

# Nucleation and crystallization process of silicon using the Stillinger-Weber potential

Philippe Beaucage and Normand Mousseau\*

*Département de Physique and Regroupement Québécois sur les Matériaux de Pointe, Université de Montréal, Case Postale 6128, succ. Centre-ville, Montréal, Québec, Canada H3C 3J7*

(Received 6 October 2004; published 4 March 2005)

We study the homogeneous nucleation process in Stillinger-Weber silicon in the canonical ensemble. A clear first-order transition from the liquid to crystal phase is observed thermodynamically with kinetic and structural evidence of the transformation. At  $0.75T_m$ , the critical cluster size is about 175 atoms. The lifetime distribution of clusters as a function of the maximum size they reach follows an inverse Gaussian distribution as was predicted recently from the classical theory of nucleation (CNT). However, while there is a qualitative agreement with the CNT, the free-energy curve obtained from the simulations differs significantly from the theoretical predictions, suggesting that the low-density liquid phase found recently could play a role at the interface between the crystallite and the surrounding liquid during the nucleation process.

DOI: 10.1103/PhysRevB.71.094102

PACS number(s): 64.70.Dv, 64.60.Qb, 82.60.Nh

## I. INTRODUCTION

The classical nucleation theory (CNT) has been extensively tested in systems with relatively simple two-body interactions such as colloids or globular proteins.<sup>1–4</sup> These molecules are large and move slowly, making it possible to follow the crystallization process experimentally using various techniques of microscopy. Moreover, these systems can also be represented accurately by theoretical models of hard and soft spheres, which can crystallize on numerical time scales. It is therefore possible to characterize fully the microscopic mechanisms responsible for nucleation in terms of the CNT, which works particular well for these systems.

There has also been a number of studies going beyond the soft-sphere models. In particular, there has been considerable work devoted to the nucleation of Lennard-Jones models.<sup>5–9</sup> Very little work has been done, however, on more complex materials such as oriented liquids—water or tetrahedral semiconductors, for example. Recently, Matsumoto *et al.*,<sup>10</sup> using considerable computing power, managed to follow one occurrence of crystallization in a 300 ns run of a 512-molecule simulation of water in the canonical ensemble at 230 K. Clearly more simulations are needed in water but also in simpler oriented liquids such as silicon, which shows a similar phases diagram around melting as both liquids show a temperature of density maximum and their density falls off by  $\sim 10\%$  from the disordered liquid to the tetrahedral crystalline structure. As with water, there have been very few works studying nucleation in this technologically important material.<sup>11</sup>

Depending on the cooling rate, previous numerical work has shown that supercooled liquid silicon transforms in a glassy<sup>12,13</sup> or amorphous<sup>14,15</sup> state. Recently, it was indicated that this transition takes place just below a liquid-liquid transition:<sup>16,17</sup> at zero pressure in the Stillinger-Weber silicon, the low-density liquid (LDL), which is thermodynamically and structurally contiguous to the amorphous solid, crystallizes rapidly (around 10 ns) at 1050 K<sup>16,17</sup> whereas the more common high-density liquid (HDL) does not at any temperature on a simulation time scale. In order to circumvent the difficulty to crystallize *l*-Si, Uttormark and

colleagues<sup>18</sup> embedded a spherical crystal seed containing 400–800 atoms in bulk liquid and analyzed the growth and dissolution of clusters. They found that the critical size for a crystallite to grow to macroscopic size was of 140 and 1400 atoms at 60% and 85% of the melting temperature ( $T_m$ ). Working with a similar method, Bording and Taftø<sup>19</sup> inserted a crystallite in an amorphous matrix of 4096 germanium atoms and estimated the critical cluster radius to be 1 nm (around 185 atoms) at 60%  $T_m$ .

In this paper, we show that liquid silicon can crystallize in the NVT ensemble on a time scale accessible by MD simulation without going through the low-density liquid phase. We also show that the nucleation process, while qualitatively consistent with CNT, differs quantitatively from it.

The organization of the paper is as follows. We show the behavior of the thermodynamic, kinetic, and structural properties during the phase transition in Sec. III A. In Sec. III B 1, we analyze the nucleation and crystallization process through the evolution of the cluster that will eventually crystallize the whole system in relation to CNT. Then, in Sec. III B 2, we compute and compare the free energy of clusters between CNT and the simulation data. Finally, we look at the lifetime of small clusters in the supercooled liquid before nucleation takes place in Sec. III B 3.

## II. METHODS

The molecular dynamical simulations (MD) for this work are performed in the canonical (NVT) ensemble at the 0 K crystalline density, i.e.,  $2.32 \text{ g/cm}^3$ , and in the isothermal-isobaric (NPT) ensemble at zero pressure. All simulations are done at 1250 K (75%  $T_m$ ) in a cubic box containing 10 648 atoms, with periodic-boundary conditions. This size is sufficiently large to avoid catastrophic crystal growth due to interactions between the images of the critical crystallite, which is estimated to be around 200 atoms (see below).

We use the extended-system method of Andersen to control pressure<sup>20–22</sup> and Hoover's constraint method for the temperature.<sup>23–25</sup> Newton's equations of motion are integrated with a fifth-order Gear predictor-corrector and a time

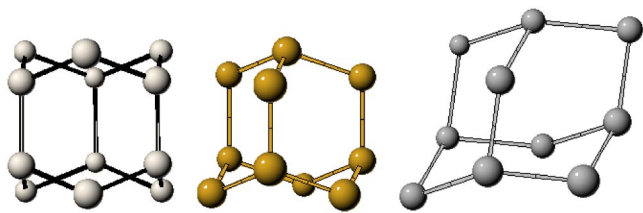


FIG. 1. (Color online) The three basic building blocks associated with the crystalline order parameter. The wurtzite basic block (left) is a 12-atom cluster composed of two sixfold rings whereas the diamond basic block (middle) is a 10-atom cluster with four sixfold rings. The  $\beta$ -tin basic block (right) is equal to a diamond basic block where the tetrahedra are compressed in one direction and elongated along the two other axes.

step  $\Delta t = 1.15$  fs. Simulations are typically equilibrated over 50 000  $\Delta t$  (58 ps) and data are accumulated over  $10^6 \Delta t$  (several ns). Atomic interactions are represented by the Stillinger-Weber potential (SW), developed to reproduce accurately the crystalline and liquid state of Si.<sup>26</sup>

Starting with a liquid well equilibrated at 2900 K, we generate nine independent trajectories in NVT conditions at 2.32 g/cm<sup>3</sup> and 75% of  $T_m$ , a degree of undercooling similar to that used for a wide variety of materials both experimentally<sup>27</sup> and numerically.<sup>6</sup> Of these nine trajectories, six crystallize within 10 ns and are numbered 1 to 6; the fastest, simulation no. 1, crystallizes within 1.5 ns.

Following previous work on liquid Si,<sup>11,17</sup> we use as an order parameter the smallest three-dimensional closed-ring structures that can be associated with a given crystalline lattice. These clusters, shown in Fig. 1, are the smallest elementary building blocks for wurtzite, diamond, and  $\beta$ -tin structures and are defined topologically: the wurtzite lattice is associated with a 12-atom cluster composed of two sixfold rings connected at three points while the diamond and  $\beta$ -tin can be described topologically by a single 10-atom cluster with four sixfold rings back to back. To establish the connectivity of these clusters, the first-neighbor cutoff is set to 2.75 Å, a value similar to that used in these high-quality amorphous networks. This is somewhat shorter than the typically nearest-neighbor distance used in liquids (which is about 3.0 Å) as it focuses on local crystalline order.

These elementary clusters are present with a low density in the liquid ( $\rho_{\text{crystal}} \approx 5\text{--}10$  at. %) as well as in high-quality amorphous models prepared using the modified Wooten-Winer-Weaire bond-switching algorithm ( $\rho_{\text{crystal}} \approx 1\text{--}5$  at. %).<sup>28</sup> These blocks provide, therefore, a much more sensitive measure of crystallinity than the structure factor or the radial distribution function (RDF).

Our criteria are different from those used in a previous study of the nucleation of crystallites implanted into a SW liquid by Uttormark, Thompson, and Clancy.<sup>18</sup> In this case, the description of a crystallite nucleus is defined uniquely based on a mixture of energetic, topological, and geometric constraints. For an atom to be part of a crystallite, (i) its three-body energy in SW potential of fourfold or fivefold coordinated atoms (within a 3.35 Å nearest-neighbor distance) must be lower than 0.4336 eV; (ii) it must possess four nearest neighbors and at least three of them are also

fourfold coordinated; (iii) its angular bond angles meet this criterion:  $\sum_{i=1}^6 (\cos \Theta_i + 1/3)^2 < 0.4$  (where  $\Theta_i$  is the angle between nearest neighbors of a fourfold coordinated atom). The crystallites identified with this method are less compact than those flagged with our topological order parameter. This is particularly true for small crystallites (fewer than 20 atoms), which tend to be open and stringy, like twisted polymers, with Uttormark's criteria. The two methods converge, however, for larger clusters, near and beyond the critical size, where a clear definition of surface is less important.

### III. RESULTS AND DISCUSSION

#### A. Phase transition

Homogeneous nucleation is often difficult to obtain numerically, especially in oriented solids such as Si and water, which display a crystalline structure far from that of the liquid phase. It took months of computer time to simulate homogeneous nucleation in TIP3P water. Studies using SW Si failed to find traces of nucleation in a 5000-atom cell after a 1-ns simulation.<sup>18</sup>

In view of these results, and because classical nucleation theory (CNT)<sup>29,30</sup> predicts that nucleation and crystallization is obtained more rapidly for strong undercooling and larger system size, we choose to simulate a larger cell, with more than  $10^4$  atoms, simulated over 10 ns at  $0.75T_m$ .

As shown in Fig. 2, this is sufficient to observe homogeneous nucleation, from the pure liquid phase, in the NVT ensemble. While the data presented in this figure are for simulation no. 1, a run that crystallizes particularly quickly, the overall properties of the transition are identical to run no. 2 to 6. The top curve shows a brutal drop in the potential energy of the system, from  $-3.75$  to  $-3.95$  eV/at, indicating a clear thermodynamic transition after 1.5 ns of simulation. The phase transition is also visible by following the change in pressure (bottom panel). As the density is maintained at the crystalline value, the pressure in the liquid phase is negative; it changes sign at the liquid-crystal transition since the crystal density at 1250 K and 0 GPa is slightly lower than at 0 K, and since the new structure contains grain boundaries. The liquid to solid phase transition is clearly seen in the kinetics of the system (middle panel): in the supercooled liquid, the diffusion is significant, with  $D = 5.4 \times 10^{-6}$  cm<sup>2</sup>/s; it drops suddenly at the transition to become vanishingly small, a clear indication of a liquid to solid transition.

Under the NVT conditions described in the Introduction, the mean pressure of the supercooled liquid is  $-1.9$  GPa. In a previous work,<sup>17</sup> we studied the transition from high-density liquid (HDL) to low-density liquid (LDL) in Stillinger-Weber Si and showed that this transition does occur at around 1250 K and  $-2$  GPa but moves to lower temperatures as the pressure is increased. The current simulations are therefore slightly above the HDL to LDL transition, and we seem to observe a pure liquid-crystalline transition: the liquid before the transition has a RDF and a diffusion constant characteristic of the HDL and there is no trace of a LDL phase during the crystallization process.

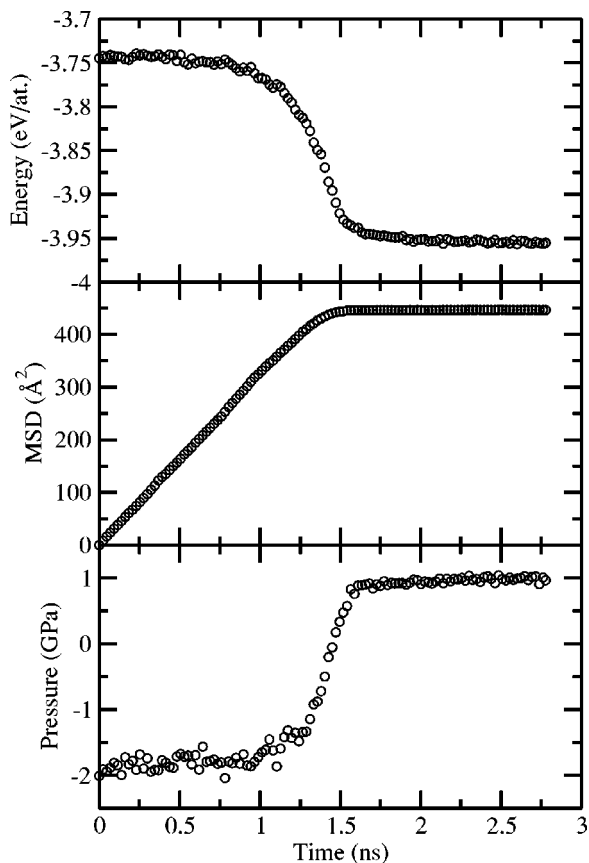


FIG. 2. Evolution of the energy (top), mean-square displacement (middle), and pressure (bottom) during the liquid-crystal phase transition of Si with NVT conditions at 1250 K and 2.32 g/cm<sup>3</sup>. These results are for simulation no. 1, which crystallizes the fastest. While the other simulations take longer to crystallize, their evolution is similar.

Changes in the structural properties of this model as the transition occurs are shown in the next two figures. At  $t=0$  ns, the RDF (see Fig. 3) is typical of that of a liquid, with little structure beyond the broad second-neighbor peak. The nature of the RDF is totally different after the transition, with well-defined crystalline peaks up to 9 Å and beyond. In the liquid phase, the system contains very few crystalline building blocks and  $\rho_{\text{crystal}}$  fluctuates between 5% and 10% of all the atoms (see Fig. 4, top panel). After the transition, more than 85% of the atoms belong to diamond and/or wurtzite crystalline blocks, with a probability higher for diamond structures except in trajectory no. 1.

The coexistence of two crystalline structures is not surprising since, with a cutoff of 3.77 Å, the SW potential cannot differentiate between the diamond and wurtzite structures at zero temperature: these two structures start to differ only at their third-neighbor shell, at 4.50 and 3.91 Å, respectively. It is therefore only the thermal vibrations, bringing the third-neighbor shell atoms inside the cutoff from time to time, that allow the potential to distinguish between these two crystalline structures. With long enough annealing, we expect the wurtzite structures to disappear completely.

For its part, the liquid phase is characterized by a low density of crystalline building blocks. Moreover, these crys-

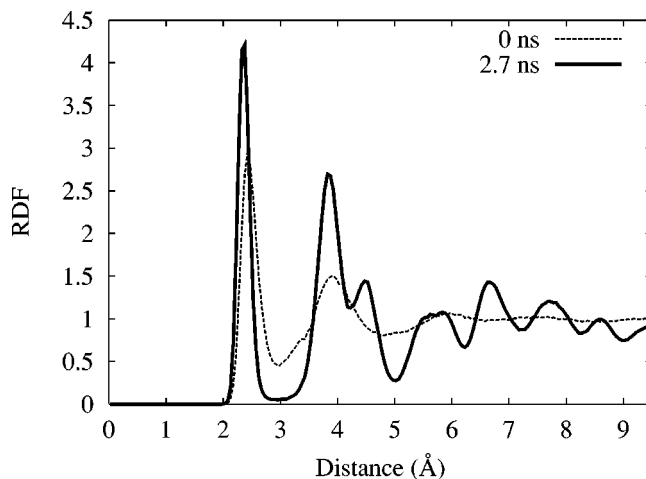


FIG. 3. Radial distribution function before and after the liquid-crystal phase transition of Si in NVT conditions at 1250 K and 2.32 g/cm<sup>3</sup>. The RDF is characteristic of a crystalline state after the transition (2.7 ns) and of a liquid before the transition (0 ns). These results are taken from simulation no. 1.

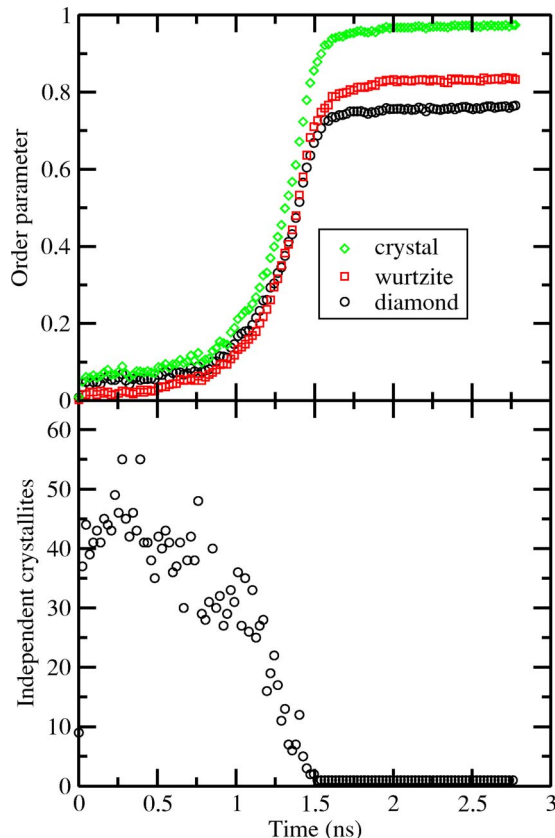


FIG. 4. (Color online) Proportion of atoms in elementary blocks (top) and number of independent clusters (bottom) during the liquid-crystal phase transition of Si in NVT conditions at 1250 K and 2.32 g/cm<sup>3</sup>. The proportion of atoms in diamond and/or wurtzite crystalline structures ( $\diamond$  crystal) increases rapidly reaching a value close to 1 after the transition. These results are for simulation no. 1.

TABLE I. Characteristic times of the crystalline precursor that gives rise to crystallization of the supercooled liquid.

Simulations	Time (ns)				
	$t_0$	$t_{200}$	$t_{\text{nuc}}$	$t_{500}$	$t_{\text{crys}}$
1	0.06	0.38	0.46	0.59	1.60
2	0.64	0.75	0.84	1.02	2.75
3	3.14	3.30	3.32	3.62	4.85
4	3.30	3.67	4.20	4.68	6.00
5	5.14	5.35	5.32	5.76	8.00
6	7.79	7.98	7.98	8.27	9.75

tallites tend to be small, counting fewer than 20 atoms, on average. Before crystallization begins, the number of independent nuclei oscillates between 40 and 50. As crystallization occurs, however, the largest nucleus grows rapidly, absorbing the smaller crystallites and forming a single system-size cluster; the number of independent crystallites decreases constantly during this process (Fig. 4, bottom panel).

## B. Characterization

### 1. Stability of crystallites

It is possible to characterize more finely the crystallization by following the crystalline precursor as it takes over the simulation cell. This is achieved by following the evolution of all crystallites by steps of 1.15 ps. During this short time some crystallites appear, other vanish, while the rest might evolve significantly; a set of rules must therefore be established to identify uniquely and reversibly each aggregate. (1) At least three atoms must remain together over one time interval for a cluster to survive; a failing test indicates that the aggregate has dissolved. (2) When two or more crystallites merge together, the one with the highest number of surviving atoms is considered the progenitor, the other one ceases to exist. (3) If, on the other hand, a cluster splits into multiple parts, the new aggregate containing the highest number of original atoms becomes the progeny and the other clusters are considered newborn. Using this analysis, we can then follow the evolution of the crystalline precursor by tracing back its ancestors.

In order to compare between the six runs that crystallize, we separate the time evolution into four periods. The instant of birth of the crystalline precursor is defined as  $t_0$  (see Table I). From this time, it may take several hundreds of picoseconds (about 200–900 ps) for this embryo to reach a critical size, at time  $t_{\text{nuc}}$ . The nucleation time  $t_{\text{nuc}}$  is defined as the point in time where the size of the aggregate starts growing steadily, as seen in Fig. 5. At this point, the system leaves the incubation regime to enter the steady state of nucleation and crystallization as such takes place.

CNT predicts that a cluster of overcritical size should grow continuously whereas undercritical size crystallites tend to dissolve, in both cases, to lower their free energy. Statistical fluctuations can foil those predictions around the critical size, however, and move from undercritical to overcritical size and vice versa. This explains why we define  $t_{\text{nuc}}$

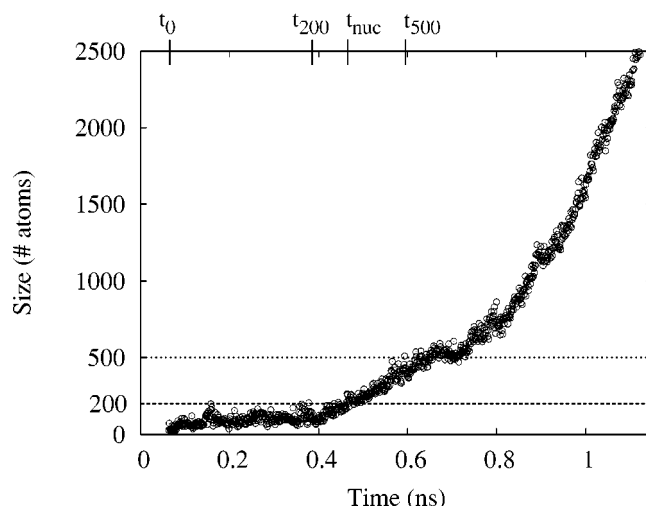


FIG. 5. Evolution of the crystalline precursor during the liquid-crystal transition of Si in NVT conditions at 1250 K and 2.32 g/cm<sup>3</sup>. These results are taken from the first simulation (no. 1) to crystallize.

not as the first time when the cluster reaches the critical size, but the first time it reaches it for good. For example, while at  $t_{\text{nuc}}$  crystalline precursors are composed in average of 160 atoms, they have often reached a size of 200 atoms or more before. This fine characterization of  $t_{\text{nuc}}$  is probably not needed, however. Looking at Table I,  $t_{\text{nuc}}$  appears closely correlated with  $t_{200}$ , the point in time where the crystallite reaches a maximum size of 200 atoms for the first time. The number of clusters reaching a 200-atom size or more and then dissolving into the liquid is extremely small. Thus, the critical cluster size should be around 175 atoms for Si at 1250 K, in agreement with the estimate of Uttormark *et al.*<sup>18</sup>

From  $t_{\text{nuc}}$ , the crystallization *per se* proceeds rapidly into a steady growth regime which lasts about 2 ns. The crystallization time,  $t_{\text{crys}}$ , is defined as the moment when the size of the largest cluster stops growing.

For all simulations, it is possible to trace back the critical cluster to its appearance as a small aggregate of about 20 atoms, at  $t_0$ . By selection, this cluster should live longer than most other undercritical crystallites. As shown in Fig. 5, the size of this cluster typically oscillates for a long time, aggregating and losing atoms until it reaches a critical size at  $t_{\text{nuc}}$ , and then starts growing for good.

Surprisingly, while the cluster size oscillates, its composition changes considerably. Throughout the incubation regime, the crystalline precursor changes its composition significantly: very few atoms of the original cluster remain part of it until the nucleation phase starts. In half the simulations, fewer than 50% of the original atoms are part of the cluster for 90% of the time interval between  $t_0$  and  $t_{\text{nuc}}$  (see Table II). Even in the steady-growth regime, starting at  $t_{\text{nuc}}$ , the crystallite continues to exchange atoms with the liquid. For most of the runs, less than half the 160 or so atoms present at  $t_{\text{nuc}}$  remain in the clusters for 90% of the time in this interval until  $t_{500}$ ; as the growth takes place, a significant fraction of the atoms move back and forth between the crystallite and the surroundings. These results are in line with a previous

TABLE II. Proportion of atoms participating in the crystalline precursor permanently and 90% of the time during the incubation and steady-state regime of nucleation, starting from atoms that belong originally to the crystallite at time  $t_0$  until  $t_{\text{nuc}}$  in the incubation phase and from  $t_{\text{nuc}}$  until  $t_{500}$  in steady state. The interval between each configuration snapshot is 1.15 ps.

Persistence of atoms in part of the crystalline precursor				
Simulations	From $t_0$ to $t_{\text{nuc}}$		From $t_{\text{nuc}}$ to $t_{500}$	
	Permanent	90% of the time	Permanent	90% of the time
1	18%	82%	52%	81%
2	4%	64%	43%	77%
3	38%	79%	18%	57%
4	0%	40%	18%	51%
5	0%	46%	13%	40%
6	0%	20%	29%	49%

study on growth and dissolution of implanted LJ crystallites with a critical size similar to that of our system,<sup>6</sup> which shows that the probability of dissolution, while decreasing rapidly with cluster size, above the critical size is still non-negligible for clusters 50% bigger than critical size. Although we follow a cluster that will not dissolve totally, the considerable atomic exchange is a reflection of this tendency. While the critical aggregate's composition changes rapidly, its position remains almost fixed in space, its center of mass hardly moving except by aggregation. The crystalline precursor is therefore not a static crystalline seed slowly growing throughout the nucleation process; there is a constant exchange of matter with the surrounding liquid even for post-critical sizes (see Fig. 6).

## 2. Free energy

It is formally straightforward to compare the simulations with the predictions of CNT on the thermodynamics of crystal growth. The free-energy curve of crystallites can be obtained from the simulations by plotting the equilibrium probability  $P_{eq}(n)$  to find a crystallite of size  $n$  in the metastable liquid.<sup>1,31</sup>

We compute  $P_{eq}(n)$  in the supercooled liquid, accumulating data until the largest cluster reaches 500 atoms, fewer than 5% of the total number of atoms but over the critical size (see Table I), and over all runs. This distribution is directly connected to the free energy  $\Delta F(n)$  associated with these clusters,

$$P_{eq}(n) \propto \exp\left(\frac{-\Delta F(n)}{k_B T}\right), \quad (1)$$

$$\frac{\Delta F(n)}{k_B T} = -\ln\left(\frac{N(n)}{\sum_n N(n)}\right) + C, \quad (2)$$

where  $N(n)$  is the number of clusters of size  $n$  present in the liquid,  $k_B T$  is the Boltzmann constant times temperature, and  $C$  is a constant.

The CNT offers another way to compute the free energy. In a simple relation, the energy gain in the formation of a

new phase is balanced by the cost to produce an interface between the old and new phases,

$$\Delta F(n) = \Delta F_{sl} n + \alpha n^{2/3}, \quad (3)$$

where  $\Delta F_{sl} = F_s - F_l$  is the Helmholtz free-energy difference between solid and liquid states in NVT conditions,  $\alpha = A\gamma$  with  $\gamma$  the surface tension,  $A = (36\pi/\rho_s^2)^{1/3}$  for spherical crystallites, and  $\rho_s$  the density of the solid phase. While the Helmholtz free-energy difference  $\Delta F_{sl}$  is relatively easy to obtain, the evaluation of the surface tension is much trickier because small crystallites are far from spherical and fluctuate considerably in shape for a given size. Crystallites become mostly spherical only well beyond the overcritical size.

Figure 7 compares the free energy for these two methods: from the equilibrium probability [Eq. (2)] and from CNT predictions [Eq. (3)]. Following standard practice, the surface energy parameter  $\alpha$  is fitted in order to obtain the best agreement with the first method. The Helmholtz free-energy difference between the crystalline and liquid phases is computed as follows.

The Gibbs free-energy difference  $\Delta G_{sl}$  between solid and liquid states in NPT conditions at zero pressure is given by the difference in chemical potential  $\Delta\mu$  between the two phases. This quantity was computed by Broughton and Li<sup>13</sup> and was found to be  $-7.697 \times 10^{-2}$  eV/at. However, we need the Helmholtz free-energy difference  $\Delta F_{sl}$  at fixed density, which we can obtain by thermodynamic integration from the zero-pressure results. Starting with the relation for the internal pressure  $(\partial F / \partial V)_{N,T} = -P$ , we use a thermodynamic integration for each phase ( $l$ - and  $s$ -Si),

$$\Delta F = \int_{F_1}^{F_2} dF = - \int_{V_1}^{V_2} P(V) dV. \quad (4)$$

The free-energy difference between our system at zero pressure and at fixed density is computed by a Gaussian integration with five values,

$$\int_{V_1}^{V_2} P(V) dV = \left(\frac{V_2 - V_1}{2}\right) \sum_{i=1}^5 w_i P(V_i), \quad (5)$$

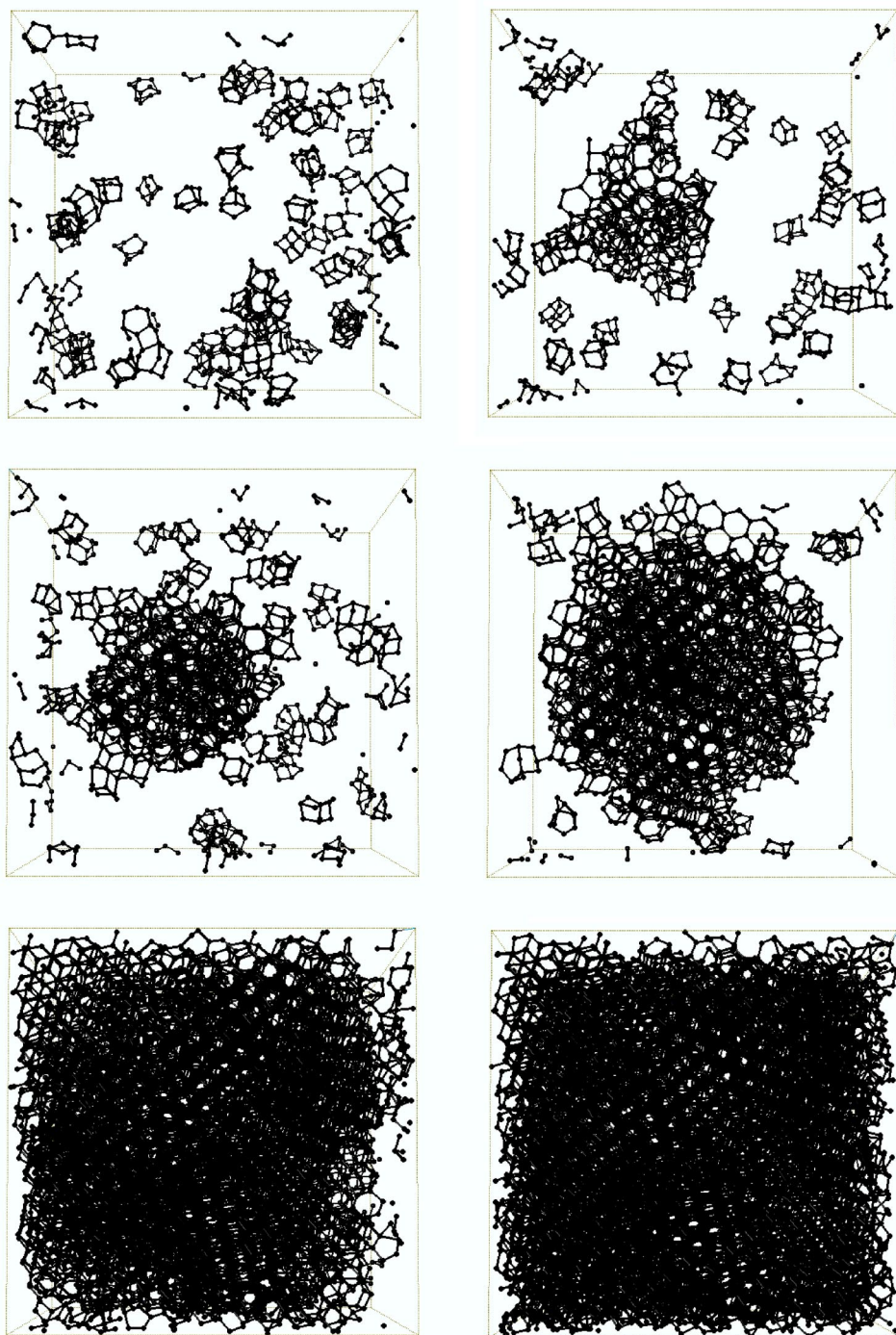


FIG. 6. Evolution of nucleation and crystallization during the liquid-crystal phase transition of SW Si at 1250 K and 2.32 g/cm<sup>3</sup>. The configurations show atoms that belong only to crystalline structures at 0, 0.58, 0.86, 1.15, 1.44, and 1.73 ns, respectively, for simulation no. 1.

$$V_i = \left( \frac{V_2 - V_1}{2} \right) x_i + \left( \frac{V_2 + V_1}{2} \right), \quad (6)$$

where  $x_i$  are the values for the Gaussian integration with their relative weight  $w_i$ . The initial volume, at zero pressure, for the liquid is  $V_{1,l} = 18\,827.9 \text{ \AA}^3$  (2.467 g/cm<sup>3</sup>) and the solid,  $V_{1,s} = 20\,277.6 \text{ \AA}^3$  (2.29 g/cm<sup>3</sup>); the final volume is  $V_2 = 20\,023.4 \text{ \AA}^3$ . Each point in the integral is simulated in NVT conditions at 1250 K for the liquid and solid. We equilibrate our 1000-atom system for 58 ps and then compute the mean pressure during 345 ps of simulation time.

After integrating, we find a free-energy difference per atom between the fixed density ( $\rho = 2.32 \text{ g/cm}^3$ ) and zero-pressure system,<sup>32</sup> for liquid and solid state,

$$\Delta F_s = 9.588 \times 10^{-4} \text{ eV/at.}, \quad (7)$$

$$\Delta F_l = 5.573 \times 10^{-3} \text{ eV/at.} \quad (8)$$

This gives a free-energy difference between the liquid and solid phase at 2.32 g/cm<sup>3</sup> and 1250 K of

$$\Delta F_{sl} = \Delta G_{sl}(P=0) + \Delta F_s - \Delta F_l, \quad (9)$$

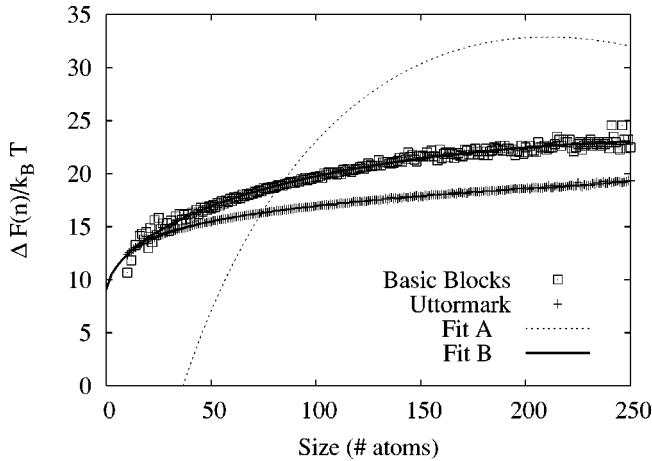


FIG. 7. Free energy (divided by  $k_B T$ ) of crystallites as a function of their size in the NVT ensemble. The simulation data are computed from the equilibrium probability of presence for clusters with the basic blocks analysis ( $\square$ ) or the criteria of Uttormark *et al.* (Ref. 18) ( $+$ ). The CNT curve computed with the  $\Delta F_{sl}$  value from thermodynamic integration is indicated as fit A. A better fit is given by fit B. Details are discussed in the text.

$$\Delta F_{sl} = -8.158 \times 10^{-2} \text{ eV/at.} \quad (10)$$

The constant-volume correction is therefore only 6% of the zero-pressure result of Broughton and Li.

As can be seen in Fig. 7, however, the CNT curve does not match the free-energy data coming from  $P_{eq}(n)$  in simulations. In order to find a better fit, the free-energy difference  $\Delta F_{sl}$  between the solid and liquid state should be nine times lower than the value computed with the thermodynamic integration.

We can verify the impact due to the choice of the order parameter on the free-energy curve by reanalyzing the data using the criteria of Uttormark *et al.*<sup>18</sup> The resulting curve is also plotted in Fig. 7 and shows an even flatter curve, away from CNT results. We also repeated the simulation at 1250 K in the NPT ensemble at zero pressure and over 10 ns. In this situation, the trajectories do not crystallize—the largest crystallite reaches about 100 atoms, well below the estimated critical size. The free-energy distribution obtained from the cluster size distribution, while more curved than that for the NVT conditions, is still far from the CNT predictions ( $\Delta G_{sl}$  is about five times too low) (see Fig. 8).

The discrepancy between the two approaches clearly indicates that the classical nucleation theory does not fully capture the nucleation process in SW Si. We identify two possible sources of the discrepancy. (1) As was demonstrated by Sastry and Angell recently,<sup>16,17</sup> SW Si undergoes a high-density to low-density liquid-liquid phase transition. The low-density phase could be stabilized at higher temperature by the presence of a crystallite. In this case, it would be necessary to take into account two interfaces instead of one in the CNT equations. (2) The CNT fails because the critical nucleus is too small breaking the approximation of spherical crystallites. At this moment, we could not verify or disprove either of these possibilities.

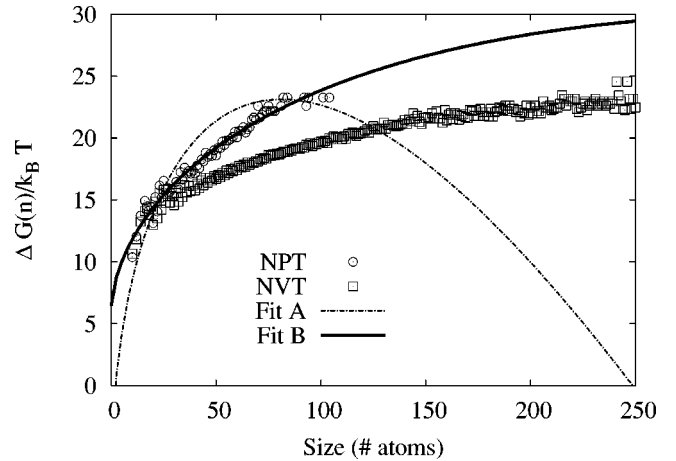


FIG. 8. Free energy (divided by  $k_B T$ ) of crystallites as a function of their size in NPT conditions (NPT) compared to NVT conditions (NVT). The simulation data are computed from the equilibrium probability of presence for clusters with the basic blocks analysis. The CNT curve computed with the  $\Delta G_{sl}$  of Broughton et Li (fit A) is closer to the free-energy data originating from  $P_{eq}(n)$ . However, a better fit (fit B) requires a value five times lower.

### 3. Lifetime of crystallites

Beyond the free-energy curve, we also analyze the dynamics of the crystallites present in the supercooled liquid.

The lifetime probability of crystallites can be derived by following the kinetic approach of Zeldovich.<sup>29</sup> This approach predicts that the evolution of the clusters can be described by a diffusion equation of the form

$$\frac{\partial c(n,t)}{\partial t} = \frac{\partial}{\partial n} \left\{ D(n) \left[ \frac{\partial c(n,t)}{\partial n} + \frac{\partial}{\partial n} \left( \frac{\Delta G(n)}{k_B T} c(n,t) \right) \right] \right\}, \quad (11)$$

where  $c(n,t)$  is the concentration of crystallites of size  $n$  at time  $t$ ,  $D(n)$  is the diffusion, and  $k_B T$  is the Boltzmann factor times the temperature.

Van Kampen<sup>33</sup> resolved the differential equation for small times by assuming the diffusion to be constant. Further approximating the potential as linear with respect to the cluster's size, van Beijeren<sup>34</sup> succeeded in finding a solution for longer times. This latter equation, which gives the distribution function for first arrival at size  $n_f$ , for crystallites starting from size  $n_0$ , is a well-known result<sup>35</sup> that confirms van Kampen short-term behavior and contains an additional friction term  $e^{-\nu_0 t}$  which becomes important for longer times,

$$P(n, n_f, t) = \frac{n_f - n_0}{\sqrt{4\pi D t^3}} e^{-(n_f - n_0)^2 / 4Dt} e^{-[\Delta G(n_f) - \Delta G(n_0)] / 2k_B T} e^{-\nu_0 t}, \quad (12)$$

where

$$\nu_0 = D \left( \frac{[\Delta G(n_f) - \Delta G(n_0)]}{2k_B T} \right)^2. \quad (13)$$

This probability distribution is formally known as an inverse Gaussian distribution (or inverse normal, Wald). It was first derived independently by Schrödinger<sup>36</sup> and Smoluchowski<sup>37</sup>

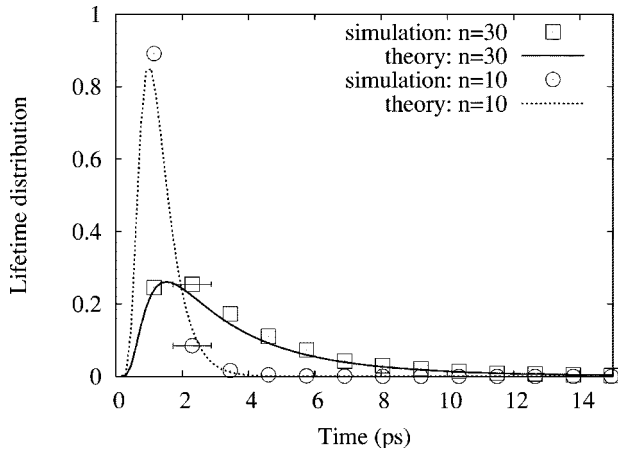


FIG. 9. Lifetime distribution of clusters reaching a maximum size of 10 and 30 atoms. Comparison between the inverse Gaussian distribution (theory) and the simulations data (simulation) with an uncertainty of  $\pm 0.58$  ps.

to describe Brownian motion in systems with a drift velocity. Hence, the development of a crystallite can be represented as a random walk in a field of force  $\Delta F$  through different size classes where small clusters have a strong tendency to dissolve into the liquid (a drift to  $n_f \rightarrow 0$ ) and supercritical nanocrystals tend to growth to macroscopic size ( $n_f \rightarrow \infty$ ). Since we do not have all the information on the free energy of crystallites  $\Delta G(n)$  (see Sec. III B 2) and the diffusion constant, it is not possible to use directly Eq. (12) to compare the lifetime behavior of clusters in the supercooled liquid during nucleation. However, we can circumvent the difficulty by writing the inverse Gaussian distribution under a parametric form where  $A$  represents the mean and  $A^3/B$  is the variance,

$$P(t) = \frac{B}{\sqrt{2\pi t^3}} \exp\left[-\frac{B}{2t} \left(\frac{t-A}{A}\right)^2\right], \quad (14)$$

$$A = \frac{-(L-n_0)k_B T}{D[\Delta G(L) - \Delta G(n_0)]}, \quad (15)$$

$$\frac{A^3}{B} = \frac{-2(L-n_0)}{D^2} \left(\frac{k_B T}{\Delta G(L) - \Delta G(n_0)}\right)^3. \quad (16)$$

We compute the mean lifetime and variance for crystallites reaching the same maximum size in order to determine the theoretical distribution and compare with the lifetime probabilities from numerical simulations. Because large clusters are not encountered frequently, the amount of data collected over all MD simulations remains small for the lifetime of cluster near the critical size. In Fig. 9, the lifetime distributions determined by Eq. 14 and the simulations data are in good agreement for small crystallites ensuring that cluster nucleation is well described by the inverse Gaussian distribution. The mean lifetimes for crystallites reaching an undercritical size of 10 or 30 atoms is  $1.32 \pm 0.6$  and  $3.79 \pm 0.6$  ps, respectively, with a variance of 1.73 and 10.01, although some rare clusters last until 30 and 50 ps (not shown). As would be expected, the mean lifetime increases with the size.

Although some approximations have been made to obtain the lifetime probabilities of clusters by the inverse Gaussian distribution and from the simulations data, the results are conclusive for crystallites reaching relatively small size. Since small clusters developed themselves in a confined range of size, we believe that the free-energy difference can be approximated by a linear relation to the crystallite size and the diffusion kept constant.

#### IV. CONCLUSIONS

There has been a lot of interest recently regarding the nature of the liquid-solid transition in oriented liquid such as water and tetrahedral semiconductors. In many systems, it appears that there exists a high-density to low-density liquid transition often leading to a glassy or amorphous phase.<sup>16,17,38</sup> Here, we reported results on a study of nucleation in liquid Si above the HDL to LDL transition.

We find that homogeneous nucleation takes place on a time scale of about 10 ns in a large enough system at constant volume. Using a topological order parameter, it is possible to follow the evolution of the crystallites through the crystallization process. Based on this analysis, we estimate the critical size to be around 175 atoms, within the limits of previous estimation of Uttormark *et al.* Surprisingly, the critical cluster, the one that will eventually crystallize the whole system, can survive at undercritical size for a long time (up to 900 ps or more) before it starts to grow steadily. Although the cluster's center of mass does not move significantly, there is a fluctuation in the composition of the cluster, as atoms move from the liquid to the crystallite and vice versa, even once the crystallite has reached an overcritical size.

A comparison of the simulation results with the classical nucleation theory indicates that the general behavior of the nucleation process is in agreement with CNT. For example, we find that the lifetime distribution of clusters reaching a specific maximum size follows the inverse Gaussian distribution predicted recently,<sup>34</sup> supporting the description of the cluster growth as a random walk in the presence of a force field associated with the free energy. However, the details of the nucleation free energy differ significantly from the theoretical predictions. While the specific origin of this discrepancy remains open, we suggest that it could be caused by the presence of a low-density liquid at the interface between the crystal and the normal liquid or by the small size of the critical nucleus. More studies are required to fully address this problem.

#### ACKNOWLEDGMENTS

The authors want to thank G.T. Barkema, H. van Beijeren, and K. Brendel for helpful discussions. This work is funded in part by NSERC, NATEQ, and the Canada Research Chair Program. N.M. is supported by the Research Corporation. Most of the simulations were run on the computers of the Réseau Québécois de Calcul de Haute Performance (RQCHP), whose support is gratefully acknowledged.



- \*Electronic address: Normand.Mousseau@umontreal.ca
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