

# **Quantized fracture mechanics and related applications for predicting the strength of defective nanotubes**

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## **Abstract**

A new energy-based theory, *Quantized Fracture Mechanics* (QFM), is presented that modifies continuum-based fracture mechanics. The differentials in Griffith's criterion are substituted with finite differences; the implications are remarkable. Fracture of tiny systems with a given geometry and type of loading occurs at *quantized* stresses that are well predicted by QFM. QFM is self-consistent, agreeing to first-order with linear elastic fracture mechanics (LEFM), and to second-order with non-linear fracture mechanics (NLFM): the equation of the *R-curve* is consequently derived. For vanishing crack length QFM predicts a finite ideal strength in agreement with Orowan's prediction. The different fracture Modes (*opening I, sliding II and tearing III*), and the stability of the fracture propagations, are treated in a simple way. In contrast to LEFM, QFM has no restrictions on treating defect size and shape. As an example, strengths predicted by QFM are compared with experimental and numerical results on carbon nanotubes containing defects of different size and shape.

## **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 Fracture Mechanics can be applied only to "large" sharp cracks, we choose to modify fracture mechanics, by accounting for the discontinuous nature of matter. By substituting the differentials in Griffith's criterion with finite differences, a much more flexible theory, without *ad hoc* assumptions (e.g., as in the well-known "Equivalent" or "Quasi" LEFM that considers *ad hoc* fictitious crack lengths (of the order of the real crack length plus the size of the plastic zone) as "Irwin suggested (rather than provided a conclusive argument)...", see [4]), results. We call this theory *Quantized Fracture Mechanics* (QFM) and show that QFM includes LEFM and Non Linear Fracture Mechanics (NLFM) as limiting cases and that it can be applied in a simple way and analytically. QFM is particularly relevant to the fracture of tiny structures, such as of nanotubes (or nanowires or nanoplates) that play, and will play, a central role in nanotechnology applications. Thus, a comparison between QFM and experimental/numerical investigations on strength and fracture of defective nanotubes concludes the paper.

## **Quantized Fracture Mechanics**

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.,  $d \rightarrow \Delta$  [5]. According to the principle of conservation of energy, Griffith's energy criterion implies a crack propagation when the sum of the variation of the total potential energy  $dW$  and of the kinetic energy  $dT$ , corresponding to a virtual increment of the crack surface  $dA$ , becomes equal to the energy spent to create the new free crack surface, i.e.,  $dW + dT + G_{IC} dA = 0$ , where  $G_{IC} = 2\gamma_{IC}$  is the fracture energy (per unit area created) of the material. The factor of 2 accounts for the creation of two surfaces during crack formation. For quasi static crack growth  $dT \approx 0$  and the energy release rate is defined as  $G_I = -dW/dA$  (where the derivation is evaluated at constant displacement), and Griffith's criterion is simply  $G_I = G_{IC}$ . The stability of the fracture equilibrium can be evaluated by the sign of the second derivative of the energy at the incipient crack propagation: if  $(d^2 W/dA^2)_C$  is positive, the fracture equilibrium is stable, if negative, unstable. It is well known that Griffith's criterion [1] is equivalent to the stress-intensity factor based criterion [2] for brittle crack propagation, if the stress-intensity  $K_I$  and its critical value  $K_{IC}$  (the fracture

toughness of the material) are assumed to be equal [3]. According to LEFM [3],  $G_I = K_I^2/E'$ , with  $E' = E$  (for plane stress) or  $E' = E/(1-\nu^2)$  (for plane strain), where  $E$  is the Young's modulus and  $\nu$  is the Poisson's ratio of the material. Because  $G_{IC} = K_{IC}^2/E'$ , the criterion  $G_I = G_{IC}$  is equivalent to  $K_I = K_{IC}$ . Generalizing for *opening* (I), *sliding* (II), and *tearing* (III) crack Modes, from LEFM  $G = \frac{K_I^2}{E'} + \frac{K_{II}^2}{E'} + \frac{1+\nu}{E} K_{III}^2$ . LEFM is thus summarized as [4]:

$$G \equiv -dW/dA = G_C; \quad (dG/dA)_C < 0 \text{ stable, if } > 0 \text{ unstable (LEFM)} \quad (1a)$$

$$K_{I,II,III} = K_{I,II,III,C}; \quad (dK_{I,II,III}^2/dA)_C < 0 \text{ stable, if } > 0 \text{ unstable (LEFM)} \quad (1b)$$

On the other hand, in QFM ( $d \rightarrow \Delta$ ) Eqs. (1) become [5]:

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

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

where  $\langle \cdot \rangle_A^{A+\Delta A} \equiv \frac{1}{\Delta A} \int_A^{A+\Delta A} \cdot dA$ . QFM assumes “dissipation energy” in quanta  $G_C \Delta A$  where  $\Delta A$  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 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]:

$$G \equiv -dW/dA = R; \quad (dG/dA)_C - (dR/dA)_C < 0 \text{ stable, if } > 0 \text{ unstable (NLFM)} \quad (3a)$$

(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

$R = G_C + \frac{\Delta W}{\Delta A} - \frac{dW}{dA}$ . 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  $\Delta G/\Delta A \equiv dG/dA$  and  $\Delta R/\Delta A \equiv dR/dA$ .

It corresponds to a second-order expansion of  $W$ , i.e.,  $\Delta W \approx \frac{dW}{dA} \Delta A + \frac{1}{2} \frac{d^2 W}{dA^2} (\Delta A)^2$ . Consequently, Eq. (2a) corresponds to Eq. (1) at the first-order approximation of QFM (i.e., 1 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:

$$R \approx G_C + \frac{1}{2} \left( \frac{d^2 W}{d A^2} \right)_c \Delta A \quad (3b)$$

The classical limit of applicability of the  $R$ -curve in the NLFM treatment is that it is found as a function of the structure's geometry and not only as a material property; until now, it has been considered an experimental parameter [8]. *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; its 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  $2l$  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  $\Delta A \equiv at$ . From LEFM,

$K_I(l) = \sigma \sqrt{\pi l}$ , where  $\sigma$  is the applied far field stress. According to LEFM the crack will propagate

when  $K_I = K_{IC}$ ; in contrast, for QFM the crack will propagate when  $K_I^*(l) = \sqrt{\frac{1}{a} \int_l^{l+a} K_I^2(l) dl} = K_{IC}$ . The

corresponding predictions for the failure strength of the plate are:

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

For  $a/l \rightarrow 0$  (i.e., large cracks) LEFM and QFM converge, whereas for  $a/l \rightarrow \infty$  (i.e., short cracks) they diverge. LEFM incorrectly predicts an infinite strength, whereas QFM (as the Quasi-LEFM, see [4]) predicts a reasonable finite strength: assuming that at the atomic scale the fracture quantum corresponds to the atomic size, the ideal strength predicted by QFM (against the considered fracture propagation) is identical to Orowan's prediction [11] if multiplied by a factor of  $\sqrt{\pi/4}$ . On the other hand from Eq. (4), at larger size scale the fracture quantum is expected to be of the order of  $a \approx 2K_{IC}^2 / (\pi\sigma_c^2)$ , with  $\sigma_c$  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.,  $(dK_I^2/dl)_c = K_{IC}^2/l > 0$  and,  $(\Delta K_I^{*2}/a)_c = K_{IC}^2/(l+a/2) > 0$ .

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:

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

where  $\rho$  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 ( $a/l, a/\rho \rightarrow 0$ ), 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  $\sigma_c/\sigma_f$  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. The result is simple but surprising: it predicts a finite (in contrast with LEFM) strength that is size-dependent (in contrast with the continuum tensional approach coupled with Elasticity) for geometrical self-similar defects in an infinite plate.

### 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: a possible explanation was that when the outer layer of the MWCNT breaks at these large stresses, the accumulated elastic energy is released and generates a stress wave that travels through the outer surface of the MWCNT permanently deforming it.

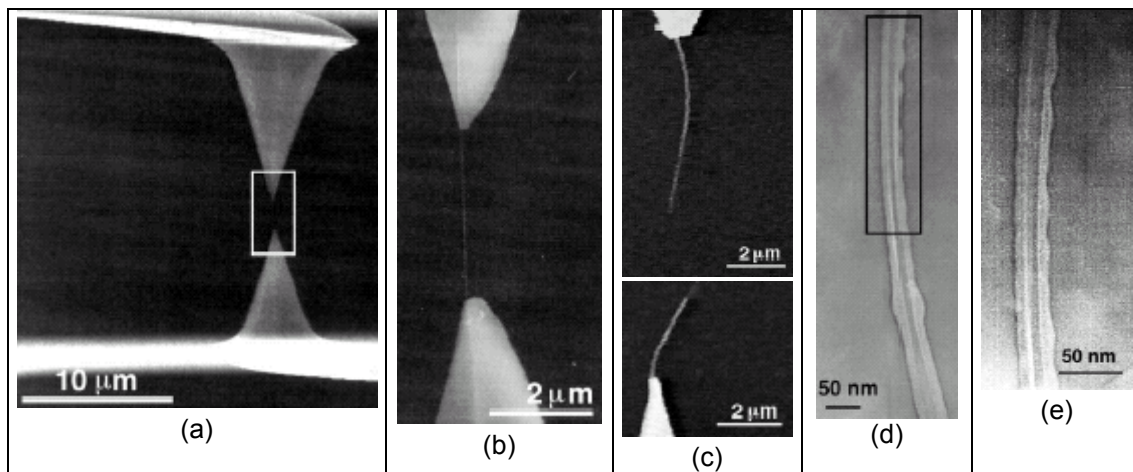


Figure 1: Experiments [13] on fracture strength of nanotubes.

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]). The tensile strength of an (8,8), thus armchair, CNT was calculated to be 114.6GPa; calculated tensile strengths of 107.5, 109.0, and 107.4GPa, respectively, were reported for 3 zig-zag CNTs: (8,0), (9,0), and (10,0). We note that the outer shell chiral angle was unknown for the 19 MWCNTs whose fracture strength was measured [13]. We speculate that the measured values are lower than the calculated ideal strength as a consequence of the presence of defects in the tested nanotubes. *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  $r_0 \approx 1.42 \text{ \AA}$ , 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  $\sigma_c$ , 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  $\sigma_c \sqrt{1+\rho/2a} = 111 \text{ GPa}$ . Molecular dynamics simulations confirms the same trend [16]. For the value of the ideal strength calculated in [15],  $\sigma_c = 93.5 \text{ GPa}$ , and thus it gives the reasonable value of  $\rho \approx 0.8a \approx 2.0 \text{ \AA}$ . 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).

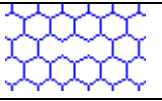
Strength[GPa]	$n=2$	$n=4$	$n=6$	$n=8$	
MM - (80,0)	64.1	50.3	42.1	36.9	
QFM	64.1	49.6	42.0	37.0	

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).

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). We estimate the radius of each hole as  $\rho_m \approx (2m-1)r_0$ . Since the ratio  $2\rho_m/\pi D$ , with  $D$  nanotube diameter, is small (0.09 and 0.18 respectively for the pinhole defects  $m=1$  and  $m=2$  analyzed in [17]), we treat the nanotube as an infinite graphene sheet (thus, by Eq. (5)). From the stress-intensity factor at the tip of a crack emanating from an hole [7] QFM (with  $a \approx \sqrt{3}r_0$ ), yields the results reported in Table 2; the strength is reduced by a factor of 1/3 (the classical value posed by Elasticity) only for very large (compared to  $a$ ) holes (the QFM asymptote is precisely 1/3.36). Even though there is reasonable agreement for the numerically computed strength reductions (0.80 for  $m=1$  and 0.55 for  $m=2$ , [17]), in our opinion these numerical results, which include a calculated strength of a defect-free nanotube of  $\sim 300 \text{ GPa}$ , do not consider an important factor: the very large computed strength (as compared to DFT calculated values of  $\sim 110 \text{ GPa}$ ) suggests that there was a problem in the cut-off of the Brenner potential used (as discussed in [16]). In this context, ab-initio and MD simulations have been recently performed [18] on nanotubes with  $m=1-6$  holes. The results are compared with QFM in Table 2, with close agreement. 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.

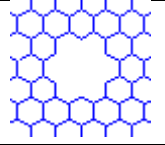
$\sigma/\sigma_c$	$m=1$	$m=2$	$m=3$	$m=4$	$m=5$	$m=6$	
QFM	0.68	0.48	0.42	0.39	0.37	0.36	
MD - (50,0)	0.64	0.51	0.44	0.40	0.37	0.34	
MD - (100,0)	0.65	0.53	0.47	0.43	0.41	0.39	

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

## Conclusions

A new energy-based theory of fracture mechanics involving a modification of the well known continuum-based approach has been developed that properly accounts for the discrete nature of matter (or energy release). The proposed *Quantized Fracture Mechanics* (QFM) of Eqs. (2) is self-consistent, and can be easily applied analytically for predicting the strength also of nanostructures. The concept of forbidden bands and quantized strength level has been also introduced, and seems to be confirmed by the experimental evidence at nanoscale.

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