

# Mechanical versus thermodynamical melting in pressure-induced amorphization: The role of defects

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We study numerically an atomistic model which is shown to exhibit a one-step crystal-to-amorphous transition upon decompression. The amorphous phase cannot be distinguished from that obtained by quenching from the melt. For a perfectly crystalline starting sample, the transition occurs at a pressure at which a shear phonon mode destabilizes, and triggers a cascade process leading to the amorphous state. When defects are present, the nucleation barrier is greatly reduced and the transformation occurs very close to the extrapolation of the melting line to low temperatures. In this last case, the transition is not anticipated by the softening of any phonon mode. Our observations reconcile different claims in the literature about the underlying mechanism of pressure amorphization.

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## I. INTRODUCTION

Since the first reports on pressure-induced amorphization (PIA), there has been an increasing interest in the phenomenon that has been observed in a large class of systems, both upon compression and decompression (see Ref. 1 for a review and references on particular materials). The experimental interest stems from the fact that PIA occurs in some extremely widespread and important materials, namely, water<sup>2</sup> and quartz and its polymorphs,<sup>3</sup> and also because PIA provides a novel route to the synthesis of amorphous materials, in addition to the traditional technique of quenching from the melt. From a basic point of view, there are controversies about the mechanism of PIA and the nature of the amorphous phase, in particular regarding whether it is equivalent or not to that obtained by quenching.<sup>4,5</sup> Since in most cases crystalline phases that undergo PIA show reentrant melting in the  $P$ - $T$  plane, it has been suggested<sup>2</sup> that PIA is nothing but melting at temperatures below the glass temperature of the supercooled fluid. Other studies (specially numerical ones<sup>6-9</sup>) have instead emphasized the relationship between PIA and mechanical instabilities. It has been observed in fact that in many cases PIA is triggered by the softening of a shear phonon mode.<sup>10</sup> In addition, some memory effects<sup>11</sup> and anisotropic properties,<sup>4</sup> although controversial,<sup>12</sup> show that many times what appears to be an amorphous phase preserves within its structure signatures of the parent crystalline phase.

In view of the broad phenomenology briefly stated above, it is highly desirable to take advantage of model systems in which amorphization can be studied in a transparent way, allowing to look in detail into the mechanisms and characteristics of the transformation. This motivates the present work, in which we study a simple two-dimensional system of identical pointlike particles interacting through a specially devised two-body potential. The simplicity of the model allows us to study large systems with some amount of defects, and observe directly the crucial role they play in the transformation.

In the model we study, there are a few different crystalline ground states depending on the applied pressure. We present here the results of the evolution of the most compact structure (stable at the highest pressures) upon pressure release.<sup>13</sup> As we will see, PIA at temperatures in which particle diffusion is negligible is always related to mechanical instabilities. For perfect lattices, PIA is reflected in the softening of a shear phonon mode. This leads to local distortions that produce the destabilization of new vibrational modes, leading to a cascade of instabilities,<sup>8</sup> which drives the system toward an amorphous structure. However, in the presence of defects, *localized* vibrational modes exist, which may become unstable before any extended vibrational mode does. This favors the nucleation of the amorphous phase at pressures much closer to the thermodynamic equilibrium value between the crystalline and amorphous phases.

The work is divided as follows. In Sec. II we present the model. The results at zero temperature are contained in Sec. III. In Sec. IV we give evidence that the disordered samples obtained can be called truly amorphous. In Sec. V we present results at finite temperatures, and Sec. VI contains some discussion and conclusions.

## II. THE MODEL

An isotropic, purely repulsive interparticle potential is used, with a strict hard core at a distance  $r_0$  plus an almost triangular repulsive shoulder. The pairwise interaction potential  $V(r)$  between two particles separated by a distance  $r$  is given by<sup>14</sup>

$$\begin{aligned}
 V(r) &= \infty & \text{for } r < r_0 \\
 V(r) &= \varepsilon_0 \left[ 1.2 - 2.8125(r/r_0 - 1.08)^2 + \frac{0.008}{r/r_0 - 1} \right]^2 \\
 & \text{for } r_0 < r < r_1 \\
 V(r) &= 0 & \text{for } r > r_1,
 \end{aligned} \tag{1}$$

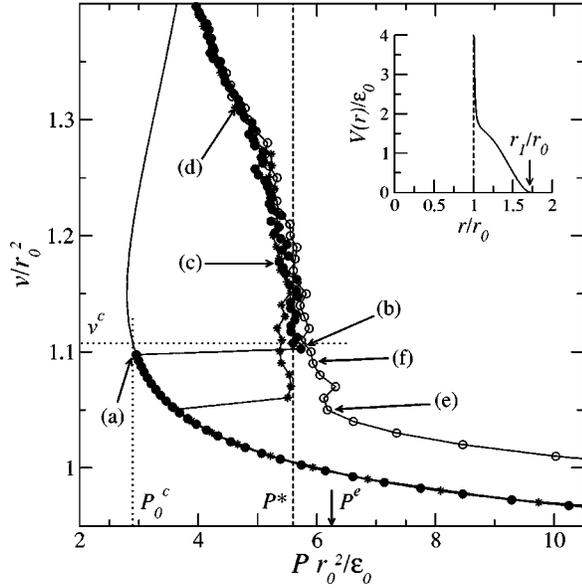


FIG. 1. Evolution of pressure  $P$  upon increasing of the specific volume  $v$ , at zero temperature. The thin continuous line is the expected evolution if the system remains always triangular. The dotted lines mark the ideal stability limit  $(v^c, P_0^c)$ , at which a phonon energy vanishes. Dots indicate results of simulation for a perfect lattice (full circles), a lattice with a single vacancy (stars) and a system with grain boundaries (open circles, see Fig. 3). Letters correspond to snapshots in Fig. 3. The inset shows the interparticle potential  $V(r)$ .

where  $r_1 = 1.17315r_0$ , and  $r_0$  sets the length unit. The potential is plotted in the inset of Fig. 1. This kind of potential has been previously used to systematize the anomalous properties of tetrahedrally coordinated materials.<sup>14–16</sup> Then we expect they are also appropriate to study amorphization under pressure, since this phenomenon occurs for most of these materials. Its crucial characteristic is the existence of two possible equilibrium distances between particles.

The system is simulated by standard molecular dynamics in the  $NVT$  ensemble with periodic boundary conditions. At a given volume, the quantities of interest are evaluated, and the volume is changed in steps of the order of 0.01% by rescaling all coordinates of the particles and the size of the simulation box. Temperature is fixed by rescaling the velocities of the particles whenever necessary. As the amorphization process implies the existence of mechanical instabilities, we typically observe that kinetic energy tends to increase during amorphization. In a real situation this energy transforms into heat. Here we simply eliminate it by the mentioned rescaling procedure. Pressure is calculated by a direct evaluation in terms of the interparticle forces. We choose to model the system at constant volume in order to survey all regions of the volume-pressure curve, including those that would be unstable in constant pressure simulations. The results to be presented correspond to a two-dimensional system, to facilitate a direct visualization of the particle configurations. We should mention, however, that the same phenomenology was observed in three-dimensional samples with the same interparticle potential.

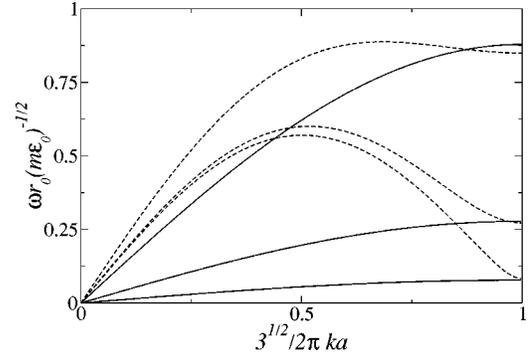


FIG. 2. The dispersion relation of phonons along one of the directions perpendicular to the densest planes of the triangular structure close to the instability pressure. Continuous lines correspond to the repulsive potential Eq. (1), and dashed lines to the same potential plus an attractive term [Eq. (2)] that includes second-nearest-neighbors interactions. Curves correspond, from top to bottom, to  $|P - P_0^c|(r_0^2/\epsilon_0) = 0.01, 0.001, \text{ and } 0.0001$ . Note that since the repulsive interaction reaches only the first neighbors, the continuous lines have an analytical form of the type  $\sim \sin(k)$ , and all phonon frequencies vanish at the same pressure  $P = P_0^c$ . For the case with second-nearest-neighbors interaction the instability occurs first for the edge zone phonon  $ka = 2\pi/\sqrt{3}$ .

### III. ZERO-TEMPERATURE RESULTS

We take as the starting configuration the one corresponding to the triangular lattice with lattice parameter  $\sim r_0$ , which is stable at high pressures. In Fig. 1 we present the results of simulations at  $T=0$  in a system of 2800 particles. The thin continuous line corresponds to the  $v$ - $P$  relation assuming the system remains always triangular. The reentrance of this line is a consequence of the particular form of the interaction potential. The numerical results for a perfect lattice (full circles) follow this line up to some maximum volume, at which they abruptly depart from it. This is the pressure in which a phonon with vanishing energy first appears in the triangular structure (see Fig. 2). Analytical evaluation shows that this instability occurs when  $3V'(a)/a + V''(a) = 0$ , where primes denotes derivatives of the potential, and  $a$  is the lattice parameter. This expression is valid as long as the interaction between next-nearest neighbors is zero, as is in the present case. The critical volume  $v^c$  and pressure  $P_0^c$  are indicated by dotted lines in Fig. 1, and they are fully compatible with the numerical results. The unstable phonons turn out to be shear phonons with the wave vector  $\mathbf{k}$  oriented perpendicularly to one of the three most compact directions in the lattice. Note that for the interparticle potential we use, the longitudinal phonon branch along these directions is of the type  $\sim \sin(k)$ , and all shear phonons—irrespective of the absolute value of  $k$ —become zero energy at the same point. Then, in the present case the instability pressure is macroscopically signaled by the vanishing of the stress dependent shear modulus of the material,<sup>17,18</sup>  $\mu = (C_{11} - C_{22})/2 - P = 0$ .

At  $v^c$  there is a sharp and abrupt increase of pressure.<sup>19</sup> Snapshots of the particle configurations give clues of what happens in the system. In Fig. 3(a) we see the triangular configuration just before the instability. Figure 3(b) shows

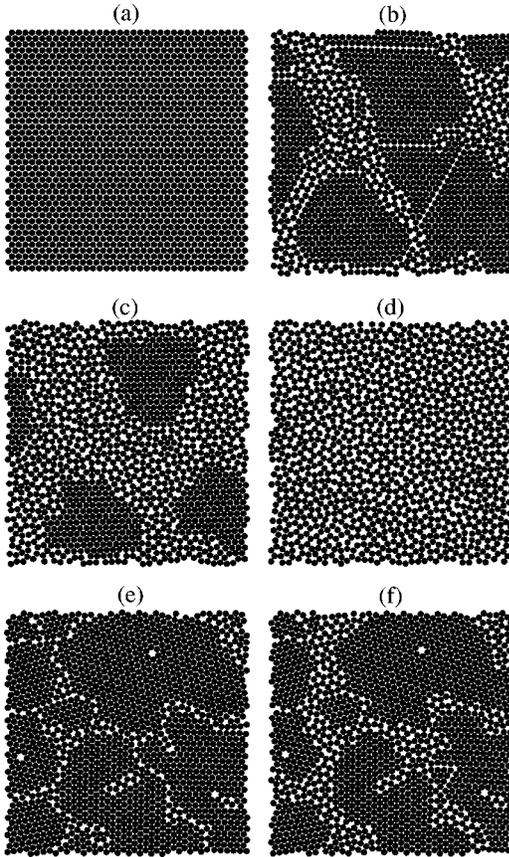


FIG. 3. Snapshots of the systems at the points indicated in Fig. 1 (only about a quarter of the full simulated system is shown). Upper four panels correspond to a perfect crystal starting sample, whereas the two lower panels are from a polycrystalline sample with grain boundaries and vacancies.

that after changing the volume a very small quantity, an instability has propagated in the system. We stress that the evolution of the system from the configuration in Fig. 3(a) to that in Fig. 3(b) is triggered by a very small volume change, and is just the steepest descend evolution toward a local energy minimum of the energy landscape. In this evolution, pressure recovers to a higher value indicated as  $P^*$  (dashed line) in Fig. 1. This value is roughly maintained<sup>20</sup> upon further volume increase up to  $v/r_0^2 \sim 1.27$ , which is close to the volume at which the disordered regions have taken over the whole system. If volume is increased further, pressure decreases noticeably.

The thermodynamic equilibrium pressure  $P^e$  at  $T=0$  between the crystalline and disordered structures is indicated by the arrow in Fig. 1. The value of  $P^e$  was calculated by enthalpy evaluations of the triangular lattice and the amorphous structure obtained by quenching from the melt. Thus,  $P^e$  represents the natural extrapolation of the melting line to zero temperature. We see that  $P^e$  is close to (though a bit higher than)  $P^*$ .

It must be noticed that constant pressure simulations would have shown at  $P_0^c$  an abrupt transition between a completely ordered and a completely disordered system, while  $P^*$  would have remained hidden. However,  $P^*$  has a clear

physical meaning as the transition pressure *once the disordered phase has been nucleated*. This suggests that if nucleation centers are present in the system,  $P^*$  will be experimentally accessible as the actual transition pressure. In fact, Fig. 1 shows also the  $v$ - $P$  evolution for a system with a single vacancy and for a system with grain boundaries. In the former case, the instability occurs before  $v^c$  is reached, and in the latter case it even occurs without any pressure reentrance.<sup>21</sup> Note that the three curves tend to coincide after the first destabilization of the original lattice. Two snapshots of the system for the polycrystalline case [Figs. 3(e) and 3(f)] show how the disordered phase grows from grain boundaries, which provide nucleation centers for the transformation. These results are a clear indication that defects are very effective in lowering the energy barrier for the transition, and also explain why, in experiments, transformation pressures close to the thermodynamic values are usually observed. The lowering of the energy barrier due to defects and its relation to thermodynamic melting has been discussed by Mizushima *et al.*<sup>22</sup> in the context of crystal-crystal pressure-induced transformations. Note that in the case in which the transformation is triggered by defects, the phonon spectrum of the system (and in particular the elastic constants) gives no indication of the instability that is about to occur. This is particularly obvious in the case of a single vacancy: a single defect cannot modify the phonon spectrum of an infinite sample, and then its effect is not seen in the elastic constants, but it produces a finite change in the value of the critical pressure  $P_0^c$ .<sup>23</sup>

It was already mentioned that for the interaction potential used, the whole branch of shear phonons become zero energy at  $P_0^c$ . We want to emphasize however that amorphization is not related to this degeneracy, as it can also be triggered by a single phonon becoming unstable. In fact, we did simulations with a modified potential in which an attractive term  $V_a$  reaching up to second-nearest neighbors was included. The actual potential used is that of the preceding section plus an attractive term given by

$$V_a(r) = 2\varepsilon_0(r-r_1)^2 \quad \text{for } r_1 < r < (r_1+2r_0)/2,$$

$$V_a(r) = -2\varepsilon_0[(r-2r_0)^2 - (r_1-2r_0)^2/2]$$

$$\text{for } (r_1+2r_0)/2 < r < 2r_0. \quad (2)$$

The instability corresponds now to the vanishing of the energy of edge zone shear phonons only, as indicated in Fig. 2. The amorphization of the system occurs precisely at the point where this phonon becomes zero energy, and it was observed to be similar to the previous case where the full shear phonon branch becomes unstable at the same pressure. This rules out an amorphization mechanism in which at the instability, arbitrary combinations of the unstable phonons generate disordered movements of the atoms, and favors a cascade mechanism as described in the discussion section below.

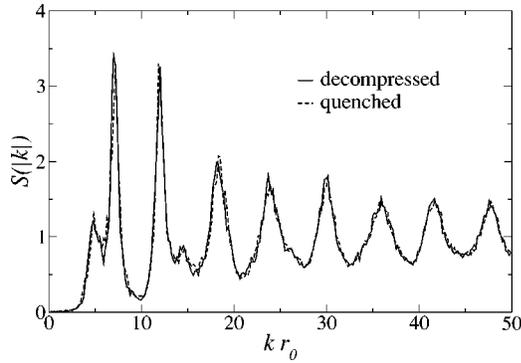


FIG. 4. The structure factor of the amorphous structure obtained by decompression of a perfect crystalline sample and that obtained by a quench from the liquid phase, at the same volume  $v/r_0^2 = 1.289$ . They coincide within the numerical precision.

#### IV. COMPARISON BETWEEN DECOMPRESSED AND QUENCHED AMORPHOUS STRUCTURES

The claim that the disordered structure we obtain upon decompression is really amorphous is supported by the following facts. We find no evidence for orientational order in the structure factor  $S(\mathbf{k})$ , even in the case in which we start with a monocrystalline sample. Moreover, a quantitative comparison with the structure factor of a system quenched from the liquid (prototypic of an amorphous sample) shows that they are indistinguishable (Fig. 4). In addition, we have failed to find any single systematic difference between the two amorphous structures.

#### V. FINITE-TEMPERATURE EFFECTS

If temperature is not strictly zero, even the perfect lattice amorphizes before the ultimate mechanical instability limit is reached. Simulations at finite temperature with perfect samples show that the amorphization occurs at a temperature-dependent critical pressure  $P^c(T)$  [such that  $P^c(T=0) = P_0^c$ ]. The temperature dependence of the critical pressure originates in the fact that a thermally activated process may destabilize the soft phonon before it actually becomes zero energy.

It is instructive to see in some more detail how this destabilization occurs. Consider the normal modes (phonons) of the system. We will study the case in which only a single phonon with wave vector  $\mathbf{k}$  perpendicular to one of the high-density planes has nonzero amplitude. We expand the energy of the lattice in powers of the amplitude of the phonon oscillation, going one order beyond the harmonic approximation. Let us call  $\delta_l$  and  $\delta_t$  the longitudinal and transverse oscillation amplitudes of that phonon. As we will see there is a nontrivial coupling between the two at the instability.

Taking into account that our potential produces interactions only among first neighbors in the lattice, the energy per particle  $e_0$  of the system up to third order in the amplitudes can be written after some lengthy but straightforward calculation as

$$e_0 = \frac{1}{8} \sin^2\left(\frac{\sqrt{3}ka}{4}\right) \left[ \delta_l^2 \left( \frac{3V'}{a} + V'' \right) + \delta_t^2 \left( \frac{V'}{a} + 3V'' \right) \right] + \frac{\sqrt{3}}{8} \sin^3\left(\frac{\sqrt{3}ka}{4}\right) \left[ \delta_l^2 \delta_t \left( -\frac{4V'}{a^2} + \frac{V''}{a} + V''' \right) \right]. \quad (3)$$

The first line in Eq. (3) is the harmonic contribution, the second is a cubic term in the displacements (there is an additional cubic term proportional to  $\delta_l^3$ , but this can be shown to be not relevant for the analysis below). The system becomes unstable when the coefficient of  $\delta_l^2$  vanishes, providing again the condition  $3V'/a + V'' = 0$ , which defines the  $T=0$  values  $P_0^c$  and  $v^c$ . Close enough to this instability point,  $3V'/a + V''$  is proportional to  $P - P_0^c$  and to lowest order all other coefficients can be considered to be constants. Then generically, the energy can be written as

$$e_0 = \sin^2\left(\frac{\sqrt{3}ka}{4}\right) [A(P - P^c) \delta_l^2 + B \delta_t^2] + \sin^3\left(\frac{\sqrt{3}ka}{4}\right) [D \delta_l^2 \delta_t]. \quad (4)$$

The existence of a  $\delta_l^2 \delta_t$  term is very important, as it indicates that for  $P$  slightly larger than  $P_0^c$  there is a saddle point (actually two, one with positive and the other with negative  $\delta_t$ ) close to  $\delta_l = 0$ ,  $\delta_t = 0$ , than can be determined requiring stationarity of Eq. (4). The result is

$$\delta_l^S = \pm \frac{\sqrt{2AB(P - P^c)}}{D \sin\left(\frac{\sqrt{3}ka}{4}\right)},$$

$$\delta_t^S = \frac{A(P - P^c)}{D \sin\left(\frac{\sqrt{3}ka}{4}\right)}, \quad (5)$$

where the superscript indicates the values at the saddle. If the system reaches this saddle it can escape from the local minimum at the origin, namely, the system destabilizes. The energy barrier  $h$  for this process is obtained by reinserting Eq. (5) into Eq. (4). The result is

$$h = \frac{4A^2B(P - P^c)^2}{D^2}. \quad (6)$$

Note that the barrier is exactly the same whatever the wave vector of the phonon considered (this is no longer true if further neighbors interactions are included, but the possibility to escape through the jump of a barrier remains). The instability mechanism is then driven by the  $\delta_l^2 \delta_t$  term in the energy, what implies a not trivial coupling of transverse modes (those actually having vanishing frequency) and longitudinal ones. At finite temperatures the barrier  $h$  can be surmounted. Nucleation theory tells that escape time  $\tau$  is proportional to  $\exp(h/T)$ . Assuming the preexponential factor is a constant  $\tau_0$  (this is certainly not true, but dependences on  $\tau_0$  become weak in the final result) we obtain that if a time  $t_0$

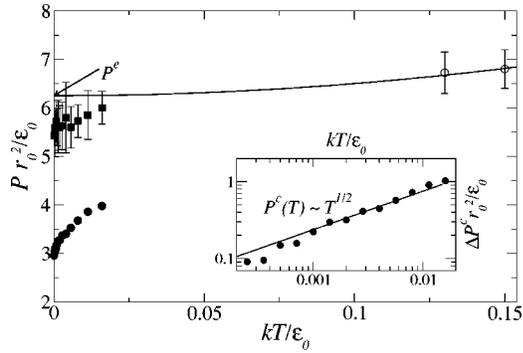


FIG. 5. Evolution of  $P^c$  (full circles) and  $P^*$  (full squares) as a function of temperature (bars in  $P^*$  indicate the whole range in which transformation occurs). The inset shows in a log-log plot that  $\Delta P^c = P^c(T) - P^c(T=0)$  increases as  $T^{1/2}$  at finite temperatures. The extrapolation of the melting line (from calculations at higher temperatures, two points are seen) is indicated by the dashed line. It goes to  $P^e$  at  $T=0$ .

is given, the system will overcome the energy barrier if  $t_0 \geq \tau$ , and from here we obtain the formula for the temperature necessary to escape a given barrier, namely,

$$T > h \ln^{-1}(t_0 / \tau_0). \quad (7)$$

For practical purposes the logarithmic factor can be usually taken to be approximately 0.1. As  $h \sim (P - P_0^c)^2$ , we obtain that the critical pressure  $P^c(T)$  increases as  $T^{1/2}$  at finite temperatures, a behavior that is well reproduced in the simulations (Fig. 5). The  $P^c(T)$  line is then the pressure amorphization line for a sample without defects, and can be properly interpreted as the “mechanical melting” line of this system. In the absence of defects, it marks the limit on which the crystalline phase destabilizes (purely mechanically at  $T=0$ , and by a thermally activated process at  $T \neq 0$ ). Note, however, that the elastic constants of the system, in particular the shear modulus  $\mu$ , do not extrapolate to zero at  $P^c(T)$ , except at  $T=0$  (see Fig. 6). In fact, the numerical evaluation by means of fluctuation formulas<sup>18,24</sup> shows that the effect of temperature in the elastic constants is very small. At  $T=0$

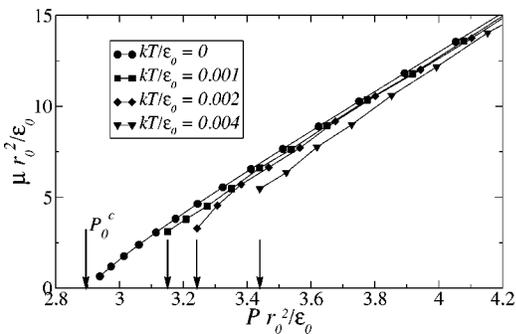


FIG. 6. Variation of the stress dependent shear modulus  $\mu$  with pressure at different temperatures. For  $T=0$ ,  $\mu$  vanishes at the critical pressure  $P^c(T=0)$ , but for increasing temperatures  $\mu$  does not tend to zero at the corresponding critical pressure  $P^c(T)$  (indicated by the arrows), showing that the transition is not macroscopically captured by the elastic constants.

the stress dependent shear modulus  $\mu$  vanishes at  $P_0^c$ , as we already knew from the phonon dispersion relation, but at  $T \neq 0$  extrapolation is consistent with a vanishing of  $\mu$  very close to  $P_0^c$ , and certainly not at  $P^c(T)$ . The thermally activated process that at finite temperatures leads to the instability at the higher pressure  $P^c(T)$  is a rare event that it is enough to occur once to completely destabilize the system. This process is not captured in the value of the elastic constants.

The results presented above correspond to samples without defects. For defective samples the amorphization line  $P^*(T)$  is only weakly dependent on  $T$ . In addition, it is very close to the extrapolation of the melting line obtained from simulations at higher temperatures (see Fig. 5).  $P^*(T)$  and  $P^c(T)$  are well different from each other, particularly at very low temperatures. Defects are responsible for this difference, and provide the link between the “mechanical” and “thermodynamical” scenarios for pressure amorphization.

## VI. DISCUSSION AND CONCLUSIONS

The experimental observation that in some materials PIA occurs roughly along the extrapolated melting line has motivated the suggestion<sup>2</sup> that “thermodynamic melting” is the underlying driving force for amorphization. Our results show that amorphization at zero temperature is always a phenomenon related to mechanical instabilities. In perfect lattices, mechanical instabilities reflect necessarily in the phonon spectrum of the material, and amorphization can be easily related to a mechanical process. However, for defective lattices, the mechanical instability that triggers amorphization is associated with localized vibrational modes around defects, and this instability occurs typically without any noticeable signature in the phonon spectrum, i.e., the mechanical nature of the process is more subtle. We emphasize that a single defect is sufficient to trigger the amorphization of a whole macroscopic sample.<sup>23</sup>

How this first instability is able to transform the highly ordered original lattice into a fully amorphous configuration is not easy to understand, specially considering that this evolution is fully deterministic from a mechanical point of view, and can be described as the steepest descendant path of the configuration point of the system onto its energy landscape. A deep understanding of this process will surely shed light also onto the very definition of what an amorphous material is, typically characterized by what it lacks, instead of what it possesses. Here we make only the following considerations.<sup>8</sup> The first instability of the lattice (at  $T=0$ ) can always be described as the vanishing of the frequency of one of the normal modes of the system. This normal mode may be a phonon for a perfect lattice or a localized mode for a defective lattice. When the coordinate characterizing the destabilizing mode grows, it typically goes beyond the applicability limit of the linear theory, and the whole mechanical stability of the system has to be reanalyzed. Then, although the analysis of Sec. V is appropriate to determine the barrier for the system to scape from its metastable equilibrium, it cannot be continued when the system actually overcomes the saddle without including the interaction with other modes. For in-

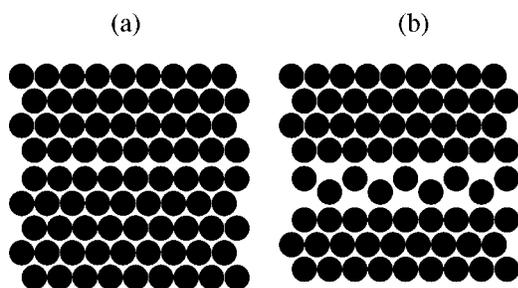


FIG. 7. The first steps in the cascade process from a perfect to an amorphous lattice: The original perfect lattice becomes unstable when the energy of a phonon vanishes, and this drives a transition to a sample with a shuffle (a). This configuration however is not stable and spontaneously evolves toward the configuration in (b). But this is not stable yet, and the process continues until equilibrium is reached when a finite fraction of the system is transformed [compare with Figs. 3(a) and 3(b)].

stance, it occurs in our system that once the coordinate of the unstable phonon starts to increase, it couples to other phonons and the result is that a shuffle of two pieces of the material develops. In this way, the instability generated by an extended object (the unstable phonon) produced a localized (one-dimensional) defect on the lattice.<sup>25</sup> But it turns out that, in the present case, the new configuration of the lattice is not stable either, and a new distortion occurs spatially close to the region already distorted (see Fig. 7). In the present case of amorphization, it is likely that a cascade of these processes occurs, which leads to an amorphous structure. The spatially localized nature of the process reflects in the fact that for partially transformed samples, transformed and untransformed regions are spatially separated, as seen in Fig. 3. We however emphasize that another possibility could be that after the first phonon instability and the first shuffle, the system reaches a mechanically stable configuration, then further increases of the volume will produce independent shuffles in the samples, along the three directions related by

symmetry. If this is the case, then this single phonon will drive a transformation (which has the character of a martensitic transformation) to a new (poly)crystalline phase. This and other intermediate cases, which in our model occur for different parameters, will be discussed separately.

In summary, we have arrived at a picture of the mechanism of PIA, reconciling mechanical and thermodynamical melting in a unifying scheme. The present model exhibits a one-step crystal-to-amorphous transition to a truly amorphous state that does not differ from the disordered structure obtained by quenching from the melt. Once the transformation is triggered, it is followed by a cascade process that produces the amorphous structure. For a perfect lattice, and vanishingly small temperatures, the transformation takes place through a shear phonon instability at a pressure far apart the thermodynamical equilibrium pressure. For defective lattices, the mechanical instability shows up by the destabilization of localized vibrational modes, close to the thermodynamical equilibrium pressure. In either case, the transformation is always triggered by mechanical instabilities. Temperature can produce the transition to occur before the mechanical stability limit is reached, due to a process of thermally activated jump over a barrier. In real samples with appropriate defects, experimental transition pressures will be seen close to the extrapolation of the melting line. These facts reconcile different claims in the literature regarding the nature of the PIA of materials. We remark that, although we presented results for a two-dimensional model system, preliminary results in three-dimensional samples qualitatively agree with the phenomenology stated above, and will be presented elsewhere. We finally stress that these considerations have potential applications in the study of melting mechanisms of crystalline materials.<sup>26</sup>

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- <sup>20</sup>A slight systematic decrease of pressure in this range can be ascribed to energy dissipation within the disordered phase. S. Bustingorry and E.A. Jagla (unpublished).
- <sup>21</sup>The upward shift of the curve for a polycrystalline sample at large  $P$  in Fig. 1 is a consequence of the fact that grain boundaries occupy a finite fraction of the system. For a system with much larger crystallites, this shift is negligible and the large  $P$  part of the  $P$ - $v$  curve coincides with that of a monocrystalline system.
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