Local Analysis of Structural Instability in Stressed Lattices: Crack Nucleation in a Covalent Solid

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For the local analysis of structural instability, a site-dependent measure of local contribution to a global mode is introduced which is decomposed into contributions from individual interatomic bonds. Since this measure incorporates both spatial and dynamical information, the method provides insight into the temporal evolution of the lattice instability. Using this method to study lattice decohesion under pure dilation, we find the crack nucleation process to consist of the onset of instabilities at several distinct sites, followed by coalescence of local instabilities which triggers the bond rupturing along a plane. [S0031-9007(97)04628-0]

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Atomistic simulations of lattice deformation phenomena, such as recent large-scale molecular dynamics (MD) studies of fracture [1–4], provide an invaluable collection of mechanistic details on the role of local processes in triggering structural and dynamical response of the entire system. Extracting physical insight from the data generally requires the identification of relevant saddle point configurations, followed by painstaking analysis of local atomic coordinates. In principle, one can also characterize the onset of instability through the softening of normal modes. At present there exists no systematic method which exploits simultaneously the spatial (configurational) and dynamical (vibrational) information to locate and elucidate the critical atomic-level events.

In this Letter we present a novel and simple approach based on the local analysis of soft modes for investigating atomic-level mechanisms in lattice deformation. While it stems from the basic idea of local density of states [5], the method focuses on the soft modes most closely associated with the lattice instability. A parameter, to be called the local participation fraction (LPF), is used to measure the fractional atomic (local) contribution to a given vibrational mode. This quantity is then decomposed into "*dynamic coupling coefficients* ($\gamma_{i\alpha,j\beta}$)" associated with individual bonds between specific pairs of atoms. These dynamic coupling coefficients have the property that a negative value identifies the specific bond which is unstable. In terms of LPF and $\gamma_{i\alpha,j\beta}$, one can conveniently define a site-specific measure of degree of instability D_i, and a criterion for bond breaking which is specific to atom pairs. Both quantities can be computed using instantaneous atomic coordinates and the eigendisplacements at the sites in question; together they provide time-dependent information which has not been recognized heretofore.

In lattice dynamics, the eigenfrequencies of the dynamical matrix are global quantities. In order to locate where the lattice instabilities originate, a local analysis of the soft modes must be carried out. The squared eigenfrequency ω_λ^2 is the eigenvalue of the equation

$$\underline{H}C_\lambda = \omega_\lambda^2 C_\lambda , \tag{1}$$

where $H_{i\alpha,j\beta} = \Phi_{i\alpha,j\beta}/\sqrt{m_i m_j}$ and $c_{i\alpha,\lambda} = \sqrt{m_i}\, u_{i\alpha,\lambda}$, with Φ being the force constant matrix, $u_{i\lambda}$ the eigendisplacement, m the mass, i (j) referring to the site, and α (β) to the x, y, or z direction. From Eq. (1), one may write

$$\omega_\lambda^2 = \sum_{i\alpha,j\beta} c_{i\alpha,\lambda} c_{j\beta,\lambda} H_{i\alpha,j\beta} = \sum_{i\alpha} \omega_{i\alpha,\lambda}^2 , \tag{2}$$

where

$$\omega_{i\alpha,\lambda}^2 = \sum_{j\beta} c_{i\alpha,\lambda} c_{j\beta,\lambda} H_{i\alpha,j\beta} . \tag{3}$$

An examination of Eq. (2) suggests that $\omega_{i\alpha,\lambda}^2$ is the local contribution at the site i along the direction α to the squared eigenfrequency ω_λ^2. From Eq. (3), it can be seen that this local contribution depends on the force constants between the locality (i) and its neighbors and the eigendisplacements at the locality and at its neighbors. These are the quantities describing the status of the local environment. Therefore, $\omega_{i\alpha,\lambda}^2$ is the logical candidate for carrying out the local analysis of the soft modes.

Instead of using $\omega_{i\alpha,\lambda}^2$ directly as the local probe of the properties of the system under consideration, we choose to consider the quantity $\Delta_{i\alpha,\lambda}$ defined as

$$\Delta_{i\alpha,\lambda} = \frac{\omega_{i\alpha,\lambda}^2}{\omega_\lambda^2} = \sum_{j\beta} c_{i\alpha,\lambda} c_{j\beta,\lambda} \frac{H_{i\alpha,j\beta}}{\omega_\lambda^2} . \tag{4}$$

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We refer to this quantity as the local participation fraction (LPF) as it quantifies the local fractional contribution to the global dynamics for a certain vibrational mode. Alternatively, it can be seen from Eq. (1) that $\Delta_{i\alpha,\lambda}$ is equivalent to the participation ratio $|C_{i\alpha,\lambda}|^2$. However, if LPF is expressed in the form as given in Eq. (4), the contribution to a given site due to its neighbors is explicit. The advantage of $\Delta_{i\alpha,\lambda}$ over $\omega^2_{i\alpha,\lambda}$ as the tool for probing the local properties includes (i) $\Delta_{i\alpha,\lambda}$ is normalized by ω^2_λ; therefore, a meaningful comparison can be made between $\Delta_{i\alpha,\lambda}$ for different eigenmode λ's to gauge the contribution made by the locality (i) to the vibrational modes under consideration; (ii) the existence of two sum rules for $\Delta_{i\alpha,\lambda}$ facilitates a systematic check on the contributions by different localities to a particular vibrational mode or how a certain locality contributes to various vibrational modes. These sum rules can be stated as $\sum_{i\alpha} \Delta_{i\alpha,\lambda} = 1$ and $\sum_\lambda \Delta_{i\alpha,\lambda} = 1$. Thus, by examining $\Delta_{i\alpha,\lambda}$ at various sites and along different directions for a given vibrational mode, one can readily identify the region or regions which contribute the most to that vibrational mode. In the meantime, the variation of $\Delta_{i\alpha,\lambda}$ as a function of λ would easily pinpoint those vibrational modes which are most affected by the environment associated with the locality in question. Therefore, an illuminating local analysis of the vibrational properties can be readily carried out by examining $\Delta_{i\alpha,\lambda}$ either as a function of $i\alpha$ for a given eigenmode λ or as a function of eigenmodes λ for a certain $i\alpha$. Equation (4) can be rewritten as

$$\Delta_{i\alpha,\lambda} = \sum_{j\beta}{}' (u_{i\alpha,\lambda} u_{j\beta,\lambda} - u_{i\alpha,\lambda} u_{i\beta,\lambda}) \frac{\Phi_{i\alpha,j\beta}}{\omega^2_\lambda} \quad (5)$$

using the relation $\Phi_{i\alpha,i\beta} = -\sum_j' \Phi_{i\alpha,j\beta}$, where prime indicates that $j = i$ is excluded in the summation. In this form, $\Delta_{i\alpha,\lambda}$ is expressed as the sum of weighted force constants, where the summation is over all neighboring pairs between a particular locality (i) along the direction (α) in question and all neighboring sites and along all directions. The weighting factor is composed of the eigendisplacements at the sites under consideration. The force constant $\Phi_{i\alpha,j\beta}$ is a measure of the coupling between vibrations at site i along direction α to that at site j along direction β. The weighting factor, through its dependence on the product of eigendisplacements at (i,α) and (j,β) relates not only to the participation of the vibrations at sites i and j but also to their relative phase. Hence the terms in the summation in Eq. (5) give a detailed description of how the couplings between the locality (i) under consideration and all its neighbors contribute to the local vibrational dynamics.

A necessary precursor to the bond rupture between a pair of atoms is the onset of the instability between the elastic coupling of the atoms. This is usually signaled by the appearance of the soft modes (negative squared eigenfrequencies) associated with the coupled vibrations of the atomic pairs. An analysis based on Eq. (5) can then be put to use to set up a quantitative measure for the onset of the bond breaking.

From Eq. (5), it can be seen that the quantity $\gamma_{i\alpha,j\beta;\lambda}$ defined by

$$\gamma_{i\alpha,j\beta;\lambda} = (u_{i\alpha,\lambda} u_{j\beta,\lambda} - u_{i\alpha,\lambda} u_{i\beta,\lambda}) \frac{\Phi_{i\alpha,j\beta}}{|\omega^2_\lambda|} \quad (6)$$

is a measure of the extent of the coupling of the vibration at (j,β) to that at (i,α) in the mode λ. This becomes apparent when Eq. (3) is rewritten using Eqs. (4)–(6) as

$$\begin{aligned} \omega^2_{i\alpha,\lambda} &= \sum_{j\beta}{}' (u_{i\alpha,\lambda} u_{j\beta,\lambda} - u_{i\alpha,\lambda} u_{i\beta,\lambda}) \Phi_{i\alpha,j\beta} \\ &= \sum_{j\beta}{}' \gamma_{i\alpha,j\beta;\lambda} |\omega^2_\lambda| . \end{aligned} \quad (7)$$

Ordinarily, the dynamic coupling coefficient $\gamma_{i\alpha,j\beta;\lambda}$ will contribute positively if the local eigenfrequency $\omega^2_{i\alpha,\lambda}$ is positive. However, if the coupling between $i\alpha$ and $j\beta$ becomes dynamically unstable for the mode ω^2_λ, $\gamma_{i\alpha,j\beta;\lambda}$ will be negative. For example, for a soft mode corresponding to a negative squared eigenfrequency ω^2_λ, the local squared eigenfrequency $\omega^2_{i\alpha,\lambda}$ will be negative in the region where the lattice instability has set in. From Eq. (7), the occurrence of the negative local squared eigenfrequency can be traced to the negative contribution by those pairs $(i\alpha,j\beta)$ which result in a negative $\gamma_{i\alpha,j\beta;\lambda}$ coupling. Hence the onset of the dynamical instability of the coupling between the pair $(i\alpha,j\beta)$ for a mode ω^2_λ is signaled by $\gamma_{i\alpha,j\beta;\lambda} \leq 0$. The zero occurs when $\Phi_{i\alpha,j\beta} = 0$, indicating that the pair is completely decoupled.

Finally, to come up with a quantitative measure to determine the onset of the bond rupture between a pair of atoms (i,j), one has to examine the correlation between the vibrations along all the directions at sites i and j for all of the vibrational modes. If $\Phi_{i\alpha,j\beta} \equiv 0$ for all α and β, the vibrations at sites i and j are, of course, entirely uncorrelated. There is therefore no "bonding" between atoms at i and j. But, even for $\Phi_{i\alpha,j\beta} \neq 0$, as long as the negative contribution to those $\gamma_{i\alpha,j\beta;\lambda}$ from the few soft modes overwhelms the positive contribution from the stable modes, it indicates that the coupling $\gamma_{i\alpha,j\beta;\lambda}$ for the stable modes must be insignificant. In this situation, the coupling between the pair (i,j) must be considered as unstable. Based on this scenario, we define a quantity

$$B_{ij} = \tfrac{1}{2} \sum_{\alpha\beta\lambda} (\gamma_{i\alpha,j\beta;\lambda} + \gamma_{j\alpha,i\beta;\lambda}) . \quad (8)$$

The appearance of the second term in Eq. (8) is to assure the symmetry of B_{ij} with respect to the interchange of i and j. In this scheme, if

$$B_{ij} \leq 0, \quad (9)$$

it signifies that the coupling between the atoms at i and j is unstable. Therefore, it gives a quantitative measure of the onset of the bond breaking.

To test the validity of our approach, we have carried out a local analysis of the lattice instability leading to lattice decohesion in a MD study of a model covalent solid β-SiC under hydrostatic tension [6–9]. By following the atomic configurations at successive time steps, one may discern the initial appearance of the crack and the subsequent formation of the crack surfaces based on whether the distances between pairs of neighboring atoms exceed a certain limit. However, such a heuristic criterion sheds no light on the atomic-level mechanisms associated with the lattice decohesion. In our approach, we organize the vast amount of information available from MD simulations in such a way that quantitative measures (e.g., $\Delta_{i\alpha,\lambda}$) based on the local properties (e.g., local force constant matrices, eigendisplacements, etc.) can be formulated to determine the location of the crack nucleation, the prediction of the bond rupture, the formation of the crack surfaces, and the associated impurity modes.

Our MD simulations of β-SiC under a hydrostatic tension were carried out with the modified Tersoff potential [6,10]. Simulations were performed for hydrostatic loading from $\sum = 0$ to 5.575. The system was found to be stable for $\sum$ up to 5.55. At $\sum = 5.575$ (0.37 Mbar), the system becomes unstable as the properties of the system show no sign of convergence for up to 5000 time steps (1 time step $= 1.45 \times 10^{-4}$ ps), indicating that the critical loading lies between 5.55 and 5.575.

Although one may examine $\Delta_{i\alpha,\lambda}$ given by Eq. (4) for each individual soft mode as a function of $i\alpha$ to identify the sites and polarizations where lattice instability is located, we have chosen to organize the information somewhat differently. In our strategy, we first consider a quantity defined by $D_i = \sum_{\alpha,\lambda<0} \Delta_{i\alpha,\lambda}$ where the summation over λ is only for the negative squared eigenfrequencies. This quantity can be used to gauge the overall effect of all of the soft modes at a given site (i). In this sense, it also provides a general measure of the degree of instability at the site i.

We have calculated D_i at all of the sites in the MD cell at various time steps for the case of $\Sigma = 5.575$, where the corresponding MD simulations suggest that lattice instability has set in. In Figs. 1(a)–1(d), we show the location of the ten largest D_i's at time steps 1500, 1900, 2400, and 2900. It can be seen that at time steps 1500 and 1900 the ten largest D_i's are scattered throughout the MD cell. At the time step 2400, these D_i's start to coalesce in the neighborhood of the (111) shuffle plane as indicated in Fig. 1, and, at the time step 2900, most of the ten largest D_i's are concentrated on this particular shuffle plane. Among the sites which exhibit the ten largest D_i's on the shuffle plane, the maximum D_i (the open circle in Fig. 1) first appears on this plane at site 70 and step 1900. This is indicated by an arrow in Fig. 1(b). While the maximum D_i shifts from one site to another during subsequent time steps, all these sites remain on the same (111) shuffle plane. This behavior is reminiscent of observations of local stress accumulations in MD studies of formation and deformation of interfacial junctions [11]. The trend of coalescence of the largest D_i's towards the (111) shuffle plane is seen to continue up to step 2900. The events in this sequence suggest that the nucleation of the crack occurs at site 70 and step 1900. Subsequently, it triggers bond rupturing along the (111) shuffle plane which eventually leads to the formation of two crack surfaces facing each other. It should be noted that the distribution of the locations of the ten largest D_i's follows a fluctuating pattern (see Table I). This, we believe, constitutes evidence suggesting that the process of crack nucleation in a homogeneous medium can have a statistical aspect characteristic of "fluctuation-stabilized stress concentration" [12].

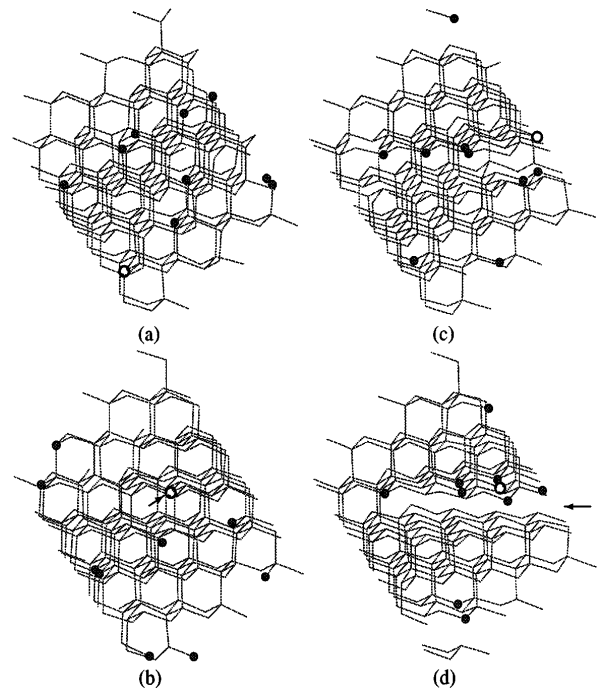

FIG. 1. The locations of the ten largest D_i's in the MD cell (216 atoms) for various time steps are shown. The maximum D_i is indicated by the open circle while the other nine largest D_i's are shown as solid circles. No connecting bond is drawn in the network between two adjacent sites if their separation exceeds 1.3 times that of the nearest neighbor separation. (a) Time step 1500; (b) step 1900; the maximum D_i occurs at the site 70 (pointed by an arrow); (c) step 2400; (d) step 2900; the (111) shuffle plane is indicated by the arrow.

We have also computed B_{ij} between site 70 and its four nearest neighbors [namely, the sites 1, 51, 30, and 69 with the bond (70,69) pointing along the $\langle 111 \rangle$ direction] at step 1900. It was found that $B_{70,69} = -6.56$, $B_{70,1} = 2.44$, $B_{70,51} = 2.60$, and $B_{70,23} = 1.08$. This shows that

TABLE I. Ten largest D_i's at various time steps.

1500	1900	2400	2900
$0.207(D_{180})$	$0.245(D_{70})$	$0.238(D_{30})$	$0.397(D_{50})$
$0.202(D_{68})$	$0.230(D_{158})$	$0.211(D_{168})$	$0.257(D_{28})$
$0.184(D_{176})$	$0.209(D_{36})$	$0.192(D_{12})$	$0.254(D_{16})$
$0.177(D_{102})$	$0.208(D_{156})$	$0.186(D_{16})$	$0.244(D_{182})$
$0.168(D_{42})$	$0.199(D_{88})$	$0.158(D_{80})$	$0.235(D_{72})$
$0.158(D_{6})$	$0.171(D_{4})$	$0.143(D_{29})$	$0.231(D_{8})$
$0.156(D_{130})$	$0.146(D_{58})$	$0.134(D_{164})$	$0.215(D_{200})$
$0.130(D_{141})$	$0.134(D_{170})$	$0.126(D_{18})$	$0.214(D_{70})$
$0.129(D_{48})$	$0.131(D_{132})$	$0.122(D_{26})$	$0.212(D_{14})$
$0.105(D_{2})$	$0.126(D_{162})$	$0.112(D_{70})$	$0.211(D_{146})$

the bond between the pair (70,69) is unstable while those for the pairs (70,1), (70,51), and (70,23) remain stable at that time step. This is to be expected because only one bond needs to be broken for a crack to form in the shuffle plane, whereas three bonds have to be broken for a crack to nucleate in the glide plane. Since the pairing of (70,69) is along the $\langle 111 \rangle$ direction, it can be concluded that the instability of the bonding between the pair (70,69) initiates the crack opening along the (111) shuffle plane. In addition, we have calculated B_{ij} between the sites on the (111) shuffle plane where site 70 resides and their neighbors in the $\langle 111 \rangle$ direction at time steps 1900, 2400, and 2900. The result shows that the number of bond ruptures increases from time step 1900 to 2900, where almost all of the bonds along the $\langle 111 \rangle$ direction are broken. This then suggests that, at the time step 2900, the crack opening is almost complete within the MD cell, leading to the appearance of two crack surfaces.

The present local analysis can also be easily applied to identify impurity modes associated with the deformed lattice, including the surface modes on the crack surfaces. For example, we may define a quantity $S(\lambda) = \sum_{i',\alpha} \Delta_{i'\alpha,\lambda}$, where i' now runs over surface atoms only, as a measure of surface fractional contribution to a particular vibrational mode. Because of the sum rule governing $\Delta_{i\alpha,\lambda}$, if $S(\lambda)$ as a function of λ exhibits a sharp peak for a particular frequency, then the corresponding mode must be a surface mode. We have calculated $S(\lambda)$ as a function of λ for the two planes facing each other across the "broken" bonds along the $\langle 111 \rangle$ direction. Our result shows that there is a superlocalized mode at $\omega^2 = 598.17$ (THz)^2 and a few other impurity modes including three prominent ones at $\omega^2 = 109.96$, 118.07, and 123.48 (THz)^2. We found that the mode at $\omega^2 = 598.17$ (THz)^2 is due to the enhanced bonding (after relaxation) between two adjacent sites across those two planes. The vibrations are practically localized on these two sites. We also found that the other three impurity modes may be construed as the precursors to the surface modes. The details will be given elsewhere.

In summary, a procedure for analyzing the structural and dynamical response of an unstable lattice is developed in terms of atom- and bond-specific measures which are both site and vibrational mode dependent. As long as the dynamical matrix for the system can be calculated, the method is general and equally applicable to disordered solids or lattices with point or extended defects. In the relatively simple process of crack nucleation in a uniformly dilated lattice, our approach gives new insight into the collective response of a lattice which then evolves into preferential bond breaking to form a crack surface, as well as identification of impurity modes associated with the lattice deformation. Such methods of data analysis and interpretation should prove particularly valuable in large-scale molecular dynamics studies of fracture [1].

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