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Unifying two criteria of Born: Elastic instability and melting of homogeneous crystals

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Abstract

The criteria formulated by M. Born for the onset of melting (1939) and lattice stability (1940) are re-examined on the basis of more general considerations of elastic instabilities. With the aid of molecular dynamics simulations, we show that (1) Born's stability criteria are valid only in the case of zero external stress, and (2) his thermoelastic melting criterion, with some modification, is valid for the homogeneous process (mechanical melting or upper limit of superheating) which can occur when the free-energy-based heterogeneous process (melting by nucleation and growth) is kinetically suppressed. These and other related recent results on crack nucleation, pressure-induced polymorphic transition and amorphization emphasize the fundamental role of elastic instabilities in triggering unstable structural responses of homogeneous crystals.

1. Introduction

In 1939, Born set forth a simple criterion for crystal melting in which he postulated that melting should be accompanied by the loss of shear rigidity [1]. Expressed in terms of the shear modulus G for a cubic crystal, the melting point T_m is that temperature at which

$$G(T_m) = 0 \,. \tag{1}$$

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A year later he extended this concept to lattice deformation [2] by deriving the well-known conditions for stability, valid for cubic crystals,

$$C_{11}+2C_{12}>0, \qquad C_{11}-C_{12}>0, \qquad C_{44}>0\,, \tag{2}$$

where C_{11}, C_{12}, and $C_{44}(=G)$ are the three distinct elastic constants (in Voigt notation).

The purpose of this discussion, contributed on the occasion of the 60th birthday celebration of W.G. Hoover, is to examine the basis on which Born's two criteria may be considered to be valid. Shortly after (1) was proposed, experimental results obtained on NaCl single crystals were presented showing that the two shear constants, C_{44} and $(C_{11}-C_{12})$, have *nonzero* values at the melting point [3]. Moreover, it was not clear how (1) could explain the presence of latent heat and volume change associated with a first-order thermodynamic phase transition. The current status with regard to the stability criteria (2) seems to be more ambiguous, neither stringent tests have been performed nor qualifications discussed concerning its possible limitations. The challenge of ascertaining whether such criteria are capable of predicting the actual onset of an instability is considerable. The difficulty, on the theoretical side, has been that stability analyses have been formulated in different ways [4], and few explicit calculations of elastic constants at the critical condition have been reported to make an unambiguous test possible. On the experimental side, competing effects frequently render the determination of the triggering instability uncertain. It is fair to surmise that while the shortcomings of (1) are well known, the predictive value of (2) has gone unscrutinized.

The approach we follow is to begin with the results of a corresponding set of elastic stability criteria for homogeneous lattices under arbitrary but uniform external load which we have recently derived [5,6]. Combining the new criteria, which may be considered as generalizations of (2), with direct molecular dynamics simulation of structural response of a perfect crystal to pure dilatation, we show that (2) is not valid except for vanishing external stress. Instead of testing (1) using experimental data, we propose next to analyze and simulate the process of isobaric heating to melting of a perfect crystal without surfaces or defects of any kind, *since for this case* (2) *would be applicable if the heating were performed at zero pressure.* As we will see below, simulation shows that at the onset of melting one of the shear constants indeed vanishes, although it is $(C_{11}-C_{12})$ rather than C_{44}. Moreover, the observed melting temperature, or equivalently critical lattice strain, is in remarkable agreement with the predictions based on the new criteria. Since the system we analyze and simulate is a defect- and surface-free lattice, the melting that is being observed here does not refer to the free-energy-based heterogeneous process involving nucleation and growth. That process, if not kinetically suppressed in simulation by virtue of elimination of all defects and surfaces, would set in at a lower temperature (the physical or actual melting point) and preclude the melting process associated with an elastic instability. Allowing for these modifications, we feel with some degree of justification that Born's concept of thermoelastic mechanism of melting, which should be applied only to mechanical and not thermodynamic melting, has been reconciled with his lattice stability criteria, which now should be understood to require generalization whenever the external stress is nonzero.

2. Elastic stability criteria at finite load

Recently, we have derived the criteria for elastic stability of a homogenous crystal under conditions of arbitrary external load [5,6]. The results are obtained systematically by formulating a Gibbs integral which combines the change in the Helmholtz free energy and the external work done during deformation; in this way one can see clearly that Born's derivation amounts to neglecting the contribution from the external work. It therefore follows that predictions of critical load in general will depend on the nature of the applied stress, in contrast to the criteria (2) which involve only the elastic constants. On the other hand, it is useful to regard the new criteria as generalizations of (2) in which the elastic constant tensor **C** is replaced by an elastic stiffness tensor **B** [7],

$$\mathbf{B} = \mathbf{C} + \Lambda\,, \tag{3}$$

where the tensor Λ depends only on the applied stress $\boldsymbol{\sigma}$. For cubic crystals and in the case of hydrostatic loading, $\boldsymbol{\sigma} = -P\boldsymbol{I}$, where $\boldsymbol{I}$ is the unit tensor and $P > 0$ for compression, the generalized stability criteria have the form [5,6,8]

$$C_{11} + 2C_{12} + P > 0, \qquad C_{11} - C_{12} - 2P > 0, \qquad C_{44} - P > 0\,. \tag{4}$$

Even though (2) and (4) have very similar appearance, the presence of the external stress obviously can alter the competition between the different modes of instability to the extent that (2) and (4) lead to different predictions, qualitatively and quantitatively.

A simple but conclusive demonstration of the validity of (4) is to consider a closed-packed lattice under pure dilatation ($P < 0$). Fig. 1 shows the variation with lattice strain of the two moduli, $B_T = (C_{11} + 2C_{12})/3$ and $G' = (C_{11} - C_{12})/2$ in the case of Born's criteria (2), and $B_T = (C_{11} + 2C_{12} + P)/3$ and $G' = (C_{11} - C_{12} - 2P)/2$ in the case of the generalized criteria (4). The third modulus, that involving C_{44}, is not shown because it is not a competing mode of instability for this particular loading. These results are obtained by molecular dynamics simulation using an interatomic potential model for fcc Au [9] (details of the potential are of no interest in the present discussion). The simulation cell is cubic and contains $N = 504$ atoms, arranged in an fcc structure with periodic border conditions. Starting with the lattice parameter a set at the equilibrium value a_0 (corresponding to zero pressure and minimum potential energy) and temperature $T = 500$ K, we equilibrate the system at incrementally larger values of a while maintaining constant temperature by velocity rescaling after every time step.

It can be seen in Fig. 1 that one would predict on the basis of (2) that the system would fail by the vanishing of the shear constant G' (known as the Born instability) at a critical strain around 1.025. On the other hand, according to (4) failure is predicted to be caused by the vanishing of the bulk modulus B_T (known as the spinodal instability) at a critical strain (extrapolated) of 1.059. To see which prediction is correct, we have run the simulations up to the point of failure by dilatation. What was observed was that at a strain of 1.053 the system responded abruptly by a sudden release of internal stress with a corresponding lowering of the enthalpy, both being consequences of lattice

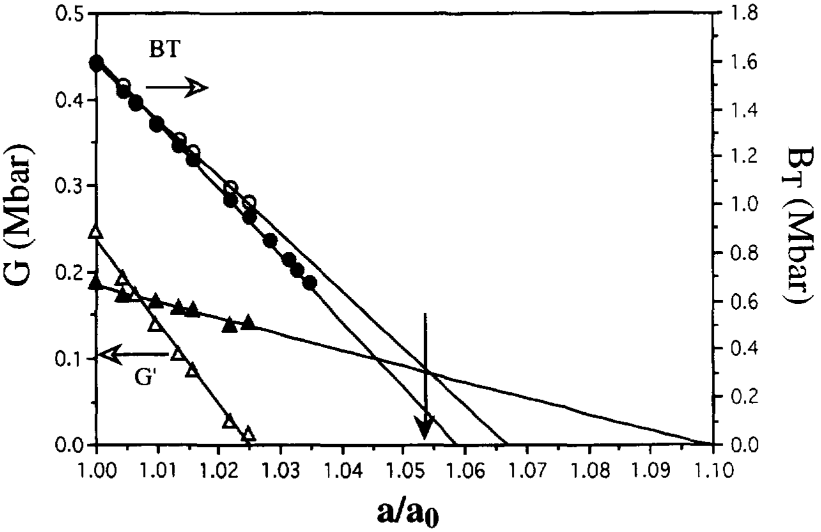

Fig. 1. Variation of elastic moduli B_T and G' with lattice strain a/a_0 in an fcc lattice under pure dilatation, where a is the lattice parameter at temperature T and a_0 is the value at $T = 0$ K. Open and closed symbols denote results from (2) and (4), respectively. Solid lines are linear extrapolations to give critical values for each instability. Arrow indicates the critical strain observed by direct simulation.

decohesion in the form of cavitation. Thus, the validity of the generalized criteria (4) is clearly established. It also follows from our finding that Born's criteria (2) should not be used to determine the theoretical strength of a crystal [10,11].

3. Isobaric heating to melting at $P = 0$

Given that the generalized criteria (4) obviously reduce to Born's results in the limit of zero load, then (2) is a valid description of lattice stability in the special case of a cubic crystal being heated to melting at zero pressure. This process is of interest because it can be studied by molecular dynamics simulation in a straightforward manner and the results would provide a clean test of the melting hypothesis stated in (1). For the simulation we use the same model already described except that the simulation cell now contains $N = 1372$ atoms and periodic border conditions are imposed in the manner of Parrinello and Rahman [12]. A series of isobaric-isothermal simulations (with velocity rescaling) are carried out at various temperatures. At each temperature the atomic trajectories generated are used to compute the elastic constants at the current state using appropriate fluctuation formulas [13].

Fig. 2 shows the variation with temperature of the lattice strain a/a_0 along the three cubic symmetry directions. The slight increase with increasing temperature merely indicates the lattice is expanding normally with temperature, and the results for the three directions are the same as they should be. At $T = 1350$ K one sees a sharp bifurcation

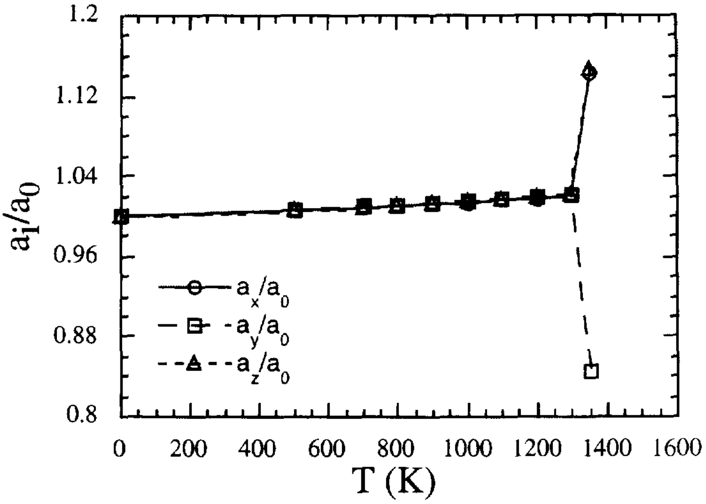

Fig. 2. Variation of lattice strain a/a_0 with temperature along three Cartesian directions in the simulation of an isobaric ($P=0$) heating process.

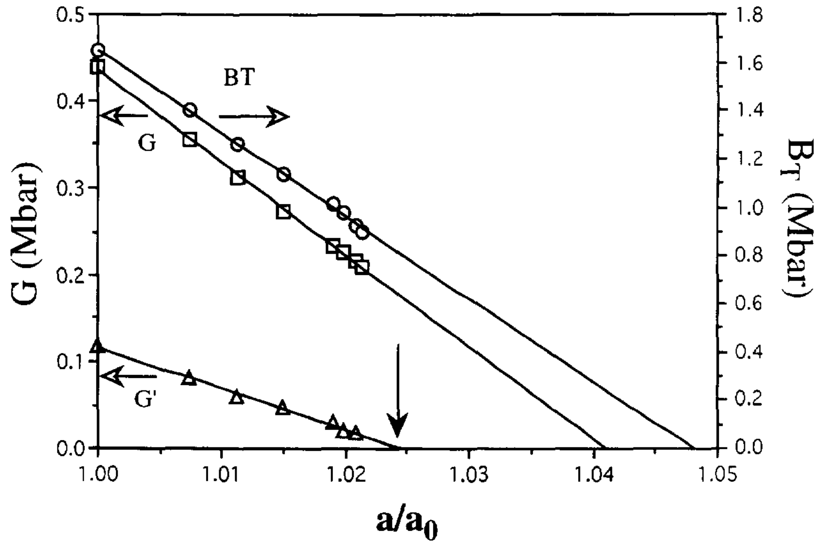

Fig. 3. Variation of B_T, G, and G' with lattice strain a/a_0 in the isobaric ($P=0$) heating process.

in the lattice dimension where the system elongates in two directions and contracts in the third. This is a clear sign of symmetry change, from cubic to tetragonal. To see whether the simulation results are in agreement with the prediction based on (2), we show in Fig. 3 the variation of the elastic moduli with temperature, or equivalently with lattice strain in view of the one-to-one correspondence shown in Fig. 2; the three moduli of interest are the bulk modulus $B_T=(C_{11}+2C_{12})/3$, tetragonal shear

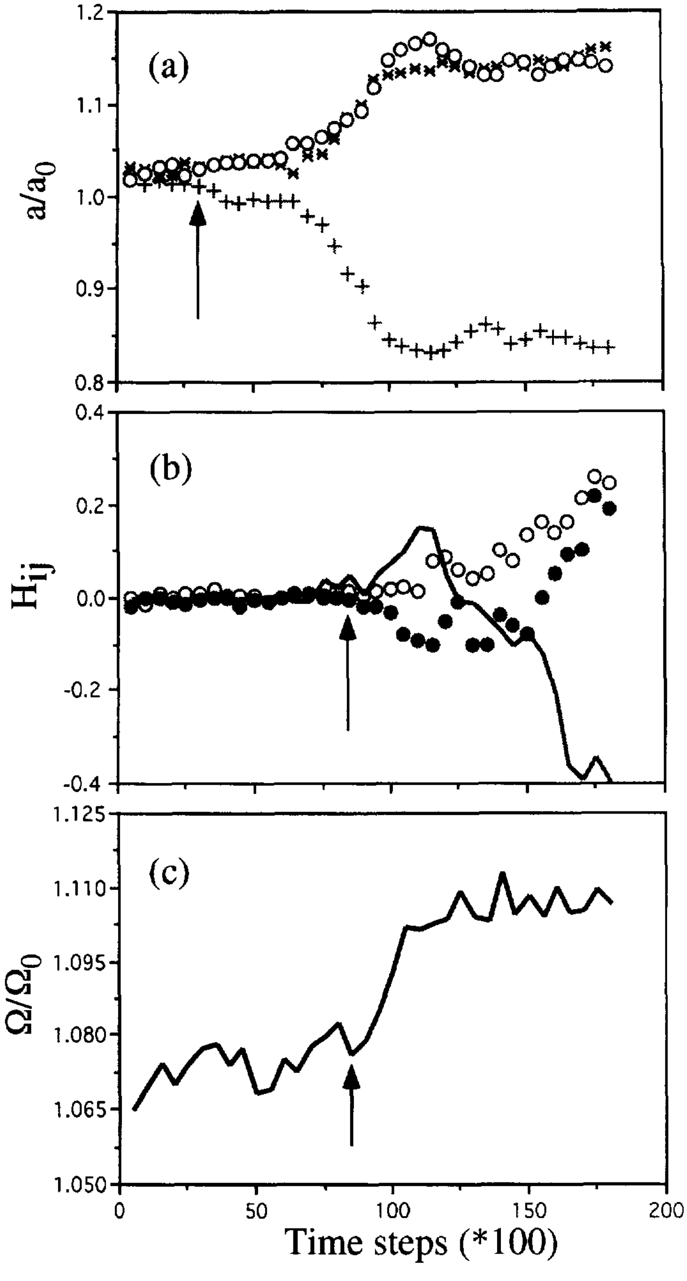

Fig. 4. Time responses of (a) lattice strain along three initially cubic directions, (b) off-diagonal elements of the cell matrix $H, H_{12}, H_{13}, H_{23}$, (c) normalized system volume. Arrows indicate the onset of Born instability in (a), shear instability in (b), and lattice decohesion in (c).

modulus $G' = (C_{11} - C_{12})/2$, and rhombohedral shear modulus $G = C_{44}$. On the basis of Fig. 3 one would predict the incipient instability to be the vanishing of G', occurring at the theoretical or predicted lattice strain of $(a/a_0)_{th} = 1.025$. From the simulation at $T = 1350$ the observed strain is $(a/a_0)_{obs} = 1.024$. Thus, we can conclude that the vanishing of tetragonal shear is responsible for the structural behavior.

For more details of the system behavior at $T = 1350$ K we show in Fig. 4 the time evolution of the lattice strain, the off-diagonal elements of the cell matrix H, and the system volume. It is clear from Fig. 4(a) that the onset of the $G' = 0$ instability triggers both a shear (cf. Fig. 4(b)) and a lattice decohesion (Fig. 4(c)), the latter providing the characteristic volume expansion associated with melting. This sequence of behavior, which has not been recognized previously, implies that the signature of a first-order transition, namely, latent volume change, is not necessarily associated with the incipient instability. Our results also provide evidence supporting Born's picture of melting being driven by a thermoelastic instability [1], recently reinterpreted by Boyer to involve a combination of loss of shear rigidity and vanishing of the compressibility [14]. Moreover, it is essential to recognize that this thermoelastic mechanism can only be applied to the process of mechanical instability (homogeneous melting) of a crystal lattice without defects, and not to the coexistence of solid and liquid phases at a specific temperature (heterogeneous melting) [15,16].

4. Implications and perspective

It is perhaps worthwhile restating what the combination of stability analysis and molecular dynamics simulation has contributed to the understanding of Born's two criteria. That the stability criteria (2) are valid only under vanishing external load is quite clear, both theoretically and in simulation studies. Since it is often advantageous to be able to predict a priori the critical stress or strain for the onset of instability, the availability of (4) could facilitate more quantitative analysis of simulation results. Although our results for an fcc lattice with metallic interactions show that homogeneous melting is triggered by $G' = 0$ and not (1), nevertheless, they constitute clear-cut evidence that a shear instability is responsible for *initiating* the transition. The fact that simulation reveals a sequence of responses apparently linked to the competing modes of instabilities (cf. Fig. 4) implies that it is no longer necessary to explain all the known characteristic features of melting on the basis of the vanishing of a single modulus. In other words, independent of whether $G' = 0$ is the initiating mechanism, the system will in any event undergo volume change and latent heat release in sufficiently rapid order (on the time scale of physical observation) that these processes are all identified as part of the melting phenomenon. Generalizing this observation further, one may entertain the notion of a hierarchy of interrelated stability catastrophes of different origins, elastic, thermodynamic, vibrational, and entropic [17].

Finally, it may be mentioned that in several recent studies, the stability criteria (4) have led to precise identifications of the elastic instability triggering a particular structural transition. In hydrostatic compression of Si, the instability which causes the transition from diamond cubic to β-tin structure is the vanishing of $G'(P) = (C_{11} - C_{12} - 2P)/2$ [18]. In contrast, compression of crystalline SiC in the zinc blende structure results in an amorphization transition associated with the vanishing of $G(P) = C_{44} - P$ [19]. For behavior under tension, crack nucleation in SiC [20] and cavitation in a model binary intermetallic [21], both triggered by the spinodal instability, vanishing of $B_T(P) = (C_{11} + 2C_{12} + P)/3$, are results which are analogous to the observations reported here. Notice also that in the present study a crossover from spinodal to shear instability can take place at sufficiently high temperature [6].

Acknowledgements

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References

[1] M. Born, J. Chem. Phys. 7 (1939) 591.
[2] M. Born, Proc. Cambridge Philos. Soc. 36 (1940) 160.
[3] L. Hunter, S. Siegel, Phys. Rev. 61 (1942) 84.
[4] R. Hill, Math. Proc. Camb. Phil. Soc. 77 (1975) 225; R. Hill, F. Milstein, Phys. Rev. B 15 (1977) 3087.
[5] J. Wang, S. Yip, S.R. Phillpot, D. Wolf, Phys. Rev. Lett. 71 (1993) 4182.
[6] J. Wang, J. Li, S. Yip, S. Phillpot, D. Wolf, Phys. Rev. B 52 (1995) 12627.
[7] D.C. Wallace, Thermodynamics of Crystals, Wiley, New York, 1972.
[8] T.H.K. Barrons, M.L. Klein, Proc. Phys. Soc. 85 (1965) 523; W.G. Hoover, A.C. Holt, D.R. Squire, Physica 44 (1969) 437.
[9] S.M. Foiles, M.I. Baskes, M.S. Daw, Phys. Rev. B 33 (1986) 7983.
[10] M. Born, R. Furth, Proc. Cambridge Philos. Soc. 36 (1940) 454.
[11] N.H. Macmillan, A. Kelly, Proc. R. Soc. London A 330 (1972) 291, 309.
[12] M. Parrinello, A. Rahman, J. Appl. Phys. 52 (1981) 7182.
[13] J.R. Ray, Comput. Phys. Rep. 8 (1988) 109.
[14] L.L. Boyer, Phase Transitions 5 (1985) 1.
[15] J.F. Lutsko, D. Wolf, S.R. Phillpot, S. Yip, Phys. Rev. B 40 (1989) 2841.
[16] D. Wolf, P.R. Okamoto, S. Yip, J.F. Lutsko, M. Kluge, J. Mater. Res. 5 (1990) 286.
[17] J.L. Tallon, Nature (London) 342 (1989) 658.
[18] K. Mizushima, S. Yip, E. Kaxiras, Phys. Rev. B 50 (1994) 14952.
[19] M. Tang, S. Yip, Phys. Rev. Lett. 75 (1995) 2738.
[20] M. Tang, S. Yip, J. Appl. Phys. 76 (1994) 2719.
[21] F. Cleri, J. Wang, S. Yip, J. Appl. Phys. 77 (1995) 1449.