Journal of
Mechanics of Materials and Structures

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Volume 1, Nº 4 *April 2006*

mathematical sciences publishers

JOURNAL OF MECHANICS OF MATERIALS AND STRUCTURES
Vol. 1, No. 4, 2006

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We present an atomic-level criterion for material stability in an atomic system. The criterion draws on the strong ellipticity condition in continuum elasticity theory; however, it is formulated directly in terms of atomic potential without resorting to the continuum concepts. Since the criterion is based on local energetics at an atomic site, we expect it to be applicable to pre-defected systems, provided that the site energy can be reasonably defined. The kinetic implication of the stability condition is also discussed. The application in nanotubes shows that the criterion can capture the tensile limit strain of both perfect and defective nanotubes, and the predictions agree well with the atomistic simulations reported in the literature.

1. Introduction

The loss of elastic stability in an atomic lattice is often a precursor to defect nucleation. For a nonhomogeneous system, lattice instability typically occurs first at "weak spots" where the local deformation has exceeded the stability limit. If loaded further, the lattice may respond by irreversible deformations such as bond breaking, defect nucleation or topological transformation. Thus, local instability provides fundamental information about elastic limit and ultimately the strength of an atomic structure. Present atomistic simulations such as molecular dynamics can provide invaluable details of the mechanical motion of atomic systems. However, to extract physical insight into the system behavior especially the onset of local irreversible motion requires the identification of indicators that characterize the critical state at which the transition occurs.

To motivate the stability condition presented in this work, it is instructive to review relevant concepts in elastic stability at continuum scale. The stability of a finitely deforming elastic body under quasistatic load is typically characterized by the positiveness of the increment of the free energy in reconfigurations from an equilibrium state [Truesdell and Noll 1965]. Stability conditions may be divided into two categories: one is for *structural stability* that characterizes the stability of the entire system including possibly the energetic contribution from the external load;

Keywords: Strong ellipticity condition, acoustic tensor, lattice stability, carbon nanotube.

the other is for *material stability* that concerns the stability of an isolated material element. In nonlinear elasticity, the material stability is characterized by the strong ellipticity condition [Ogden 1997; Ciarlet 1988]. Van Hove [1947] showed that the strong ellipticity condition guarantees the uniqueness of solution for Dirichlet boundary value problems. In the context of stability, the condition precludes the existence of any nonzero reconfiguration that does not alter its boundary. The loss of strong ellipticity, on the other hand, indicates that the stationary acceleration wave [Hill 1962] or locally supported discontinuous bifurcation [Rice 1976] becomes admissible in an initially homogeneous deformation field. The stability governed by the strong ellipticity condition, therefore, corresponds to Gibbs' notion of internal stability that requires a system be stable under arbitrary reconfigurations that leave the boundary unaltered [Gibbs 1993]. The condition is intrinsic to the material since the energetic influence from the external environment is excluded.

The local stability considered in this work can be intuitively understood as material stability in atomic systems. Numerous studies have reported on the elastic stability of crystal lattice. Born and Huang [1954] and others [Hill and Milstein 1977; Wang and Yip 1993; Wang et al. 1995; Morris and Krenn 2000] treated a unit cell as an elastic system, and derived stability conditions for perfect crystals. These criteria are formulated in terms of the local stress and the elasticity tensor; however, they are derived under the assumption that the unit cell deforms homogeneously, which is valid only for simple lattice. The analysis of material stability can be further complicated by the presence of defects. Presently, there is no unified method for local stability in defective systems. Kitamura et al. [2004a; 2004b] proposed to detect the instability by the singularity of the *global* tangent stiffness matrix. The method applies to general systems; however, it is for structural stability and the detected unstable motions include global modes such as elastic buckling. Dmitriev et al. [2004] proposed a scheme of local analysis that considers only atoms in a small region of interest. The method, strictly speaking, is not of material stability analysis. Yashiro and Tomita [2001] used Wang's criteria [Wang and Yip 1993; Wang et al. 1995], which are for defect-free simple lattice, to predict the material stability in defective system. The results showed a reasonable correlation with molecular dynamics simulations, however, the theoretical basis remains unclear.

In a series of papers, Li and others [Li et al. 2002; Van Vliet et al. 2003; Zhu et al. 2004; Li et al. 2004] have proposed a local condition (called Λ criterion therein) for detecting the nucleation of point defect in perfect crystals. The criterion is based on the strong ellipticity condition, but evaluated using the stress and elasticity tensor derived from the atomic description. Li and others [Li et al. 2002; Van Vliet et al. 2003] speculated that the loss of strong ellipticity indicates the admissibility of nonhomogeneous bifurcation modes, which could occur at atomic spacing and result in a single dislocation or microcrack. While the exact nature

of the localized singularity remains debatable, this line of thinking suggests that the atomistic displacement singularity and the continuum scale strain localization may be analyzed in the same theoretical framework. A similar approach has been applied to predict the strain-localization and crack initiation in atomic-informed continuum models [Klein and Gao 1998; Gao and Klein 1998].

In this contribution, we further explore this line of thinking and propose an alternative form of atomic material stability condition. The condition is based on the local energy landscape and is formulated directly in atomistic description without resorting to continuum concepts and homogenization. We also discuss the kinetic implication of the condition, and show that the condition corresponds to a monotonicity condition in a properly defined atomic stress. The critical state signifies the stationary point in the response of "atomic traction". We utilize the criterion to analyze the stability of carbon nanotubes (CNT). The application improves a recent work by the same authors [Lu and Zhang 2006] where they used the strong ellipticity condition based on a continuum elasticity model to predict the failure strain of CNTs. The tensile failure strains in [Lu and Zhang 2006] compare well with the stability limits obtained from crystal elasticity models [Zhang et al. 2002a] as well as early molecular dynamics simulations [Yakobson et al. 1997]; however, they appear higher than those reported in recent publications [Troya et al. 2003; Zhang et al. 2005; Mielke et al. 2004]. In the present work, the analysis is performed directly in the discrete setting and comparable results are obtained. In addition, the method in [Lu and Zhang 2006] is limited to perfect tubes. Here, both perfect and defective tubes are considered.

2. Atomistic material instability condition

As discussed above, the strong ellipticity condition characterizes material stability in an finitely deforming elastic body. With reference to the strain energy function $W = W(\boldsymbol{F})$ where $\boldsymbol{F}$ is the deformation gradient, the strong ellipticity condition is given by

$$A_{iIkK}\, b_i b_k N_I N_K > 0 \quad \text{with } A_{iIkK} = \frac{\partial^2 W}{\partial F_{iI}\, \partial F_{kK}}$$

for all arbitrary nonzero vectors $\boldsymbol{b}$ and $\boldsymbol{N}$. A_{iIkK} is the (Cartesian) component of the fourth-order elasticity tensor, F_{iI} is the component of the deformation gradient, and (b_i, N_I) are the components of the vectors $\boldsymbol{b}$ and $\boldsymbol{N}$. The summation convention applies to repeated indices unless stated otherwise. Introducing $\boldsymbol{n} = \boldsymbol{F}^{-T}\boldsymbol{N}$, the condition can be written in spatial form, as

$$(C_{ijkl} + \delta_{ik}\tau_{jl})\, b_i b_k n_j n_l > 0, \tag{1}$$

where $C_{ijkl} = (\det \boldsymbol{F})^{-1} A_{iIkK} F_{jI} F_{lK}$ is the spatial elasticity tensor and τ_{jl} is the component of the Cauchy stress. This condition is often stated alternatively in

terms of the positive-definiteness of the acoustic tensor

$$Q_{ik}(\boldsymbol{n}) = (C_{ijkl} + \delta_{ik}\tau_{jl})n_j n_l. \tag{2}$$

If the energy function is sufficiently smooth, the strong ellipticity condition is equivalent to the rank-one convexity of the energy function, which can written

$$\frac{\partial^2}{\partial \varepsilon^2}\bigg|_{\varepsilon=0} W(\boldsymbol{F} + \varepsilon \boldsymbol{b} \otimes \boldsymbol{N}) > 0 \tag{3}$$

for arbitrary nonzero vectors $\boldsymbol{b}$ and $\boldsymbol{N}$, see [Ciarlet 1988, Section 5.10]. In this paper, the operator $\otimes$ means the standard tensor product.

There are several justifications for the strong ellipticity condition. At continuum scale, the strong ellipticity condition guarantees the uniqueness of solution for Dirichlet boundary value problems [Van Hove 1947]. In the context of stability, the condition precludes any nonzero incremental motion that leaves the boundary unaltered. The loss of strong ellipticity condition indicates that the energy surface is locally concave, and a particular form of local discontinuous bifurcation become admissible even if the material element is subjected to all round displacement boundary conditions [Hill 1962; Rice 1976]. In [Li et al. 2002; Van Vliet et al. 2003; Zhu et al. 2004; Li et al. 2004], the condition (1) is utilized in atomic system, with the continuum stress and elasticity tensor being evaluated using the Ray sum [Ray et al. 1986; Lutsko 1988].

Here, we propose a direct atomic level stability condition without resorting to the concepts of stress and elasticity tensor. We focus on models in which the system potential can be expressed as a sum of bond potentials. For such systems one can define the energy of an atomic site and partition the total potential into contributions from the site potentials. Consider such a system at an equilibrium state (temperature $T = 0$). Let $\boldsymbol{r}_a$ be the position of atom a and let $\boldsymbol{r}_{ab} := \boldsymbol{r}_b - \boldsymbol{r}_a$ be the bond vector. The potential of bond ab is

$$V_{ab} = V_{ab}(\boldsymbol{r}_{pq}).$$

For many-body interaction, the potential V_{ab} depends not only on bond $\boldsymbol{r}_{ab}$, but also on other bonds in the potential range. The potential of an atom site can be defined by

$$W_a = \tfrac{1}{2}\sum_b V_{ab}(\boldsymbol{r}_{pq}). \tag{4}$$

The summation runs over all bonds connecting to atom a.

Motivated by the strong ellipticity condition, we postulate that for an atomic site to be locally stable, the equilibrium state must satisfy the condition

$$\boldsymbol{b} \cdot \boldsymbol{Q}_a(\boldsymbol{n})\boldsymbol{b} > 0 \tag{5}$$

for arbitrary nonzero vectors $\boldsymbol{n}$ and $\boldsymbol{b}$. Here,

$$\boldsymbol{Q}_a(\boldsymbol{n}) = \frac{1}{2}\sum_b \sum_{p,q} \sum_{s,t} (\boldsymbol{r}_{pq}\cdot\boldsymbol{n}) \frac{\partial^2 V_{ab}}{\partial \boldsymbol{r}_{pq}\partial \boldsymbol{r}_{st}} (\boldsymbol{r}_{st}\cdot\boldsymbol{n}) \tag{6}$$

is the atomistic counterpart of the acoustic tensor, which depends quadratically on $\boldsymbol{n}$. The condition (5) is equivalent to the positive-definiteness of the atomistic acoustic tensor $\boldsymbol{Q}_a$.

The condition can be stated alternatively as a convexity condition for W_a. If the site energy W_a is at least twice differentiable, the condition (5) is equivalent to

$$\frac{\partial^2}{\partial \varepsilon^2}\Big|_{\varepsilon=0} W_a\big(\boldsymbol{r}_{pq} + \varepsilon \boldsymbol{b}(\boldsymbol{r}_{pq}\cdot\boldsymbol{n})\big) > 0 \tag{7}$$

for arbitrary nonzero vectors $\boldsymbol{b}$ and $\boldsymbol{n}$. The equivalence can be directly verified. This representation corresponds directly to the rank-one convexity condition (3). The rank-one deformation gradient increment, in a discrete setting, corresponds to the atomic displacement increment

$$\delta \boldsymbol{r}_{ab} = \boldsymbol{b}(\boldsymbol{r}_{ab}\cdot\boldsymbol{n}). \tag{8}$$

We refer to (7) as a *mono-mode convexity condition*.

Several remarks on the condition (5) or (7) are in order. First, the stability condition is postulated based on the premise that the stability of a site is determined by the local energy landscape. If the condition (5) is violated for certain vectors $\boldsymbol{b}$ and $\boldsymbol{n}$, the energy surface is locally concave, and bifurcation into lower energy modes becomes possible. The displacement mode (8) is chosen to test the convexity as it naturally corresponds to the rank-one deformation gradient in the continuum theory. In simple crystals $\boldsymbol{b}$ and $\boldsymbol{n}$ retain the physical explanation as wave vectors [Li et al. 2002; Van Vliet et al. 2003]. Second, as will be discussed in Section 3, the condition is related to the monotonicity of a properly defined atomic stress that characterizes the average intensity of interaction between an atom and the surrounding atoms. In particular, the singularity in $\boldsymbol{Q}$ signifies the state where the traction is momentarily stationary in a mono-mode incremental displacements. Thirdly, the condition coincides with Li's criterion for simple crystals (see Appendix). However, they may differ in complex lattices depending on how the atomic stress and elasticity tensor are evaluated in Li's approach. The atomistic form (6) has the advantage of being free from continuum concepts. More importantly, since the condition is based on the local property of the energy function, we expect it to be applicable to defective systems provided that the site energy can be reasonably defined.

3. Kinetic implications

The condition (5) can be further examined from the standpoint of atomic stress, which provides information about the local kinetics in some average sense. For systems that admit the site energy of the form (4), the static atomic stress at site a can be defined as

$$\boldsymbol{\sigma}_a = \frac{1}{2\omega} \sum_b \sum_{p,q} \frac{\partial V_{ab}}{\partial \boldsymbol{r}_{pq}} \otimes \boldsymbol{r}_{pq},$$

where ω is the volume of atomic site a. This expression of stress can be derived from an energetic argument by considering the mechanical power in a superposed affine incremental motion. The quantity represents the average intensity of interaction between the atom a and the surrounding atoms. The stress so defined is symmetric, and the symmetry follows from the invariant requirement $V_{ab}(\boldsymbol{r}_{pq}) = V_{ab}(\boldsymbol{R}\boldsymbol{r}_{pq})$ for any rotation tensor $\boldsymbol{R}$. Intuitively, if the atomic system is mechanically stable, one expects the stress to satisfy the *monotonicity condition*

$$\delta\boldsymbol{\sigma}_a \cdot \delta\boldsymbol{\epsilon} > 0$$

for properly defined strain increment $\delta\boldsymbol{\epsilon}$.

The stress increment under incremental atomic displacements $\delta\boldsymbol{r}_{pq}$ is given by

$$\delta\boldsymbol{\sigma}_a = \frac{1}{2\omega} \sum_b \sum_{p,q} \sum_{s,t} \Big(\frac{\partial^2 V_{ab}}{\partial \boldsymbol{r}_{pq} \partial \boldsymbol{r}_{st}} \delta\boldsymbol{r}_{st} \Big) \otimes \boldsymbol{r}_{pq} + \frac{1}{2\omega} \sum_b \sum_{p,q} \frac{\partial V_{ab}}{\partial \boldsymbol{r}_{pq}} \otimes \delta\boldsymbol{r}_{pq} - \frac{\delta\omega}{2\omega^2} \sum_b \sum_{p,q} \frac{\partial V_{ab}}{\partial \boldsymbol{r}_{pq}} \otimes \boldsymbol{r}_{pq}. \quad (9)$$

Consider the mono-mode displacement increment (8). Since this incremental displacement field is affine, we can define the corresponding strain increment, as

$$\delta\boldsymbol{\epsilon} = \tfrac{1}{2}(\boldsymbol{b} \otimes \boldsymbol{n} + \boldsymbol{n} \otimes \boldsymbol{b}). \quad (10)$$

Regardless of how the atomic volume ω is defined, the volume increment is given by the formula $\delta\omega = \omega(\operatorname{tr} \delta\boldsymbol{\epsilon})$, which yield

$$\delta\omega = \omega(\boldsymbol{b} \cdot \boldsymbol{n}). \quad (11)$$

Substituting (8) into (9), and invoking equations (10), (11), a straight forward calculation yields

$$\delta\boldsymbol{\sigma}_a \cdot \delta\boldsymbol{\epsilon} = \tfrac{1}{\omega}\, \boldsymbol{b} \cdot \boldsymbol{Q}_a(\boldsymbol{n})\boldsymbol{b}.$$

Hence, the positiveness of $\boldsymbol{Q}_a$ ensures that the atomic stress is at least monotonic in the incremental mode (8).

Alternatively, the definition of stress motivates the introduction of atomic traction in an imaginary plane of normal $\boldsymbol{n}$:

$$\boldsymbol{t}_a^{\boldsymbol{n}} := \boldsymbol{\sigma}_a \boldsymbol{n} = \frac{1}{2\omega} \sum_b \sum_{p,q} \frac{\partial V_{ab}}{\partial \boldsymbol{r}_{pq}} (\boldsymbol{r}_{pq} \cdot \boldsymbol{n}). \tag{12}$$

This quantity represents the contribution of the atom a to the macroscopic traction in the direction $\boldsymbol{n}$. Similarly to (9), the increment under incremental atomic displacements $\delta \boldsymbol{r}_{ab}$ is

$$\delta \boldsymbol{t}_a^{\boldsymbol{n}} = \frac{1}{2\omega} \sum_b \sum_{p,q} \sum_{s,t} (\boldsymbol{r}_{pq} \cdot \boldsymbol{n}) \frac{\partial^2 V_{ab}}{\partial \boldsymbol{r}_{pq} \partial \boldsymbol{r}_{st}} \delta \boldsymbol{r}_{st} + \frac{1}{2\omega} \sum_b \sum_{p,q} \frac{\partial V_{ab}}{\partial \boldsymbol{r}_{pq}} (\delta \boldsymbol{r}_{pq} \cdot \boldsymbol{n}) - \frac{\delta \omega}{2\omega^2} \sum_b \sum_{p,q} \frac{\partial V_{ab}}{\partial \boldsymbol{r}_{pq}} (\boldsymbol{r}_{pq} \cdot \boldsymbol{n}). \tag{13}$$

Again, consider the mono-mode (8). Recalling (11), the last two terms in equation (13) cancel each other and the traction increment (13) takes the form

$$\delta \boldsymbol{t}_a^{\boldsymbol{n}} = \tfrac{1}{\omega} \boldsymbol{Q}_a(\boldsymbol{n}) \boldsymbol{b}. \tag{14}$$

If at a point along a loading path the acoustic tensor becomes singular, namely $\boldsymbol{Q}_a(\boldsymbol{n})\boldsymbol{b} = \boldsymbol{0}$ for a pair of direction vectors $(\boldsymbol{b},\ \boldsymbol{n})$, then, according to equation (14), the atomic traction is momentarily stationary. This is another important indicator for the onset of instability in atomic systems, since the stationary point in atomic force often marks the incipiency of softening response.

4. Application in carbon nanotubes

The validity of the stability condition is assessed with application in carbon nanotubes. The criterion is utilized to identify the critical load of elastic instability in defective carbon nanotubes under tension. In this study, we are concerned with the stability of CNT at lower temperatures where the system is in quasistatic state, and its stability is determined primarily by the mechanical characteristics of the interatomic potential. The atomic coordinates are computed using molecular mechanics (MM). The analysis does not consider thermal effects, however, we expect that at low temperatures the influence of thermal contribution to the local stability of CNT is negligibly small. The first generation Tersoff–Brenner potential [Brenner 1990; 1992] is used to model CNT bond energy. The parameters listed as potential-I in [Brenner 1990] are utilized in the computation, as in [Zhang et al. 2002a; 2002b]. This empirical potential has been widely used in studying carbon nanotubes and is found to be able to accurately describe the bond energy, elastic modulus and even defect nucleation. With Brenner's potential the interatomic energy between atom

a and b is expressed by the function

$$V(r_{ab}) = V_R(r_{ab}) - \bar{B}V_A(r_{ab}),$$

where r_{ab} is the length of the covalent bond, V_R and V_A are the repulsive and attractive terms depending on the bond length, and $\bar{B}$ models the multibody coupling between bond ab and its environment, which depends on angles between ab and adjacent bonds. At an atomic site of a CNT, one can distinguish the three bond vectors in the unit cell of the honeycomb lattice of graphene by bond vectors $\boldsymbol{r}_\alpha$, $\alpha = 1, 2, 3$ which makes three angles, labeled such that $\theta_{\alpha\beta}$ is the angle between bond α and β. The site energy is

$$W_a = \tfrac{1}{2}\sum_{\alpha=1}^{3}\left(V_R(r_\alpha) - \bar{B}(\cos\theta_{\alpha\beta}, \cos\theta_{\alpha\gamma})V_A(r_\alpha)\right) \qquad (\beta \neq \gamma).$$

It has been observed that the cutoff function in Brenner's bond-order potential produces unphysical results [Shenderova et al. 2000; Belytschko et al. 2002]. Recent studies [Troya et al. 2003; Zhang et al. 2005; Mielke et al. 2004] have used a modification originally suggested in [Shenderova et al. 2000], which removes the cutoff function but retains the interactions only for atoms initially within a 2 Å cutoff distance. The present work also follows this approach. The summation over the bonds pq and st in (6) is truncated accordingly. Nevertheless, the resulting stress and acoustic tensor include the contributions from the derivatives of the bond order function $\bar{B}(\theta_{\alpha\beta}, \theta_{\alpha\gamma})$. These contributions can not be omitted because π bond characterized by the function $\bar{B}$ plays an important role in strengthening the cohesive interaction between carbon atoms.

To simulate uniaxial tension, the atoms at the two ends are subjected to prescribed displacement increments while the coordinates of the interior atoms are computed using molecular mechanics. The convexity condition (5) is monitored by the smallest eigenvalue of $\boldsymbol{Q}_a(\boldsymbol{n})$. To find the minimum eigenvalue at a given atomic configuration, the vector $\boldsymbol{n}$ is swept through the admissible range with a pre-set increment and a bi-section process is used to locate the critical direction, as in [Lu and Zhang 2006]. The procedure is performed at every atom site and at every load increment. Although the process can be computationally intensive, it is a mere postprocessing of the molecular mechanics data and therefore doesn't interfere with MM solution process.

We begin by considering pristine tubes. Figure 1 shows the values of the smallest eigenvalue of $\boldsymbol{Q}_a$ at different elongation in an armchair [10, 10] and a zigzag [17, 0] tube. Black circles indicates unstable atoms at which the smallest eigenvalue becomes negative. Stable atom sites are denoted by grey or hollow circles, where the grey scale is obtained by scaling the (positive) eigenvalue of $\boldsymbol{Q}_a$ from 0 to 1, with increasing grayness for decreasing eigenvalues. Our analysis finds that the pristine

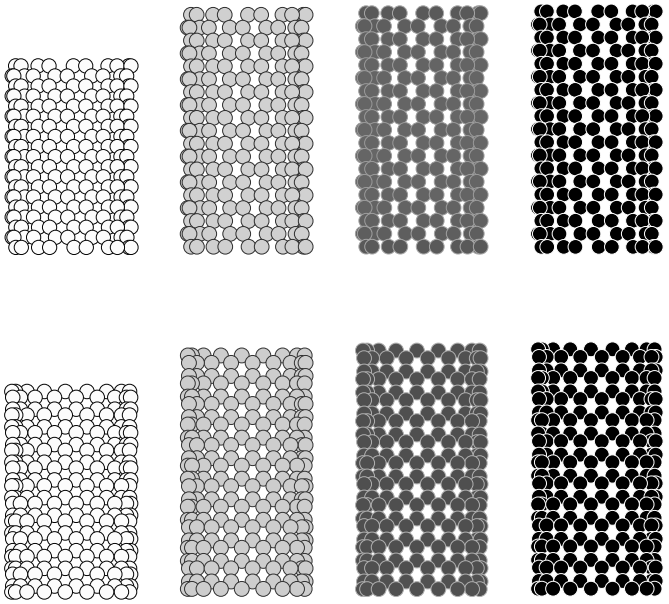

Figure 1. Stability of perfect armchair [10, 10] (upper row) and zigzag [17, 0] tubes (lower row) under various tensile strains. Black circles indicate the unstable sites where the smallest eigenvalue of the acoustic tensor is negative. The grey scale is obtained by scaling the (positive) eigenvalues inversely against the largest positive value in the loading process.

tubes lose stability uniformly when stretched to a critical strain. Particularly, the armchair [10, 10] becomes unstable at 29.8%. In comparison, numerous studies reported the critical tensile strain values close to 30% [Yakobson et al. 1997; Marques et al. 2004; Mielke et al. 2004; Zhang et al. 2005]. The critical strain for the zigzag tube [17, 0] is found to be 19.1%, again the value is consistent with the reported range of 16–20% [Dumitrica et al. 2003; Mielke et al. 2004; Zhang et al. 2005]. See Table 1. The molecular dynamics simulations by Yakobson et al. [1997] and recently by Marques et al. [2004] showed that the deformation is initially homogeneous till the critical strain is reached. Upon further stretching, a largely distorted neck appears and the tube quickly breaks into segments. As in [Lu and Zhang 2006], the critical directions $\boldsymbol{b}$ and $\boldsymbol{n}$ are found to be parallel to the tube axis, indicating that the unstable model corresponds to an incipient mode-I crack.

The same analysis is conducted for nanotubes embedded with a single Stone-Wales (SW) defect [Stone and Wales 1986]. Existing studies suggest that the

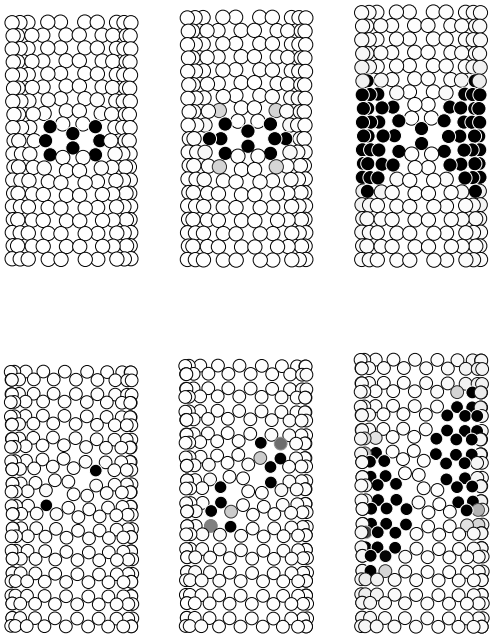

Figure 2. Evolution of unstable zone in CNTs with Stone-Wales defect. Upper row: [10, 10] armchair tube. Lower row: [17, 0] zigzag.

5/7/7/5 ring may behave as a dislocation core and weakens the strength moderately [Buongiorno Nardelli et al. 1998; Yakobson 1998; Mielke et al. 2004; Troya et al. 2003]. Figure 2 shows the evolution of instability zone during stretching. Unlike the pristine tubes which lose stability uniformly, here the unstable sites appear first at the SW ring; when loaded further the unstable zone quickly spreads out and results in global instability (MM computation fails to converge). For the [10, 10] armchair, the initial instability is found to occur at 21% strain, and the tube loses global stability at 26% strain. As shown in Table 1, the lower limit compares well with the reported yield strain obtained from molecular and quantum mechanics simulations. The upper limit 26% also corresponds nicely with break strain of SW defective tubes reported by Marques et al. [2004]. For the zigzag tube [17, 0], the initial instability is found to be 14%. In comparison, other studies [Mielke et al. 2004; Troya et al. 2003] found the critical strains of zigzag tubes to be close to 14%.

Recent simulations have reported that vacancy defects can significantly reduce the strength of CNTs. Mielke et al. [2004] predicted the limit strain of 11–15% for [5, 5] armchair tubes with one-atom vacancy, and 9–13% limit strain for [10, 0] tubes with the same defect. Zhang et al. [2005] reported moderately lower limit

Critical Tensile Strains of SWCNTs				
Tube type	Defect	$\varepsilon_{\text{crit}}(\%)$	Method	Reference
[17, 0]	pristine	19.1	MM (TB-G1)	present work
[10, 0]	pristine	16.0	QM-AM1	[Dumitrica et al. 2003]
[10, 0]	pristine	20.0	QM-PM3	[Mielke et al. 2004]
[10, 0]	pristine	18.1	MM (MTB-G2)	[Zhang et al. 2005]
[10, 10]	pristine	29.8	MM (TB-G1)	present work
[5, 5]	pristine	27.9	QM-MSINDO	[Troya et al. 2003]
[5, 5]	pristine	30.0	QM-DFT	[Mielke et al. 2004]
[5, 5]	pristine	29.7	MM (MTB-G2)	[Zhang et al. 2005]
[17, 0]	SW	14.1	MM (TB-G1)	present work
[10, 0]	SW	13.9	QM-PM3	[Mielke et al. 2004]
[10, 10]	SW	21.3	MM (TB-G1)	present work
[5, 5]	SW	24.4	QM-MSINDO	[Troya et al. 2003]
[5, 5]	SW	22.0	QM-PM3	[Mielke et al. 2004]
[17, 0]	vacancy	13.0	MM (TB-G1)	present work
[10, 0]	vacancy	13.0	QM-PM3	[Mielke et al. 2004]
[10, 10]	vacancy	12.8	MM (TB-G1)	present work
[5, 5]	vacancy	15.3	QM-PM3	[Mielke et al. 2004]
[5, 5]	vacancy	11.4	MM (MTB-G2)	[Zhang et al. 2005]

Table 1. Tensile failure strain of CNTs and comparison with predictions of molecular mechanics (MM), molecular dynamics (MD) and quantum mechanics (QM) simulations. TB-G1 and MTB-G2 stand for the first- and modified second-generation Tersoff-Brenner potentials.

strain for the zigzag tubes. We consider the [17, 0] zigzag tube with a symmetric, reconstructed one-atom vacancy. The initial instability is found to occur at 13.0% strain. When loaded further, the unstable zone spreads and the tube loss global stability at about 17% strain. Figure 3 shows the distribution of unstable sites at various strains. We also consider the [10, 10] armchair tube with an asymmetric one-atom vacancy. The onset of unstable atoms is captured at 12.8% strain, and the tube quickly loss global stability when loaded slightly further. The limit strains for both the armchair and the zigzag tubes compare reasonally well with Mielke's predictions. The armchair result also agrees with the range reported in [Zhang et al. 2005].

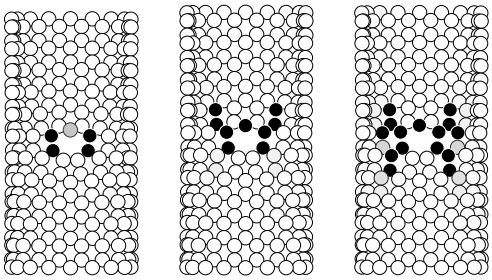

Figure 3. Evolution of unstable zone in the $[17, 0]$ tube with a symmetric one-atom vacancy.

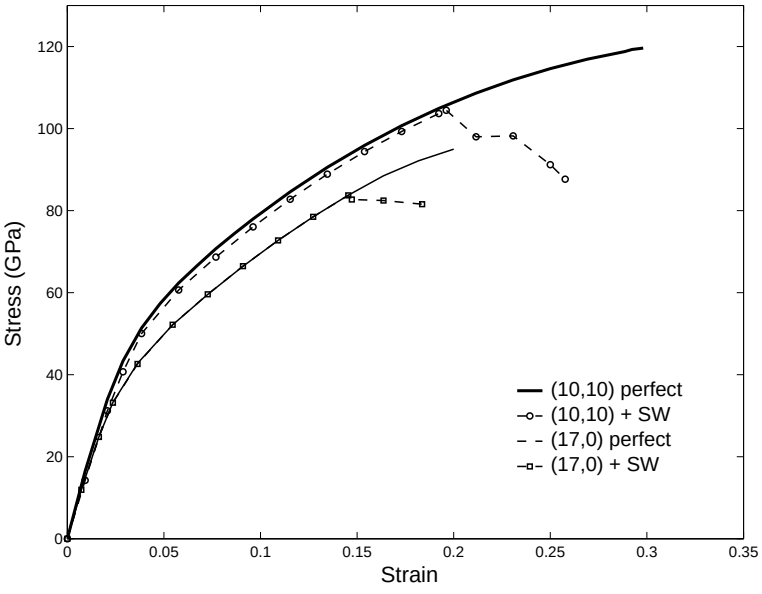

Figure 4. Stress versus strain in perfect and SW defective tubes. The instability points detected by the stability criterion correlate directly to the sudden stress drop in the response.

Figure 4 shows the (engineering) tensile stress as a function of strain for the pristine and SW defective tubes. The limit strains correlate nicely to the sudden loss of stress in the response. The stress is computed by dividing the resultant end reaction force by the tube's original circumference and the shell thickness of 0.34 nanometer.

5. Summary

An atomic level stability condition has been presented for predicting the local elastic instability of an atomic system. The criterion corresponds to the strong ellipticity condition in continuum elasticity, but is formulated directly in terms of atomic quantities without explicit reference to continuum stress and elasticity tensor. Being essentially a generalization of the continuum condition for material stability, the criterion is expected to capture the onset of local failure in atomic systems. Also, since the criterion is directly based on the site potential, we expect it to be applicable in complex lattices and defective systems provided that the site energy can be reasonably defined.

Preliminary applications in tensile CNTs has shown promising results. For pristine tubes, the predicted limit strains are in excellent agreement with the reported values from molecular and quantum mechanics simulations. For SW defective tubes, the lower limits (at the onset of unstable sites) agree very well with the reported failure strains. A single one-atom vacancy in the [10, 10] is found to reduce the limit strain significantly, consistently with the findings in recent publications. The spatial distribution of the stability indicator also provides useful information about the unstable zone and its evolution during a loading course.

Appendix

In this appendix we provide an explicit expression for the acoustic tensor $\boldsymbol{Q}_a$ in the context of pairwise potentials and show that in this case the condition coincides with the criterion in [Li et al. 2002; Van Vliet et al. 2003]. Fir a pairwise potential, the bond energy V_{ab} depends only on the bond length $r_{ab} = \sqrt{\boldsymbol{r}_{ab} \cdot \boldsymbol{r}_{ab}}$, namely $V_{ab} = V(r_{ab})$. The site energy therefore is $W_a = \sum_b V(r_{ab})$. Using the chain rule and invoking the identity $\partial r_{ab}/\partial \boldsymbol{r}_{ab} = \boldsymbol{r}_{ab}/r_{ab}$, we find

$$\frac{\partial V}{\partial \boldsymbol{r}_{ab}} = \frac{\partial V}{\partial r_{ab}} \frac{\boldsymbol{r}_{ab}}{r_{ab}}.$$

Furthermore,

$$\frac{\partial^2 V}{\partial \boldsymbol{r}_{ab} \partial \boldsymbol{r}_{ab}} = \frac{1}{r_{ab}^2} \frac{\partial^2 V}{\partial r_{ab}^2} \boldsymbol{r}_{ab} \otimes \boldsymbol{r}_{ab} + \frac{1}{r_{ab}} \frac{\partial V}{\partial r_{ab}} \Big(\boldsymbol{I} - \frac{1}{r_{ab}^2} \boldsymbol{r}_{ab} \otimes \boldsymbol{r}_{ab} \Big),$$

where $\boldsymbol{I}$ is the second order identity tensor. It follows that, for this system the atomistic acoustic tensor (6) takes the form

$$\boldsymbol{Q}_a = \frac{1}{2} \sum_b \Bigg(\frac{1}{r_{ab}^2} \Big(\frac{\partial^2 V}{\partial r_{ab}^2} - \frac{1}{r_{ab}} \frac{\partial V}{\partial r_{ab}} \Big) (\boldsymbol{r}_{ab} \cdot \boldsymbol{n})^2 \boldsymbol{r}_{ab} \otimes \boldsymbol{r}_{ab} + \frac{1}{r_{ab}} \frac{\partial V}{\partial r_{ab}} (\boldsymbol{r}_{ab} \cdot \boldsymbol{n})^2 \boldsymbol{I} \Bigg). \quad (15)$$

The summation runs over all bonds emanating from atom a.

According to the recipe of Li and others [Li et al. 2002; Van Vliet et al. 2003], the stability condition is evaluated using the continuum acoustic tensor (2) in conjunction with derived atomic stress and elasticity tensor. For this system, the static Virial stress [Irving and Kirkwood 1950; Cheung and Yip 1991; Shen and Atluri 2004] or BDT stress [Basinski et al. 1971; Shen and Atluri 2004] is given by

$$\boldsymbol{\sigma} := \frac{1}{2\omega}\sum_b \frac{\partial V}{\partial \boldsymbol{r}_{ab}} \otimes \boldsymbol{r}_{ab} = \frac{1}{r_{ab}}\frac{\partial V}{\partial r_{ab}} \boldsymbol{r}_{ab} \otimes \boldsymbol{r}_{ab}, \tag{16}$$

where ω is the volume of atomic site a. The isothermal elastic tensor at $T = 0$ can be obtained from the Ray sum [Ray et al. 1986; Lutsko 1988], as

$$\mathbb{C} = \frac{1}{2\omega}\sum_b \frac{1}{r_{ab}^2}\Big(\frac{\partial^2 V}{\partial r_{ab}^2} - \frac{1}{r_{ab}}\frac{\partial V}{\partial r_{ab}}\Big) \boldsymbol{r}_{ab} \otimes \boldsymbol{r}_{ab} \otimes \boldsymbol{r}_{ab} \otimes \boldsymbol{r}_{ab}. \tag{17}$$

Li's procedure results in an expression identical to (15) modulo a volume factor, as can be readily checked by substituting (16) and (17) into (2). The two criteria coincide in this special case.

Acknowledgments

The work was partially supported by a Scientific Research Initiative Grant from the University of Iowa.

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Received 29 Sep 2005.

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