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PII: S0020-7683(13)00433-2
DOI: http://dx.doi.org/10.1016/j.ijsolstr.2013.10.038
Reference: SAS 8171

To appear in: *International Journal of Solids and Structures*

Please cite this article as: Todt, M., Bitsche, R.D., Hartmann, M.A., Fischer, F.D., Rammerstorfer, F.G., Growth limit of carbon onions - A continuum mechanical study, *International Journal of Solids and Structures* (2013), doi: http://dx.doi.org/10.1016/j.ijsolstr.2013.10.038

Growth limit of carbon onions - A continuum mechanical study

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Abstract

The growth of carbon onions is simulated using continuum mechanical shell models. With this models it is shown that, if a carbon onion has grown to a critical size, the formation of an additional layer leads to the occurrence of a structural instability. This instability inhibits further growth of carbon onions and, thus, can be a reason for the limited size of such particles. The loss of stability is mainly evoked by van der Waals interactions between misfitting neighboring layers leading to self-equilibrating stress states in the layers due to mutual accommodation. The influence of the curvature induced surface energy and its consequential stress state is investigated and found to be rather negligible. Furthermore, it is shown that the nonlinear character of the van der Waals interactions has to be considered to obtain

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maximum layer numbers comparable to experimental observations. The proposed model gives insight into mechanisms which are assumed to limit the size of carbon onions and can serve as basis for further investigations, e.g., the formation of nanodiamonds in the center of carbon onions.
Keywords: carbon nanostructures, finite element modeling, shell buckling, van der Waals interactions

1. Introduction

Carbon based nanostructures like graphene (Cadelano et al., 2009; Geim and Novoselov, 2007; Geim, 2009; Novoselov et al., 2004; Zhang et al., 2011), carbon nanotubes (Baughman et al., 2002; Iijima, 1991; Pantano et al., 2004; Yakobson et al., 1996), fullerenes (Kroto et al., 1985; Tang and Huang, 1995a), and carbon onions (Banhart and Ajayan, 1996; Kroto, 1992; Ugarte, 1992, 1995) have been intensively studied within the last decades. Graphene is the main building material of all of these carbon nanostructures (Geim and Novoselov, 2007) and is stated to be the strongest and thinnest material ever discovered (Geim, 2009). Nanotubes, fullerenes, and carbon onions should inherit the exceptional mechanical, electrical and electronic properties of graphene, due to their similar structure.

Fullerenes and carbon onions take an exceptional position among the carbon nanostructures. Graphene and carbon nanotubes have an hexagonal atomic arrangement, whereas fullerenes and carbon onions also contain pentagonal atomic rings to form closed cell structures. Fullerenes must contain 12 pentagons to be stable (Tang and Huang, 1995a); therefore, these particles are of polyhedral shape. Polyhedral closed cell particles also occur in

multi-layered arrangements (Blank et al., 2007; Fu et al., 2007; Kroto et al., 1985; Zhao et al., 2007), which can be transformed to perfectly spherical carbon onions by intense electron irradiation (Banhart and Ajayan, 1996; Ugarte, 1992). Currently, several techniques are available to produce multi-layered closed cell arrangements and carbon onions like electron irradiation of graphite at elevated temperatures ($\geq 300°C$) (Banhart and Ajayan, 1996; Banhart et al., 1997b), annealing of diamond nanoparticles (Joly-Pottuz et al., 2008; Tomita et al., 2002), high pressure transformation of single-crystal graphite (Blank et al., 2007), using a radio frequency plasma process (Fu et al., 2007), or synthesis by decomposition of phenolic resin (Zhao et al., 2007). The different production techniques lead to different growing scenarios of such multi-layered particles. Onions produced by high-pressure transformation of single-crystal graphite or from coal in a radio frequency plasma reactor are assumed to grow from the inside to the outside (Blank et al., 2007; Du et al., 2007). Carbon onions produced by high-temperature annealing of nanodiamonds start their formation at the boundaries of the nanodiamond (Kuznetsov et al., 1994; Tomita et al., 2002) and have a diameter being almost equal to that of the initial nanodiamond (Los et al., 2009). This growing scenario is also proposed in (Ugarte, 1995).

The multi-layered particles have a high local electronic density and consequently a high ability to absorb electromagnetic radiation. Thus, they can be used as fillers in composites for electromagnetic shielding (Macutkevic et al., 2009). Furthermore, carbon onions have a potential application as additives in lubricants (Joly-Pottuz et al., 2008), as solid lubricants (Hirata et al., 2004), or as nanoscopic pressure cells to produce nanodiamonds (Ban-

hart and Ajayan, 1996; Banhart et al., 1997a; Redlich et al., 1998). In all applications the size of the multi-layered particles is of substantial interest.

Carbon onions observed in experiments can consist only of a few layers (Joly-Pottuz et al., 2008; Ugarte, 1995), be of intermediate size (Banhart et al., 1997a; Blank et al., 2007), or consist of many layers (Wesolowski et al., 1997; Zwanger et al., 1996) with diameters up to 50 nm. The different sizes are probably a result of the different production techniques and, hence, of the different growing mechanisms. In (Zwanger et al., 1996) it is shown that the precursor material and the irradiation dose influence the size of the particles. But, what limits the size of the particles? Is there something like a growth limit, and if yes, what triggers this limit? To the best of the authors' knowledge these questions are not clarified so far in the literature.

Theoretical predictions about the maximum number of layers to which carbon onions can grow can be found in (Tang and Huang, 1995b), where it is shown that this number can reach a big value. However, in this study the deformations of the layers due to the van der Waals (vdW) interactions are not considered and the layers are assumed to remain spherical during the growth. Thus, a possible occurrence of structural instabilities, e.g., buckling of layers, is not incorporated in the theoretical models by Tang and Huang (1995b).

In the current paper, we propose that exactly such an occurrence of a structural instability limits the size to which carbon onions can grow. The instability is assumed to be evoked by the formation of an additional layer onto an onion which has grown to its maximum layer number. Due to the expected large number of layers the application of atomistic simulation tech-

niques would lead to enormous computational efforts. Hence, continuum mechanical shell models of carbon onions of various sizes are used to investigate whether or not these assumptions for a growth limit are reasonable.

Continuum mechanical shell models have shown to give reliable results for buckling of carbon nanostructures, such as single and multi-layered carbon nanotubes (Pantano et al., 2004; Yakobson et al., 1996), single layer graphene (Hartmann et al., 2013), or carbon crystallites (Todt et al., 2010). Continuum mechanical shell models are also applicable to investigate the mechanical properties of carbon fullerenes as shown in (Todt et al., 2013 in press) by comparison with Monte Carlo simulations. However, using continuum mechanical models of carbon onions involves some basic assumptions about the structure of the individual layers, the vdW interactions and the growth of carbon onions, which are addressed in the following sections.

2. Methodology

For studying the growth and, hence, a possible growth limit of carbon onions using continuum mechanics the finite element method is employed. The onion layers are assumed to be deformable and the vdW interactions between the layers are taken into account. Buckling eigenvalue prediction is used to check if the occurrence of a structural instability can be the reason for the limited size of carbon onions. The finite element analyses are performed with the commercial finite element program ABAQUS[2]. The general concept proposed for studying the growth limit of carbon onions was already briefly

[2]http://www.3ds.com/products/simulia/portfolio/abaqus/overview/

discussed by the authors in (Todt et al., 2011b), where also preliminary results were presented.

2.1. Axisymmetric Shell Model

In many cases the observed carbon onions are almost perfectly spherical in shape (Banhart and Ajayan, 1996; Kroto, 1992; Ugarte, 1992, 1995). Thus, the assumption of perfectly spherical onions seems to be admissible in the finite element model. Consequently, axisymmetric models are used in the computational analysis reducing the computational requirements significantly (see Fig. 1). In any case, the assumption of axisymmetry is justified as long as stable, i.e., pre-buckling states are considered. The axisymmetric model is used for stability considerations, too. This is because for a single thin-walled spherical shell under a constant external pressure the lowest and, therefore, relevant buckling eigenvalue appears with an extremely high multiplicity, see (Drmota et al., 1987). This high multiplicity of the eigenvalue leads to a high number of eigenfunctions being orthogonal to each other. Among these eigenfunctions several axisymmetric ones can be found, which have the same physical relevance as non-axisymmetric eigenfunctions. Regardless, whether an axisymmetric or non-axisymmetric buckling mode is considered, an imperfect shell most likely forms a single dimple in the post-buckling regime (Drmota et al., 1987), which represents an axisymmetric deformation, too. Thus, axisymmetry is also a reasonable assumption for the buckled configuration of a single spherical shell. Complete spherical shells filled with elastic media also show axisymmetric buckling modes if subjected to external pressure (Sato et al., 2012). A carbon onion can be considered as the outermost shell filled with an elastic medium formed by the layers below

and the vdW interactions between these layers.

Each layer of the onion is denoted an index $i \in [1, N]$, with N being the total number of layers forming the onion, see Figure 1. The layers are modeled as thin elastic shells with a membrane stiffness $C = Eh$ and bending stiffness $D = \frac{Eh^3}{12(1-\nu^2)}$, where E, ν, and h are the elastic modulus, the Poisson's ratio, and the layer thickness, respectively. For sake of simplicity, standard shell elements are used in the analyses requiring the direct input of parameter set E, ν, and h. However, the values found in literature for these parameter set differ strongly, e.g., $E = 1050\,\mathrm{GPa}$, $\nu = 0.186$, $h = 0.334\,\mathrm{nm}$ (Liu et al., 2007) or $E = 4840\,\mathrm{GPa}$, $\nu = 0.19$, $h = 0.075\,\mathrm{nm}$ (Pantano et al., 2004). A more detailed list of parameter sets can be found, e.g, in (Huang et al., 2006). Although the different parameter sets give almost the same values for C, the obtained values for D are significantly different having a remarkable influence on the stability behavior of onion layers. For a single, perfectly spherical onion layer (i.e., without the supporting layers underneath) the critical pressure can be estimated as (Pflüger, 1975)

$$p_i^* = \frac{2Eh^2}{\sqrt{3(1-\nu^2)}(R_i^{(0)})^2}\ , \tag{1}$$

where $R_i^{(0)}$ is the radius of layer i. As can be seen from Eq. (1) the pressure p_i^* is quite sensitive to E and h. Consequently, also the occurrence of a structural instability in a carbon onion is likely to be sensitive to these parameter sets. Thus, a different choice of E, h, and ν will lead to different proposes on the critical size of the onions. Parameter sets with $E \approx 1000\,\mathrm{GPa}$ and $h \approx 0.34\,\mathrm{nm}$ strongly overestimate the bending stiffness and, hence, the critical pressure of fullerenes, i.e., single onion layers as shown in (Todt et al.,

2013 in press). Thus, also the critical size of the onions might be strongly overestimated by such parameter sets. A good representation of the stiffness properties of fullerenes and their critical pressure can be obtained with $E \approx 5000\,\mathrm{GPa}$ and $h \approx 0.07\,\mathrm{nm}$ (Todt et al., 2013 in press). On account of this the parameter set proposed in (Pantano et al., 2004) ($E = 4840\,\mathrm{GPa}$, $\nu = 0.19$, $h = 0.075\,\mathrm{nm}$) is used to describe the layer properties.

Although the layers are modeled as spherical shells it is assumed that their number of atoms is equal to those of icosahedral fullerenes with the same mean radii. According to (Tang and Huang, 1995a) the number of atoms, n, forming fullerenes with icosahedral symmetry can be calculated using $n = 60k^2$ or $n = 20m^2$, with $k, m \in \mathbb{N}$. The radius $R_i^{(0)}$ of an undeformed, i.e, stress free layer i can than be evaluated as (Voytekhovsky, 2003)

$$R_i^{(0)} = a^{(0)}\sqrt{0.103374\ n_i - 0.424548}\ , \tag{2}$$

where $a^{(0)} = 0.142\,\mathrm{nm}$ is used as carbon-carbon bond length in the undeformed configuration and n_i is the number of atoms forming this layer.

2.2. Excess Surface Energy

In (Holec et al., 2010) it is shown that a curvature-dependent excess surface energy is active in curved carbon nanostructures. As a consequence of the excess surface energy the layers are subjected to surface stresses leading to a non-zero membrane stress state in the layers.

The dependency of the excess surface energy $E_i^{(S)}$on the layer radius R_i can be described using a power law $E_i^{(S)} \propto R_i^{\beta}$ (Holec et al., 2010). For $E_i^{(S)}$ being expressed in $\mathrm{J/(nm)^2}$ an average value of $\beta = -1.83$ is evaluated for the whole fullerene model; for more details see (Holec et al., 2010). Consequently

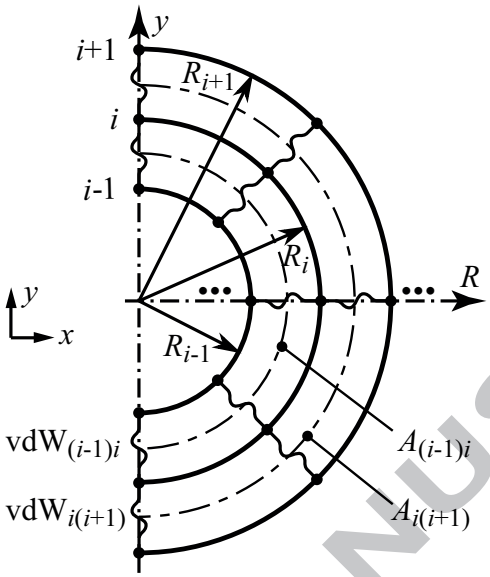

Figure 1: Axisymmetric model of a carbon onion consisting of N layers.

a surface stress $\bar{\sigma}_i^{(S)}$ (being a membrane force per unit length) develops in the onion layers according to the Shuttelworth equation (Fischer et al., 2008),

$$\bar{\sigma}_i^{(S)} = E_i^{(S)} + \frac{\mathrm{d}E_i^{(S)}}{\mathrm{d}\bar{\varepsilon}_i^{(S)}} \ . \tag{3}$$

The parameter $\bar{\varepsilon}_i^{(S)}$ is the in-plane strain in a small strain setting (Fischer et al., 2008). For a first estimate usually the second term of the right hand side of Eq. (3) can be neglected, and the relation

$$\bar{\sigma}_i^{(S)} = E_i^{(S)} \tag{4}$$

can be used. Note that in Eqs. (3) and (4) the quantities $E_i^{(S)}$ and $\bar{\sigma}_i^{(S)}$ are physically different but have the same unit, namely force per unit length.

In the finite element model the surface stress $\bar{\sigma}_i^{(S)}$ is taken into account by applying a corresponding inwards oriented pressure $p_i^{\mathrm{S}} = 2\bar{\sigma}_i^{(S)}/R_i$ (Fischer

et al., 2008) onto layer i, resulting with Eq. (4) in

$$p_i^{\mathrm{S}} = 2A\ R_i^{-2.83}. \tag{5}$$

The factor $A \approx 0.36\,\mathrm{nN\ nm/(nm)^{0.17}}$ is estimated form Fig. 7 in (Holec et al., 2010). As can be seen from Eq. (5), the pressure p_i^{S} decreases fast with increasing layer radius R_i and, thus, is only of relevance for the innermost layers of a carbon onion.

2.3. Van der Waals Model

For carbon onions the vdW interactions between neighboring layers must be considered as well. From an atomistic point of view the vdW interactions between two neighboring layers result from vdW interactions between the atoms forming these layers. This atom-atom interactions, however, are not applicable in continuum mechanical models, for which a pressure-distance relation is required. Appropriate continuum vdW models for different carbon nanostructures can be found in literature, see, e.g., (He et al., 2005; Kelly, 1981; Lu et al., 2009; Todt et al., 2011a). In (Lu et al., 2009; Todt et al., 2011a) the curvature of the carbon nanostructures is taken into account in the formulation of the vdW interactions. In the present study this curvature influence on the vdW interactions is neglected for the sake of simplicity, and pressure-distance relations derived for planar graphene are used (Kelly, 1981; Todt et al., 2011a). With increasing layer radii the curvature effect in the vdW interactions vanishes and, thus, for the outer layers this simplification is admissible. Onion layers with small radii, i.e., the innermost layers, are much stiffer and have a much higher resistance against buckling than the outermost layers, see Eq. (1). Therefore, it seems unlikely that buckling starts at the

center of the onion. Consequently, the simplified representation of the vdW interactions in the inner region is assumed to be of minor influence.

The pressure-distance relations used for describing the vdW interactions read according to (Kelly, 1981)

$$p(\alpha) = \frac{C_{33}}{6} \left[\left(\frac{\sigma}{\alpha}\right)^{10} - \left(\frac{\sigma}{\alpha}\right)^{4} \right] , \tag{6}$$

or (Todt et al., 2011a)

$$p(\alpha) = C_0 \left[\left(\frac{\sigma}{\alpha}\right)^{11} - \left(\frac{\sigma}{\alpha}\right)^{5} \right] , \tag{7}$$

respectively, where α is the current interlayer distance and σ is a Lennard-Jones Parameter. The parameters C_{33} and C_0 are compressive constants. In (Kelly, 1981; Zhao and Spain, 1989) a value of 36.5 GPa is reported for C_{33}, whereas C_0 is obtained as $C_0 = 8\,\epsilon\,\sigma\,\pi\,(\rho_\infty)^2$ (Todt et al., 2011a) and, thus, depends on the atom density per unit area, $\rho_\infty = 38.18\,\text{atoms/nm}^2$, and another Lennard-Jones parameter ϵ. In the literature different values can be found for σ and ϵ, see, e.g., $\sigma = 0.3415\,\text{nm}$, $\epsilon = 0.00239\,\text{eV}$ in (Lu et al., 2009) and $\sigma = 0.3345\,\text{nm}$, $\epsilon = 0.00319\,\text{eV}$ in (Zhang et al., 2007). Thus, it is unlikely that $C_{33}/6$ and C_0 have the same value. VdW models described by Eqs. (6) and (7) not only differ in their compressive constants but also in their exponents. This differences may lead to different results for the growth limit of carbon onions as considered in the following. It should be noted that both models give the same interlayer distance $\alpha_{\text{eq}} = \sigma$ for which $p(\alpha) = 0$. The distance α_{eq} is referred to as equilibrium vdW distance.

2.3.1. Linear van der Waals Model

Taking the nonlinear behavior of the vdW interactions into account is a computationally intensive task. Thus, the vdW interactions are linearized

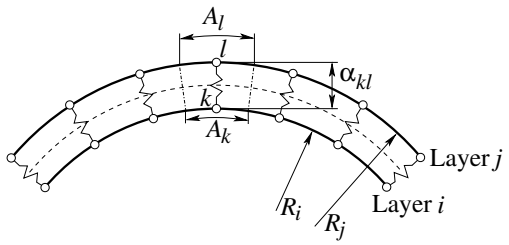

Figure 2: Areas associated to nodes k and l in curved structures.

around the vdW equilibrium distance α_{eq} for performing principle model analyses in a first attempt. This linearization is admissible if the distances α between neighboring layers are close to α_{eq} and the deviations $\Delta\alpha$ in the interlayer distances are small. The linearized vdW interactions can be interpreted as some sort of elastic bedding, and linear spring elements are used to model this bedding. The modeling procedure of the linear vdW bedding is described for Eq. (6) only, but can be easily transferred to Eq. (7), too.

Under the above assumptions the linearized pressure-distance relation corresponding to Eq. (6) reads

$$p_{\mathrm{lin}} = \hat{k}\Delta\alpha \ , \tag{8}$$

with $\hat{k} = \frac{\mathrm{d}p}{\mathrm{d}\alpha}|_{\alpha=\alpha_{\mathrm{eq}}} = \frac{C_{33}}{\alpha_{\mathrm{eq}}}$ being the linearized stiffness of the vdW bedding. With Eq. (8) the vdW force F_{kl} acting on a single finite element node of the layers can be obtained as

$$-F_{kl} = p_{\mathrm{lin}} A_{kl} = \hat{k} A_{kl}(\alpha_{kl} - \alpha_{\mathrm{eq}}), \tag{9}$$

where α_{kl} and $A_{kl} = \frac{A_k + A_l}{2}$ are the current distance between and the area associated to nodes k and l, respectively linked by the spring element, see

Figure 2. The area A_{kl} accounts for the curvature dependent difference between areas A_k and A_l related to nodes k and l, respectively. The negative sign in Eq. (9) means that forces in the springs are positive for attraction and negative for repulsion. From Eq. (9) it follows that the stiffness , k_{kl}, of the spring element linking nodes k and l reads

$$k_{kl} = -\hat{k} A_{kl} \ , \tag{10}$$

In contrast to more advanced models (Todt et al., 2011a), this vdW model leads to equal forces on opposite faces of neighboring layers $p_i A_i = p_j A_j = p_{\text{lin}} \frac{A_i + A_j}{2}$, where p_i and p_j are the vdW pressures acting on the layers with areas A_i and A_j, respectively.

2.3.2. Nonlinear van der Waals Model

In more advanced simulations the nonlinear behavior of the vdW interactions is taken into account. For this purpose the vdW interactions are modeled in ABAQUS as user defined contact interface UINTER (Pantano et al., 2004; Yao et al., 2008) for which the "contact" stresses in normal and tangential direction have to be defined. Although, the vdW interactions are treated as contact, the layers i and j are still separated by the interlayer distance α. The stresses in normal direction, i.e., the "contact" pressures on neighboring layers, can be directly defined by using either Equation (6) or Equation (7). The shear stiffness of the vdW interface is small compared to the normal stiffness and is neglected in the vdW model (Pantano et al., 2004). Therefore, the tangential stresses in the interface are set to zero corresponding to a frictionless "contact" between the layers. To ensure proper convergence characteristics, also the incremental, i.e., tangent interface stiff-

ness matrix $\underset{\approx}{\mathbf{K}}^{(\mathrm{I})}$ has to be implemented by the user. The matrix element $K_{ij}^{(\mathrm{I})}$ defines the change in the i-th stress component due to an infinitesimally small perturbation of the j-th component of the array of relative displacements between adjacent layers. Thus, the current component $K_{11}^{(\mathrm{I})}$ is equal to the current stiffness of the vdW bedding in normal direction in terms of a pressure-distance relation

$$K_{11}^{(\mathrm{I})} = \frac{\partial p(\alpha + \Delta\alpha)}{\partial \Delta\alpha} \ . \tag{11}$$

All other components of the interface stiffness matrix are set to zero, as the vdW interface is assumed to have zero shear stiffness. Like for the linear vdW model the vdW forces on opposite faces of neighboring layers are equal.

2.4. Simulating the growth of carbon onions

Starting with the outermost layer in the growth simulations seems to be problematic as the size of the carbon onion at its growth limit is a priori not known. Thus, it is assumed that in the model the carbon onion grows layer-by-layer starting with the innermost one.

For the first, i.e., the innermost layer the C60 fullerene is used. This layer is assigned the layer index $i = 1$. Further layers are deposited one after the other. Each new layer $i = N$ with radius $R_N^{(0)}$ in the stress free configuration is concentrically located outside onto the surface of the current onion consisting of $N-1$ layers. The pressure p_N^{S} due to the surface stress is applied and kept constant during the whole growth simulation. Usually, the interlayer distance $\alpha_{(N-1),N}^{(0)} = R_N^{(0)} - R_{N-1}$ between layers N and $N-1$ is not equal to the vdW equilibrium distance α_{eq}. Thus, the new layer N does not exactly fit the onion. Due to this misfit the vdW interactions lead, in

combination with the surface stress, to either tensile or compressive stresses in this new layer. Additionally, the stresses in the layers underneath are changed, too. The new equilibrium configuration of the N-layered onion is calculated in a geometrically nonlinear analysis step and evaluated regarding its stability by performing a buckling eigenvalue analysis. The formulation of the eigenvalue problem depends on the type of model used for describing the vdW interactions between adjacent layers.

Simulations with the Linear van der Waals Model

In the linear vdW model the spring elements between the layers are introduced with a stress free length of $\alpha^{(0)}_{(N-1),N}$. The vdW interactions due to $\alpha^{(0)}_{(N-1),N} \neq \alpha_{\mathrm{eq}}$ are calculated using Eq. (9) and are, like the surface stress being active in layer N, considered as perturbation loads in the buckling eigenvalue prediction. The corresponding eigenvalue problem reads

$$\left(\underset{\approx}{\mathbf{K}}_{N-1} + \bar{\lambda}^j_N \Delta\bar{\underset{\approx}{\mathbf{K}}}_N\right) \bar{\underset{\approx}{\mathbf{\Phi}}}^j_N = \underset{\sim}{\mathbf{0}} \; . \tag{12}$$

In Eq. (12) $\underset{\approx}{\mathbf{K}}_{N-1}$ is the tangent stiffness matrix of the system with N layers including the effects of the surface stress and the vdW forces acting in the configuration of the carbon onion with $N-1$ layers. The matrix $\Delta\bar{\underset{\approx}{\mathbf{K}}}_N$ represents the contribution of the vdW interactions between layer $N-1$ and N and the surface stress in layer N. The parameters $\bar{\lambda}^j_N$ are the eigenvalues and $\bar{\underset{\approx}{\mathbf{\Phi}}}^j_N$ are the corresponding eigenfunctions. The smallest eigenvalue $\bar{\lambda}^1_N$ is the factor by which the contribution of the N-th layer has to be multiplied in order to bring the onion consisting of N layers to an unstable state. Thus, layer N cannot be added without surpassing the stability limit if $\bar{\lambda}^1_N < 1.0$. The corresponding eigenvector $\underset{\sim}{\mathbf{\Phi}}^1_N$ characterizes the buckling mode of the

N-layered carbon onion.

Simulations with the Nonlinear van der Waals Model

In the nonlinear vdW model the vdW interactions due to the difference $\alpha^{(0)}_{(N-1),N} \neq \alpha_{\mathrm{eq}}$ become active directly after the new layer is added. They are, thus, not available as perturbation loads in the eigenvalue buckling prediction. To overcome this problem an external pressure $p_N^{(\mathrm{ext})}$ is applied to the outermost layer N in the stability analysis. The pressure $p_N^{(\mathrm{ext})}$ is defined to be equal to the critical pressure p_i^* of this layer without its supporting layers underneath and is calculated with Eq. (1). The choice of $p_N^{(\mathrm{ext})} = p_i^*$ is not based on any necessity but provides information about the effect of bedding due to the inner layers.

The corresponding eigenvalue problem is then defined as

$$\left(\underset{\approx}{\mathbf{K}}_N + \bar{\lambda}^j_N \Delta\bar{\underset{\approx}{\mathbf{K}}}_N\right) \bar{\underset{\sim}{\mathbf{\Phi}}}^j_N = \underset{\sim}{\mathbf{0}} \tag{13}$$

with $\underset{\approx}{\mathbf{K}}_N$ being the tangent stiffness matrix of the N-layered onion in its equilibrium state including the vdW interactions between all N layers. The matrix $\Delta\bar{\underset{\approx}{\mathbf{K}}}_N$ represents the change in the stiffness of the onion due to the external pressure $p_N^{(\mathrm{ext})}$. The variables $\bar{\lambda}^j_N$ and $\bar{\underset{\sim}{\mathbf{\Phi}}}^j_N$ again are the eigenvalues and the corresponding eigenvectors, respectively. For this model the smallest eigenvalue $\bar{\lambda}^1_N$ is the factor by which the pressure $p_N^{(\mathrm{ext})}$ on the outermost layer has to be multiplied to bring the N-layered onion to a critical state. In contrast to the linearized model, $\bar{\lambda}^1_N = 0$ indicates that the carbon onion has grown to its critical size, whereas $\bar{\lambda}^1_N <= 1$ means that the critical pressure of the onion is equal to or smaller than the buckling pressure of the outermost layer. For the linearized vdW model the eigenvalue analysis is used to check

if another layer can be added without provoking a structural instability. For the nonlinear model it is checked if an existing onion is still stable when its outermost layer is subjected to an external pressure $p_N^{(\mathrm{ext})}$. Thus, if $\bar{\lambda}_N^1 = 0$ no external pressure is required to provoke a structural instability. This means that the section forces, i.e., the membrane forces per unit length of section line, introduced due to the mutual accommodation of the layers are then sufficient to evoke buckling and, hence, the onion has grown to its critical size.

3. Results and Discussion

3.1. Simulations with the Linear van der Waals Model

For the linear vdW model adding a further layer to the onion requires only a single linear solution step, leading to low computational requirements. This model is used to check if the surface stress has an influence on a possible growth limit of carbon onions. Furthermore, the number of atoms n_i forming the new layer to be added is calculated in two different ways. (i) It is assumed that every new layer is an icosahedral fullerene where $n_i = 60\ i^2$, with i being the layer index. (ii) The new layer belongs either to the group of $n_i = 60\ m^2$ or $n_i = 20\ k^2$ fullerenes ($k, m \in \mathbb{N}$), where the fullerene with the smallest accommodation effort is chosen. In the following (i) and (ii) are referred to as "pure" and "mixed" configuration, respectively. The linear vdW model used is based on Eq. (6) with $\sigma = 0.3415\,\mathrm{nm}$ (Lu et al., 2009).

The obtained eigenvalues related to buckling are depicted in Fig. 3. An eigenvalue $\bar{\lambda}_N^1 > 1.0$ means that the onion is in a stable equilibrium configuration. On one hand, the surface stress only has an influence on $\bar{\lambda}_N^1$ if

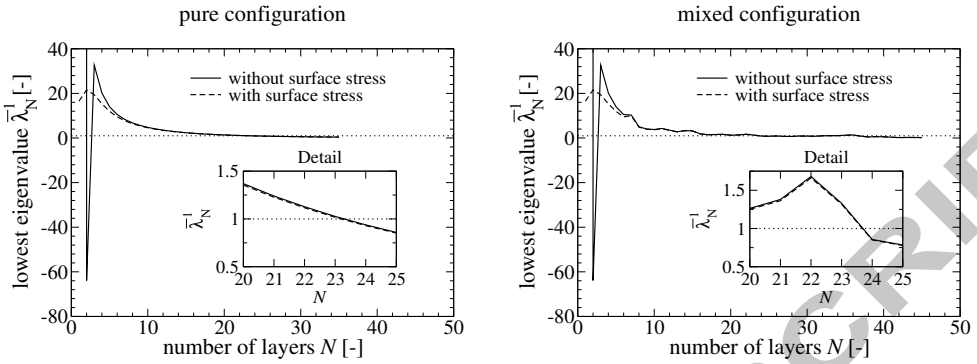

Figure 3: Lowest eigenvalue $\bar{\lambda}^1_N$ depending on the number of layers N forming a carbon onion for the pure (left) and mixed (right) configuration. Insets show a magnification, when the eigenvalue drops below one, i.e., the onion approaches its stability limit.

the onions consists of less than six layers and, on the other hand, it "stabilizes" the model by preventing the solution from running into the negative peak which represents an artifact. For $N \geq 6$ the influence of the surface stress becomes negligible. The lowest eigenvalue $\bar{\lambda}^1_N$ approaches 1.0, if the onion has grown to a size of $N = N_{\text{crit}} = 23$ layers, for both configurations independent of the surface stress. As can be seen from Fig. 4 only a few outer layers buckle in an interactive way, whereas the inner layers remain unaffected. The observed buckling mode is comparable to buckling modes observed for complete spheres filled with elastic media (Sato et al., 2012). This confirms the applicability of of the axisymmetric model as discussed in Subsection 2.1.

The difference between pure and mixed configurations becomes obvious if the section forces f_i in the layers (Figure 5) and the resulting interlayer

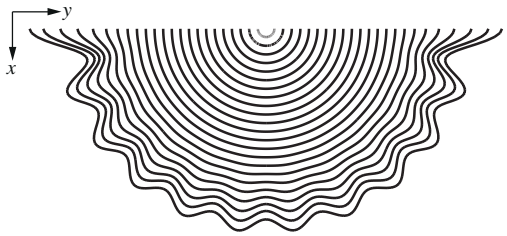

Figure 4: Buckling mode of a carbon onion of pure configuration corresponding to the lowest eigenvalue $\bar{\lambda}_N^1 = 1.0$ at the growth limit $N_{\text{crit}} = 23$ achieved by using a linear vdW model.

distances α_{ij} (Figure 6) are considered. Instead of stresses σ_i stress resultants in terms of section forces $f_i = \sigma_i h$ are used since the layer thickness h is just an effective value, see Section 2.1.

Figure 5 shows the evolution of the section forces f_i in the individual layers during the growth of the onion. In case of the pure configuration each newly added layer k is first subjected to compressive section forces f_k whether or not the surface stress is considered. During further growth of the onion the compressive section forces are reduced and, if sufficient layers are added, tensile section forces develop in layer k. Thus, only the outer layers of the onion are under compression. The influence of the formation of a new layer on the section forces of the layers underneath vanishes towards the center. At the growth limit $N = N_{\text{crit}}$ only the four outer layers are under compression.

Taking the surface stress into account leads to a relatively large compressive section force in the innermost layer, which is reduced after the second layer is added but does not become a tensile section force during the growth of the onion. In this case also the second layer remains under compression during the growing process. The influence of the surface stress on the section

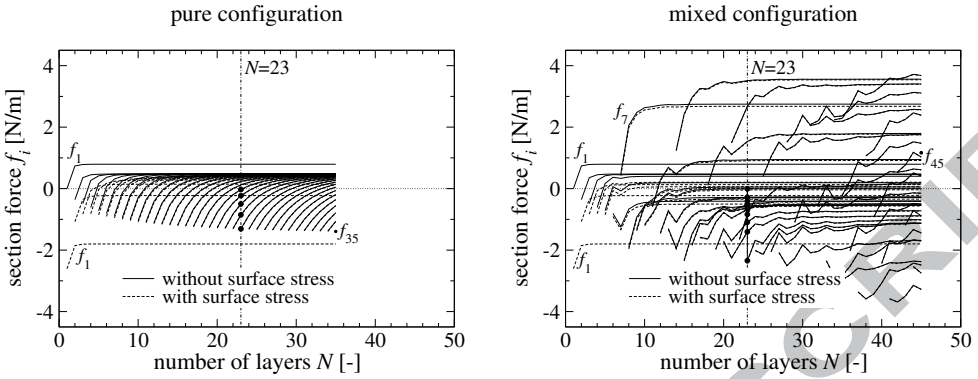

Figure 5: Section forces f_i in the i-th layer of an N-layered onion for the pure (left) and mixed (right) configuration. Negative values of f_i denote compression. For $N = 23$, compressive section forces in the layers are marked with • for the case where no surface stress is considered.

forces f_i vanishes fast with increasing size of the layers, and and for layers with $i > 8$ the section forces are unaffected by the surface stress. Although the surface stress introduces substantial compressive section forces in the two innermost layers, it has no influence on the growth limit of the onion. The pressure p^* required to introduce buckling in a layer with radius R scales with $\frac{1}{R^2}$, see Eq. (1). Thus, layers in the outer region of the onion are much more sensitive to buckling than those in the inner region. The radius of the outermost layer R_{23} is about 23 times the radius of the innermost layer $R_1 \approx 0.341\,\text{nm}$ and, therefore, the critical pressure of the innermost layer is about 530 times higher than that of layer $i = 23$. Thus, the influence of the compressive section forces in the inner layers and, hence, the surface stress is negligible, and buckling is introduced in the outer region of the onion.

For the mixed configuration (Figure 5, right) a newly added layer is not

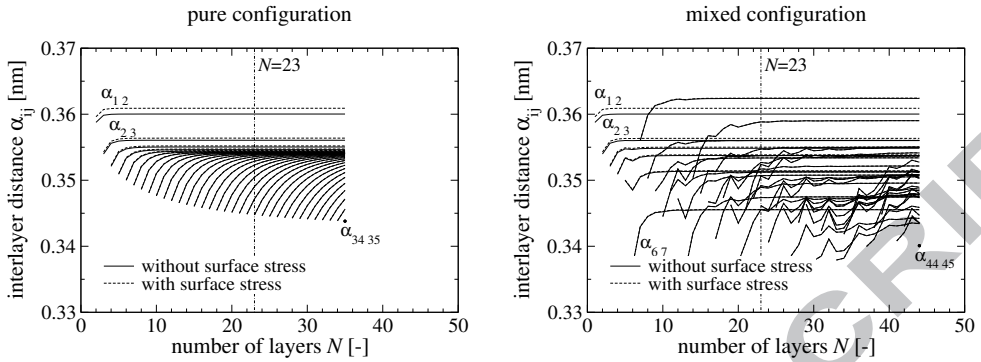

Figure 6: Interlayer distances α_{ij} between layers i and $j = i+1$ depending on the number of layers N for the pure (left) and mixed (right) configuration.

a priori under compression. At the stability limit 11 layers are under compression, not all of them being located in the outer region of the onion. The absolute values of the compressive and tensile section forces are generally higher than those observed for the pure configuration.

Figure 6 shows the current interlayer distances α_{ij} after layer N has been added and the N-layered onion has reached its new equilibrium configuration.

For the pure configuration the interlayer distance $\alpha_{ij}^{(0)} = R_j^{(0)} - R_i$ ($i = j - 1$) between the newly formed layer $j = N$ and the onion consisting of $N - 1$ layers is always larger than the equilibrium distance of the vdW interactions, $\alpha_{\mathrm{eq}} = 0.3415\,\mathrm{nm}$. This leads to attractive vdW forces between the $(N-1)$-layered onion and the new layer, introducing compressive section forces in the new layer and tensile section forces in the $N - 1$ layers forming the onion. As a consequence also the interlayer distances in the outer region of the $(N - 1)$-layered onion increase, whereas the interlayer distances in the inner region remain almost unaffected. All interlayer distances α_{ij} of an

N-layered onion in its equilibrium state are larger than α_{eq}, see Figure 6 (left). The interlayer distances decrease from the inner region of the onion to the outer region, which is in contrast to experimental observations, see e.g. Banhart (1997). However, also in Baowan et al. (2007) a decrease in layer spacing from the inner region to the outer region of a carbon onion is calculated using analytical continuum mechanical models. The surface stress has an influence on the interlayer distances $\alpha_{1\ 2}$ and $\alpha_{2\ 3}$ only. The interlayer distances in the outer region of an N-layered onion are completely unaffected by the surface stress.

For onions of the mixed configuration (Figure 6, right) the interlayer distances α_{ij} do not decrease continuously from the inner region to the outer region. Generally, the formation of layers j from the series $n_j = 20\ k^2$ leads to a smaller interlayer distances α_{ij} than the formation of layers belonging to the $n_j = 60\ m^2$ series and, consequentially, to a mixture of interlayer distances being smaller and larger than α_{eq}. The waviness of the interlayer distance curves and the section force curves is a consequence of this.

Although, the interlayer distances and section forces obtained for the pure and mixed configurations are different, both configurations give quite the same growth limit $N_{\text{crit}} = 23$ layers. This growth limit is significantly lower than the number of layers found in reality Banhart (1997); Banhart et al. (1997a); Blank et al. (2007); Wesolowski et al. (1997); Zwanger et al. (1996). The reason for the difference between experimentally observed and simulated values of N_{crit} is the simplification of the vdW interactions. The linear vdW model is only valid for interlayer distances α_{ij} close to α_{eq}, but the obtained interlayer distances differ considerably from α_{eq}, see Figure 6.

If α_{ij} is larger than α_{eq} the linear vdW model overestimates the stiffness of the vdW bedding and, as a consequence, the vdW interaction forces between the layers. Thus, the vdW induced section forces in the layers are too high. Since the compressive section forces in the outer layers are responsible for the occurrence of the instability, overestimating these forces introduces the instability too early. This leads to a value N_{crit} which is much lower than the experimentally observed maximum number of layers.

Nevertheless, the linear model shows that the occurrence of a structural instability most likely limits the size of carbon onions. The vdW interactions, leading to self-equilibrating stress states in the layers due to mutual accommodation, have shown to be responsible for the loss of stability, whereas the curvature induced surface stress plays only a minor role. Using a nonlinear vdW model should lead to more realistic values of N_{crit}.

3.2. Simulations with the Nonlinear van der Waals Model

As the vdW interactions are the driving forces behind the growth limit of carbon onions their influence is investigated in more detail. Due to the minor influence of the surface stress on the growth limit it is neglected in the following. Furthermore, it seems to be of no importance if the carbon onion belongs to the pure or mixed configuration. Thus, only onions of pure configuration are considered.

The two different vdW models, given by Equations (6) and (7) are used to describe the vdW interactions and are referred to as M1 and M2, respectively. For the required Lennard-Jones parameters σ and ϵ two different sets, S1 ($\sigma = 0.3415\,\mathrm{nm}$ and $\epsilon = 0.00239\,\mathrm{eV}$ (Lu et al., 2009)) and S2 ($\sigma = 0.3345\,\mathrm{nm}$ and $\epsilon = 0.00319\,\mathrm{eV}$ (Zhang et al., 2007)) are taken from literature. The

Table 1: Nonlinear vdW models used in the stability analysis of carbon onions.

Model	Equation	σ in nm	ϵ in eV	$C_{33}/6$ in GPa	C_0 in GPa
M1S1	(6)	0.3415	0.00239	$6.08\dot{3}$	-
M2S1	(7)	0.3415	0.00239	-	4.79
M1S2	(6)	0.3345	$0.00319eV$	$6.08\dot{3}$	-
M2S2	(7)	0.3345	0.00319	-	6.26

two vdW models M1 and M2 in combination with the parameter sets S1 and S2 lead to four different vdW interfaces which are defined according to Sec. 2.3.2. The parameters and compressive constants used in the interface definitions are summarized in Table 1.

Figure 7 shows the results of the computational stability analysis based on Eq. (13) for the different vdW interfaces. A value $\bar{\lambda}_N^1 \geq 1$ indicates that the critical pressure of the onion is larger than the buckling pressure of the outermost layer, i.e., the outermost layer is sufficiently supported by the inner layers to prevent buckling. For a low number of layers the supporting effect becomes larger with increasing layer numbers. After reaching a certain number of layers, the inner layers are still supporting the outermost one, but the effect is reduced by every layer added. The numerical analysis terminates close before $\bar{\lambda}_N^1 = 0$ is reached due to ill-condition of the algebraic system (the matrix $\underset{\approx}{\mathbf{K}}_N$ approaches a singularity) describing the boundary value problem which arises when the next layer is added. The abort of the analysis implies that the onion is very close to its stability limit. Thus, the critical size of the onion can be extracted by extrapolation of the eigenvalue curves.

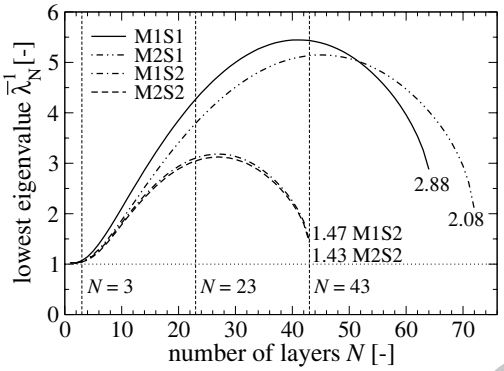

Figure 7: Lowest eigenvalue $\bar{\lambda}_N^1$ versus the current number of layers N forming the carbon onion. The different curves correspond to the different vdW interface models.

The vdW interface M1S1 is the nonlinear counterpart to the linear vdW interactions used in Section 3.1. For M1S1 a growth limit of $N_{\text{crit}} \approx 64$ is estimated which is much larger than the value $N_{\text{crit}} = 23$ calculated with the linear model. N_{crit} extracted with the improved interface M1S1 is comparable to numbers of layers of large onions found in experiments (Banhart et al., 1997b). The highest critical number of layers, $N_{\text{crit}} \approx 72$, is estimated with the interface M2S1. The vdW interfaces M1S2 and M2S2 show similar eigenvalue curves, and both interfaces lead to $N_{\text{crit}} \approx 43$, although the exponents of the vdW models M1 and M2 are different. The corresponding buckling mode of M1S2 at the growth limit is depicted in Fig. 8. The same buckling patterns can be observed for all vdW interfaces. The outermost layers buckle in an interactive way, whereas the inner layers remain almost unaffected. This corresponds to the buckling behavior observed already in Section 3.1.

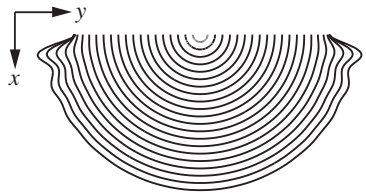

Figure 8: Buckling mode of a carbon onion modeled with interface M1S2. Only each second layer is displayed.

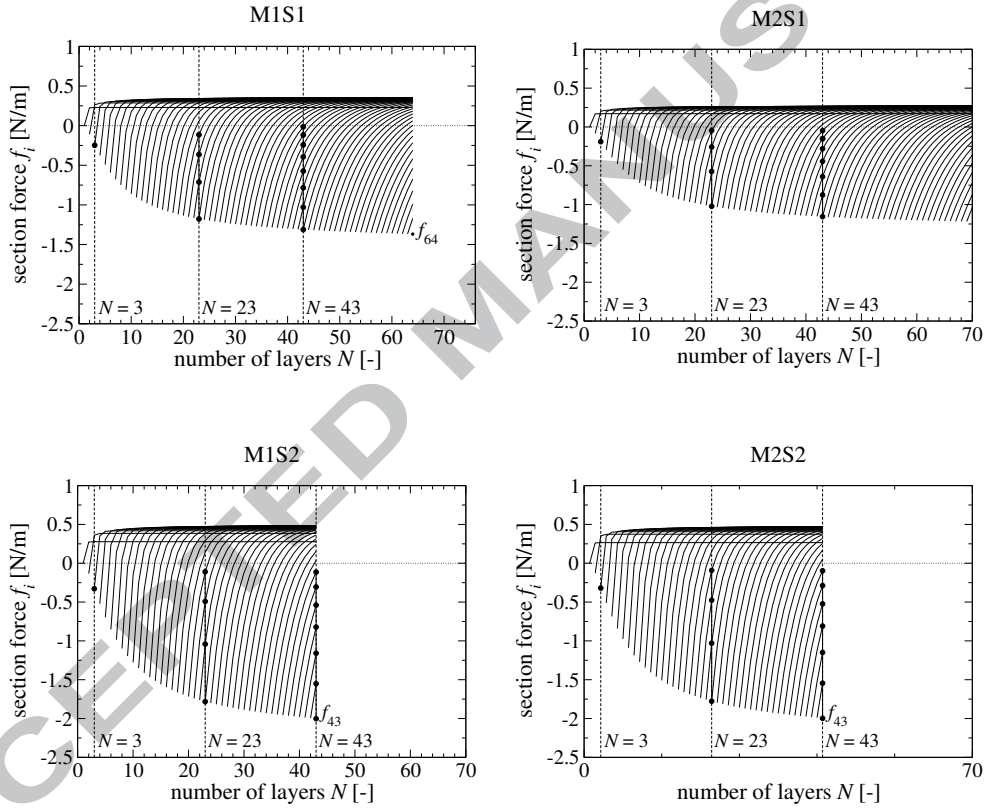

Figure 9: Section forces f_i in the i-th layer of an N-layered onion for all vdW interfaces. Negative values of f_i denote compression. Layers under compression are marked with • for $N = 3,\ 23$ and 43.

Figure 9 shows that, a newly added layer $i = N$ is always under compression. Adding further layers reduces the compressive section force in layer N, and if sufficient layers are added a tensile section force develops. If the onion has become large enough, adding of further layers does not lead to a further change in the section force of layer N, anymore, and also its distance to the layer underneath remains unaffected. The number of layers to be added until a tensile section force develops or until the layer remains unaffected by a new layer depends on the position of the layer in the onion. Only layers in the outer region are subjected to compressive section forces and their number increases with the size of the onion. This fact is illustrated in Fig. 10 for M1S1.

Although the qualitative behavior of all models with different nonlinear vdW interfaces is the same, their quantitative behavior is different. A higher value of the compressive constants C_{33} and C_0 leads to higher vdW pressures and, therefore, to higher compressive section forces in the layers, see Figure 9. Higher vdW pressures are also observed if a smaller vdW equilibrium distance $\alpha_{\text{eq}} = \sigma$ is used, as the initial interlayer distance α_{ij} between a newly added layer and the layers underneath is always larger than α_{eq}; compare M1S1 and M1S2 in Fig. 11. Higher values of the vdW pressures imply that higher compressive section forces are introduced in the outer layers and, hence, evoke the occurrence of a structural instability at lower layer numbers. If the vdW interfaces have (almost) the same compressive constant and vdW equilibrium interlayer distance (e.g., M1S2 and M2S2) the results of the eigenvalue problem, the interlayer distances, and the section forces are almost equal, too. This leads to the conclusion, that the different exponents of the

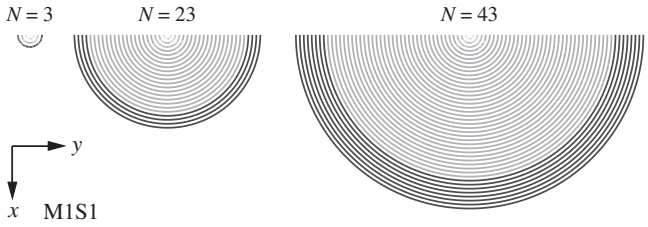

Figure 10: Number of layers under compression (black) and tension (gray) for onions of different sizes.

vdW models M1 and M2 have only a minor influence.

The obtained maximum number of layers forming the onions is highly sensitive to the vdW parameters used. Thus, the calculated growth limits have rather a qualitative than a quantitative character. Nevertheless, the results indicate that the occurrence of a structural instability is a possible explanation for the limited size of carbon onions. The obtained results for N_{crit} are in the range of the sizes of carbon onions observed in experiments (Banhart et al., 1997b), although much larger onions, e.g., consisting of 115 layers (Zwanger et al., 1996), have been observed. Possibly this high layer numbers can be achieved by allowing layers which are not a spherical representation of icosahedral fullerenes. These single layers need not to be thermodynamically stable if isolated, but may lead to a better accommodation of the different layers. This possibility is neglected in the presented model.

4. Conclusion

By using an axisymmetric continuum shell model it is shown that the occurrence of a structural instability is a possible explanation for the limited size of carbon onions. The instability is introduced by self-equilibrating stress

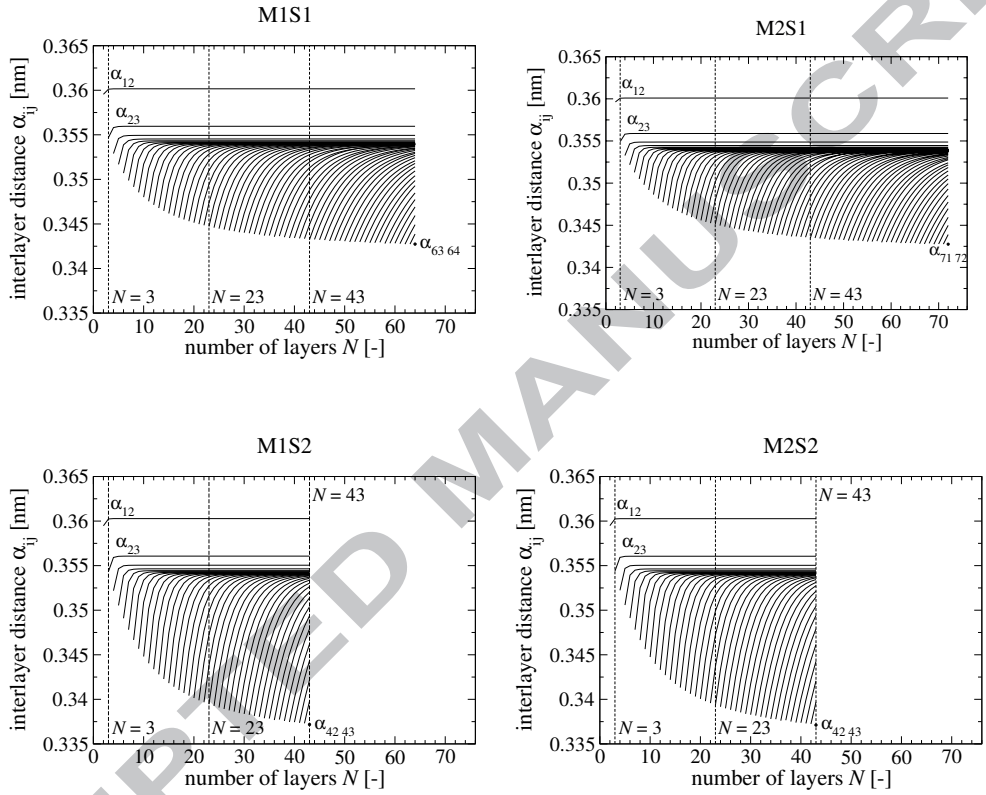

Figure 11: Interlayer distances α_{ij} between layers i and $j = i + 1$ depending on the number of layers N for all vdW interfaces.

states emerging due to accommodation of misfitting carbon layers during the growing process. The stresses are mainly introduced by van der Waals interactions between adjacent layers, whereas the influence of the curvature induced surface stress has shown to be negligible. Under the assumption that carbon onions grow from the inside to the outside, loss of stability is introduced in the outer layers whereas the innermost layers remain unaffected. Other growing scenarios might lead to different buckling patterns and should be considered in further studies. To obtain reasonable results for the growth limit the nonlinear character of the van der Waals interactions has to be taken into account. The so obtained critical sizes of the onions are highly sensitive to the interlayer distances and compressive constants used in the van der Waals models and, thus, rather have a qualitative than a quantitative character. To obtain a better representation of reality also the assumption of the layers being icosahedral fullerenes should be abandoned in further studies. Nevertheless, the used models clearly indicate a growth limit of carbon onions and can serve as basis for further investigations concerning the growth of such particles.

Acknowledgments

The first author, Melanie Todt, is grateful for funding by the fFORTE WIT - Women in Technology Program of the Vienna University of Technology and the Austrian Federal Ministry of Science and Research.

Vitae

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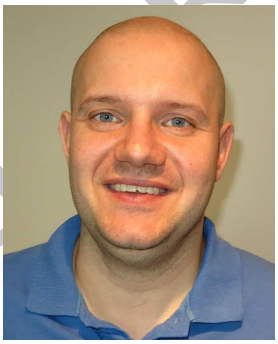

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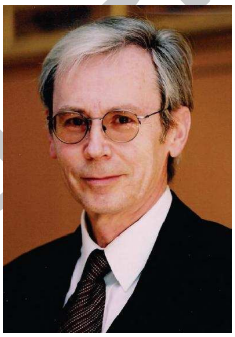
F.G. Rammerstorfer



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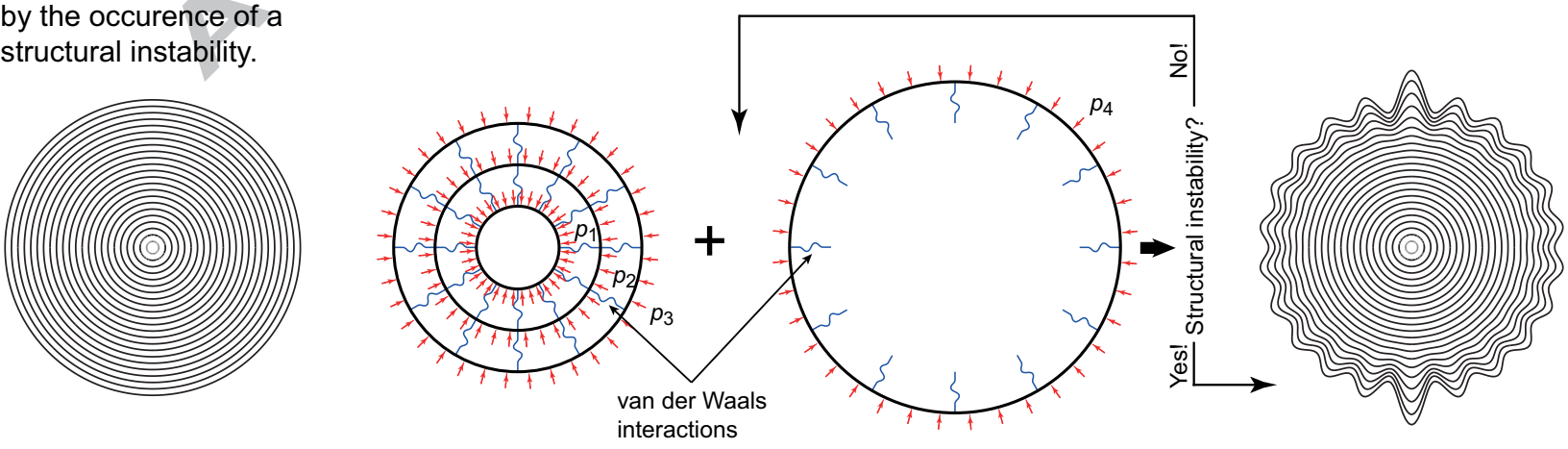
Hypothesis: Size of carbon onions is limited to N layers by the occurence of a structural instability.

Continuum mechanics model:

Adding a further layer enforcing additional van der Waals interactions and surface stress



Structural instability is found for a critical layer number.

p_i ... external pressure representing the surface stress due to layer curvature

The number of layers forming carbon onions seems to be limited.
The occurence of a structural instabilitiy can be a reason for this limitation.
The van der Waals interactions are the main reasons for the loss of stability.
The vdW parameters used have significant influence on the stability limit.
The influence of the curvature dependent surface stress is negligible.