QUANTIZED FRACTURE MECHANICS AND STRENGTH OF DEFECTIVE NANOTUBES

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ABSTRACT

A new energy-based theory, *Quantized Fracture Mechanics* (QFM), is presented. In contrast to Linear Elastic Fracture Mechanics (LEFM) QFM has no restrictions on treating defects of any size and shape. An application for predicting the strength of defective nanotubes concludes the paper.

INTRODUCTION

Two classic treatments of Linear Elastic Fracture Mechanics (LEFM) are Griffith's criterion [1], an energy-based method, and a method based on the stress-intensity factor [2]; as a matter of fact, they are equivalent [3]. Since LEFM can be applied only to "large" and perfectly sharp cracks, we choose to modify it, by accounting for the discontinuous nature of crack propagation and matter.

QUANTIZED FRACTURE MECHANICS

The energy release rate is defined as $G = \frac{K_I^2}{E'} + \frac{K_{II}^2}{E'} + \frac{1+\nu}{E} K_{III}^2$, 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 $E' = E/\left(1-\nu^2\right)$ (for plane strain), where E is the Young's modulus and ν is the Poisson's ratio of the material. LEFM is summarized as [4]:

$$G \equiv -\mathrm{d}W/\mathrm{d}A = G_C; \quad \left(\mathrm{d}G/\mathrm{d}A\right)_C < 0 \text{ stable, if } > 0 \text{ unstable (LEFM)} \tag{1a}$$

$$K_{I,II,III} = K_{I,II,IIIC}; \quad \left(\mathrm{d}K_{I,II,III}^2/\mathrm{d}A\right)_C < 0 \text{ stable, if } > 0 \text{ unstable (LEFM)} \tag{1b}$$

where W is the total potential energy and the pedex C denotes a critical condition for the crack propagation. We assume a quantization of Griffith's criterion to account for discrete crack propagation, and thus in the continuum hypothesis, differentials are substituted with finite differences, i.e., $\mathrm{d} \to \Delta$ [5]. Accordingly:

$$G^* \equiv -\Delta W/\Delta A = G_C; \quad \left(\Delta G^*/\Delta A\right)_C < 0 \text{ stable, if } > 0 \text{ unstable (QFM)} \tag{2a}$$

$$K_{I,II,III}^* \equiv \sqrt{\left\langle K_{I,II,III}^2 \right\rangle_A^{A+\Delta A}} = K_{I,II,IIIC}; \left(\Delta K_{I,II,III}^{*2}/\Delta A\right)_C < 0 \text{ stable, if } > 0 \text{ unstable (QFM)} \tag{2b}$$

where $\left\langle \cdot \right\rangle_A^{A+\Delta A} \equiv \frac{1}{\Delta A} \int_A^{A+\Delta A} \cdot \, \mathrm{d}A$. QFM assumes "dissipation energy" in quanta $G_C \Delta A$ where ΔA is the fracture quantum. Eqs. (1b) and (2b) are valid only for pure modes of crack propagation. For mixed modes, Eqs. (1a) and (2a) can in principle be applied; the crack should propagate in the direction (that at nanoscale could be quantized) that maximizes the energy release rate *G* (LEFM, [6]) or correspondingly G^* (QFM). Values for the stress intensity factors $K_{I,II,III}$ are available [7] for the most interesting cases. QFM involves simply evaluating $K^*_{I,II,III}$ according to Eq. (2b), which also allows the stability of the process to be predicted in an analytical way. *We thus propose QFM as a useful method for studying the strength of solids containing any shape or size defects*. The hypothesis on which QFM is based is simply on discrete crack propagation in a linear elastic continuum medium.

Finally we show that LEFM and Non Linear Fracture Mechanics (NLFM) are limit cases of QFM. In NLFM the material property G_C is replaced by an *ad hoc* "material" resistance *R* (known as the *R-curve*) that increases, tending to G_C, by increasing the crack length. NLFM can be summarized as [8]:

$$G \equiv -\mathrm{d}W/\mathrm{d}A = R; \quad \left(\mathrm{d}G/\mathrm{d}A\right)_C - \left(\mathrm{d}R/\mathrm{d}A\right)_C < 0 \text{ stable, if } > 0 \text{ unstable (NLFM)} \tag{3a}$$

(Dynamic crack propagation is characterized by an excess of energy $G - R$, which is converted into kinetic energy.) Combining the conditions for crack propagation in Eq. (2a) and Eq. (3a), it follows that $R = G_C + \frac{\Delta W}{\Delta A} - \frac{\mathrm{d}W}{\mathrm{d}A}$. Applying the operator $\Delta/\Delta A$ to the previous equation, it is clear that the conditions for stability in Eq. (2a) and Eq. (3a) are equivalent if $\Delta G/\Delta A \equiv \mathrm{d}G/\mathrm{d}A$ and $\Delta R/\Delta A \equiv \mathrm{d}R/\mathrm{d}A$. It corresponds to a second-order expansion of *W*, i.e., $\Delta W \approx \frac{\mathrm{d}W}{\mathrm{d}A}\Delta A + \frac{1}{2}\frac{\mathrm{d}^2 W}{\mathrm{d}A^2}\left(\Delta A\right)^2$. Consequently, Eq. (2a) corresponds to Eq. (1) at the first-order approximation of QFM (i.e., I order QFM $\rightarrow$ LEFM), and to Eq. (3a) at the second order approximation of QFM (i.e., II order QFM $\rightarrow$ NLFM), so that the equation of the *R-curve* in our treatment becomes:

$$R \approx G_C + \frac{1}{2}\left(\frac{\mathrm{d}^2 W}{\mathrm{d}A^2}\right)_C \Delta A. \tag{3b}$$

Thus, *QFM clarifies and quantifies in a very simple way the meaning of the R-curve (and why it must be expected a function of the geometry and, as a consequence, not a material property!).*

In the context of discrete approaches, we have to note that Seweryn [9] proposed a similar non-local approach based on energy, but without reaching our final analytical result; it formulation is

complex also to be treated numerically. On the other hand, Novozhilov [10] proposed a simple discrete approach but based on stresses: not the maximum stress but its mean value along a fracture quantum becomes critical during fracture propagation; it can be considered the QFM stress analog. Similarly, the QFM strain analog has been also proposed [5].

THE EXAMPLE OF THE GRIFFITH'S CASE

Consider Griffith's case of a linear elastic infinite plate in tension, of uniform thickness *t*, with a crack of length 2*l* orthogonal to the applied far field (crack opening Mode I). The material is described by the fracture toughness K_{IC} and by the fracture quantum at the considered size-scale For LEFM and QFM the predictions of the failure stresses are respectively:

$$\sigma_{f-LEFM}(l)=\frac{K_{IC}}{\sqrt{\pi l}}, \qquad \sigma_{f-QFM}(l)=\frac{K_{IC}}{\sqrt{\pi(l+a/2)}} \tag{4}$$

From Eq. (4), $a \approx 2K_{IC}^2/\left(\pi\sigma_C^2\right)$, with σ_C material strength at the considered size scale.

For Griffith's case, brittle crack propagation is predicted to be unstable for both LEFM and QFM theories, i.e., $\left(\mathrm{d}K_I^2/\mathrm{d}l\right)_C = K_{IC}^2/l > 0$ and, $\left(\Delta K_I^{*2}/a\right)_C = K_{IC}^2/(l+a/2) > 0$. Applying Eq. (3b) to this case, we find the *R-curve* as: $R = G_{IC}/(1+a/2l)$, exactly of the expected form [8].

Extending the QFM result from sharp to blunt-cracks (using the asymptotic correction for the stress-intensity factor derived in [12]), we find:

$$\sigma_f(l,\rho)=K_{IC}\sqrt{\frac{1+\rho/2a}{\pi(l+a/2)}}=\sigma_C\sqrt{\frac{1+\rho/2a}{1+2l/a}} \tag{5}$$

where ρ is the tip radius and $\sigma_C=\sigma_f(l=0,\rho=0)$ (coincident with the ideal strength at nanoscale). Note that, if the continuum hypothesis is made ($a/l, a/\rho \to 0$), Eq. (5) yields practically the same result as the classical tensional approach (maximum stress equal to material strength) coupled with Elasticity, for which the stress concentration σ_C/σ_f is $1+2\sqrt{l/\rho} \approx 2\sqrt{l/\rho}$ (small radii). On the other hand, Eq. (5) reduces to the correct prediction of QFM for a sharp crack. *Thus, Eq. (5) represents the link between concentration and intensification factors.*

AN APPLICATION FOR PREDICTING THE FRACTURE STRENGTH OF DEFECTIVE NANOTUBES

A pioneer experimental work on strength and fracture of nanotubes is reported in [13]. The tensile strengths of individual multiwalled carbon nanotubes (MWCNTs) were measured with a *nanostressing stage* composed by two opposing atomic force microscope (AFM) tips, Fig. 1a,b, and located within a

scanning electron microscope (SEM). The tensile experiment was prepared and observed entirely within the microscope and was recorded on video until fracture. 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 (in particular, values of 63, 43, 39, 37, 37, 35, 34, 28, 26, 24, 24, 21, 20, 20, 19, 18, 18, 12, 11 GPa were measured). Analysis of the stress-strain curves for individual 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, Fig. 1d,e.

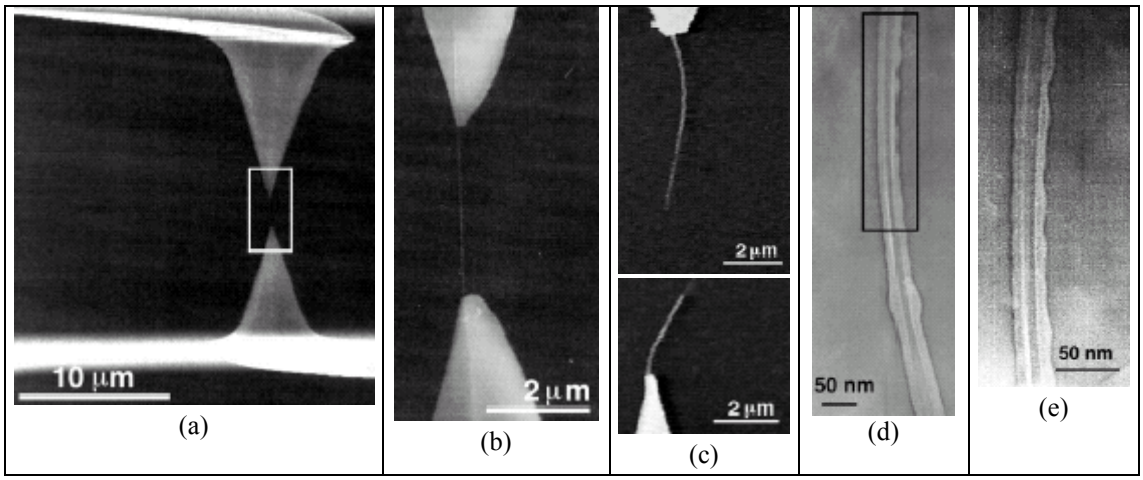


Figure 1: Experiments [13] *on fracture strength of nanotubes*.

The experimental results on nanotubes [13] show distinct clusters about a series of decreasing values of strength, with the maximum 63GPa, and the other values "quantized" at 43, 36-37, 25-26, 19-20 and 11-12GPa. The measured strength of 63GPa is not in agreement with the ideal tensile strength of small diameter carbon nanotubes (CNTs), recently obtained with density functional theory (DFT, [14], around one hundred GPa). *The observed strength quantization could be related to the quantization in the size of the defects*. For example, assuming defects like adjacent vacancies ($2\rho \approx a$, where we assume for the fracture quantum the distance between two adjacent broken chemical bonds, i.e., $a \approx \sqrt{3} r_0$, with $r_0 \approx 1.42\,\text{Å}$, interatomic length, see Table 1), the crack length in Eq. (5) must be $2l = na$ with n integer number (non integer values of n thus represent forbidden bands for the strength related to the type of defect and structure considered); accordingly, the strength is predicted to follow a $(1+n)^{-1/2}$ dependence. With 115 GPa for σ_C [14], the measured value of 63GPa is fit with n=3 and the next highest experimental value of 43GPa is fit with n=8, and so on. Note that these 19 outer shells, of different dimensions, were composed of between 4 and 54 million

atoms, thus also large defects are likely. It appears that none of the 19 MWCNTs had defect-free outer shells.

We now compare QFM with molecular mechanics (MM) and dynamics (MD) simulations. The simulations ([15]; MM, 0K) on a large diameter zig-zag (80,0) CNT, which has a diameter of 6.3nm, treated the reduction in strength due to missing pairs of carbon atoms. In the simulations, an *n*-atom defect was created by removing *n* adjacent atoms along the circumference of the nanotube; 2-, 4-, 6-, and 8-atom defects were treated. The comparison between these MM simulations and Eq. (5) (we thus neglect here boundary effects) is summarized in Table 1; the MM-calculated strengths clearly follow the $(1+n)^{-1/2}$ dependence predicted by QFM with a fit of $\sigma_C\sqrt{1+\rho/2a}=111\,\mathrm{GPa}$. Molecular dynamics simulations confirms the same trend [16]. For the value of the ideal strength calculated in [15], $\sigma_C=93.5\mathrm{GPa}$, and thus it gives the reasonable value of $\rho\approx 0.8a\approx 2.0\,\mathring{\mathrm{A}}$. Note that in addition, this comparison represents an alternative (even if qualitatively similar) scenario for understanding the experimental evidence [13] (measured strengths of 63 and 43 GPa, and so on).

Different kinds of defects, as holes, might be more stable than crack-like defects at the nanoscale [17, 18]. Nanotubes with "pinhole" defects, involving removal of 6 (defect *m*=1) or 24 (defect *m*=2) carbon atoms have been recently investigated in a (10, 10) nanotube by MD simulation [17]. We here investigate also larger values of *m* where the next larger hole is generated from the previous one by removing the "next perimeter" of carbon atoms (*m*=3, 56 atoms removed; *m*=4, 96 atoms removed; *m*=5, 150 atoms removed; *m*=6, 216 atoms removed, see Table 2). From the stress-intensity factor at the tip of a crack emanating from an hole [7] QFM (with $a\approx\sqrt{3}r_0$, Eq. (5)), yields the results reported in Table 2 and compared with ab-initio and MD simulations [18]. Note in addition that in [18] strength reductions due to one vacancy by factors of 0.81 for (10,0) and 0.74 for (5,5) nanotubes are again close to our QFM-based prediction, that yields 0.79.

We finally note that assuming an ideal strength for the MWCNTs experimentally investigated [13] of 93.5GPa, as computed in [15], the corresponding strength for a pinhole *m*=1 defect is 64GPa (against the measured value of 63GPa), for an *m*=2 defect is 45GPa (against the measured value of 43 GPa) and for an *m*=3 defect is 39 GPa (as the measured value), and so on. This could represent another plausible scenario compared to the assumed linear defects that were discussed above.

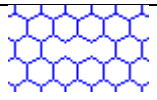
Strength [GPa]	*n*=2	*n*=4	*n*=6	*n*=8	
MM - (80,0)	64.1	50.3	42.1	36.9	
QFM	64.1	49.6	42.0	37.0	

Table 1: MM [15] *and QFM comparison on fracture strength of nanotubes with n adjacent vacancies (the graph reports the example of n=2, the applied load is vertical).*

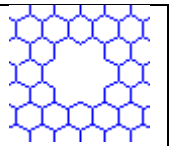
σ/σ_C	*m*=1	*m*=2	*m*=3	*m*=4	*m*=5	*m*=6	
QFM	0.68	0.48	0.42	0.39	0.37	0.36	
MD - (50,0)	0.64	0.51	0.44	0.40	0.37	0.34	
MD - (100,0)	0.65	0.53	0.47	0.43	0.41	0.39	

Table 2: MD [18] *and QFM comparison on fracture strength of nanotubes with holes of size m (the graph reports the example of m=1).*

ACKNOWLEDGEMENTS

The authors would like to thank A. L. Ruoff, A. Carpinteri, P. Cornetti and E. Zimney.

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