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# Phonon, Cauchy-Born and homogenized stability criteria for a free-standing monolayer graphene at the continuum level

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ABSTRACT

The purpose of the present work is the study of three stability criteria for a free standing monolayer graphene modelled as a monoatomic hexagonal 2-lattice at the continuum level. The criteria treated are: the phonon stability, the Cauchy-Born stability and the homogenized stability criteria. Phonon stability requires plane progressive waves to propagate along the material with real velocities. The outcome consists of necessary and sufficient conditions for the wave speed to be real in terms of graphene's acoustic tensors. Requiring energy's second variation to be positive render the Cauchy-Born stability criterion. The outcome consist of a Hessian matrix whose components are derivatives of the energy with respect to its arguments. The Cauchy-Born stability criterion stipulate this Hessian matrix to be positive semi-definite. Solving the equations ruling the shift vector, enable to rule the shift vector out of the energy. The Cauchy-Born stability criterion for this homogenized energy renders the homogenized stability criterion. These three stability criteria are lied down for graphene for both the geometrically and materially linear and the nonlinear case. For the phonon stability study the equation ruling the shift vector has two alternatives: an equilibrium equation and a rate equation according to a gradient flow law.



## 1. Introduction

Stability of crystalline solids is the purpose of the study of Elliott et al. (2006a). These authors examine three crystalline stability criteria: phonon stability, Cauchy-Born stability and homogenized stability. Their theory is applicable at the atomic/discrete level: energy is measured thought a potential describing the interatomic force every atom experiences by its environment. The field equations are the equilibrium equations for the discrete body: Newton's second law for each particle. The main difference in-between these three criteria is the perturbations they allow which result to some modes (acoustic or optic) being excluded from the analysis. The authors conclude that the Cauchy-Born stability is recommended as the relevant and the more general stability criterion. Their approach is successfully applied to martensitic transformations taking place in shape memory alloys for both temperature induced (Elliott et al., 2006b; Elliott, 2007) as well as stress induced (Elliott et al., 2011) martensitic phase changes for bi-atomic crystals.

The present work is motivated by the above analysis (Elliott et al., 2006a) and applies to the continuum case for a free standing monolayer graphene. We start by viewing graphene as a monoatomic hexagonal 2-lattice (Fadda and Zanzotto, 2000) in line with our previous works on the topic (Sfyris and Galiotis, 2015; Sfyris et al., 2014a, 2014b, 2015a, 2015b, 2015c). The “2” in 2-lattice refers to the presence of two atoms in the unit translation cell of graphene, while “monoatomic” refers to the fact that these two atoms belong to the same species: they are both carbon atoms. Confinement to weak transformation neighborhoods (Ericksen, 1979; Parry, 1978; Pitteri, 1984, 1985; Pitteri and Zanzotto, 2003) and adoptment of the Cauchy-Born rule (Ericksen, 2008; Pitteri and Zanzotto, 2003) enable working with an energy at the continuum level depending on three arguments: an in-surface strain measure, an out-of-surface measure and the shift vector. The in-surface strain measure is the standard Cauchy-Green deformation tensor, $\mathbf{C}_S$, now being two-dimensional. The out-of-surface measure is graphene's curvature tensor, $\mathbf{b}_0$, viewed as a 2-dimensional surface. Energy's dependence on curvature is motivated by the works of Steigmann and Ogden (Steigmann and Ogden, 1997a, 1999, 1997b) as well as earlier approaches on the topic (Gurtin and Murdoch, 1975; Murdoch and Cohen, 1979; Cohen and DeSilva, 1966). Energy's dependence on the shift vector, $\mathbf{p}$, result from well established theories of multilattices (Pitteri, 1985; Pitteri and Zanzotto, 2003).

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Specific expressions for such continuum energies for graphene are given in Sfyris and Galiotis (2015). For the nonlinear theory (Sfyris et al., 2014b) we present some simple closed form solutions such as: biaxial tension/compression, simple shear, as well as a specific buckling/wrinkling mode. The geometrically and materially linear counterpart of this theory is presented in Sfyris et al. (2014a). There, the assumption of linearity simplifies the analysis and facilitates analytical results for biaxial tension/compression, simple shear and a specific out-of-plane buckling/wrinkling mode. We here utilize these energies to constitutively describe graphene at the continuum level. The field equations for our framework are the momentum, the moment of momentum and the equation ruling the shift vector. The first two come from the relevant work of Chhapadia et al. (2011) while for the equation ruling the shift vector there are two options. In one case, one can assume that the shift vector adjust so as equilibrium is reached (Pitteri and Zanzotto, 2003, p. 338). Alternatively, one can use a rate equation for the shift vector according to a gradient flow law (Pitteri and Zanzotto, 2003, p. 350).

Thus, our framework is designed for the continuum case, in contrast to the discrete approach of Elliott et al. (2006a). The interatomic potential used there, is for our continuum framework the constitutive law describing graphene. The discrete field equations are substituted by their continuum analogs: momentum, moment of momentum and the equation ruling the shift vector. Passage from atomic to continuum theory is treated elegantly in the works of Bhattacharya and James (1999) and Friesecke and James (2000) using the mathematical tool of Gamma convergence. In our framework here, we do not prove such a multiscale limit. We take graphene's energy (Sfyris and Galiotis, 2015; Sfyris et al., 2014b, 2014a, 2015a) as the starting point and lay down the continuum counterparts of the stability criteria of Elliott et al. (2006a). These criteria should mark the initiation of martensitic transformations for graphene at the continuum level, in line with the approach of Elliott et al. (2006a, 2006b, 2011) (Elliott, 2007).

At the continuum level graphene experiences weak phase changes when the matrix of matrices $\partial W/\partial y_i \partial y_j$, $\mathbf{y} = (\mathbf{C}_S, \mathbf{p})$ is singular (see Sfyris, 2015). Being a multilattice one may separate these phase changes into two categories: structural phase changes and configurational phase changes (Pitteri, 2003). During configurational weak phase changes the motif (the extra atom in graphene's unit cell) follow the deformation of the skeleton, at least in the beginning. On the other hand, structural weak phase transitions are driven by the deformation of the motif followed by a suitable consequent deformation of the skeleton. Therefore, since $\mathbf{C}_S$ describe the skeleton deformation and $\mathbf{p}$ the motif deformation, by means of matrices, $\partial^2 W/\partial \mathbf{C}_S^2$ being singular mark the initiation of configurational weak phase changes. Singularity of the matrix $\partial^2 W/\partial \mathbf{p}^2$, on the other hand, is related with the initiation of structural weak phase changes.

In the present framework graphene's energy depend on three arguments: $(\mathbf{C}_S, \mathbf{b}_0, \mathbf{p})$. Thus, in general, weak phase changes happen when the matrix of matrices $\partial W/\partial y_i \partial y_j$, $\mathbf{y} = (\mathbf{C}_S, \mathbf{b}_0, \mathbf{p})$ is singular. Since in our analysis here we perturb all three fields our stability arguments give conditions such that the quantity $\partial W/\partial y_i \partial y_j$, $\mathbf{y} = (\mathbf{C}_S, \mathbf{b}_0, \mathbf{p})$ is non-singular. So, when these conditions fail, phase changes take place. If only the field $\mathbf{C}_S$ is perturbed, then failure of the conditions we obtain mark the initiation of configurational weak phase changes. If only the field $\mathbf{p}$ is perturbed, then we obtain conditions for the initiation of structural weak phase changes. All in all, the need for stability criteria, is that they mark the initiation of phase changes, in the sense that their failure provide conditions for the phase changes to take place. If not all the fields are perturbed we obtain as special cases the conditions for configurational and structural weak phase changes.

The phonon-stability criterion at the continuum level is the seeking for plane progressive waves (Hayes and Rivlin, 1961; Sawyers and Rivlin, 1973, 1978, 1977; SawyersRivlin, 1977; Knops and Wilkes, 1973; Sfyris, 2011) as candidate solutions for the theory of small deformations superimposed upon large (Green et al., 1952; England and Green, 1961; Toupin and Bernstein, 1961; Knops and Wilkes, 1973). The starting point is the assumption that the small deformation is a plane wave. Substituting this to the equations of small upon large, we obtain a set of equations for the amplitude of the wave. Requiring a non-trivial solution for it, we obtain the secular equation. From the secular equation we obtain necessary and sufficient conditions for the velocities of the wave to be real. These conditions are given in terms of graphene's acoustic tensors and constitutes the continuum analog of Elliott et al. (2006a) phonon approach which requires the phonon frequencies to be real.

Essentially, at the continuum level, we generalize the approach of Rivlin and co-workers (Hayes and Rivlin, 1961; Sawyers and Rivlin, 1973, 1977, 1978; SawyersRivlin, 1977) to graphene modelled through its continuum energy (Sfyris and Galiotis, 2015; Sfyris et al., 2014b, 2014a, 2015a). The generalization lies in the fact that we perturb the 2-dimensional in-surface displacement field as well as the curvature tensor and the shift vector. Also, we use the moment of momentum equation in addition to the momentum equation and the equation ruling the shift vector as well. For the last equation we have two options: a static and a dynamic one and we study both in the phonon method approach. Ultimately, we obtain conditions for having real wave velocities. Failure of these conditions means that weak phase changes take place. When only the field $\mathbf{C}_S$ is perturbed these phase changes should be configurational, while when only the field $\mathbf{p}$ is perturbed, the phase changes should be structural.

For the Cauchy-Born stability criterion we generalize the Legendre-Hadamard condition of E and Ming (2007) to our Hessian matrix that contains terms related with the curvature as well, in addition to terms related with the right Cauchy-Green tensor and the shift vector. The elegant proof given by these authors (E and Ming, 2007) is based on specific assumptions for the acoustic and the optical branch of the spectrum of the dynamical matrix. Thus, it renders an interesting relation between phonon and Cauchy-Born stability criteria for the discrete case. Our approach for obtaining the continuum Legendre-Hadamard condition is slightly different. We assume generalized perturbations, in line with Steigmann and Ogden (1997b) and evaluate the second variation of the energy. We then keep the matrix we need and simplify all non-relevant terms as much as possible using the Gauss formula for the surface. What it remains is set equal to zero, rendering a sufficient condition for the Cauchy-Born stability criterion to be expressed through the Hessian of the energy.

Certainly, this line of attack is mainly based on intuition rather than mathematical arguments. Nevertheless, it seems reasonable, since it combines the approach of Steigmann and Ogden (1997b) with the one of E and Ming (2007). The Hessian matrix of Steigmann and Ogden (1997b) contains terms related with curvature in addition to the one's from the in-surface strain, while the approach of E and Ming (2007) contains terms related with the shift vector in addition to the one's related with in-surface strain. Our Hessian matrix contains all of these terms. We note that an alternative though not straightforward path for proving our claim may be through the quasiconvexity condition as Steigmann and Ogden (1997a, 1999) do, noting that higher-order quasiconvexity reduce to quasiconvexity for symmetric matrices (DalMaso et al., 2004). Our Cauchy-Born stability criterion is the continuum analog of the corresponding one of Elliott et al. (2006a). These authors use the second derivative test using the