasing external pressure crystals usually undergo structural phase transitions. Often, the final structure is unknown and simulations can be very useful in identifying possible candidates. This task represents a challenge for computational physics. Great progress was achieved with the introduction of constant-pressure molecular dynamics (MD) [1] and, in particular, the Parrinello-Rahman method [2] where the box is allowed to change its shape in order to comply with a new structure. The Parrinello-Rahman method is now described in textbooks and widely used also in different variants [3–10]. However, structural transitions are often first order. Since for crystal simulations periodic boundary conditions are commonly used, heterogeneous nucleation is suppressed and the system has to cross a significant barrier in order to transform from one structure to another. As a consequence, large hysteretic effects are observed within the above approaches. In order to observe the transition within the accessible simulation time [11] one often has to overpressurize the system close to the point of mechanical instability. Under such conditions one or more intermediate phases may be skipped [10,12], which reduces the predictive power of the method.

In the work of Parrinello and Rahman [2] it was realized that in an MD simulation of a crystal phase transition it is necessary to treat the MD supercell edges $\vec{a}, \vec{b}, \vec{c}$ as dynamical variables. These variables were arranged to form a matrix $\mathbf{h} = (\vec{a}, \vec{b}, \vec{c})$, and extending the work of Andersen [1] a Lagrangian was introduced that coupled the $\mathbf{h}$ degrees of freedom with the microscopic motion of the atoms under the condition of constant pressure. Because of the time-scale problem mentioned earlier, this approach tends to be ineffective at pressures close to the critical transition pressure. As the origin of the problem is the lack of efficiency of standard molecular dynamics in crossing high barriers, we adopt here a conceptually different strategy. Since our aim is to simulate a phase transition at a pressure P and a temperature T we consider the Gibbs potential $\mathcal{G}(\mathbf{h}) = \mathcal{F}(\mathbf{h}) + PV$ as a function of $\mathbf{h}$ where $\mathcal{F}(\mathbf{h})$ is the Helmholtz free energy of the system at fixed box and $V = \det(\mathbf{h})$ is the volume of the box. We assume, following Nosé and Klein [3], that the matrix $\mathbf{h}$ is symmetric in order to eliminate rotations of the supercell. This reduces the number of collective variables to 6. These 6 independent components of $\mathbf{h}$ now represent collective coordinates, or order parameters, which distinguish the different minima of $\mathcal{G}$. We note that the derivative

$$-\frac{\partial \mathcal{G}}{\partial h_{ij}} = V\{[(\mathbf{p} - P)\mathbf{h}^{-1}]_{ij} + [(\mathbf{p} - P)\mathbf{h}^{-1}]_{ji}\}\left(1 - \frac{1}{2}\delta_{ij}\right), \tag{1}$$

where $\mathbf{p}$ is the internal pressure tensor, can easily be evaluated from microscopic MD or Monte Carlo runs at constant $\mathbf{h}$ by averaging the microscopic virial tensor. Making use of Eq. (1) we now construct an algorithm, based on the recently introduced method of Ref. [13], that is able to explore the surface $\mathcal{G}(\mathbf{h})$ efficiently and, in particular, can identify the local minima which correspond to stable or metastable crystal structures at a given pressure P. The method [13] has been shown to be able to dramatically speed up the simulation of activated processes and is therefore well suited for simulating first-order phase transitions. We describe here the basic ideas and refer to the original paper for more details.

Following Ref. [13], the collective variables that are now arranged to form a six-dimensional vector $\mathbf{h} = (h_{11}, h_{22}, h_{33}, h_{12}, h_{13}, h_{23})$ are evolved according to a steepest-descent-like discrete evolution with a stepping parameter δh (*metadynamics*),

$$\mathbf{h}^{t+1} = \mathbf{h}^t + \delta h \frac{\phi^t}{|\phi^t|}. \tag{2}$$

Here the driving force $\phi^t = -\frac{\partial \mathcal{G}^t}{\partial \mathbf{h}}$ is derived from a history-dependent Gibbs potential $\mathcal{G}^t$ where a Gaussian has been added to $\mathcal{G}(\mathbf{h})$ at every point $\mathbf{h}^{t'}$ already visited in order to discourage it from being visited again. Hence we have

$$\mathcal{G}^t(\mathbf{h}) = \mathcal{G}(\mathbf{h}) + \sum_{t'<t} W e^{-|\mathbf{h}-\mathbf{h}^{t'}|^2/2\delta h^2}, \tag{3}$$

and the force ϕ^t is therefore a sum of a thermodynamical driving force $\mathbf{F} = -\frac{\partial \mathcal{G}}{\partial \mathbf{h}}$ and the term $\mathbf{F}_g$ coming from a potential constructed as a superposition of Gaussians. As time proceeds, the history-dependent term in Eq. (3) fills the initial well of the free-energy surface and the system is driven along the lowest free-energy pathway out of the local minimum. The passage through the transition state can be detected by monitoring the relative orientation of the forces $\mathbf{F}$ and $\mathbf{F}_g$. While a well is being filled, these two forces approximately balance each other, $\mathbf{F} + \mathbf{F}_g \approx 0$, and the two vectors have roughly opposite directions. After crossing the saddle point this is no longer true, and $\mathbf{F}$ and $\mathbf{F}_g$ become almost parallel and oriented along the eigenvector corresponding to the negative eigenvalue of the Hessian matrix. The indicator $\mathbf{F} \cdot \mathbf{F}_g/(|\mathbf{F}||\mathbf{F}_g|)$ develops a sharp spike which can be used to signal the transition from one basin to the other.

The choice of the parameters W and δh depends on the $\mathcal{G}(\mathbf{h})$ landscape. In order to achieve the necessary energy resolution, W should be chosen as a fraction of the relevant energy barriers. The parameter δh, on the other hand, determines the resolution in $\mathbf{h}$. However, a very small value of δh is not to be recommended. In fact, a small δh requires longer runs. Furthermore, for an optimal filling the curvature of the Gaussians should be smaller than that of the well. This leads to the condition $\frac{W}{\delta h^2} \leq K$ where K is the smallest eigenvalue of the $\mathcal{G}(\mathbf{h})$ Hessian at the minimum $\mathbf{h}_0$. For a cubic system we can estimate K from the approximate expansion of $\mathcal{G}(\mathbf{h})$ around $\mathbf{h}_0$,

$$\mathcal{G}(\Delta\mathbf{h}) \approx \mathcal{G}(\mathbf{h}_0) + \frac{1}{2} V c \left(\frac{\Delta \mathbf{h}}{L}\right)^2, \tag{4}$$

where L is the cell edge and c is of the order of magnitude of the elastic constants. This leads to the estimate $K \approx Lc$ and to the condition $\frac{W}{\delta h^2} \lesssim Lc$. A more general discussion of the choice of W and δh can be found in Ref. [13].

In practice the metadynamics simulation proceeds as follows. We start from an equilibrated value of $\mathbf{h}$ at a given pressure P and temperature T and evaluate the pressure tensor $\mathbf{p}$ in a constant $\mathbf{h}$ MD run long enough to allow relaxation to equilibrium and sufficient averaging of $\mathbf{p}$. The $\mathbf{h}$ is updated using the forces (1) and metadynamics Eqs. (2) and (3) to a new value $\mathbf{h}'$. After the box is modified, the particle positions are rescaled in order to fit into the new box using the relation $\vec{r}' = \mathbf{h}'\mathbf{h}^{-1}\vec{r}$. As the initial free-energy well is gradually filled, the box undergoes a set of deformations until a transition state is reached and the system enters into the basin of attraction of a new state. In order to characterize the new phase it is often useful at this stage to switch off the Gaussian term, so that the metadynamics becomes purely steepest-descent-like and drives the system towards the equilibrium state for the new structure. In this equilibrium state the pressure will be equal to P. However, during the metadynamics the pressure tensor can become anisotropic and the internal pressure may be different from P. Once the new structure is characterized, one can switch the Gaussians on again, thus filling the new minimum, and move to other minima, if available. The metadynamics is capable of reconstructing the free-energy profile [13], since the sum of the Gaussians in Eq. (3) converges to $-\mathcal{G}(\mathbf{h})$ up to an additive constant, if W and δh are properly chosen. This will not be used here since once the structures are known it is relatively straightforward to calculate their free energy [14]. We emphasize, however, that free-energy calculations alone do not provide an alternative to our method since they assume knowledge of the final crystal structure.

We have tested our method on several model Hamiltonians. Here we report only a simulation of a tight-binding model of Si [15] at a pressure very close to the theoretical transition pressure. This tight-binding parametrization captures some of the main features of the Si phase diagram and provides a convenient test model. In the following we shall use a supercell of 216 atoms and only the Γ point of the Brillouin zone. The $T = 0$ phase diagram for this model system can be found by performing energy versus volume calculations in the three relevant structures, namely, the $P = 0$ equilibrium diamond structure and the two high-pressure phases, β-tin and simple hexagonal (SH). The latter two are almost degenerate in energy, β-tin being only metastable. A common tangent construction gives a critical pressure of 15.5 GPa for the transition from the diamond to the SH phase. Applying the Parrinello-Rahman method to the same model and system size, the transition from diamond to the SH phase is found to occur at 44 GPa [16], which corresponds to an overpressurization of almost a factor of 3. Here we show instead that with our new method the transition can be observed with affordable computational effort at $T = 300$ K and $P = 16$ GPa, i.e., very close to the critical pressure.

A metadynamics simulation was run with the parameters $W = 8.6$ eV and $\delta h = 1$ Å which are compatible with the guidelines given earlier, taking into account that $L \approx 15$ Å and a typical Si elastic constant value is $c \approx 100$ GPa. We have preferred a relatively large value for δh in order to enhance volume fluctuations and thus to favor the change of volume which accompanies the pressure-induced transformation of diamond Si. This choice is also instrumental in avoiding that the system makes a fake transition to the same crystal structure, since such a transition obviously conserves volume. The origin of these fake transformations is to be found in the fact that a given crystal structure can correspond to different values of **h**. This problem, which is a consequence of what is known as modular invariance [6], can be fixed in many different ways. However, in view of the simple solution found here we have not pursued these alternatives, which will be discussed elsewhere.

At each metadynamics step we equilibrated the system for 1 ps and averaged the pressure tensor for another ps; temperature was controlled by Nosé-Hoover chains [17]. The history of the run is shown in Fig. 1. The indicator $\mathbf{F}\cdot\mathbf{F}_g/(|\mathbf{F}||\mathbf{F}_g|)$ [Fig. 1(e)] clearly shows that at metastep 35 there is a phase transition [see also Figs. 1(d) and 2(a)–2(d)]. Consequently, after this step we switched off the Gaussians to let the system evolve towards the new structure in a steepest-descent-like manner till metastep 50 [see Figs. 2(e)–2(h)]. This final structure was then evolved for 5 ps with a Parrinello-Rahman simulation. During this time very little relaxation of the cell parameters took place, which confirms that we have reached a minimum of $\mathcal{G}(\mathbf{h})$. A visual inspection of the final structure [Fig. 2(h)] as well as an analysis of the diffraction peaks showed that the system had made a transition to the SH structure, whose parameters are $a = 2.61$ Å and $c = 2.48$ Å. We also calculated the atomic volume, shown in Fig. 1(c). After step 34 we observe a pronounced drop, agreeing well with the results of the $T = 0$ calculation which predicts a change from 17.5 Å^3 per atom in the diamond to 14.8 Å^3 per atom in the SH phase.

Another run was carried out in which after metastep 35 the Gaussians were kept switched on. This metadynamics led to a series of transitions between the stable SH and metastable β-tin structures with different orientations. We also performed a simulation of decompression of the SH structure at $p = 5$ GPa which after 48 metadynamics steps transformed into a tetrahedrally coordinated amorphous structure. Experimentally Si upon decompression also does not come back from the β-tin to the diamond structure but transforms to a series of metastable structures [18]. These two examples demonstrate that the method is able to find also metastable crystalline and amorphous phases.

This calculation shows that the method overcomes many of the limitations of the previous approaches. It must be stressed that, in contrast to previous work [1–10], it is not a constant-pressure simulation method but rather a method for exploring the dependence of the Gibbs free energy on the **h** variables. The use of the history-dependent metadynamics allows large energy barriers to be overcome in a short time and makes this approach very efficient. If other internal slow degrees of freedom besides the **h** variables are present, as in molecular crystals, these can naturally be added and taken into account within the general scheme [13]. Metadynamics is in principle able to visit any crystalline structure that is at least metastable at a given pressure; however, use of pressures considerably different from the critical one may result in the need for a longer time in order to escape from the initial minimum. In the example presented here the total aggregated simulation time is about 100 ps. This makes the method suitable also for an *ab initio* MD simulation of systems containing about 100 atoms. Another advantage is that *ab initio* constant-volume

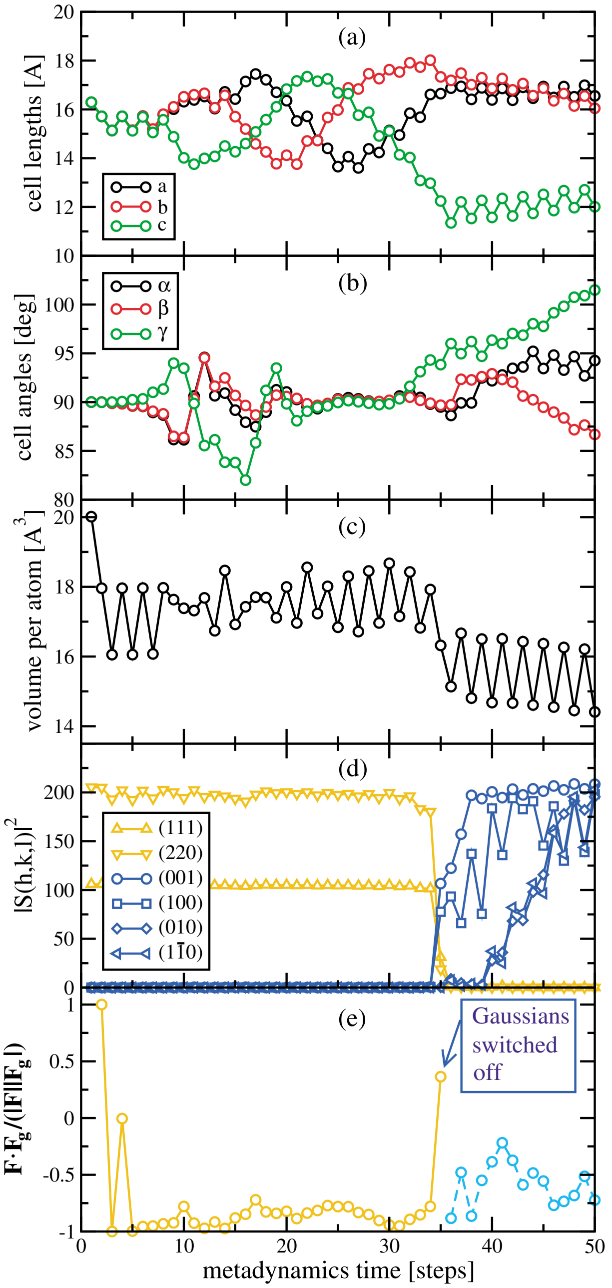

FIG. 1 (color). Evolution of cell lengths (a), cell angles (b), atomic volume (c), selected peaks of the diamond (averaged over all equivalent directions, orange) and SH (blue) structure factor (d), and relative orientation of forces **F** and $\mathbf{F}_g$ (e) during the metadynamics. Note the structural transition at step 35. The Gaussian term in Eq. (3) is switched off after step 35. The light blue curve in (e) shows the continuation of the orange run in the mode in which the Gaussians are added at every metadynamics step.

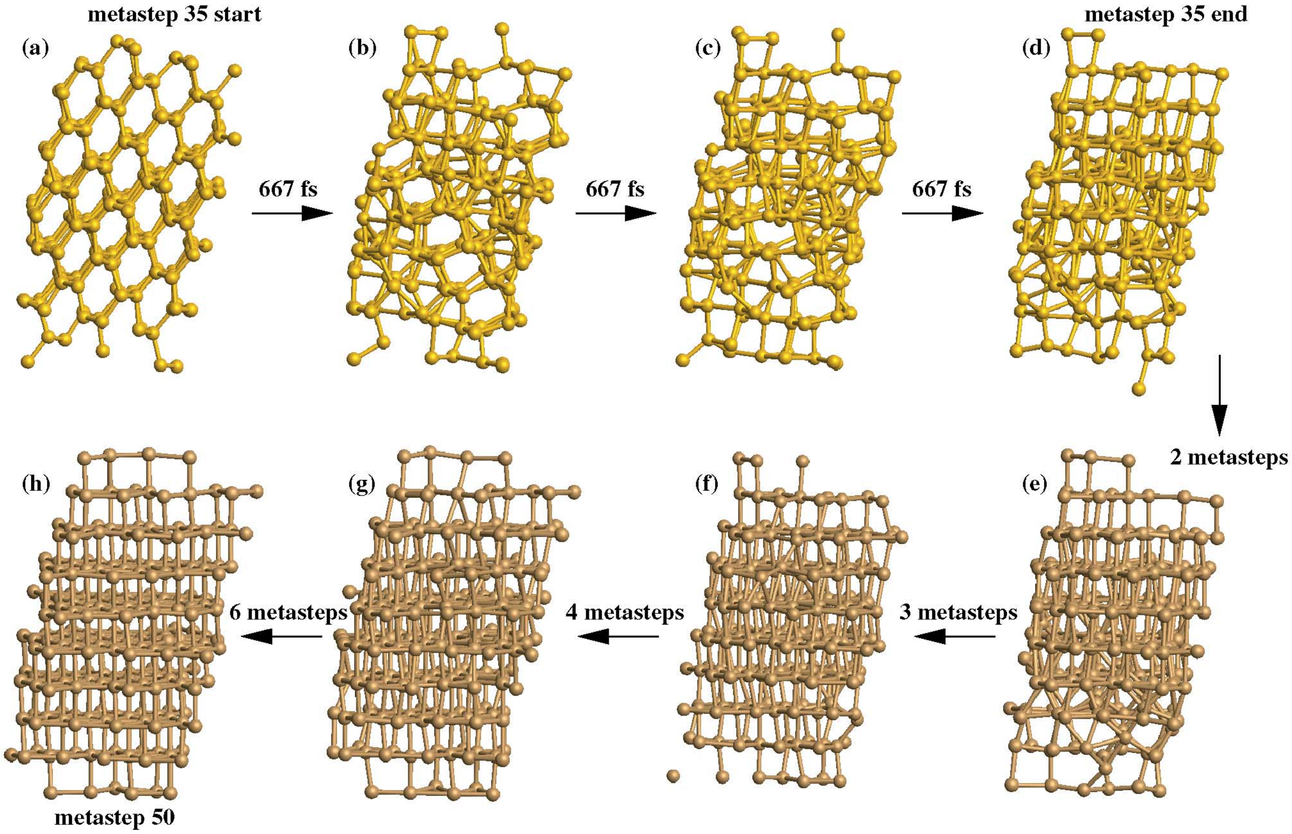

FIG. 2 (color). (a)–(d) Evolution of atomic configurations during 2 ps of microscopic dynamics (at intervals of 667 fs) across the transition at metastep 35. The initial diamond structure (a) is strongly strained, compressed along one axis, and elongated along perpendicular ones [see also Fig. 1(a)]. In the next two snapshots (b),(c) the gradual disappearance of the diamond structure can be observed; at the same time, a new periodic structure emerges (d). (e)–(h) Evolution during 15 subsequent steps of metadynamics. Note the gradual formation of the simple hexagonal phase. From the analysis of diffraction peaks the final supercell (h) was found to contain 222 primitive cells; therefore 6 vacancies are actually present in the structure.

codes can be used, avoiding the need to use expensive tricks to deal with the Pulay correction [12]. In conclusion, it can be confidently stated that this new method, with its ability to induce structural transitions at equilibrium conditions, can substantially improve the predictive power of solid-state simulations.

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