Bond energy effects on strength, cooperativity and robustness of molecular structures

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A fundamental challenge in engineering biologically inspired materials and systems is the identification of molecular structures that define fundamental building blocks. Here, we report a systematic study of the effect of the energy of chemical bonds on the mechanical properties of molecular structures, specifically, their strength and robustness. By considering a simple model system of an assembly of bonds in a cluster, we demonstrate that weak bonding, as found for example in H-bonds, results in a highly cooperative behaviour where clusters of bonds operate synergistically to form relatively strong molecular clusters. The cooperative effect of bonding results in an enhanced robustness since the drop of strength owing to the loss of a bond in a larger cluster only results in a marginal reduction of the strength. Strong bonding, as found in covalent interactions such as disulphide bonds or in the backbone of proteins, results in a larger mechanical strength. However, the ability for bonds to interact cooperatively is lost, and, as a result, the overall robustness is lower since the mechanical strength hinges on individual bonds rather than a cluster of bonds. The systematic analysis presented here provides general insight into the interplay of bond energy, robustness and other geometric parameters such as bond spacing. We conclude our analysis with a correlation of structural data of natural protein structures, which confirms the conclusions derived from our study.

Keywords: molecular mechanics; strength; robustness; failure; deformation; materiomics

1. INTRODUCTION

Functional properties of materials in biology feature an astounding range and play a central role in realizing a diversity of functional properties, such as gene regulation, catalysis, signal transmission, material transport, structural support or locomotion, many of them simultaneously, to yield multi-functional materials [1–10]. The structure of biological materials has evolved under evolutionary pressures and is often governed by the quest for a species’ survival, often in adverse environments where energy, material quality and quantity as well as time scales available to produce materials are exceedingly scarce [5,11,12]. These intrinsic limitations explain why many material constituents found in biology are functionally inferior material building blocks themselves that are exceptionally brittle (e.g. silica or other minerals) or extremely weak (e.g. H-bonding, van der Waal forces or weak covalent interactions, such as disulphide bonds). Comparative studies of protein materials show that most biological materials are made up from only a few select universal elements such as \( \approx 20 \) natural amino acids, despite their great functional diversity [13,14]. The development of high-performance nanoscale materials, such as bioinspired polymers or organic–inorganic hybrid materials, with exceptional strength, robustness and ductility has recently generated enormous interest [15–18]. A fundamental challenge in engineering biologically inspired materials is the identification of molecular structures to define fundamental building blocks, realized through the establishment of chemical bonds that drive, for example, interparticle adhesion at larger scales [19–21]. Understanding the effect of varied bond strength on the resulting mechanical properties of bond cluster is crucial for designing the nanoscale structure of natural and synthetic polymer materials to achieve desired mechanical properties. Earlier theoretical calculations have been put forth to provide a concept for designing extremely high strength or high adhesion strength materials, especially for nanotube and adhesive gloves [22–24]. A recent study based on a fractal approach is also related to the calculation of the mechanical properties, strength, stiffness and toughness, of nanoscale structure, especially for nanotube composites materials [25]. Such fundamental knowledge is important in the design of nanocomposites, fibres or self-assembled hierarchical materials. Here, we
propose a simple and systematic analysis of the effect of bond strength and geometry on the mechanical properties of a small bond cluster, used to derive generic insight into this question. The key objective of this paper is to answer a fundamental question: what kinds of bonds does Nature choose to generate desired material behaviours, such as deformability, high strength or toughness?

2. RESULTS AND DISCUSSION

We consider a double-stranded system as a simple model to study the mechanical properties of molecular structures, as shown in Figure 1. The figure shows the geometry and loading condition of the molecular cluster with key model parameters summarized in Table 1. Figure 1a shows the geometry of the double-stranded protein domain stabilized by an array of bonds deformed by an external force \( F \). Before rupture, the structure features free ends with an initial contour length of \( \lambda_1 \) and an end-to-end distance of \( x_1 \). The distance between two neighbouring bonds is \( L_0 \), the dissociation energy is \( E_b \) and the persistence length of the peptide chain is \( \xi_p \). When the force reaches a critical value (strength) the structure breaks (b), and a number of bonds break and the contour length increases owing to the detachment of a piece of the chain \( d \lambda \). Thus, the end-to-end distance becomes \( x_2 = x_1 + dx + d\lambda \), where \( dx \) is the initial end-to-end distance of detachment of a piece of the chain, \( dx \) is the elongation of initial free molecule and \( dx \) is the elongation of detachment of a piece of the chain. After the bonds break (c), the system has slipped and bonds may reform. The cooperativity index \( N_c \) is defined as the number of bonds that break concertedly during the rupture process and is obtained using equation (4.5). (d) WLC force-displacement behaviour of the cluster during the rupture process (dark line, before rupture; grey line, after rupture; shaded area, energy released).

Figure 1. Geometry and loading condition of the molecular cluster. (a) Geometry of the double-stranded protein domain stabilized by an array of bonds deformed by an external force \( F \). Before rupture, the structure features free ends with an initial contour length of \( \lambda_1 \) and an end-to-end distance of \( x_1 \). The distance between two neighbouring bonds is \( L_0 \), the dissociation energy is \( E_b \) and the persistence length of the peptide chain is \( \xi_p \). When the force reaches a critical value (strength) the structure breaks (b), and a number of bonds break and the contour length increases owing to the detachment of a piece of the chain \( d \lambda \). Thus, the end-to-end distance becomes \( x_2 = x_1 + dx + d\lambda \), where \( dx \) is the initial end-to-end distance of detachment of a piece of the chain, \( dx \) is the elongation of initial free molecule and \( dx \) is the elongation of detachment of a piece of the chain. After the bonds break (c), the system has slipped and bonds may reform. The cooperativity index \( N_c \) is defined as the number of bonds that break concertedly during the rupture process and is obtained using equation (4.5). (d) WLC force-displacement behaviour of the cluster during the rupture process (dark line, before rupture; grey line, after rupture; shaded area, energy released).
end-to-end distance becomes $x_2 = x_1 + dz' + dx_1 + dx_2$, where the $dz'$ is the initial end-to-end distance of detachment of a piece of the chain, $dx_1$ is the elongation of initial free molecule and $dx_2$ is the elongation of detachment of a piece of the chain. After the bonds break (figure 1c), the system has slipped and bonds may reform if admissible; otherwise, the cluster will fail catastrophically immediately after the first rupture event. Figure 1d shows the worm-like chain (WLC) force-displacement behaviour of the cluster during the rupture process. The critical force to rupture is given by the condition that the energy dissipated must equal the energy stored in the bonds per unit contour length. The cooperativity index $N_{cr}$ is defined as the number of bonds that break concerted during the rupture process and is calculated by considering how many bonds participated cooperatively in the failure process, similar to the calculation of a fracture process zone in fracture mechanics. An important parameter varied in the study presented here is the bond energy, $E_b$. An overview of different bond energies is given in table 2, showing the broad range of bond energies found in Nature [1,26,27]. Further details regarding the model used here are given in §4. We also refer the reader to the original papers in which the model used here was derived [28,29] and validated against experiment [30]; and compared against other models for further support [22–24,31].

Figure 2 shows the dependence of the strength on the number of bonds in the cluster, for varied bond energies $E_b$. The strength increases while $N \leq N_{cr}$. When $N > N_{cr}$, the strength saturates a constant value because the maximum number of bonds that participate in a unit rupture process is reached. For clusters with more

Table 1. Summary of all parameters used (see figure 1a for the geometry).

<table>
<thead>
<tr>
<th>parameter</th>
<th>dimension</th>
<th>description</th>
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</thead>
<tbody>
<tr>
<td>$E_b$</td>
<td>energy</td>
<td>dissociation energy of each bond</td>
</tr>
<tr>
<td>$L_0$</td>
<td>length</td>
<td>distance between two bonds in structure</td>
</tr>
<tr>
<td>$\xi_p$</td>
<td>length</td>
<td>persistence length of polypeptide</td>
</tr>
<tr>
<td>$L_m$</td>
<td>length</td>
<td>length of molecular cluster</td>
</tr>
<tr>
<td>$N_{cr}$</td>
<td></td>
<td>critical number of bonds that rupture concurrently</td>
</tr>
<tr>
<td>$F_{break}$</td>
<td>energy</td>
<td>rupture force</td>
</tr>
</tbody>
</table>

Table 2. Summary of typical bond energies (listed from weakest to strongest).

<table>
<thead>
<tr>
<th>bond type</th>
<th>bond energy range (in kcal mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Van der Waal bond (e.g.</td>
<td>0.0654 (e.g. for C–C stacking in graphene)</td>
</tr>
<tr>
<td>bond in graphene [26])</td>
<td>0.0654 (e.g. for C–C stacking in graphene [26])</td>
</tr>
<tr>
<td>H-bond</td>
<td>2 –10 [1]</td>
</tr>
<tr>
<td>disulphide (S–S) bond</td>
<td>51 [27]</td>
</tr>
<tr>
<td>C–C bond</td>
<td>83 [27]</td>
</tr>
<tr>
<td>C=C bond (double bonds)</td>
<td>146 [27]</td>
</tr>
<tr>
<td>C=C bond (triple bonds)</td>
<td>195 [27]</td>
</tr>
</tbody>
</table>

than $N_{cr}$ bonds only $N_{cr}$ bonds actually contribute to resist deformation and thus do not lead to a further increase of the strength. It can be seen that the slope of strength becomes larger with an increase of $E_b$. For example, the strength per bond is roughly 31 pN for $E_b = 2.84$ kcal mol$^{-1}$ and it is almost 821 pN for $E_b = 51$ kcal mol$^{-1}$, more than 25 times larger. For the data shown here, we considered a bond spacing of $L_0 = 0.3$ nm and a persistence length of $\xi_p = 0.4$ nm (the reference persistence length found for the backbone of polypeptides, for example).

We proceed with a presentation of an analysis of key mechanical properties as a function of relevant parameters, most importantly $E_b$ (bond energy), $L_0$ (distance between two bonds in the cluster) and $\xi_p$ (persistence length of the polypeptide chain). Figure 3 shows the cooperativity index $N_{cr}$ as a function of $E_b$, $L_0$ and $\xi_p$. Figure 3a,b shows the cooperativity index
as a function of $E_{b}$ and $L_0$ for two different values of the persistence length $\xi_p$. The overall behaviour is similar, but a smaller persistence length yields a higher cooperativity index for all other parameters being equal. This suggests that a softer polymer enhances the cooperativity of the bond cluster since $\xi_p \sim EI$.

Figure 3c,d shows the cooperativity index $N_c$, as a function of $E_{b}$ and $\xi_p$ for two different values of $L_0$. The data show that a smaller $L_0$, resembling a tighter packing of bonds, leads to a higher cooperativity index. Figure 3e,f shows the cooperativity index $N_c$, as a function of $\xi_p$ and $L_0$ for two different values of the bond energy $E_{b}$. The data show that the cooperativity index $N_c$ is almost independent with respect to changes in the persistence length from 1 to 10 nm.

A critical property of bond clusters is the maximum strength it can reach, reflecting the strength saturation at a constant value as shown in figure 2 (for the following analysis, we focus on the maximum strength a cluster reaches when the number of bonds is $N_c$ or larger). Figure 4 shows the strength of the cluster under varied $E_{b}$, $L_0$ and $\xi_p$. The strength is shown as a function of $E_{b}$ and $L_0$ (figure 4a,b), $E_{b}$ and $\xi_p$ (figure 4c,d) and $L_0$ and $\xi_p$ (figure 4e,f). When bonds have a larger bond energy $E_{b}$, the breaking force becomes larger, in all cases studied here. The local maximum of the strength is located in the region which $L_0$ is small and $E_{b}$ is large, reflecting the situation of the highest bond energy density. As shown in figure 4a,b, for smaller distances between two bonds $L_0$, the system requires a larger rupture force. Figure 4c,d shows that a larger $E_{b}$ or smaller $L_0$ yields a larger strength as the persistence length $\xi_p$ varies. For $\xi_p < 2$ nm, the strength becomes smaller as $\xi_p$ increases. As $\xi_p$ is larger than 2 nm, the dependence of strength on the persistence length becomes rather weak.

The discussion of the results presented in the preceding two paragraphs shows that cooperativity and strength are competing effects. An increase in $E_{b}$ yields a greater strength; however, the cooperativity is reduced. Bond cooperativity has implications on the robustness of the system. To demonstrate this, we consider a cluster with $N_c$ bonds, reflecting a system that features a strength at its theoretical limit (see figure 2 that shows how the strength saturates when $N = N_c$ bonds). We define the robustness $R$ as the ratio of the strength of a defected system, $F(N_c - 1)$, compared with the strength of an intact system, $F(N_c)$ (for equations on how these strengths are calculated see §4):

$$R = \frac{F(N_c - 1)}{F(N_c)}.
$$

It is noted that, in principle, there exist many definitions for robustness [32–34]. The concept used here is based on the idea to assess how the emergence of a flaw (a lost bond) would change the strength of the system. It can thus be seen as a flaw sensitivity parameter.

If the robustness $R$ is close to one, the strength of a defected system is close to the strength of a defect-free system, which implies that the system is stable despite the presence of a defect. Conversely, if $R$ is close to zero, the system tends to be unstable as a larger fraction of the strength is lost under the pressure of a ‘defect’. Figure 5a shows the relation of robustness as a function of $E_{b}$ for different choices of bond spacings $L_0$. The robustness is a monotonically decreasing function. Conversely, the strength is a strictly increasing function as shown in the same plot. In a system with bonds with higher bond energies, although the strength is larger, the strength loss by a defect is relatively higher so that the robustness decreases significantly. As $L_0$ increases, the systems with stronger bonds become more and more unstable under the existence of defects, and the robustness drops to zero. One possible measure to express the overall performance of the system is to compute the product of the strength and the robustness, $P = RF$. The product of robustness and strength is plotted with varied $E_{b}$ and $L_0$ in figure 5b. For $L_0 = 0.3$ and 0.4 nm, the performance is a monotonically increasing function. However, the function becomes anti-monotonic for $L_0 = 0.5$ and 0.6 nm (see inset in figure 5b). For larger $L_0$, the bond energy $E_{b}$ corresponding to the maximum performance becomes smaller. We emphasize that there are many possible measures for robustness one can define, and that the definition put forth in equation (2.1) is only one possible choice. Similarly, the calculation of the overall performance as done above can be defined differently, in principle, if a better understanding of the relative weight of robustness and strength is incorporated.

The analysis reported here shows that weaker bonds and a softer polymer chain provide a greater capacity to work cooperatively (figure 3). The cooperative nature of
Clusters to resist force results in a greater robustness as shown in figure 5, reflecting the fact that the loss of a single bond in a cluster of many does not severely compromise its strength. The reduction of bond energy, however, comes at a price of reduced cluster strength as shown in figures 4 and 5. The key result of this analysis is thus that robustness and strength are competing properties. Another aspect related to the emergence of cooperative behaviour is that the relative weakness of bonds in this regime (we have shown that cooperativity is enhanced by weak bonding) leads to the emergence of stick-slip mechanisms of deformation, which can increase the energy dissipation capacity of materials. Stick-slip motion is not possible (or more unlikely) for strong bonds since such bonds cannot easily reform upon breaking. Conversely, weak bonds can break and reform easily and thus mediate this mechanism of deformation, synergistically supporting the emergence of highly

Figure 3. Cooperativity index $N_{cr}$ as a function of $E_b$, $L_0$ and $\xi$. We plot the cooperativity index $N_{cr}$ as a function of $E_b$ and $L_0$ $(a,b)$, $E_b$ and $\xi$ $(c,d)$, $L_0$ and $\xi$ $(e,f)$ for fixed $E_b$, $L_0$ and $\xi$, respectively. $(a,b)$ Fixed $\xi$, when the distance between two bonds $(L_0)$ is smaller, the cooperativity index $N_{cr}$ increases and maintains a value larger than one as long as $L_0 < 0.5$ nm. For a stronger bond (larger $E_b$), the cooperativity index becomes smaller. It is worth noting that $N_{cr} < 1$ for small $E_b$, even when $L_0$ is larger. The cooperativity index drops dramatically for larger $E_b$ as $L_0$ increases. If the distance between two bonds is small, they tend to break concurrently. $(c-f)$ Dependence of cooperativity index on $E_b$ and $L_0$ is similar as in the results shown in $(a,b)$. The cooperativity index is almost independent with respect to changes in the persistence length from 1 to 10 nm.
dissipative stick-slip deformation. Table 3 summarizes the key results of our study as discussed above.

3. CONCLUSION

From a general perspective of material design, our results imply the softer bonds should be used in a cluster geometry and stiffer bonds should exist individually. This concept is indeed found in the structure of natural biological materials. H-bonds (with bond energies in the range of 2–10 kcal mol\(^{-1}\) as shown in Table 1) tend to exist in clusters. This can be seen in \(\alpha\)-helices (3–4 H-bonds per cluster or ‘turn’) [35], \(\beta\)-sheets (4–6 H-bonds per \(\beta\)-strand cluster) [36] and many other protein structures [37]. Conversely, stronger bonds such as covalent bonds exist as single bonds. This can be seen in the backbone of polypeptides or disulphide bonds. The backbone of proteins, for example, features a linear one-dimensional array of amino acids that are
Strength, cooperativity and robustness

C.-C. Chou and M. J. Buehler

4. MATERIAL AND METHODS

4.1. Worm-like chain-based fracture theory

We briefly review the WLC model-based fracture theory ([40,41]; as reported in a series of earlier publications [28,29]) and which predicted and confirmed the intrinsic strength limit for an assembly of bonds in shear. The theory adopts Griffith’s theory of fracture mechanics for nanoscale phenomena pertaining to the rupture of a cluster of bonds in the geometry shown in figure 1 [42–44]. The onset of failure is characterized by the condition that the change in free energy owing to the extension of the fracture balances the energy necessary to create new surfaces, \( \gamma_s \) (the parameter \( \gamma_s \) is the one-dimensional equivalent of surface energy and is defined as \( \gamma_s = E_b/L_0 \), where \( E_b \) is the dissociation energy of a bond, and \( L_0 \) is the distance between two bonds). The negative of the expression for the free energy \( W_p \) change with respect to a rupture advance of one unit distance, \( \delta a \), is called the energy release rate \( G = -\delta W_p/\delta a \). At the onset of failure the condition

\[
G = -\frac{\delta W_p}{\delta a} = \gamma_s
\]

connected by single covalent bonds. Similarly, disulphide bonds [38] serve as mechanical clamps in enzymes and are typically found as individual bonds. These examples show qualitatively that covalent bonds appear as single elements, in agreement with our hypothesis. We conclude that from a biological point of view, the choice of bond strength indeed controls the functionality of materials. For example, covalent bonds form the backbone of intermediate filament proteins, which play a significant role in the cell mechanical behaviour at large deformation, to resist the rupture. Weaker H-bonds that connect the dimers in intermediate filament proteins facilitate interdimer sliding behaviour under stretching and contribute to the enhanced stability and toughness as they can be sacrificed to mediate highly dissipative deformation mechanisms [39].

While covalent bonds are much stronger than, for example, low-energy H-bonds they lack a greater level of robustness. In biological materials such as spider silk, this issue is circumvented in an intriguing way since weak bonds are used to define key mechanical properties such as strength or toughness, and strong bonds are mainly used to define the backbone structure of proteins. Our basic model applied here could be directly extended to other protein and polypeptide materials and could perhaps explain the fracture behaviour in these proteins. This presents an exciting opportunity for future work. The insight derived here could be applied to designing the nanoscale structure of peptide-based and other materials consisting of the different bonds to achieve desired mechanical properties, and in particular strength, robustness and the ability to feature highly dissipative deformation behaviours as mediated by stick-slip rupture of key molecular domains. Possible applications range from the design of novel composites, fibre materials, to adhesion systems.

Figure 5. Comparison of robustness and strength for varied \( E_b \) and \( L_0 \), and combined measurement of robustness and strength as a function of \( E_b \) and \( L_0 \). (a) Competition of the robustness (solid lines) and strength (dotted lines). The robustness is a monotonically decreasing function and the strength is a strictly increasing function. However, the function becomes anti-monotonic for \( L_0 = 0.5 \) and \( 0.6 \) nm. (c) Detailed view of the data depicted in (b) for small bond energies in the range of 1–10 kcal mol\(^{-1}\). The plot confirms that there is a transition between \( L_0 = 0.4 \) and 0.5 nm. When \( L_0 \) is larger than 0.5 nm, the \( E_b \) corresponding to the maximum performance becomes smaller with an increase of \( L_0 \).
must be satisfied. At low force levels, the Marko–Siggia worm-like chain model (often abbreviated as WLC) is adopted to describe the elastic behaviour of the backbone of the polypeptide chains. The force in WLC theory is a function of end-to-end distance (x), contour length (λ) and persistence length (ξp) of a polypeptide:

$$ F = \frac{k_B T}{4\xi_p} \left( 1 - \frac{x}{\lambda} + \frac{4x}{\lambda} - 1 \right), \quad (4.2) $$

where $k_B$ is the Boltzmann constant and T is the temperature. In the rupture event (figure 1), the free energy change $\Delta A$ can be computed as a function of the extension dx in a polypeptide chain. The energy release rate can then be expressed as

$$ G = \frac{-\Delta A + Fdx}{dx}, \quad (4.3) $$

where $\Delta A = A_2 - A_1$. The parameters $A_2$ and $A_1$ are the free energies after and before bond rupture, and $A$ is obtained by the integral of the force $F$ in equation (4.2). Here, considering the geometry of the attached segment in polypeptide chain, we extend the free energy change equation in [28,29] and introduce a parameter, s, which is the ratio of the end-to-end distance to the contour length of the attached segment, dx/da, where 0 ≤ s ≤ 1. For a fully relaxed segment, there is no force exerting on the segment so the end-to-end distance is zero and s = 0 is obtained. On the other hand, for a fully extended segment, the end-to-end distance is equal to the contour length (dx = dλ), so that s = 1. The extended energy release rate is given by $G = (-\Delta A + F(\alpha - s))/dx$, where $\alpha$ is the ratio of end-to-end length of the free chain to the contour length (x/λ). In the one-dimensional WLC theory, the physically averaged end-to-end distance of a WLC is zero and it is also true for every segment of WLC.

If the attached segment with contour length dλ is treated as a part of a WLC, the averaged end-to-end distance of the segment, dx, should be zero but not is directly obtained from the geometry of the model. It is notable that the parameter s cannot be one because the fully extended WLC would yield an infinite force. If we assume the attached chain is fully relaxed (reflecting $s = 0$), G is exactly the same as the equation reported in references [28,29]. The force can be expressed in terms of $\alpha$, where [26]

$$ F(\alpha) = \frac{k_B T}{4\xi_p} \times [(1 - \alpha)^2 + 4\alpha - 1] \quad (4.4) $$

Table 3. Summary of key results of this study.

<table>
<thead>
<tr>
<th>parameter change</th>
<th>effect on cooperativity index</th>
<th>effect on robustness</th>
<th>effect on strength</th>
</tr>
</thead>
<tbody>
<tr>
<td>bond energy $E_0$ higher cooperativity at smaller bond energy</td>
<td>higher robustness at smaller bond energy</td>
<td>lower strength at smaller bond energy</td>
<td></td>
</tr>
<tr>
<td>bond spacing $L_0$ higher cooperativity at small bond spacing</td>
<td>higher robustness at small bond spacing</td>
<td>higher strength at small bond spacing</td>
<td></td>
</tr>
<tr>
<td>persistence length $\xi_p$ (measure of stiffness of polypeptide chain since $\xi_p \sim EL$) higher cooperativity at smaller persistence length</td>
<td>higher robustness at smaller persistence length</td>
<td>higher strength at smaller persistence length</td>
<td></td>
</tr>
</tbody>
</table>

and can then be substituted into the extended G function. This yields

$$ G = \left( \frac{k_B T}{4\xi_p} \right) \times [\alpha (1 - \alpha)^2 + (1 - \alpha)^{-1} + 2\alpha^2 + 1 - s (1 - \alpha)^{-2} + 4\alpha s - s]. \quad (4.5) $$

At the critical point of rupture, $\alpha_c$ and from that the breaking force $F_{\text{breaking}}$ are obtained by solving $G = \gamma_c$. The number of bonds that participate ($N_{\text{cr}}$, cooperativity index) in the rupture event is obtained by

$$ N_{\text{cr}} = \frac{k_B T}{E_b} \left[ \frac{2k_B T}{4\xi_p} [(1 - \alpha_{\text{cr}})^2 + 4\alpha_{\text{cr}} - 1] - \ln \left( \frac{1}{\sigma T} \right) \right]. \quad (4.6) $$

See table 1 for an overview of all parameters used in the model.

4.2. Robustness calculation

As defined in equation (2.1) the robustness is defined as the ratio of strength of a defected system $F(N_{\text{cr}} - 1)$, to an intact system, $F(N_{\text{cr}})$. The strength, $F(N_{\text{cr}} - 1)$, is the rupture force of the system when there is a defect present in the system and can be obtained from the equation of Bell’s model ([for details, see references [28,29]]). It is worth noting here that the domain and the value of the equation of Bell’s model must be positive. The force, $F(N_{\text{cr}} - 1)$, is defined as zero if the values are negative; reflecting the physical situation that the force is zero.

4.3. Combined measure of robustness and strength

For the ‘best’ performance of a system, both the robustness and strength must be maximized to optimize the overall behaviour of the system. The most stable system is defined as the one with the maximum value of the product of robustness and strength. We therefore define a combined measurement, $P$, as the product of robustness and strength:

$$ P = RF. \quad (4.7) $$

The combined measurement is a function of $E_b$ and $L_0$ and other model parameters. We emphasize that there are many possible measures for how robustness can be defined, and that the definition put forth in equation (2.1) in the main text is only one possible choice. Similarly, the calculation of the overall
performance as done in equation (2.1) can be done differently, in principle, and a more detailed understanding of the relative weight of robustness and strength can be incorporated.

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