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ORIGINAL ARTICLE

New quantized failure criteria: application to nanotubes and nanowires

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Abstract In this paper new quantized failure criteria are proposed, also for nanoscale applications. The main theories in the context of the strength of solids, i.e., of brittle fracture, dynamic fracture, fatigue and Weibull Statistics are reconsidered according to the proposed "quantization rules". The "corresponding principle" is verified and thus the classical theories are found to be the limit cases of the quantized counterparts. As an example, our treatment is applied to very recent experimental results on carbon or WS_2 nanotubes and to futurist ultra-nanocrystalline diamond nanowires, for which the tensile, bending and ideal strength are estimated.

Keywords Quantized fracture mechanics · Size-effects · Nanoscale strength · Nanotubes · Nanowires · Ultra nano crystalline diamond

1 Introduction: a review

According to continuum based fracture mechanics (Griffith 1921), the strength of a structure can be computed by an energy balance during crack propagation, or equivalently by setting the stress-intensity factor K equal to its critical value, the fracture toughness of the material K_C, i.e., $K = K_C$. The stress-intensity factor K, for crack propagation modes I, II or III, is a function of the geometry and applied load. On the other hand, if the hypothesis of the continuous crack advancement is relaxed, and thus a quantized energy balance is assumed (Pugno 2002), a more general Quantized Fracture Mechanics (QFM; Pugno and Ruoff 2004) is formulated:

$$K^* = \sqrt{\langle K^2 \rangle_l^{l+\Delta l}} = K_C, \quad \text{Modes I–III}, \tag{1}$$

where K^* is the square root of the mean value of the square of the stress-intensity factor along a fracture quantum Δl, for a crack of length l. The effectiveness of this approach has been demonstrated at the nanoscale (Pugno and Ruoff 2004) but also by fitting experimental results at larger size scales (Pugno and Ruoff 2004; Taylor et al. 2005); at macroscale the theory was called finite fracture mechanics. An application of Eq. 1 is reported in Sect. 3. Note that the integral in Eq. 1 has to be evaluated properly, that is, the calculation must be equivalent to evaluate the difference in the energy release rates between the finale $(l + \Delta l)$ and initial (l) states. For example, the external loads directly applied at the crack faces have not to be considered acting on Δl; or for mixed mode crack propagation, the advancement Δl is in general not collinear with the crack, and so on.

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For dynamic loads the "mean" value of the stress-intensity factor must be considered also along the time quantum Δt, connected to the time $\Delta l/c$—with c crack speed—to generate a fracture quantum (i.e. dynamic QFM; Pugno 2006, submitted):

$$K_d^* = \sqrt{\left\langle \left\langle K^2 \right\rangle_l^{l+\Delta l} \right\rangle_{t-\Delta t}^{t}} = K_C, \quad \text{Modes I–III.} \qquad (2)$$

Note that Eq. 2, in analogy to Quantum Mechanics that is erected on the Planck's constant $\hbar$, is based on the existence of the action quantum $G_C \Delta l \Delta t$, where G_C is the fracture energy of the material. Classical dynamic fracture mechanics would imply $K = K_{dC}$ with K_{dC} an a priory unknown dynamic fracture initiation toughness, different from K_C, especially for severe loading rates, e.g., impacts. On the other hand, Eq. 2 reproduces very well the experimental observations on times to failure also for severe loading rates (see Pugno 2006, submitted). An application is reported in Sect. 4.

For taking into account also negative stress-intensity factor regimes, i.e., crack closure, in addition to the crack opening assumed by Griffith, K^2 should have to be considered with the algebraic sign of K (Petrov, private communication): fracture does not occur if negative and positive stages compensate each other during the fracture and time quanta. In fact note that, according to Griffith $K^2 = K_C^2$ whereas in general, $K = K_C$, where K can be positive or—for crack closure—negative.

Classical fracture mechanics, that corresponds to the limit case of Eq. 1 for $\Delta l = 0$, can be applied only to "large" and sharp cracks, i.e., to cracks having length larger than the fracture quantum and vanishing tip radius. In contrast, QFM has no restriction in treating defects with any size and shape (Pugno and Ruoff 2004). Furthermore, dynamic QFM can treat also severe loading rates, e.g., impacts, in contrast to classical dynamic fracture mechanics. It corresponds to the limit case of Eq. 2 for $\Delta t = 0$, and becomes not predictive for severe impacts, requiring an ad hoc dynamic fracture initiation toughness. In the dynamic QFM treatment the dynamic fracture initiation toughness is identical to its static value, as must physically be.

Instead of a classical maximum stress criterion, i.e., $\sigma_{max}=\sigma_C$, where σ_C is the strength of the material, the stress analog of the energy-based criterion (1) must be written as (Neuber 1958; Novozhilov 1969):

$$\sigma^* = \left\langle \sigma_{tip} \right\rangle_0^{\Delta l} = \sigma_C$$
$$\text{Mode I, for Modes II and III: } \sigma \to \tau \qquad (3)$$

where σ_{tip} is the opening—for mode I—stress at the tip of a defect, where is located the origin of the reference system; for mode II or III the normal stress and strength must be evidently replaced by the corresponding shear stress τ and strength τ_C. This criterion, the first "quantized" one, was introduced by Neuber (1958) and Novozhilov (1969). In particular Novozhilov introduced the term "fracture quantum", that he assumed coincident with the interatomic spacing; however, his school and his apprentices widely applied this method during 1970–1980 years removing such an hypothesis, thus assuming the fracture quantum not restricted to the atomic spacing (Morozov 1984). Only later other authors applied this modified criterion (e.g., Seweryn 1998; Taylor, 1999; Carpinteri and Pugno 2005a). For a quantum analogy on Eq. 3 (see Petrov 1996; Petrov et al. 2003).

For dynamic loads this stress criterion has to be rewritten as (Morozov et al. 1990):

$$\sigma_d^* = \left\langle \left\langle \sigma_{tip} \right\rangle_0^{\Delta l} \right\rangle_{t-\Delta t}^{t} = \sigma_C$$
$$\text{Mode I, for Modes II and III: } \sigma \to \tau, \qquad (4)$$

representing the stress analog of the action-based Eq. 2 (see also Petrov 1996).

Equations 1 and 2 are based on stress-intensity factors, whereas Eqs. 3 and 4 on stress. However note that considering, for example QFM, the free-parameter Δl can be fixed to reproduce for $l \to 0$ the classical criterion $\sigma_{max} = \sigma_C$ (where σ_{max} is the maximum stress in the structure): thus, the QFM criterion implies a smooth transition between $\sigma_{max} = \sigma_C$ for vanishing crack length to $K = K_C$ for large cracks (where $K^* \approx K$). On the other hand at the question "strength or toughness?" Leguillon (2002) replied suggesting to consider both the criteria simultaneously. Accordingly, imposing that the criteria of Eqs. 1 and 3 have to predict the same failure for each value of l corresponds to a mixed criterion (Cornetti, private communication; Cornetti et al. 2005). The corresponding fracture quantum capable of ensuring such an equality for each

value of l can be derived consequently: in this case, the fracture quantum $\Delta l\,(l)$ becomes, more than a material constant, a well-defined structural parameter. In formulae:

$$K^* = K_C \text{ and } \sigma^* = \sigma_C \quad \Delta l: \text{ same predictions}$$
$$\text{Model I, for Modes II and III: } \sigma \to \tau. \tag{5}$$

We finally note that Eqs. 1 and 3 have been successfully applied also for fatigue limit predictions by Taylor et al. (2005) and Taylor (1999), respectively. The corresponding fatigue limit criteria can be formally written considering the variations Δ of in front of the symbols, interpreting ΔK^*, $\Delta\sigma^*$ as the amplitude ranges of K^*, σ^* in a cycle, ΔK_C as the threshold value of the stress-intensity factor and $\Delta\sigma_C$ as the plain-specimen fatigue limit.

2 New quantized criteria: towards a complete picture

In this section we briefly introduce new quantized failure criteria (Pugno 2004a) towards the realization of a complete picture. The details and applications will be reported in future publications.

Fracture. As suggested by Eq. 5, imposing the same strength and/or time to failure predictions from Eqs. 2 and 4 a new dynamic mixed criterion, in which both the fracture and time quanta are derived to ensure the equality of such predictions, is formulated:

$$K_d^* = K_C \text{ and } \sigma_d^* = \sigma_C \quad \Delta l,\ \Delta t: \text{ same predictions}$$
$$\text{Mode I, for Modes II and III}: \sigma \to \tau. \tag{6}$$

In addition, substituting the stress with the corresponding strain in Eqs. 3 and 4, normal, ε, for modes I, or shear, γ, for mode II and III, a strain static:

$$\varepsilon^* = \left\langle \varepsilon_{tip} \right\rangle_0^{\Delta l} = \varepsilon_C$$
$$\text{Mode I, for Modes II and III: } \varepsilon \to \gamma \tag{7}$$

and dynamic criteria:

$$\varepsilon_d^* = \left\langle \left\langle \varepsilon_{tip} \right\rangle_0^{\Delta l} \right\rangle_{t-\Delta t}^{t} = \varepsilon_C$$
$$\text{Mode I, for Modes II and III: } \varepsilon \to \gamma \tag{8}$$

are derived. Thus, the picture on stress, strain and energy (or toughness) based criteria for static and dynamic fracture seems to be rather complete. Obviously, the strain criteria themselves could be "mixed" with the other ones, as done for strength and toughness.

The quantized criteria of Eqs. 3–8 require in general the expression of the complete—and not only asymptotic—stress field around the tip of the defect, well-known only for the simplest cases. On the other hand, the criteria of Eqs. 1 and 2 can be applied in a very simple way, by starting from the well-known solutions for the stress-intensity factors; for example, hundreds of static and dynamic solutions are reported in the classical Murakami's Handbook (1986). Obviously, the predictions of the different criteria are not coincident, but similar; a comparison between Eqs. 1 and 3 for predicting the strength of defective nanotubes was reported by Pugno and Ruoff (2004).

Fatigue. Here we note that not only Eqs. 1 and 3 but all the criteria (1–8) can be rewritten for fatigue limit predictions, formally introducing the variations Δ in front of the symbols. However, such criteria estimate the beginning of the fatigue crack growth but not its evolution. On the other hand, regarding the evolution of the fatigue crack, substituting the stress-intensity factor K with its "quantized" version K^* in the Paris' law—or in its classical extensions—we formulate a quantized Paris' law, to be applied also to short cracks (Pugno 2004a; Pugno et al. 2005):

$$\frac{dl}{dN} \approx A\left(\Delta K^*\right)^{\alpha} \tag{9}$$

where N is the number of cycles, A, α are the Paris' constants and ΔK^* is the amplitude range of the "quantized" stress-intensity factor in a cycle.

For very short cracks $K^* \propto \sigma$ (see next section) and Eq. 9 resembles the classical Whöler's law, i.e., $N_f\left(\Delta\sigma\right)^{\beta} = B$, with B, β constants and N_f life time. Note that, similarly to brittle fracture, the fracture quantum itself could be fixed in fatigue to derive from Eq. 9 and in the limit case of crack length tending to zero, the same Whöler's prediction for the life time N_f. On the other hand, for very large cracks ($K^* \approx K$) Eq. 9 becomes the classical Paris' law. Equation 9 is a stress-intensity factor based quantized criterion for fatigue crack growth. The stress analog can be formulated substituting $\Delta\sigma$ with $\Delta\sigma^*$ in the classical Whöler's law, i.e.:

$$N_f\left(\Delta\sigma^*\right)^{\beta} = B. \tag{10}$$

Equations 9 and 10 corresponds in fatigue crack growth to Eqs. 1 and 3 or 2 and 4 in static or dynamic fracture. Accordingly, starting from these two analogs, it is clear that all the analogs of Eqs. 1–8 can be easily formulated also for fatigue crack growth; for example the mixed criterion of Eq. 5, ensuring the same fatigue life prediction N_f, has to be written as:

$$\frac{\mathrm{d}l}{\mathrm{d}N} \approx A\left(\Delta K^*\right)^{\alpha} \text{ and } N_{\mathrm{f}}\left(\Delta\sigma^*\right)^{\beta} = B$$
$$\Delta l: \text{ same predictions.} \tag{11}$$

Weibull's statistics. Weibull (1939) formulated the most popular statistical theory for the strength of solids. According to Weibull the probability of failure F of a specimen of volume V under uniaxial stress σ is given by $F=1-\exp(-\frac{1}{V_0}\int_V \left(\sigma/\sigma_0\right)^m \mathrm{d}V)$, where V_0 is a reference volume and σ_0, m are two constants. If stress-intensifications are present, as in cracked structures, the Weibull's integral does not converge: this represents a limit of the classical Weibull's statistics and can automatically be removed if instead of σ its "quantized" version σ^* (or σ_{d}^*) is considered:

$$F = 1 - \exp\left(-\frac{1}{V_0}\int_V \left(\sigma^*/\sigma_0\right)^m \mathrm{d}V\right). \tag{12}$$

Thus the quantized crack advancement removes a paradox and a new statistics is generated.

Quantization rules. In general, we conclude emphasizing that our definition of K^* and σ^* (also in dynamics) allow one to "quantize" classical well-known criteria based on stress and/or on stress-intensity factor. More powerful quantized approaches will result and the classical ones will be automatically recovered for the limit case of vanishing quanta, as required by the "corresponding principle".

3 Nano-fracture and nano-fatigue for nanotubes

By applying Eq. 1 to an infinite plate with a "predominant" symmetric crack of half-length l and blunt tip radius ρ, subjected to a remote axial stress σ perpendicular to the crack, we derive the failure load σ_{f} corresponding to the crack propagation in the form of (Pugno and Ruoff, 2004):

$$\sigma_{\mathrm{f}}(l,\rho) = K_{\mathrm{IC}}\sqrt{\frac{1+\rho/(2\Delta l)}{\pi\left(l+\Delta l/2\right)}} = \sigma_{\mathrm{C}}\sqrt{\frac{1+\rho/(2\Delta l)}{1+2l/\Delta l}}, \tag{13}$$

where K_{IC} is the fracture toughness for mode I and $\sigma_{\mathrm{f}}(l=\rho=0)=\sigma_{\mathrm{C}}$ is by definition the strength of the material for the plain structure; in general, it differs from the ideal strength since other minor defects could exist in the plate.

Particularizing to the case of a sharp crack, $K=\sigma\sqrt{\pi l}$ and by a simple integration $K^* = \sigma\sqrt{\pi\left(l+\Delta l/2\right)}$, from which the prediction of the strength is derived as the corresponding particular case of Eq. 13. $K^* \approx K$ only for very large cracks whereas $K^* \propto \sigma$ for very short cracks. The identical strength prediction is obtained—but with a more tedious calculation—by applying Eq. 3 (Taylor et al. 2005) and thus also by applying Eq. 5. On the other hand, classical fracture mechanics would yield Eq. (13) with $\Delta l \to 0$, and $\rho = 0$, predicting an infinite strength for the plain structure, i.e., $\sigma_{\mathrm{f}}(l=0) = \infty$, clearly a paradox; in addition, the classical maximum stress criterion simply would imply a vanishing strength, i.e., again a paradox. In contrast, eq. (13) does not present paradoxes. It unifies stress-concentration and-intensification factors. It suggests that for $2l \ll \Delta l$, i.e., very short cracks, materials become insensitive to flaws, as deduced by Carpinteri (1982) by analyzing the competition between ductile and brittle collapses; such "flaw tolerance concept" seems to become nowadays crucial in the design of innovative nano-biocomposites (Gao et al. 2003). For short cracks the fundamental critical parameter is σ_{C}, whereas for very large cracks it becomes K_{IC}. Making an analogy, this explains why similar phenomena, but arising at different size scales, are governed by different competing parameters: for example for fracture and wear—that is fracture at a smaller size scale—by K_{IC} and hardness $H \propto \sigma_{\mathrm{C}}$, respectively.

More importantly, the fracture quantum is itself a size dependent parameter, that increases by increasing the size scale as suggested by its prediction in brittle fracture (for the considered

structure), i.e., $\Delta l \approx \frac{2K_{IC}^2}{\pi\sigma_C^2}$ (see Eq. 13), in which we must remember that σ_C is the strength of the plain structure; it increases by decreasing the size scale as a consequence of approaching the defect-free condition, for which σ_C becomes coincident with the ideal material strength.

Applying Eq. 1 for fatigue limit and denoting with ΔK_C the threshold value of the stress-intensity factor, for very large cracks $\Delta K_C \approx \Delta K_C^*$, whereas for very short cracks $\Delta\sigma_C \approx \Delta K_C/\sqrt{\pi\,\Delta l/2)}$, where $\Delta\sigma_C$ is the plain-specimen fatigue limit. This yields an estimation of the fracture quantum during fatigue crack propagation (for the considered structure) as $\Delta l \approx \frac{2\Delta K_C^2}{\pi\Delta\sigma_C^2}$. Thus, in general the fatigue limit $\Delta\sigma_f$ for a cracked large plate is predicted as $\Delta\sigma_f \approx \Delta K_C/\sqrt{\pi(l+\Delta l/2)}$, exactly as experimentally observed (see Taylor 1999; Taylor et al. 2005).

At macroscale the fracture quanta for brittle and fatigue crack propagation are different; since usually $\frac{K_C}{\Delta K_C} > \frac{\sigma_C}{\Delta\sigma_C}$, the fracture quantum in fatigue is smaller than in brittle fracture. But at nanoscale we conjecture that they could become coincident to the distance between adjacent chemical bonds, as well as the time quantum is expected to be the time needed to break a bond, finite as a consequence of the finite crack speed. For example, for nanotubes the fracture quantum for brittle fracture truly becomes identical to the distance between adjacent chemical bonds, as demonstrated by comparing Eq. 13 with atomistic simulations of various types (Pugno and Ruoff 2004). For example, considering defects like n adjacent vacancies implies $2l = n\Delta l$ in Eq. 13. In Table 1 the complete experimental data set by Yu et al. (2000) is rationalized according to QFM. We have assumed $n = 2\,(1)$ related to the highest measured value of 63 GPa, to get a reasonable ideal strength of 97.6 GPa; the case of $n = 3$ (2), corresponding to an ideal strength of 112.7 GPa is also considered. In Table 1 the very recent experimental results by Kaplan-Ashiri et al. (2005, submitted) on WS_2 nanotubes and by Barber et al. (2005a, submitted) on carbon nanotubes (see Barber et al. 2005b), are similarly rationalized. For WS_2 nanotubes (Kaplan-Ashiri et al. 2005, submitted), the authors presumed to have observed the ideal material strength, i.e., assumed $n = 0\,(1)$ for the highest measure value of 16.3 GPa (see Barber et al. 2005b). An alternative plausible scenario is also considering for the highest measured value $n = 1$ (2) finding out an ideal strength of 20.6 GPa; the case of $n = 3$ would correspond to an ideal strength of 25.3 GPa, probably too high, since a 10% of the Young modulus would give ~16 GPa. For carbon nanotubes (Barber et al. 2005a, submitted) the highest measured value cannot be considered the ideal material strength. As emphasized by the same authors (Barber et al. 2005b) sites of interactions between the two external layers have to be postulated. Thus, the case reported in Table 1 of $n = 0$ (1) for the highest measure value of 259.7 GPa (ideal strength) is unrealistic. A more plausible scenario assumes the ideal strength coincident with the measured value of 109.5 GPa (2), as suggested by our previous considerations on the experiments by Yu et al. (2000). Thus, in this last case and for the higher values of strengths, the number of sites of interaction (treated as "negative" vacancies) between the two external layers can be deduced: roughly speaking the number of interaction sites can be estimated as the differences between the previous two cases, as described in Table 1.

These examples clearly show that "materials become insensitive to flaws at nanoscale" (Gao et al. 2003), is an interesting finding on nano-biocomposites but not of absolute validity. As previously emphasized the reason is that a "crack insensitiveness zone" exists but only for flaws smaller than the fracture quantum $\Delta l \approx \frac{2K_C^2}{\pi\sigma_C^2}$, and for nanotubes $\Delta l = \sqrt{3}a \approx 2.5$ Å.

Similarly, Eq. 9 could in the future play an interesting role for nano-fatigue. Incidentally, note that we have extended the concept of flaw tolerance also for fatigue limits, by defining $\Delta l \approx \frac{2\Delta K_C^2}{\pi\Delta\sigma_C^2}$: it is the analog of $\Delta l \approx \frac{2K_C^2}{\pi\sigma_C^2}$, the parameter regulating the competition between ductile and brittle collapses. Thus, also in dynamic fracture an intrinsic characteristic time $\Delta t \propto \Delta l/c$ emerges. And for fatigue crack growth the same concept could be discussed by considering the competition between the Whöler and Paris regimes, or simply the unified law of Eq. 9.

Table 1 The QFM applied to multi-walled carbon nanotubes, grown by arc-discharge method (Yu et al. 2000), by chemical vapor deposition (Barber et al. 2005a, submitted) and WS_2 nanotubes (Kaplan-Ashiri et al. 2005, submitted). Note that if the highest measured strength for WS_2 nanotubes corresponds to a single vacancy defect, the ideal strength for WS_2 nanotubes is estimated to be ∼21 GPa

Case	Strength (GPa) Yu et al. (2000)	Number of atomic vacancies QFM		Strength (GPa) Kaplan-Ashiri et al. (2005, submitted)	Number of atomic vacancies QFM		Strength (GPa) Barber et al. (2005a, submitted)	Number of atomic vacancies (if negative correspond to "interactions between layers")QFM	
1	11	97	130	3.8	22	36	17.4	277	49
2	12	82	109	6.7	6	11	22.3	169	29
3	18	36	48	7.7	5	8	23.7	149	26
4	18	36	48	8.4	4	7	30.0	93	16
5	19	32	43	8.7	3	6	44.2	42	7
6	20	29	39	9.8	2	5	49.3	34	5
7	20	29	39	11.1	2	3	52.7	29	4
8	21	26	35	12.5	1	2	54.8	27	4
9	24	20	27	13.3	1	2	62.1	21	3
10	24	20	27	13.6	1	2	66.2	18	2
11	26	17	22	15.0	0	1	84.9	11	1
12	28	14	19	15.1	0	1	90.1	9	1
13	34	9	13	15.1	0	1	90.3	9	1
14	35	9	12	15.8	0	1	91.1	9	1
15	37	8	11	16.1	0	1	99.5	8	1
16	37	8	11	16.3	0	1	101.6	7	0
17	39	7	9				108.5	6	0
18	43	5	8				109.5	6	0
19	63	2	3				119.1	5	−1
20							127.0	4	−2
21							132.9	4	−2
22							140.8	3	−3
23							141.0	3	−3
24							175.0	2	−4
25							231.8	1	−5
26							259.7	0	−6
Predicted ideal strength (GPa)		97.6	112.7		16.3	20.6		259.7 (Unrealistic)	109.5

4 "Doubling" of the impact strength

Let us consider as a simple example a semi-infinite crack in an otherwise unbounded body. The body is initially stress free and at rest. At time $t = 0$ a pressure σ begins to act on the crack faces. In this case, as it is well-known, $K_{\mathrm{I}}(t) = 2\sigma\frac{\sqrt{c_{\mathrm{D}}t(1-2\nu)/\pi}}{(1-\nu)}$ (see Freund 1990), where c_{D} is the dilatational wave speed of the material and ν is its Poisson's ratio. Applying Eq. 2 we find the failure for a given time $t_{\mathrm{f}} > \Delta t$, satisfying:

$$K_{\mathrm{I}}(t) = \frac{K_{\mathrm{IC}}}{\sqrt{1 - \Delta t/(2t_{\mathrm{f}})}} \equiv K_{\mathrm{dIC}}. \tag{14}$$

Thus, if classical dynamic fracture mechanics is applied, i.e., $K_{\mathrm{I}}(t) = K_{\mathrm{dIC}}$, the "measured" fracture initiation toughness K_{dIC} will be observed, according to dynamic QFM, time to failure dependent. In addition, note that, according to our time quantization, a minimum time to failure exists and it must be of the order of $t_{\mathrm{fmin}} \approx \Delta t$. Considering

very severe impacts ($t_f \to t_{fmin} \approx \Delta t$), the dynamic strength ($\propto K_{dIC}$) is expected for this scheme $\sqrt{2}$ times larger than its static value ($\propto K_{IC}$). For an applied pressure linearly increasing with time, the factor $\sqrt{2}$ is replaced by the factor 2 (Pugno 2006, submitted). For different schemes a slightly different factor is expected. Roughly speaking we could call this effect as the "doubling" of the dynamic strength. This is a well-known experimental phenomenon; recently Owen et al. (1998) have confirmed this finding on microsecond range dynamic failure tests of 2024-T3 aircraft aluminum alloy, where the dynamic strength was observed increasing by a factor of ~ 2 by varying the time to failure by ~ 8 order of magnitudes. Also, Owen et al. (1998) reported the observation of a minimum time to failure. Their results were similarly rationalized by Petrov and Sitnikova (2004), on the basis of Eq. 4. However, note that there are some experiments showing a quite different behavior, e.g., a decreasing and/or a non-monotonic variation of the fracture toughness versus the time to failure.

As demonstrated for Eq. 1, the dynamic criterion of Eq. 2 could in the future hold an interesting role also for nanostructures. Regarding this point it would be very interesting comparing our prediction for the fracture initiation toughness with the results of molecular dynamics and/or quantum mechanical atomistic simulations.

5 Correlation between Weibull and fractal statistics

Statistical failures can be well described by the widely used Weibull (1939) statistics, as briefly discussed in Sect. 2. Weibull statistics allow examination of strength, or time to failure or fatigue life, in the sense of failure probability at a certain stress level. The simplest Weibull distribution, is defined as $F = 1 - \exp\left(-\left(R/R_0\right)^n \left(\sigma_f/\sigma_0\right)^m\right)$, where σ_f is the stress at failure, assumed here to be a constant in the specimen volume $V = R^3$; σ_0 is the stress scaling parameter, in other words, the nominal stress that would result in 63% (i.e.,$\left(1 - e^{-1}\right) \cdot 100\%$) of the specimen to fail; m is the Weibull modulus; R_0 is the reference size on which the Weibull parameters are identified; $n = 3$ if we classically assume volume predominant defects. For predominant surface defects $n = 2$ with $A = R^2$, indicating with A the specimen surface area. Accordingly, the size-effect on the strength σ_f, at a specified F, is predicted as $\sigma_f \propto R^{-n/m}$. Even if at smaller size-scales surface defects should become predominant (higher surface/volume ratio) for nearly defect free-structures no dependence from volume and surface is expected, as confirmed by experimental results on fracture strength of nanotubes (see Pugno and Ruoff 2006).

On the other hand, fractal statistics, assumes energy dissipation in a fractal domain of dimension $n - 1 \le D \le n$, e.g., comprised between Euclidean surface ($D = 2$) and volume ($D = 3$), if a three-dimensional object ($n = 3$) is considered (Carpinteri and Pugno 2002, 2004). Accordingly, if the size-effect on Young's modulus is neglected, we have:

$$\sigma_f \propto R^{\frac{D-n}{2}}, \quad n - 1 \le D \le n. \tag{15}$$

Thus, we can demonstrate the equivalence between the size-effects predicted by the Weibull and fractal statistics—if the Young's modulus scaling is neglected—in terms of:

$$m = \frac{2n}{n - D}. \tag{16}$$

Note that Eq. 15 can be applied also to one-dimensional objects, for which $n = 1$, and that considering the force- instead of the energy-balance would yield the factor of 1 instead of the factor of 2 in Eqs. 15 and 16; the proof of this is left up to the reader.

The advantage of the fractal statistics, Eq. 15, is the clear interpretation of D, whereas the physical meaning of m remains partially unclear. If the fractal approach is correct, the experimental size-effect must give good fits with fractal exponents in the ranges $(n - 1, n)$. On the other hand, Weibull's statistics can in principle give information on size-effects also by testing specimens with the same size.

Note that integrating the Paris' law in the Griffith's hypothesis, for the classical case of $\alpha > 2$, considering the initial crack length to be much larger than the fracture quantum and proportional to the structural dimension R would correspond to a size-effect in the form of $\sigma_f \propto R^{2-\alpha/2\alpha}$; it gives the correlation—based on the previous hypotheses—$\alpha \approx 2/(D - n + 1)$ between fatigue and fractals. For the classical case of fractal exponent equal

to the corresponding Euclidean dimension, i.e., $D = n$, that corresponds to vanishing size-effects, we find $\alpha = 2$, in agreement with the classical models developed for interpreting the Paris' law, that in fact do not consider the size-effect on material strength. Since D is expected to slightly increase from $n-1$ to n by increasing the size-scale (Carpinteri and Pugno 2005b), we expect a size-effect on m and α, according to the previous correlation; i.e., m will increase whereas α will decrease with the size-scale.

Note that if a statistical fractal nature for the energy dissipation during a crack advancement $\Delta l' > \Delta l$ is assumed in the quantized deterministic criteria, for example due to the formation of a fractal crack surface (Carpinteri and Chiaia 1996) and/or due to the emanation of secondary fractal cracks, the "apparent" fracture energy G'_C, dissipated per unit area created, will refer to the increasing $\Delta l'$ of the nominal crack length. The energy equivalence $G_C \Delta L = G'_C \Delta l'$ must hold, where G_C and ΔL are the real fracture energy and the real total crack length increment. The smallest crack length increment coincides with the fracture quantum Δl, so that $\Delta L = \left(\Delta l'/\Delta l\right)^{D-1} \Delta l$ (Kashtanov and Petrov 2004), where D is the fractal exponent describing the fractal nature of the crack. Accordingly, we derive:

$$G'_C = G_C \left(\frac{\Delta l'}{\Delta l}\right)^{D-n+1}, \tag{17}$$

where usually n, the topologic dimension of the object, is equal to 3 (or 2) and D belongs to the range (2, 3) (or (1, 2)). In this case, Eq. 17 predicts $G'_C = G_C$ only if the classical Euclidean crack surface, i.e., $D = 2$, is considered, whereas for larger value of D, describing a fractal surface area, we have $G'_C > G_C$. Fractals and fracture quantum are embedded into Eq. 17. Larger fracture energy, or fracture toughness, must thus be considered to account for fractal cracks.

6 Ultra-nanocrystalline diamond nanowires: a statistical prediction of their tensile, bending and ideal strength

Ultra-nanocrystalline diamond (UNCD) material (Gruen 1999) has been recently developed at Argonne National Laboratory and possesses unique properties particularly suitable to the design of novel micro-electromechanical systems. The UNCD films can be doped with nitrogen using a CH_4 (1% Ar) gas mixture and nitrogen gas added. In order to investigate the strength of freestanding UNCD thin films at microscale, the membrane deflection experiment was considered (Espinosa et al. 2003; Pugno et al. 2004; Peng and Espinosa 2004).

The strength of UNCD membranes of 1 μm thick with width/length of 5/100, 10/200, 20/200, and 40/400 μm, also with nitrogen gas added of 5, 10, 15, and 20% in the atmosphere has been recently measured (Peng and Espinosa 2004). Thirty tests were performed for specimens with specified doping and size, for a total of 480 tests. We apply statistical concepts to these results for predicting the strength of UNCD at nanoscale (for details see Pugno 2005). The coefficient of correlations are found basically identical to 1, showing that such a method can be applied with confidence to these tests.

In particular we consider Eq. 15 with $n = 3$; $R = \sqrt[3]{WLt}$, where t, L and W are the thickness, length, and width of the film. The fits are reported in Fig. 1: the fractal approach seems to be consistent, showing a very good fit, the coefficient of correlation is basically identical to 1 for all the fits, with $2 \le D \le 3$. Clearly the doping decreases the fractal dimension of the domain in which the energy dissipation occurs. In particular for (undoped) UNCD the fit yields for a nanowire of characteristic size R a tensile failure stress of $\sigma_f^{(UNCD)}$ [MPa] ≈ 8525 $(R\,[\mu\,\mathrm{m}])^{-0.258}$. For example, considering a UNCD nanowire with $W = t = 10\,\mathrm{nm}$ and $L = 100\,\mathrm{nm}$, the formula predicts a tensile failure of $\sim$23 GPa, against the maximum value observed at microscale, of $\sim$ 5 GPa; from the fractal exponent $D = 2.48$, the Weibull modulus, estimated on the basis of the correlation of Eq. 16, is $m = 11.6$. For cantilever nanowires the nanoscale bending strength σ_{fB} is of particular interest. It is expected to be larger than the corresponding tensile strength σ_f as a consequence of the reduced volume undergoing larger stresses. According to Weibull (1939) $\sigma_{fB} = \sigma_f\,(2m+2)^{1/m}$ that in ourcase gives $\sigma_{fB}^{(UNCD)}/\sigma_f^{(UNCD)} \approx 1.32$ and thus a bending strength for the previous analysed nanowire of $\sim$30 GPa. Similarly

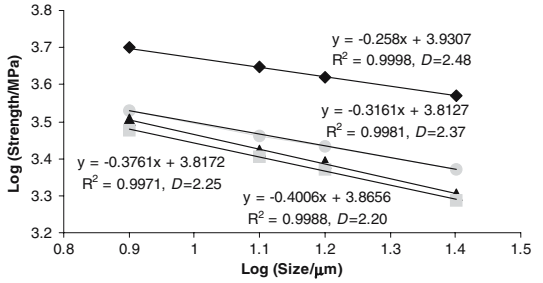

Fig. 1 Comparison between fractal statistics (*straight lines*) and experimental size-effects (*data points*) on UNCD strength for undoped (fractal exponent $D = 2.48$) and nitrogen doped (5%, $D = 2.37$; 10%, $D = 2.25$; and 20%, $D = 2.20$) specimens at microscale; such specimens are here treated as three-dimensional structures, i.e., as microbeams

we could treat also doped UNCD nanowires (Fig. 1; for details see Pugno 2005).

The estimated high strength value confirms that UNCD nanowires can be considered a valid alternative to nanotubes for NEMS applications (Pugno 2004b, c; Ke et al. 2005).

The computed nanoscale UNCD strength is compatible with a simple estimation of the UNCD ideal strength σ_C, obtained by applying eq. (1). Assuming the fracture quantum coincident with the UNCD grain size d (~ 3 nm), the ideal strength is estimated according to Eq. 1 as:

$$\sigma_C \approx \frac{\sqrt{2/\pi}}{\chi}\frac{K_{IC}}{\sqrt{d}} \tag{18}$$

where $K_{IC} \approx 4\,\mathrm{MPa}\sqrt{\mathrm{m}}$ is the fracture toughness for mode I of the UNCD and χ is a parameter that takes into account the "edge effect": it is equal to 1 for structures "without free surface", e.g., the previously treated infinite plate, or to 1.12 for structures "with free surface", e.g., a finite plate; thus $\sigma_C^{(\mathrm{UNCD})}\,[\mathrm{GPa}] \approx 90/\sqrt{d\,[\mathrm{nm}]}$. According to Eq. 18 the surfaces are predicted weaker than the inner parts of a solid by a factor of $\sim 10\%$. For finite structures, we find a reasonable estimation of the ideal UNCD strength of ~ 52 GPa. If the structure is assumed infinite the result would be ~ 58 GPa. The size R in Eq. 15 corresponding to a strength equal to the ideal strength of the solid fixes the limit size that can be treated by the fractal approach. From Eq. 18 $\sigma_C \propto d^{-1/2}$, that suggests nanostructured materials, i.e., small grain size d, for high strength applications; however, we have to note that the constant of proportionality is basically K_{IC}, that we have assumed as a constant, and could decrease itself by decreasing the grain size, limiting the fracture toughness and the applicability of nanostructured materials (Carpinteri and Pugno 2005c). Thus, the fracture toughness more than the strength could be the real critical point in designing nanostructured materials. Consequently, zones with high stress-concentrations and -intensifications, as for example surface steps, re-entrant corners (see Pugno et al. 2004; Carpinteri and Pugno 2005a), must be avoided, e.g., with high quality surface polishing.

7 Concluding remarks

Let us summarize our results with an eye to the reported equations. The quantized failure criteria of Eqs. 1–12—and especially those based on stress-intensity factors that are given in Handbooks for hundred of cases—are useful tools for the predictions of the strength of defective solids, in quasi-static, dynamic and fatigue fracture, also at the nanoscale.

We have shown that solids can be sensitive to flaws also at nanoscale (see Eq. 13), in which, for example, for nanotubes the fracture quantum Δl becomes of the order of the atomic spacing. Ideal strength estimations can be accordingly deduced. The concept of flaw tolerance has been extended to fatigue limit and crack growth and a characteristic time in dynamic fracture has been introduced. The increasing of the dynamic strength has also been rationalized (see Eq. 14).

From the fractal statistics, Eq. 15, the nanoscale strength of UNCD material is estimated; thus, it is demonstrated that the proposed methodology can be applied in general for estimating the nanoscale tensile and bending strength of materials, experimentally investigated at the more accessible microscale. Weibull statistics would give the same prediction, on the basis of the correlation derived in Eq. 16. The role of a fractal secondary crack emanation and/or crack surface formation is also described, according to Eq. 17.

A simple QFM application is demonstrated to be able to give estimations for the ideal material strength, Eq. 18. Accordingly, the surfaces are pre-

dicted weaker than the inner parts of a solid by a factor of ∼10%.

The extrapolation of the nanoscale strength from Eq. 15 is based on the assumption that the dimension of the fractal domain, related to the exponent in Eq. 15 or to the slope of the straight lines in Fig. 1, can be considered as a constant from micro- to nano-scales. And this could be not fully verified especially for the more complex case of doped UNCD films. Similarly, the validity of the simple approach summarized in Eq. 15, that assumes fracture quantum identical to the grain size for UNCD, is approximated. Thus, the UNCD predictions here reported must be considered simple reasonable estimations. Detailed quantum mechanical calculations are needed for deriving better predictions.

However, the described quantized criteria and statistical/experimental procedure are in general useful tools in the study of the strength of solids, also at the nanoscale. Since the "corresponding principle" is automatically verified for vanishing quanta the classical theories are obtained as limit cases of the quantized counterparts.

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