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STRENGTH OF NANOSTRUCTURES

Do materials become insensitive to flaws at nanoscale? An answer based on Quantized Fracture Mechanics and Nanoscale Weibull Statistics

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Abstract Quantized Fracture Mechanics is applied for predicting the strength of nanostructures. An application to defective carbon nanotubes, compared with atomistic simulations and experiments, clearly shows that atomistic flaws in nanotubes can strongly reduce their strength, e.g., by a factor of $\sim$20 % if just one atom vacancy is considered. The analysis suggests that very few defects, relatively small in size, were responsible for breaking of the tested nanotubes. This result is confirmed by an application of "Nanoscale Weibull Statistics". Thus, it seems to us that the answer to the question posed in the title is – at least in general – "no".

Keywords: Nanomechanics, nanostructures, nanotubes, quantized fracture mechanics, nanoscale Weibull statistics, quantized strength

1. Introduction

In Linear Elastic Fracture Mechanics [1], the energy release rate is defined as $G = K_I^2/E' + K_{II}^2/E' + K_{III}^2(1+\nu)/E$, where $K_{I,II,III}$ are the stress-intensity factors for modes I, II, III of crack propagation, with $E' = E$ (for plane stress) or $E' = E/(1-\nu^2)$ (for plane strain), where E is the Young's modulus and ν is the Poisson's ratio of the material.

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According to classical Fracture Mechanics, the crack propagation will arise for [1]:

$$G \equiv -dW/dA = G_C \quad \text{or} \quad K_{I,II,III} = K_{I,II,IIIC} \tag{1}$$

where W is the total potential energy and the subscript C denotes a critical condition for the crack propagation (G_C and $K_{I,II,IIIC}$ are the fracture energy and toughness of the material). On the other hand, according to Quantized Fracture Mechanics [2] (QFM) the crack propagation will arise for:

$$G^* \equiv -\Delta W/\Delta A = G_C \quad \text{or} \quad K^*_{I,II,III} \equiv \sqrt{\langle K^2_{I,II,III}\rangle_A^{A+\Delta A}} = K_{I,II,IIIC} \tag{2}$$

where

$$\langle\cdot\rangle_A^{A+\Delta A} \equiv \frac{1}{\Delta A}\int_A^{A+\Delta A} \cdot \,\mathrm{d}A.$$

QFM assumes "dissipation energy" in quanta $G_C\Delta A$ where ΔA is the fracture quantum. Values for the stress intensity factors $K_{I,II,III}$ are available for the most interesting cases [3]: thus QFM can be applied by integration (Eq. (2)) in a very simple way. In contrast to classical fracture mechanics, that can treat only "large" (with respect to the fracture quantum) and sharp (vanishing tip radius) cracks, QFM has no restriction in treating defects with any size and shape [2]. Thus, QFM can be applied also at nanoscale, where classical fracture mechanics does not work [4].

2. Do Materials Become Insensitive to Flaws at Nanoscale?

Consider a linear elastic infinite plate in tension, of uniform thickness t, with a blunt crack with tip radius ρ and length $2l$, orthogonal to the applied far field σ (crack opening mode I). The material is described by the fracture toughness K_{IC} and by the fracture quantum at the considered size-scale $\Delta A = at$. Applying QFM, the failure strength is predicted as [2]:

$$\sigma_f\,(l,\rho) = K_{IC}\sqrt{\frac{1+\rho/2a}{\pi\,(l+a/2)}} = \sigma_C\sqrt{\frac{1+\rho/2a}{1+2l/a}} \tag{3}$$

where σ_C is the strength of the plain structure (coincident with the ideal material strength only at a very small scale); accordingly, the fracture quantum is estimated as $a \approx 2K^2_{IC}/\left(\pi\sigma^2_C\right)$. Equation (3) shows that

for $2l \ll a$ ("short" cracks) the structure becomes insensitive to flaws, whereas for $2l \gg a$ (and $\rho = 0$) QFM recovers classical fracture mechanics, that is not able to predict such "short crack behaviour". Roughly speaking, it is clear that structures having characteristic size of the order of the fracture quantum are predicted to be insensitive to flaws. Thus materials with a large value of $a \approx 2K_{IC}^2/\left(\pi\sigma_C^2\right)$ present a significant zone in which they become insensitive to flaws, in agreement to what has been recently observed in bio-nanocomposites [4]. On the other hand, at nanoscale such a parameter can be *of the order of* the interatomic spacing, as observed for nanotubes (see next section). Thus, the statement reported in the title of Ref. [4] ("materials become insensitive to flaws at nanoscale") cannot be considered to be true in general, as demonstrated in the next section.

The Counterexample of Carbon Nanotubes

The tensile strengths of individual multiwalled carbon nanotubes (MWCNTs) were measured [5] with a *nanostressing stage* composed of two opposing atomic force microscope (AFM) tips, Fig. 1a,b, located in a scanning electron microscope (SEM).

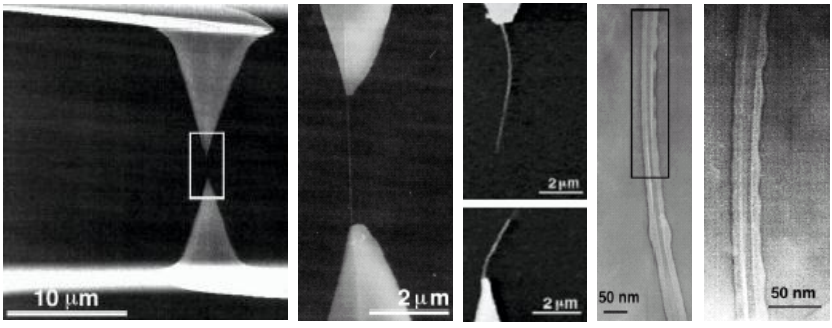


Figure 1. Experiments on fracture strength of nanotubes, [5].

The tensile experiment was prepared and observed entirely within the microscope and was recorded on video until fracture, [5]. The sum of the fragment lengths, Fig. 1c, far exceeded the original nanotube length. This apparent discrepancy was explained by a *sword-in-sheath* type fracture mechanism, similar to that observed in carbon fibers, i.e., the MWCNTs broke in the outermost layer. The tensile and fracture strength of this layer ranged from 11 to 63 GPa for the set of 19 MWCNTs that were loaded (Table 1). Analysis of the stress-strain curves for indivi-

dual MWCNTs indicated that the Young's modulus E of the outermost layer varied from 270 to 950 GPa. Transmission electron microscopic (TEM) examination of the broken nanotube fragments revealed a variety of structures, such as a nanotube ribbon, a wave pattern, and partial radial collapse, Figs. 1d,e.

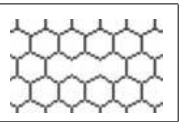
The experimental results on nanotubes [5] show distinct clusters about a series of decreasing values of strength, with the maximum 63 GPa, and the other values "quantized" at 43, 36–37, 25–26, 19–20 and 11–12 GPa, see the complete data set collection reported in Table 1. The measured higher strength of 63 GPa is not in agreement with the ideal tensile strength of nanotubes (∼100 GPa). Moreover, the observed strength quantization could be related to the quantization in the size of the defects.

Table 1. Experiments on fracture strength of nanotubes [5].

Test number	**Diameter [nm]**	**Length [μm]**	**Strength [GPa]**
1	28.0	4.10	11
2	28.0	6.40	12
3	19.0	3.03	18
4	31.0	1.10	18
5	28.0	5.70	19
6	19.0	6.50	20
7	18.5	4.61	20
8	33.0	10.99	21
9	28.0	3.60	24
10	36.0	1.80	24
11	29.0	5.70	26
12	13.0	2.92	28
13	40.0	3.50	34
14	22.0	6.67	35
15	24.0	1.04	37
16	24.0	2.33	37
17	22.0	6.04	39
18	20.0	8.20	43
19	20.0	6.87	63

We apply QFM assuming the fracture quantum to be identical to the distance between two adjacent broken chemical bonds, i.e., $a \approx \sqrt{3}r_0$, with $r_0 \approx 1.42$ Å interatomic length. For example, considering defects like n adjacent vacancies $2l = na$ in Eq. (3). This case was also treated by molecular mechanics (MM) atomistic simulations [6]. The comparison between these MM simulations and the predictions of Eq. (3) (we thus neglect here boundary effects) is summarized in Table 2;

Table 2. MM [6] and QFM [2] comparison of fracture strength of nanotubes with n adjacent vacancies (the graph reports the example of n=2, the applied load is vertical). The observed strengths are in parentheses [5].

Strength [GPa]	n=2 (63)	n=4 (...)	n=6 (43)	n=8 (39)	
MM – (80,0)	64.1	50.3	42.1	36.9	
QFM	64.1	49.6	42.0	37.0	

the MM-calculated strengths clearly follow the $(1+n)^{-1/2}$ dependence predicted by QFM with a fit of $\sigma_C\sqrt{1+\rho/2a} = 111\,\text{GPa}$. Starting from the value of the ideal strength [6] $\sigma_C = 93.5\,\text{GPa}$, it gives a reasonable tip radius of the atomistic flaws as $\rho \approx 0.8a \approx 2.0\,\text{Å}$. In Table 2 between brackets are reported the measured strengths. The first three values are well fitted assuming atomistic flaws having lengths of $n = 2, 4, 8$ (in units of fracture quanta). Thus, it is clear that atomistic flaws affect the strength of nanotubes. For a more detailed comparison, including also atomistic pinhole defects, see the QFM paper [2].

3. Nanoscale Weibull Statistics

Weibull statistics [7] for strength (or time to failure) of solids and deterministic Linear Elastic Fracture Mechanics do not apply properly at the nanoscale. Weibull statistics assumes that the number of critical flaws is proportional to the volume or to the surface area of the structure, whereas single crystal nanostructures are anticipated to be either defect-free or to have a small number of (critical) defects. As classical Fracture Mechanics has been modified (also) for nanoscale applications (by QFM [2]), similarly Weibull statistics has been modified by Nanoscale Weibull Statistics [8] (NWS) for describing the distribution of the strength of solids (also) at the nanoscale.

The simplest form of the volume-flaw based Weibull distribution [7] is

$$F(\sigma) = 1 - \exp\left[-V\left(\frac{\sigma}{\sigma_0}\right)^m\right],$$

where $F(\sigma)$ is the probability that a fiber will fail under tensile stress σ, σ_0 and m are Weibull's scale (with anomalous physical dimension) and shape (dimensionless) parameters respectively, and V is the fiber volume. The surface-flaw based Weibull distribution simply replaces V with the surface area S of the fiber (note that σ_0, m are then different compared to the σ_0, m obtained from the volume-flaw based Weibull distribution).

The cumulative probability $F(\sigma_i)$ can be obtained experimentally as

$$F(\sigma_i) = \frac{i - 1/2}{N},$$

where N is the total number of tests and the observed strengths $\sigma_1, \ldots, \sigma_N$ are ranked in ascending order [9]. The volume- and surface-based approaches become identical for the case of fracture of the external wall of nanotubes under tension, such as for the 19 nanotubes experimentally investigated [5]. This is true because $V = St = \pi DLt$, where t is the constant spacing between nanotube walls ($\sim$0.34 nm) and thus assigned as the shell thickness, and D and L are the nanotube diameter and length, respectively.

In terms of the number n of critical defects, Weibull statistics becomes:

$$F(\sigma) = 1 - \exp\left[-n\left(\frac{\sigma}{\sigma_0}\right)^m\right]. \tag{4}$$

Weibull statistics applied to fibers assumes $n = kD^\alpha L^\beta$, with $\alpha = 2$ and $\beta = 1$ if volume-flaws are considered, or $\alpha = 1$ and $\beta = 1$ if surface-flaws are considered (and k is a constant). On the other hand, we note that for nearly defect-free structures, one may assume "point-flaws" defects, i.e., that failure occurs at $n = 1$ (or equivalently at a value of n which is independent of the specimen size) for which $\alpha = 0$, $\beta = 0$, so that in general, it may be more appropriate to expect $0 \leqslant \alpha \leqslant 2$ and $0 \leqslant \beta \leqslant 1$. For example, if "length-flaws" defects are considered $\alpha = 0$ and $\beta = 1$. We note that the proposed NWS, that is, Eq. (4) with $n = kD^\alpha L^\beta$ and $0 \leqslant \alpha \leqslant 2$, $0 \leqslant \beta \leqslant 1$ (or $n = kH^\alpha L^\beta W^\gamma$ for rectangular cross-section areas $W \times H$, with $0 \leqslant \alpha, \beta, \gamma \leqslant 1$), corresponds for the limiting case of $\beta = 1$ to the modified Weibull distribution proposed for the study of the strength of sapphire whiskers [9].

Defining the nominal strength σ_n of the material for a specified value of F, e.g., $F(\sigma = \sigma_n) = \left(1 - e^{-1}\right) = 0.63$ (σ_n is thus defined as the strength corresponding to the 63% probability of failure), the corresponding size/shape-effect is predicted according to Eq. (4) as:

$$\sigma_n = \sigma_0 k^{-1/m} D^{-\alpha/m} L^{-\beta/m}. \tag{5}$$

The corresponding size-effect (that considers self-similar structures, i.e., $D \propto L$) is a power-law, in agreement with the Carpinteri's fractal law [10]. Strictly speaking Eq.(4) is defined for $\sigma < \sigma_C$, where σ_C is the (finite) ideal strength of solids, whereas obviously $F(\sigma \geqslant \sigma_C) \equiv 1$. Accordingly, in Eq. (5) σ_n is limited by σ_C. Note that the ratio between the exponents of D and L in Eq. (5) is equal to α/β. In the classical Weibull

statistics this ratio is set equal to 2 (volume-flaws) or 1 (surface-flaws). In contrast, as recently emphasized in [9], the ratio α/β can also be significantly different (for example for sapphire (α–Al_2O_3) whiskers it was observed to be equal to 7 or 15). Thus, it is clear that such size/shape effects cannot be explained by Weibull statistics, whereas Eq. (5) is compatible with the observations.

The standard Weibull statistics [7] applied to nanotubes [5] (Table 1) is shown in Fig. 2. The Weibull modulus is found to be $\sim$3. This represents the first estimation of the Weibull modulus for nanotubes. However, the correlation is very poor, showing a coefficient of correlation $R^2 = 0.67$.

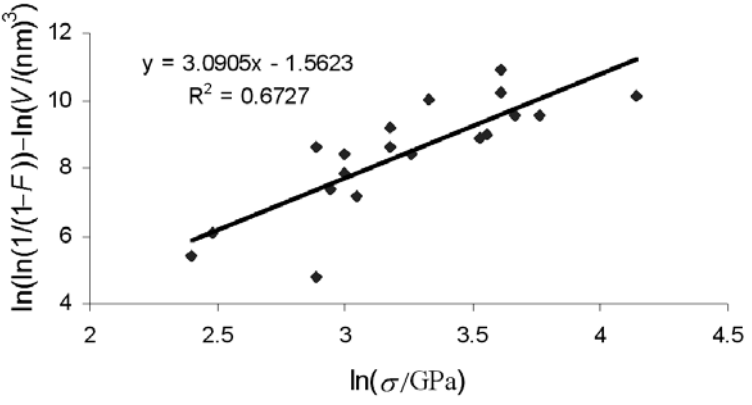


Figure 2. Weibull Statistics [7] applied to the observations on nanotubes [5].

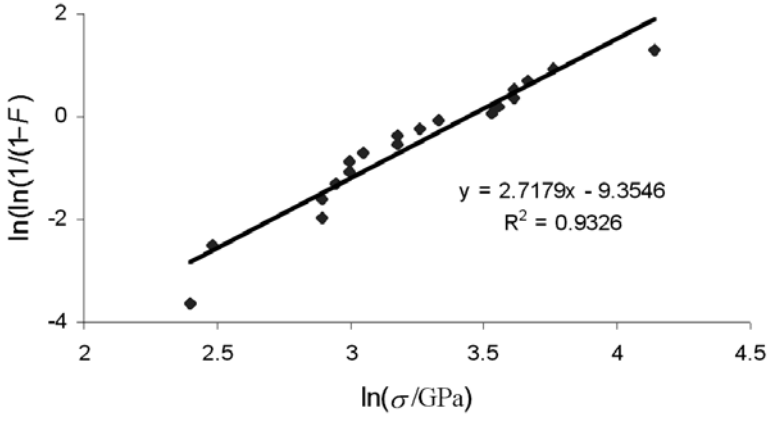


Figure 3. Nanoscale Weibull Statistics [8] applied to the observations on nanotubes [5].

In contrast, applying the NWS [8] with $n = 1$, we find $m \sim 2.7$ (and $\sigma_0 \approx 31\,\mathrm{GPa}$) with a significantly better correlation of $R^2 = 0.93$ (Fig. 3; please compare also Figs. 2 and 3).

In particular, the statistical data analysis suggests that a small number of defects (perhaps simply one critical nanoscale defect in each of the 19 different carbon nanotubes that were fractured) were responsible for these nanotubes breaking. The QFM deterministic argument is assessed by the NWS approach. Small numbers of atomistic defects can be crucial for the strength of nanostructures.

4. Concluding Remarks

The analysis, based on Quantized Fracture Mechanics and Nanoscale Weibull Statistics, corroborated by atomistic simulations and direct measurements, suggests that the answer to the question posed in the title must be considered – at least in general – to be "no".

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