

## Nanoscale Weibull statistics

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(Received 15 April 2005; accepted 29 November 2005; published online 17 January 2006)

In this paper a modification of the classical Weibull statistics is developed for nanoscale applications. It is called nanoscale Weibull statistics. A comparison between nanoscale and classical Weibull statistics applied to experimental results on fracture strength of carbon nanotubes clearly shows the effectiveness of the proposed modification. A Weibull's modulus of  $\sim 3$  is deduced for nanotubes. The approach can treat (also) a small number of structural defects, as required for nearly defect-free structures (e.g., nanotubes) as well as a quantized crack propagation (e.g., as a consequence of the discrete nature of matter), allowing to remove the paradoxes caused by the presence of stress intensifications. © 2006 American Institute of Physics. [DOI: 10.1063/1.2158491]

### I. INTRODUCTION

Weibull statistics<sup>1</sup> for strength (or time to failure, fatigue life, etc.) of solids and deterministic linear elastic fracture mechanics<sup>2</sup> (LEFM) 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. Recently LEFM, which assumes infinite ideal strength of solids, as well as large (with respect to the so-called “plastic zone”) and perfectly sharp cracks, has been modified and a theory, quantized fracture mechanics<sup>3</sup> (QFM), has been presented that quantizes the crack advancement. QFM is intended for treating defects of any size and shape (e.g., atomic vacancies and nanoholes). In this paper we present a modification of the Weibull statistics for describing the strength of solids (also) at the nanoscale. We apply this statistical treatment to the largest collection of carbon nanotube strengths available.<sup>4</sup> The Weibull modulus for nanotubes is obtained as  $\sim 3$ ; furthermore, the statistical data analysis suggests that a small number of defects were critical for such nanotubes. An application to different types of whiskers is also discussed. The proposed approach, coupled with quantized fracture mechanics, can treat stress distribution also if dominant stress intensifications are present, thus removing the classical paradoxes related to the nonconvergence of the Weibull integrals.

### II. CLASSICAL WEIBULL STATISTICS

Classical *Weibull statistics*<sup>1</sup> assumes the probability of failure  $P_f$  for a specimen of volume  $V$  under uniaxial stress  $\sigma(P)$  (a function of the considered point  $P$  in the volume  $V$ ) as

$$P_f(\sigma) = 1 - \exp \left\{ - \int_V \left[ \frac{\sigma(P)}{\sigma_{0V}} \right]^m dV \right\}, \quad (1a)$$

or equivalently,

$$P_f(\sigma) = 1 - \exp \left[ - V^* \left( \frac{\sigma}{\sigma_{0V}} \right)^m \right], \quad (1b)$$

where  $\sigma_{0V}$  and  $m$  are Weibull's scale (with anomalous physical dimension) and shape (dimensionless) parameters, respectively, and  $V^*$  is an “equivalent” volume that refers to a reference (e.g., the maximum) stress  $\sigma$  in the specimen,<sup>5</sup> defined by comparing Eqs. (1a) and (1b). If the specimen is under uniform tension  $\sigma(P) \equiv \sigma$  and  $V^* \equiv V$ .

The surface-flaw-based Weibull distribution simply replaces the volume  $V$  in Eqs. (1) with the surface area  $S$  of the specimen (and  $\sigma_{0V}$  with a new constant  $\sigma_{0S}$ ),

$$P_f(\sigma) = 1 - \exp \left\{ - \int_S \left[ \frac{\sigma(P)}{\sigma_{0S}} \right]^m dS \right\}, \quad (2a)$$

$$P_f(\sigma) = 1 - \exp \left[ - S^* \left( \frac{\sigma}{\sigma_{0S}} \right)^m \right]. \quad (2b)$$

Note that  $\sigma_{0V}$  or  $\sigma_{0S}$  have the anomalous physical dimensions of a stress times a volume or a surface raised to  $1/m$ , so that the exponents in Eqs. (1) and (2) are evidently dimensionless.

The cumulative probability  $P_f(\sigma_i)$  can be obtained experimentally as<sup>6</sup>

$$P_f(\sigma_i) = \frac{i - 1/2}{N}, \quad (3)$$

where  $N$  is the total number of tests and the observed strengths  $\sigma_1, \dots, \sigma_N$  are ranked in ascending order.

The volume- and surface-based approaches become identical for the case of fracture of the external wall of nanotubes under (nearly) uniform tension, such as for the 19

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TABLE I. Experimental results on strength of multiwalled carbon nanotubes (only the external wall was fractured) and nanotube outer diameters and lengths (Ref. 4).

| Test No. | Diameter (nm) | Length ( $\mu\text{m}$ ) | 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             |

nanotubes experimentally investigated<sup>4</sup> (Table I). 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 ( $V^* \equiv V$ ,  $S^* \equiv S$ ).

A thorough discussion of the experimental configuration and method of tensile loading is provided by Yu *et al.*<sup>4,7</sup> Briefly, the method involves a nanomanipulator device that operates in a scanning electron microscope. We also note the supplemental information,<sup>4</sup> which provides the geometry of each of the 19 multiwalled carbon nanotubes (MWCNT's) tested (<http://www.sciencemag.org/feature/data/1046083.shl>).

The standard Weibull statistics applied to this set of fracture strength data is shown in Fig. 1. The Weibull modulus is found to be  $\sim 3$ . However, the correlation is very poor, showing a coefficient of correlation  $R^2=0.67$ . Perhaps such a statistics does not describe the real nature of strength of materials at the nanoscale.

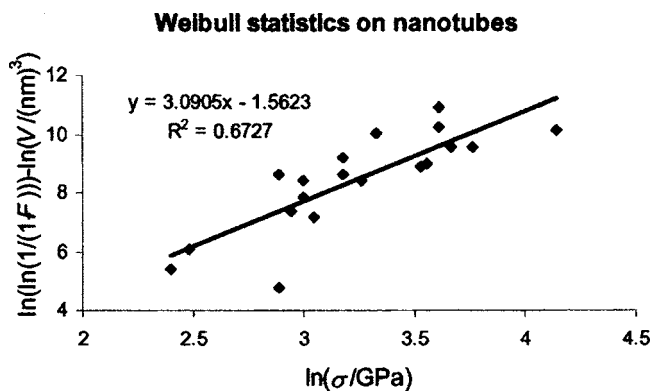


FIG. 1. Weibull statistics for strength of carbon nanotubes (Table I).

### III. NANOSCALE WEIBULL STATISTICS

According to QFM (Ref. 3) a quantized crack propagation has to be considered. QFM yields a better understanding of the experimental results and agrees with numerical simulations based on molecular mechanics and *ab initio* quantum mechanics.<sup>8</sup> The existence of a fracture quantum suggests that just a very small defect can cause the failure of a nearly defect-free structure. For example, a single atomic vacancy (a very small hole) in an infinitely large graphene sheet reduces its strength by  $\sim 20\%$  from the ideal strength.<sup>3</sup> Thus, at the nanoscale just a few defects can be responsible for the failure of the specimen, regardless its volume or surface. In addition, the tensional analog of the energy-based QFM suggests that not the stress  $\sigma$  but its mean value  $\sigma^*$  along a fracture quantum has to reach a critical value to cause the failure of the specimen. Note that replacing  $\sigma$  with  $\sigma^*$  in the Weibull approach is sufficient to remove the classical paradoxes associated with the nonconvergence of the Weibull integrals at stress intensifications (where the integral of  $\sigma^m$  diverges whereas the integral of  $\sigma^{*m}$  is finite).

Correspondingly, taking into account directly the number  $n$  of critical defects and the quantized stress  $\sigma^*$ , from Eqs. (1) and (2) we can formulate the *nanoscale Weibull statistics* (NWS) as

$$P_f(\sigma^*) = 1 - \exp\left\{-\sum_n \left[\frac{\sigma^*(n)}{\sigma_0}\right]^m\right\}, \quad (4a)$$

$$P_f(\sigma^*) = 1 - \exp\left[-n^* \left(\frac{\sigma^*}{\sigma_0}\right)^m\right], \quad (4b)$$

where  $n^*$  is defined by comparing Eqs. (4a) and (4b) and can be considered an equivalent number of defects;  $\sigma_0$  and  $m$  are two constants.

As an example we apply NWS to the experimental results on fracture strength of nanotubes.<sup>4</sup> As previously described, the application of the Weibull statistics (identical for surface- or volume-based defects, as a consequence of the two-dimensional nature of the experimentally stretched external nanotube walls) is shown in Fig. 1.

The nanotubes were basically in uniform tension, thus  $\sigma^*(n) \equiv \sigma^* \equiv \sigma$  and  $n^* \equiv n$ , where  $\sigma$  is the applied load and  $n$  is the number of critical defects. By applying NWS simply considering  $n=1$ , we find  $m \sim 2.7$  (and  $\sigma_0 \approx 31$  GPa, see Fig. 2) with a significantly better correlation of  $R^2=0.93$  with respect to the interpretation based on the classical Weibull statistics (please also compare Figs. 1 and 2).

### IV. COMPARISON BETWEEN CLASSICAL AND NANOSCALE WEIBULL STATISTICS

Let us assume fibers with circular cross-sectional area (e.g., nanotubes) under uniform tension, i.e.,  $\sigma^*(n) \equiv \sigma^* \equiv \sigma$  and  $n^* \equiv n$ . The Weibull statistics assumes that  $n=kD^\alpha L^\beta$ , 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 have noted 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  $n$  independent from the specimen size) for which  $\alpha=0$  and

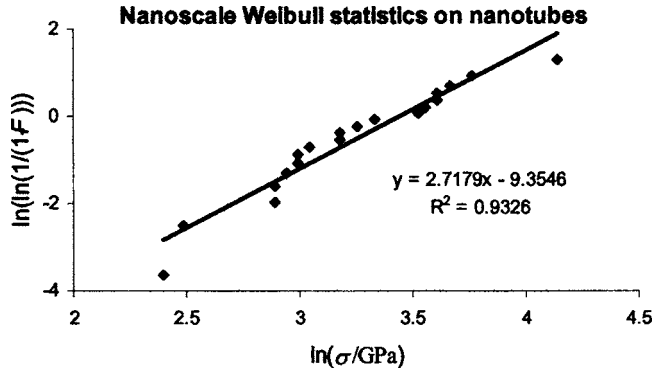


FIG. 2. Nanoscale Weibull statistics for strength of carbon nanotubes (Table I;  $\sigma^*(n) \equiv \sigma^* \equiv \sigma_{\text{applied}}$  and  $n^* \equiv n=1$ ).

$\beta=0$ , so that, in general, it may be more appropriate to expect  $0 \leq \alpha \leq 2$  and  $0 \leq \beta \leq 1$ . Note that this corresponds to substituting the volume/surface in the Weibull integrals with a fractal volume, always intermediate between a geometrical point and an Euclidean volume.<sup>9</sup> For example, if “length-flaws” defects are considered  $\alpha=0$  and  $\beta=1$ , i.e.,  $n \propto L$ ; for example, for the nanotubes previously investigated this assumption would lead to  $m \sim 2.7$  and  $R^2=0.74$ . Thus, in our hypotheses, NWS considers  $n=kD^\alpha L^\beta$  with  $0 \leq \alpha \leq 2$  and  $0 \leq \beta \leq 1$  (or  $n=kH^\alpha L^\beta W^\gamma$  for rectangular cross-sectional areas  $W \times H$ , with  $0 \leq \alpha, \beta, \gamma \leq 1$ , e.g., nanowires). Accordingly, it is clear that NWS can be applied not only at nanoscale. We note that for such an example Eq. (4) would correspond, for the limiting case of  $\beta=1$ , to the modified Weibull distribution proposed by Zhu *et al.*<sup>10</sup> in the study of the strength of sapphire whiskers and Nicalon SiC fibers. They showed that such a statistics includes all the three effects that have to be incorporated<sup>11</sup> for a correct description of the strength of solids: (i) extreme value statistics,<sup>12</sup> (ii) fracture mechanics,<sup>2</sup> and (iii) material characterization (e.g., dependence between length of the critical defect and specimen geometry). Thus, evidently, such effects are also included in our generalization, in which fracture mechanics is replaced by QFM.

Defining the nominal strength  $\sigma_N$  of the material for a specified value of  $P_f$ , e.g.,  $P_f(\sigma=\sigma_N)=(1-e^{-1})=0.63$  ( $\sigma_N$  is thus defined as the strength corresponding to the 63% probability of failure;  $n=kD^\alpha L^\beta$ ) the corresponding size/shape effect is predicted according to Eq. (4) as

$$\sigma_N = \sigma_0 k^{-1/m} D^{-\alpha/m} L^{-\beta/m}. \quad (5)$$

Strictly speaking Eq. (4) is defined for  $\sigma < \sigma_C$  (here  $\sigma^* \equiv \sigma$ ), where  $\sigma_C$  is the (finite) ideal strength of solids, whereas obviously  $P_f(\sigma \geq \sigma_C) \equiv 1$ . Accordingly, in Eq. (5)  $\sigma_N$  is limited by  $\sigma_C$ . We note that the size effect (thus assuming self-similar structures, i.e.,  $D \propto L$ ) predicted by Eq. (5) is a power law, in agreement with the fractal size-effect law proposed by Carpinteri<sup>13,14</sup> (for a unified approach see also the works of Carpinteri and Pugno<sup>9,15</sup>). Note that the ratio between the exponents of  $D$  and  $L$  is equal to  $\alpha/\beta$ . In the classical Weibull statistics this ratio is set equal to 2 (volume flaws) or 1 (surface flaws). As emphasized by Zhu *et al.*,<sup>10</sup> the ratio  $\alpha/\beta$  was observed to be significantly different for sapphire ( $\alpha\text{-Al}_2\text{O}_3$ ) whiskers.<sup>16,17</sup> These whiskers were

chemically polished to remove surface flaws, so that according to Weibull  $\alpha/\beta \approx 1$  was expected. On the other hand, such a ratio was observed as even larger than 2 (that corresponds to volume flaws): 7.0 for A type (fiber axis orientations  $\langle 11\bar{2}0 \rangle$  and  $\langle 10\bar{1}0 \rangle$ ,  $\sigma_N \propto D^{-0.21} L^{-0.03}$ ), again 7.0 for C type (axis orientation  $\langle 0001 \rangle$ ,  $\sigma_N \propto D^{-0.14} L^{-0.02}$ ), or 15.4 for A-C type (axis orientation  $\langle 10\bar{1}1 \rangle$ ,  $\sigma_N \propto D^{-2.47} L^{-0.16}$ ). Furthermore, only for unpolished A-type sapphire whiskers a value of  $\alpha/\beta \sim 1.43$  ( $\sigma_N \propto D^{-0.56} L^{-0.39}$ ), thus in the range expected by the Weibull statistics, was observed.<sup>16,17</sup> For unpolished C type they observed no length dependence at all, and  $\sigma_N \propto D^{-0.64}$ . A similar strength dependence, as  $\sigma_N \propto D^{-1}$ , was observed in iron or copper whiskers.<sup>18</sup> Thus, it is clear that such size/shape effects cannot be explained by Weibull statistics, whereas Eq. (5) is compatible with the observations reported in the whisker literature (see also Levitt<sup>19</sup>), as emphasized by Zhu *et al.*<sup>10</sup> to demonstrate on sapphire whiskers the effectiveness of their Weibull modification (limit case of NWS for  $\sigma^*(n) \equiv \sigma^* \equiv \sigma$  and  $n^* \equiv n=kD^\alpha L^\beta$  with  $\beta=1$ ).

As a final example, we consider the  $\alpha\text{-Si}_3\text{N}_4$  whiskers investigated by Iwanaga and Kawai and Ogata and Shibutani;<sup>20</sup> they observed a maximum value of the strength equal to 59 GPa (evidently close to the expected ideal material strength, see the first-principles calculations<sup>21</sup>). A linear dependence for the whisker  $\alpha\text{-Si}_3\text{N}_4$  strengths on their diameter was clearly observed (the whisker lengths were approximately constant and around 1–2 mm). We first assume the volume-flaw-based Weibull statistics, fitting their data yields  $m \sim 3.3$  ( $R^2=0.89$ ) and  $\sigma \propto D^{-0.61}$ . Assuming surface flaws we find  $m \sim 2.9$  ( $R^2=0.89$ ) and  $\sigma \propto D^{-0.34}$ . Even if the observed dependence between strengths and diameters suggest that here considering  $n=1$  is not realistic, since it would correspond to a size-independent strength such a case would correspond to  $m \sim 2.5$  ( $R^2=0.88$ ). Furthermore, fitting their experimental results on size effects, we find  $\sigma \propto D^{-0.4}$ , suggesting that these failures were probably surface dominated. The example shows that for larger structures in general  $n=kD^\alpha L^\beta$  has to be considered in the NWS rather than simply  $n=1$  (we note that the availability of only six strength values means that one should be cautious in “overinterpreting” the statistical fits).

## V. CONCLUSIONS

The comparison between classical and nanoscale Weibull statistics applied to nanotubes clearly shows the effectiveness of the proposed modification (also) for nanoscale applications. The Weibull’s modulus for nanotubes is deduced as  $\sim 3$ . Comparing classic and nanoscale Weibull statistics makes clear the role of the fracture quantization: this is crucial to treat stress intensifications in the specimen, for which the classical Weibull integrals do not converge, in contrast to what happens in our treatment. Finally, the nanoscale statistical data analysis suggests that a small number of defects, perhaps simply one critical defect in each of the 19 different carbon nanotubes that were fractured, were responsible for breaking of these nanotubes.

## ACKNOWLEDGMENTS

The authors would like to thank S. Puzzi and A. Carpinteri for the helpful scientific discussions. One of the authors (R.S.R.) appreciates support from the NASA University Research, Engineering and Technology Institute on Bio Inspired Materials (BIMat) under Award No. NCC-1-02037.

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