Model studies of instabilities in heterogeneous materials systems

by

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Abstract

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Heterogeneous materials may become structurally unstable under an applied stress. In this thesis, the effects of two dissimilar stresses are studied. First, the methods of statistical mechanics are used to analyze the effects of mechanical stress on the strength of heterogeneous materials. A phenomenological multi-scale model is presented that analyzes inelastic deformation in a model natural composite, nacre. A kinetic Monte Carlo technique is developed to study the mechanical response of the biopolymer. The results of this model are used to generate a cellular automata model of the composite material. Under certain conditions, the sizes of plastic events in this model follow an apparent power-law distribution. The dynamics are found to be similar to earthquakes, where the slip sizes exhibit a scale-free distribution.

Second, a continuum theory is generated to understand how a model microstructure responds to thermal stresses. At elevated temperatures, a structure may spontaneously change shape in order to minimize its overall surface energy. To this end, the stability of a hollow-core dislocation to pearling and coarsening is considered using a linear stability analysis. There is a competition between elastic energy and the anisotropic surface energy. It is shown that sufficiently small hollow-core dislocations are stable with respect to both forms of structural instability, suggesting a route to stabilize nanometer-scale wires.
For my parents
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Chapter 1

Introduction

The last thing one discovers in composing a work is what to put first.

— T. S. Eliot

A fundamental problem of materials science is understanding how and why materials fail. The microstructure and properties of a materials system may degrade under stress, whether the driving force is mechanical, thermal, or electrical. The nature of the breakdown can determine the performance of the material. For instance, a heterogeneous material such as concrete can develop microcracks under an applied strain, failing gradually before a critical crack becomes unstable and propagates. Likewise, at elevated temperature, mass diffusion can become activated, causing a desirable microstructure to evolve into a less favorable one. Unfortunately, the theoretical understanding of these processes can be difficult. Breakdown is often a non-equilibrium process that cannot be fully described by thermodynamics. Further, the macroscopic behavior can be affected strongly by complex interactions between small-scale features.

One illustrative example of mechanical failure is the earthquake, where discrete bursts of energy are released due to the jerky, stick-slip motion of seismic plates. Empirical laws have been found regarding the distributions of earthquakes. The Gutenberg-Richter law, for instance, relates the size of an earthquake to the frequency with which it is observed. The size of an earthquake is characterized by its moment $\mu ad$, where $\mu$ is the shear modulus of the rock, $a$ is the area of the fault that slips, and $d$ is the displacement through which this area slips. The earthquake distribution $N(M_0)$ is defined to be the number of earthquakes with moment $M_0$ and may be written in the form:

$$N(M_0) = \alpha_{GR} M_0^{-B}$$

where $B$ and $\alpha_{GR}$ are empirically determined parameters (Wyss, 1973). Eq. 1.1 is a power-law distribution, which exhibits the property of scale-invariance. This is the statement that if the size of the earthquake is scaled by some factor $\lambda$, that the shape of the distribution will not change and will instead be scaled by a factor,

$$N(\lambda M_0) = \lambda^{-B} N(M_0)$$

In other words, the earthquake size distribution will show the same properties if examined on different size scales. $N(M_0)$ is said to have the property of generalized homogeneity: it is a scaling law that has no inherent size scale.
As stated by Barenblatt (2003), these scaling laws do not occur by accident. Their existence
reflects self-similarity, a physical property of the process. To study the nature of scaling laws in
earthquakes, simple models were proposed that involved dragging blocks along a surface (Burridge
and Knopoff, 1967). The deformation of these models is jerky. This is because the motion of
a single block can cause avalanches. When a block slips, it changes the forces on its neighbors,
and can consequently cause them to move as well. Direct numerical simulation of the equations
of motion (Carlson and Langer, 1989; Carlson et al., 1994) as well as their corresponding cellular
automaton models (Olami et al., 1992) were found to reproduce the Gutenberg-Richter law.

This example illustrates that an appropriately simplified model can exhibit the same scaling
behavior as a real system. This is understood by analogy to phase transformations. If the behavior
of these systems is in some way critical, some properties of the deformation will not depend on
the microscopic details of the interactions. For example, in earthquakes, the avalanche behavior
disappears under a sufficiently large force. Under certain conditions, this pinning-depinning transition
has been interpreted as a stress-induced phase transition (Cule and Hwa, 1996). This type
of behavior is common to a variety of dynamic systems. For instance, nonlinear conductivity in
some systems has been attributed to the non-uniform sliding of charge density waves. These waves
are pinned at crystallographic defects and are prevented from moving if the applied field is below a
threshold field (Fisher, 1985). The analogous phenomenon in magnetization has also been observed,
and is known as Barkhausen noise (O’Brien and Weissman, 1994).

Dislocation plasticity on the nanoscale also progresses in discrete bursts. The force-displacement
curve from nanoindentation experiments in ductile metals exhibits a “staircase” structure (Bahr
et al., 1998), where each step corresponds to a plastic event. Dislocation dynamics simulations
have suggested that a pinning-depinning transition occurs in various metal systems (Chrzan and
Mills, 1996; Koslowski et al., 2004). Similarly, the compression of micron-sized single pillars of
Ni (Dimiduk et al., 2006) and Ni superalloy (Uc hic et al., 2004) have exhibited size effects that
are consistent with properties of finite size scaling. Under certain conditions, avalanche dynamics
may cause serrations in the stress-strain curves. One example is the Portevin-Le Châtelier effect
(Mazot, 1973; Balik and Lukáč, 1993). In other cases, the large avalanches may be cut-off, causing
the plastic behavior to be smooth at macroscopic length scales (Zaiser and Nikitas, 2007).

Inherently stochastic phenomena, therefore, determine a physical length scale for deformation.
This means that the parameters that control the engineering properties of a material may be
determined by the statistical properties of the system. This thesis attempts to use these concepts
to understand two examples of breakdown: one mechanical and one microstructural.

The first example of breakdown considers the effects of mechanical stresses on nacre, a natural
composite present in mollusk shells. Nacre consists of polycrystalline aragonite platelets connected
by an organic adhesive. It is of considerable engineering interest because its toughness is remark-
ably high in comparison to the toughness of its component materials (Jackson et al., 1990). The
dominant mechanism of inelastic deformation is the sliding of these platelets. This is an inher-
tenly discrete process that contains a strong resemblance to the spring block model of earthquakes
described earlier. As a result, phenomenological models of nacre are developed to study the conse-
quences of discrete deformation events.

The second example of breakdown focuses on the effect of diffusion on a model microstructure,
the hollow-core dislocation. Under certain conditions, this structure is unstable to shape changes.
For instance, this structure may evolve to form an array of pores. The nature of the break-up
affects the geometry of this pore array. In particular, the mass transport mechanism determines
the rate at which a particular perturbation grows, and so affects the final spacing of the pore array.
Chapter 2

Background

Existence is a series of footnotes to a vast, obscure, unfinished masterpiece.

— Vladimir Nabokov

2.1 Mechanical instabilities in biological composites

2.1.1 Mechanical properties of nacre

Many structural biological materials are composites consisting of a mineral phase in an organic matrix (as reviewed in Meyers et al., 2008). One well-studied example is nacre, which exhibits a remarkably large toughness compared to its constituent materials (Jackson et al., 1990). The reason for this toughness is still somewhat controversial, but is usually attributed to the hierarchical microstructure. As a result, there have been many attempts to replicate the properties of nacre by mimicking its structure (Deville et al., 2006; Bonderer et al., 2008; Jackson et al., 1989; Wang et al., 2007). However, there is currently no recipe to reproduce the mechanical properties of biological materials. Features at many different length scales play roles in the overall mechanical behavior of the material, and it is difficult to identify their relative importance (Wang et al., 2001). Some arguments exist for intrinsic length scales determined by static properties. The point of view of the present work is that the dynamic properties of the process may help to set these length scales as well.

Nacre consists of polycrystalline aragonite platelets, with thickness ranging between $t_p = 200 - 500$ nm, separated by a layer of biopolymer approximately 10 nm in thickness. The width of a typical platelet, $L_p$, is several microns. These platelets are more ductile than typically expected for a polycrystalline ceramic (Li et al., 2004b). This is attributed to the in situ observations of grain rotation during macroscopic deformation (Li et al., 2006). On the micron length scale, platelet sliding has been identified as the primary mechanism of inelastic deformation. Sliding, however, is resisted by various features on several length scales, as summarized in Fig. 2.1. Nanoasperities have been suggested to contribute to the sliding friction (Evans et al., 2001). The aragonite tablets have also been observed to be macroscopically wavy, leading to progressive locking during deformation (Barthélat et al., 2006). Mineral bridges between platelets are also believed to contribute to the strength of the composite (Meyers et al., 2007).
Several observations have also indicated the importance of the biopolymer. The mechanical response of the tablets (Mohanty et al., 2006) as well as the composite (Menig et al., 2000) have shown rate-dependent behavior under compression. The average strength was found to increase with increasing loading rate. *In situ* electron microscopy experiments have revealed polymer ligaments between platelets during deformation (Sumitomo et al., 2008). The biopolymer contains a mechanism for increasing the energy dispersed during deformation (Smith et al., 1999; Fantner et al., 2006). A single polymer strand contains sacrificial bonds that break discretely, leading to a saw-tooth load-displacement curve. This mechanism of “hidden length” has been proposed to add toughness to biological composites (Fantner et al., 2006). Sacrificial bonds have been observed in other mechanical studies of biological polymers. Rief et al. (1997b,a) first identified such behavior in the muscle protein titin and developed a two-state statistical model to study the effects of these unfolding events on the mechanical response of the single polymer.

### 2.1.2 Continuum theories

Most existing theories of nacre have attempted to use continuum mechanics to analyze its mechanical properties. There are two primary points of view. The first approach, known as the shear-lag model, is derived from theories of composites. It considers a force balance on each individual platelet, and estimates the properties of the material based on the bulk properties of the constituent materials. The second approach, or fracture mechanics approach, attempts to calculate the resistance of the composite to the growth of a crack. This is done by approximating the properties of the composite as a continuum, then finding the degree to which stresses are localized in the material.
Shear-lag model

The elastic modulus of nacre has been described using a semi-empirical shear-lag model (Gao, 2006; Jäger and Fratzl, 2000). Here, the mineral platelets are assumed to bear tensile loads, and the organic is assumed to bear shear loads only. Under these assumptions, the Young's modulus $E_c$ of the composite can be calculated to be

$$\frac{1}{E_c} = \frac{4(1 - \Phi)}{G_p \Phi^2 \rho^2} + \frac{1}{\Phi E_m}$$

(2.1)

where $\Phi$ is the volume fraction of mineral, $\rho$ is the aspect ratio of the platelets, $G_p$ is the shear modulus of the polymer, and $E_m$ is the Young's modulus of the mineral. In the limit that the mineral is infinitely stiff, the modulus reduces to $E_c \approx G_p \Phi^2 \rho^2 / 4(1 - \Phi)$. This model is very successful in describing the modulus of natural composites. The measured shear moduli of wet and dry nacre are reproduced well with the shear-lag model (Gao, 2006).

A related model for the strength of nacre is named the shear-transfer model (Glavinechevski and Piggott, 1973). It is a modified rule of mixtures that extrapolates between the strength of the mineral and the strength of the organic matrix. The overall strength of the composite $\sigma_f$ is given by

$$\sigma_f = \alpha \Phi + (1 - \Phi) \sigma_m$$

(2.2)

where $\sigma_m$ is the strength of the mineral, and $\alpha$ is a parameter that depends on the failure mode of the composite. The shear strength of the organic matrix is given by $\tau_y$. If the aspect ratio of the platelet, $s = L_p / t_p$ is larger than a critical ratio $s_c = \sigma_m / \tau_y$, the platelets will fracture and $\alpha$ will be given by

$$\alpha = 1 - \frac{\sigma_m}{2 \tau_y s}.$$  

(2.3)

If the aspect ratio is smaller than $s_c$, pull-out will occur and

$$\alpha = \frac{\tau_y s}{2 \sigma_m}.$$  

(2.4)

This model identifies a transition between platelet pull-out and platelet fracture that is determined by the geometry of the platelets. The effect of aspect ratio on the failure mode is illustrated in Fig. 2.2.

More detailed calculations have been made using the finite-element method (FEM), several authors have performed calculations incorporating contact physics (Barthelat et al., 2006; Evans et al., 2001; Katti and Katti, 2001; Katti et al., 2001, 2004). Evans et al. (2001) performed initial studies considering the effects of nanometer-scale asperities. Barthelat et al. (2006) instead considered microscopic tablet waviness, and found that these microstructural features were more important than the nanoscale ones. More complicated models of the organic matrix were incorporated by Katti and Katti (2001).

Fracture mechanics

The modern understanding of fracture mechanics was first developed by Inglis (1913), who realized that local stresses are concentrated around flaws. Griffith (1920) used this fact to determine a quantitative dependence of the stress at which a sample fails based on the size of existing flaws. Irwin (1956) then extended Griffith’s theory to applications in ductile materials. These analyses
Figure 2.2: Shear transfer model indicating crossover between pull-out and platelet fracture. The solid portions of the curves depict the prediction for the strength of the composite.

set an energetic criterion for fracture, defining a strain energy release rate $G$ available for extending a crack. For a simple geometry, such as a plate in plane stress with an internal crack of length $2a$,

$$G = \frac{\pi \sigma^2 a}{E} \quad (2.5)$$

under a uniform, externally applied stress $\sigma$, where $E$ is the Young's modulus of the material. For the crack to extend, the driving force $G$ must be larger than some critical value, $G_c$. In this case, $G_c = 2\gamma$, the energy penalty due to the creation of new surface, twice the surface energy $\gamma$. This leads to a plate fracture strength

$$\sigma_f = \left( \frac{2\gamma E}{\pi a} \right)^{1/2}. \quad (2.6)$$

The Griffith criterion is a statement about the global energy balance in the system. Irwin made a connection between the energy release rate and the stress intensity factor $K$. The stress intensity factor for various crack geometries may be calculated and is of the form

$$K = Y \sigma \sqrt{a} \quad (2.7)$$

for a crack of given length $a$, where $Y$ is a numerical factor that depends on geometry. In order for a given crack to propagate, the stress intensity must be larger than some critical fracture toughness $K_c = \sqrt{G_c E'}$, where $E'$ is the appropriate elastic constant. The toughness is a size-independent materials property that is strongly dependent on the microstructural mechanisms of fracture. These may be divided into intrinsic mechanisms, that operate ahead of the crack tip, and extrinsic mechanisms, that operate behind the crack tip. An example of an intrinsic mechanism is crack blunting, and an example of an extrinsic mechanism is platelet pull-out.

These classical ideas of fracture mechanics have been applied successfully to artificial composites (Dharan, 1978). They have also been utilized by Gao et al. (2003) to determine an engineering criterion for natural composites, the critical platelet thickness $h^*$. This is found by considering the Griffiths criterion for a platelet with a crack extending through half of its thickness. If the fracture stress is equal to the theoretical stress of the mineral $\sigma_{th}$, then

$$h^* = \frac{\sqrt{2\gamma E_m}}{\sigma_{th}} \quad (2.8)$$
where $\zeta$ is a numerical factor of order one, and $E_m$ is the Young's modulus of the mineral. $\gamma$ is the surface energy of the mineral. Gao et al. (2003) argues that the strength of platelets larger than this length will be determined by internal flaws. So, $h^*$ defines an inherent length scale of the platelets. Assuming $\gamma = 1 \text{ J/m}^2$, $\zeta = 1$, $E_m = 100 \text{ GPa}$, and $\sigma = E_m/30$, $h^*$ is estimated to be about 30 nm. One of the attractive aspects of this theory is that all of the parameters in Eq. 2.8 may be calculated through direct atomistic scale simulations.

Other researchers have attempted to consider alternate theories of elasticity. One such theory is the Cosserat, or micropolar theory of elasticity (Eringen, 1966). This theory incorporates local rotations into its formalism. This leads to elastic deformation of materials exhibiting an inherent length scale. Using elasticity theory, the stress concentration factor depends only on the shape of the hole or inclusion. However, under Cosserat theory, the stress concentration factor also is found to depend on the size of the inhomogeneity. This theory has been used to address how microscopic features in bone such as osteons introduce a size scale into the elastic response of the material (Lakes, 1995).

### 2.1.3 Statistical mechanics approach

Fracture in metals has been understood as a phase transformation (Hilarov, 2005). This suggests another way to understand the size dependence of the strength of solids. This point of view was also suggested by Mandelbrot et al. (1984), who found that fracture surfaces in metals have a fractal shape, and further claimed the fractal dimension of the surface is correlated to the toughness of the material. In other words, there is a possible connection between the engineering property of toughness and the self-similar characteristics of the fracture process. This suggests the utility of applying techniques of statistical mechanics to the problem of fracture.

A few studies have specifically considered the consequences of the random microscopic properties on the engineering properties of nacre. Nukala and Šimunović (2005) proposed a statistical model for nacre using an electrical analogue of fuses and resistors. By modeling the material as a set of elements that fail completely at a threshold extension, a design criterion for the maximum load on each platelet can be predicted. Because the material properties are inhomogeneous, it is not trivial to calculate this quantity from the shear-lag model.

Another indication of the importance of distributions of material properties on the structural properties of nacre comes from the continuum elastic calculations of Barthelat et al. (2006). The strength of an array of perfect, hexagonal platelets was found to be lower than that of a more realistic microstructure. This result suggests that the randomness in the structure is connected to the mechanical response of the system.

A third important observation is that a power-law relationship exists between the size and frequency of acoustic emission events in bone and deer antler (Zioupos et al., 1994) during fracture. This suggests that plastic events in natural composites are discrete, analogous to earthquakes.

Because of these issues, it is difficult to study statistical effects using the traditional methods of continuum mechanics. As a result, simplified models were developed to study fracture in other systems (as reviewed in Herrmann and Roux, 1990; Krajinović and Mier, 2000). In particular, fracture has been studied in the context of earthquakes, textiles, and dielectric breakdown. Some important results of these theories are described in this section. There are a large variety of techniques that have been developed: this is partly because disorder may be incorporated in two different ways. *Quenched* disorder refers to properties that are initially set randomly then not
changed for the remainder of the simulation. This may be used to simulate inhomogeneous materials properties. *Annealed* disorder is set at every time step. This type of disorder reflects randomness of the dynamic process, such as the stick-slip friction. In general, both types of randomness must be incorporated into a useful model (see, for example Scorretti et al., 2001).

**Brittle solids**

The cleavage of brittle materials has been described through "weakest-link" statistics. The failure of the sample is determined by the probability that a critically large defect is sampled. The distribution in strengths can be quite wide: it has empirically been shown to be described by the two-parameter Weibull probability distribution function (Weibull, 1951).

$$f_{\text{Weibull}}(\sigma; \lambda, k) = \begin{cases} \frac{k}{\lambda} \left(\frac{\sigma}{\lambda}\right)^{k-1} e^{-\left(\frac{\sigma}{\lambda}\right)^k} & \sigma \geq 0 \\ 0 & \sigma < 0 \end{cases}$$  

(2.9)

$f_{\text{Weibull}}(\sigma; \lambda, k)d\sigma$ may be interpreted as the probability that the sample will fail in the range of stresses between $\sigma$ and $\sigma + d\sigma$. The parameters of this distribution are the Weibull modulus $k$, and the scale parameter $\lambda$. The modulus $k$ determines the shape of the function, $\lambda$ determines the overall scale of the distribution. The value of $k$ can change the shape of the distribution dramatically. In Fig. 2.3, the probability distribution function are plotted for various values of the Weibull modulus.

**Earthquake models**

An important characteristic of earthquakes is that their frequency follows a power-law distribution. One example is the Gutenberg-Richter law, an empirical law for $N(M)dM$, the number of seismic events measured with magnitude between $M$ and $M + dM$. It is normally written in the form:

$$\log_{10} N(M) = A - bM$$  

(2.10)
Figure 2.4: A schematic of a velocity-dependent friction law that leads to stick-slip behavior. This diagram represents a linear approximation that has been used previously in the model of Carlson and Langer (1989).

where $A$ and $b$ are empirically determined parameters (Gutenberg and Richter, 1954). The physical meaning of this expression is not very transparent: the magnitude of an earthquake is measured logarithmically. A linear measure of strength of an earthquake is the moment $M_0$, which may be defined relative to $M$ using the relation

$$\log_{10} M_0 = c + dM$$  \hspace{1cm} (2.11)

where $c$ and $d$ are two other empirically determined parameters (Wyss, 1973). Using this definition, the Gutenberg-Richter equation may be rewritten as a power-law distribution,

$$N(M_0) = \alpha_{GR} M_0^{-B}$$  \hspace{1cm} (2.12)

where $B = b/d$ and $\alpha_{GR} = 10^{a+bc/d}$ (Wyss, 1973). It is important to note that it is possible to perform a continuum analysis of earthquakes by solving a corresponding set of elastodynamic equations (Rice and Ben-Zion, 1996). However, these models do not reproduce the Gutenberg-Richter law. This type of behavior may, however, be replicated by discrete models.

The Burridge-Knopoff (BK) model is one such discrete model, which treats seismic plates as an array of blocks elastically coupled by springs. A square lattice of blocks are attached to a plate moving at a constant velocity $v$ by an array of leaf springs with spring constant $k_p$. The blocks are also coupled to each other: the nearest neighbors are coupled with springs with spring constant $k_c$. The blocks interact with a surface according to a stick-slip friction law that depends on the velocity of the block, $F_f(v)$. This law is highly nonlinear, as sketched in 2.4.

As a result, the block will remain stationary until static friction is overcome, then it will move to a position that relieves the force. In a one-dimensional (1-d) BK model consisting of $N$ blocks arranged linearly, the position of the $j$th block $X_j$ may be described by a set of $N$ differential equations

$$m\ddot{X}_j = k_c(X_{j+1} - 2X_j + X_{j-1}) - k_pX_j - F_f(v + \dot{X}_j)$$  \hspace{1cm} (2.13)

where $m$ is the mass of the block, $\dot{X}_j = \partial X_j / \partial t$ and $\ddot{X}_j = \partial^2 X_j / \partial t^2$. The dynamics of the BK model have been explored with the direct numerical integration of Eq. 2.13 (Carlson and Langer, 1989; Carlson et al., 1994).
Because Eq. 2.13 is highly nonlinear, it is computationally expensive to simulate large systems. To this end, Olami et al. (1992) (OFC) introduced a cellular automaton version of the BK model. They considered the BK model in an adiabatic limit. Blocks are assumed to not slip until they reach some critical threshold force, $F_{th}$. At this point, they are allowed to slip to the position such that there is zero force on the block. Since the other blocks are stationary during this time step, the load is redistributed to its nearest neighbors. The OFC model is a good example of the incorporation of annealed order: $F_{th}$ is reset after a block slips. The energy spectra from the two methods both obey similar power-law distributions. This power-law behavior has been observed over several decades (de Carvalho and Prado, 2000).

**Fiber bundle model**

The family of models known as fiber bundle models (FBM) were initially introduced to study the behavior of threads loaded in parallel (Daniels, 1944). Each fiber is assigned a failure threshold from a distribution. The system is then loaded until a fiber breaks. After each breakage event, the load is then redistributed among the remaining fibers. One example is the equal load-sharing model, wherein all fibers share the same extension $x$. This is a mean-field model, where only one effective interaction coupling all fibers is considered.

This type of model is exactly solvable (Alava et al., 2006). Consider a system where $N$ fibers each have the same elastic modulus $k$, but a random distribution of strengths. A fiber will fail and be removed from the simulation if the force on it exceeds some threshold $f_t$, defined by a distribution. Each fiber has a failure strength assigned by some distribution $p(f)$. The number of surviving fibers $n$ at a given load is given by

$$n = N \left(1 - \int_0^{F/n} p(f)df\right) \quad (2.14)$$

where the overall load on the bundle is given by $F$. If the distribution is taken to be uniform in $[0,f_0]$, this may be integrated to find

$$\frac{F}{N} = k \epsilon \left(1 - \frac{k \epsilon}{f_0}\right) \quad (2.15)$$

This may be inverted to find that

$$\frac{n}{N} = \frac{1}{2} + \frac{1}{2} \sqrt{\frac{4}{N f_0} \left(\frac{N f_0}{4} - F\right)^{1/2}} \quad (2.16)$$
This form suggests that there is a critical load on a fiber bundle $F_c = N f_0 / 4$, above which the deformation causes catastrophic failure. It is interesting to note that

$$\frac{\partial n}{\partial F} = \frac{N}{4f_0} (F_c - F)^{-1/2}$$

This analysis demonstrates that the rate of bond fractures increases very rapidly as the system approaches catastrophic failure.

Because of the simplicity of the FBM, a variety of modifications have been proposed and studied. In order to incorporate spatial effects, local load-sharing models have also been proposed. In such models, instead of the load being distributed equally among the survivors, the load is shed to the nearest neighbors. Changing to a local load-sharing condition changes the size dependence of the properties. In particular, the average bundle strength scales as $1 / \log(N)$ (Kloster et al., 1997).

Allowing local redistributions of strain allows the organization of the fibers within the bundle to affect the mechanical behavior of the bundle. To this end, hierarchical distributions of fiber bundles have been studied computationally (Newman and Gabriellov, 1991). FBM have also been used to study dynamic fracture. Marder (1993) considered a 1-d dynamic version of a local-load sharing FBM that included inertial masses at each node.

**Random-fuse model**

A statistical method that allows the study of spatial correlations between failure events is the random-fuse model (RFM). An electrical network of resistors is connected through fuses (de Arcangelis et al., 1985). The threshold of each fuse is taken from a statistical distribution. This was introduced as an analogue to mechanical fracture. Unlike the equal-load sharing FBM discussed earlier, the RFM is inherently non-local.

Random properties may be incorporated into this model in multiple ways. For instance, the *diluted model* contains fuses with uniform failure thresholds. The term dilution refers to prebreaking a certain number of bonds. These models are brittle. Alternatively, the failure strengths of the fuses may be taken to be random. In this case, the inhomogeneous fuse strengths can cause crack deflection and a more gradual failure (Kahng et al., 1988; Sahimi and Goddard, 1986). This limit is known as *strong disorder*. Other models have explicitly incorporated other toughening mechanisms. For instance, fiber bridging in fiber-reinforced composites may be modeled by introducing a remnant resistivity that remains after the initial fuse fails (Li and Duxbury, 1988).

Using an RFM where the strengths of the fuses are drawn from a random distribution, some scaling behavior was identified. (de Arcangelis et al., 1989). The RFM may be thought of as a discrete elastic model. It may be similarly modified extensively because of its simplicity. For instance, the fuses of the RFM may be replaced with elastic beams in the *bond-bending model*. It may be shown that in the continuum limit the beam and bond-bending models reduce to the micropolar theory of elasticity (Herrmann and Roux, 1990).

Another important generalization of the RFM is the inclusion of plasticity. One example is the continuous-damage random-fuse model (CDRFM), as introduced by Zapperi et al. (1997). This model was formulated in order to simulate plastic deformation: it allows each spring to fail multiple times.
2.1.4 Summary

Nacre is a natural composite with an inherently discrete, hierarchical structure. A number of models have been developed in order to study the mechanical deformation of various materials with discrete elements. They exhibit complex stick-slip dynamics. The consequences of this jerky deformation process on the mechanical properties of nacre have not yet been fully understood. By doing so, it may be possible to determine engineering criteria that may be used to explain the toughness of nacre.

2.2 Capillary instabilities in strained systems

Under elevated temperatures, mass-transport mechanisms such as diffusion become active. Most technically important microstructures are not thermodynamically stable with respect to surface energy, and will therefore evolve to minimize the surface energy of the system. This is known as a capillary instability. In solid materials, there is often a competition between surface energy and strain energy. For instance, Cahn (1957) proposed that strain energy can modify the kinetics of heterogeneous nucleation. If a precipitate forms on a dislocation, strain energy is relieved at the expense of generating new interfaces. This idea has recently been exploited as a route to fabricate nanometer-scale wires (Nakamura et al., 2003).

In order to study these phenomena theoretically, it is necessary to make simplifying assumptions. In particular, the dynamics are assumed to be self-similar. This approach was initially used in the context of powder processing by Herring (1950). Under this assumption, the morphological evolution of a system undergoing sintering may be described by a scaling law. The exponent of this scaling law is determined by identity of the dominant mass transport process.

2.2.1 Hollow-core dislocations

A technologically important microstructural feature is the hollow-core dislocation, or “nanopipe.” Interest in these defects has recently been revived due to their detrimental presence in electronic materials. For instance, Neudeck and Powell (1994) claimed that the presence of nanopipes can be the limiting factor in the performance of SiC power devices. Hollow-core dislocations have been observed in SiC at growth spirals (Verma, 1953). Further, hollow-core dislocations have been observed as defects in AlN thin films (Tokumoto et al., 2008) and GaN thin films (Qian et al., 1995).

Frank (1951) first proposed that material near the dislocation core may be transported away and the core may open, decreasing the elastic-strain energy at the expense of creating free surfaces. In particular, a thermodynamically stable radius is predicted that depends on the size of the Burgers vector of the dislocation, the elastic moduli, and the surface energy. However, the theory of Frank (1951) does not quantitatively predict the sizes of experimentally observed hollow-core dislocations. As a result, more detailed theories have been proposed. In particular, the stability of these defects has been considered when the crystal is growing or evaporating (Cabrera and Levine, 1956). This model was improved to better treat the non-linear behavior near the core by (Schaarichter, 1965a,b). van der Hoek et al. (1982) introduced a strain energy function for the dislocation core that sets a different thermodynamic condition for nanopipe stability.

More detailed formation mechanisms for the hollow-core dislocation have been proposed, incor-
porating the crystallography and the chemistry of the materials system. Segregation of Si, Mg, and O to the dislocation core in GaN has been suggested to affect both the morphology and number of the defects (Cherns, 2000; Liliental-Weber et al., 1997). Observations of oxygen segregation to hollow-core dislocations in GaN led to a proposed mechanism involving oxygen diffusion to surface pits (Hawkridge and Cherns, 2005). Pirouz (1998) pointed out inconsistencies with the character of observed hollow-core dislocations and normal closed-core dislocations. To resolve this, a mechanism based on dislocation attraction to triple junctions was proposed. The implication is that these structures may be formed through non-diffusional processes, and are not necessarily stable or metastable structures.

Pailloux et al. (2005) recently observed an instability in nanopipes in GaN under electron irradiation. By considering the surface-energy anisotropy, a “bamboo” structure was found to be energetically favorable. This is analogous to the pearling, or Rayleigh instability observed in fibrous microstructures, in which a rod breaks up into spheres. The morphology of the pipes suggests that it may undergo another microstructural instability. In particular, the structures may coarsen, where larger nanopipes will grow at the expense of smaller ones.

2.2.2 Rayleigh instability

Rayleigh (1878) proposed a theory describing a phenomenon in which fluid jets decompose into spheres to minimize the surface energy of the system. An infinite cylinder of initial radius $R_0$ is unstable to perturbations of wavelength greater than $\lambda_{\text{min}}^{\text{isotropic}} = 2\pi R_0$ (Fig. 2.6). This minimum wavelength depends only on the initial size of the cylinder. It is independent of the actual mechanism through which mass transport proceeds. This theory was extended to isotropic solids by Nichols and Mullins (1965b). The dominant mass-transport mechanism was found to change the fastest-growing perturbation, while the minimum wavelength was still predicted to be $\lambda_{\text{min}}^{\text{isotropic}}$. Surface diffusion was found to have a fastest-growing wavelength of $2\sqrt{2}\pi R_0$. 

Figure 2.6: Schematic of hollow-core dislocation with initial radius $R_0$ undergoing Rayleigh breakup. The periodicity of the perturbation is $\lambda$. 

$$\lambda$$

$$2R_0$$

$$2R_{\text{mat}}$$

$$\lambda$$

$$z$$

$\lambda$
Cahn (1979) further noticed that anisotropic surface energies may influence the value of the minimum wavelength. Stöckken and Glaeser (1992) confirmed the effect of the surface-energy anisotropy on the fastest growing wavelength for surface-diffusion limited breakup.

2.2.3 Coarsening

As first observed by Ostwald (1900), the solubility of a particle depends on its size. Therefore, for a given ensemble of particles, there is a thermodynamic driving force for the size distribution to change. Larger particles may grow at the expense of the smaller ones in a process known as coarsening, as illustrated in Fig. 2.7. The size dependence of the chemical potential can be described quantitatively by the Gibbs-Thompson equation,

$$\Delta G_\gamma = \frac{2\gamma V_m}{R}. \quad (2.18)$$

This expression describes the free energy increase $\Delta G_\gamma$ associated with a spherical particle with radius $R$ and molar volume $V_m$. Because $\Delta G_\gamma$ decreases with larger particles, there is a thermodynamic driving force for a system to increase its size.

A complete theoretical understanding of coarsening seeks to calculate the evolution of the particle-size distribution, $f(R, t)$, where $f(R, t) dR$ is the number of clusters per unit volume with radius between $R$ and $R + dR$ at time $t$. First, because of mass conservation, $f$ must obey a continuity equation:

$$\frac{df}{dt} + \frac{d}{dR} \left( \frac{dR}{dt} f \right) = 0 \quad (2.19)$$

To solve Eq. 2.19, it must be combined with a local rate law $dR/dt$, which determines the rate at which a particular particle grows depending on its size. $dR/dt$ is determined by kinetics and geometry.

Quantitative theories explaining this process were first developed by Lifshitz and Slyosov (1956) and independently by Wagner (1961) in the limit that the precipitates are infinitely dilute. The
The diffusion equation is solved for an isolated particle. This leads to a simple form for the rate law. For instance, \( \frac{dR}{dt} \) for spheres undergoing diffusion-limited growth may be written as:

\[
\frac{dR}{dt} = \frac{K_{\text{diff}}}{R^2} \left( \frac{R}{R_c} - 1 \right)
\]

where \( K_{\text{diff}} \) is a rate constant, and \( R_c \) is the critical radius. This so-called LSW theory predicts the average particle radius increases with time according to a power law \( \langle R(t)^n \rangle \propto t \), where the value of \( n \) depends on the dominant growth mechanism. For the coarsening of spheres under a diffusion-limited growth law, \( n = 3 \).

The classical LSW theory does not quantitatively reproduce \( f \), predicting a much narrower particle-size distribution than what is experimentally observed. One of the reasons for this comes from the assumption of self-similarity. Snyder et al. (2001) found that under some practical conditions, the asymptotic regime may not be reached. Instead, transient effects may dominate the coarsening process. The LSW approach presumes the existence of an asymptotic limit, when \( f \) reaches a self-similar shape.

Another limitation of LSW comes from neglecting the local environment about each particle. It breaks down in the limit that the separation between particles becomes finite: this is known as the finite-volume-fraction limit. In this case, \( R_c \) is a function of the volume fraction. Additionally, spatial correlations may develop between particles. To this end, a number of extensions to LSW have been proposed. The two most prominent modern theories of coarsening either use statistical averaging to represent an effective medium about each particle (Brailsford and Wynblatt, 1979; Yao et al., 1993), or instead use statistical mechanics to directly analyze the microscopic diffusion problem (Marqusee and Ross, 1984). Attempts have also been made to include the effects of other interactions between particles, such as strain (Sagui and Desai, 1995).

Although the LSW theory was originally developed for spherical particles interacting through a 3-d diffusion field, theories of coarsening have been developed for alternative geometries. In particular, the coarsening of fibrous microstructures has also been of great interest (Ardell, 1972; Cline, 1971). Progress on these theories has been slowed because of peculiarities of the mathematics of 2-d diffusion. The applicable local rate law is:

\[
\left. \frac{dC_r}{dr} \right|_{r=R} = \frac{C_{R'} - C_R}{R \ln (R'/R)}
\]

where the concentration at the surface of a cylinder with radius \( r \) is \( C_r \). This analysis also introduces a distance \( R' \). In the limit that \( R' \to \infty \), the growth rate drops to zero. As noted by Ardell (1972) as well as Marqusee (1984), this means that it is not possible to calculate a steady-state growth rate for an isolated particle. So, another length scale is introduced that corresponds to the average distance to the next-nearest particle.

### 2.2.4 Summary

Hollow-core dislocations are defects that arise due to a competition between surface energy and strain energy. Similar rod-like microstructures have been observed to be unstable to morphological changes such as pearling and coarsening. By considering the possibility that hollow-core dislocations may undergo such microstructural instabilities, it may be possible to explain the observation of defects like the bamboo structure observed by Pailloux et al. (2005).
Chapter 3

Dynamic model of plastic deformation in nacre

The first man gets the oyster, the second man gets the shell.

— Andrew Carnegie

One mechanism that has been proposed as the reason for the high toughness for nacre is that energy may be dispersed during the inelastic deformation of the biopolymer. In particular, discrete domains on the matrix biopolymer Lustrin A may unfold, effectively increasing the length of the chain (Smith et al., 1999). There is inelastic deformation associated with sacrificial bonds that causes the dissipation of energy during deformation. A closely related mechanism has been used to understand the deformation of biopolymers in bone. The side groups in proteins such as osteopontin and dental matrix protein 1 have similarly been proposed to interact, leading to another type of sacrificial bond that may affect the mechanical behavior of bone (Fantner et al., 2007; Adams et al., 2008).

3.1 Dynamic response of a single biopolymer

The breaking of sacrificial bonds in a biopolymer is an inherently stochastic process. It may be interpreted as a phase transition from an intact state to a broken state. One theoretical approach to understanding how the biopolymer deforms mechanically is to use rare event, or Poisson statistics, where transitions between states are assumed to be fast compared to the time the system resides in a particular state. In this case, the “state” refers to the configuration of sacrificial bonds present. The initial state of the biopolymer is taken to have all sacrificial bonds intact. For simplicity, the irreversible limit is taken, and these sites are only allowed to unfold. Each site for sacrificial bonds may undergo a reaction, changing between the folded and unfolded states. $P_u(t)dt$, the probability of an element unfolding between times $t$ and $t + dt$, is assumed to obey an exponential dependence on the applied force (Evans and Ritchie, 1997; Zhurkov, 1984). From these analyses, the frequency of an unfolding event $\omega = 1/P_u(t)$ on a folded domain is

$$\omega_u(t) = \alpha_u \exp \left( \frac{F_{ext}(t)\Delta x_u}{k_BT} \right)$$

(3.1)
Figure 3.1: Force-extension curve of a single polymer using the worm-like chain approximation. The entropic force $F_{wlc}$ diverges as the displacement approaches the contour length, $x = L_c$.

Figure 3.2: Schematic diagram of measurement of the mechanical response of a modular polymer chain. The circles on the chain represent modules that may unfold discretely. The polymer may be strained under load-controlled (specified $F$) or displacement-controlled (specified $x$) conditions.

where $\alpha_u$ and $\Delta x_u$ are empirical parameters used to fit the rate dependence. The elastic behavior of the single molecule is assumed to follow the worm-like chain model (Marko and Siggia, 1995). This is a well-known statistical model of the elastic response of a semi-flexible polymer chain. As illustrated in Fig. 3.2, the entropic force $F_{wlc}$ for a polymer chain of contour length $L_c$ held at a displacement $x$ is

$$F_{wlc}(x, L_c) = \frac{k_B T}{p} \left[ \frac{1}{4} \left( 1 - \frac{x}{L_c} \right)^{-2} - \frac{1}{4} \frac{x}{L_c} \right]$$

(3.2)

where $p$ is the persistence length, a parameter characterizing the stiffness of the polymer. $p$ sets a length scale, above which the properties of the polymer are governed by configurational entropy. Below this length, the polymer appears to be a rigid rod. The unfolding events occur independently of each other, and are said to be described by a Poisson process. The time between individual events is stochastic and may be found by drawing a random number from the appropriate probability distribution. This is equivalent to numerically solving

$$\int_t^{t+\Delta t} N_f \omega(t) dt = -\log u$$

(3.3)
Table 3.1: Polymer parameters used in KMC model derived for titin (from Rief et al., 1997a).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T$</td>
<td>298° K</td>
</tr>
<tr>
<td>$\alpha_u$</td>
<td>$3 \times 10^{-5}$ s$^{-1}$</td>
</tr>
<tr>
<td>$p$</td>
<td>0.4 nm</td>
</tr>
<tr>
<td>$\Delta x_u$</td>
<td>0.3 nm</td>
</tr>
<tr>
<td>Initial $n_f$</td>
<td>7</td>
</tr>
<tr>
<td>$L_0$</td>
<td>28 nm</td>
</tr>
<tr>
<td>$\Delta L$</td>
<td>28 nm</td>
</tr>
</tbody>
</table>

where $u \in (0,1]$ is a uniform variate and we have assumed that $N_f$ links may unfold. Since the rate depends on time, this is known as a non-homogeneous process. Likewise, by noting that $\langle -\log u \rangle = 1$, the average time between events $\overline{\Delta t}$ is given by:

$$
\int_t^{t+\Delta t} N_f \alpha_u \exp \left( \frac{\phi t \Delta x_u}{k_BT} \right) dt = -\log u
$$

By integrating Eq. 3.5, the time to the next unfolding event is:

$$
\Delta t = -t + \frac{k_BT}{\Delta x_u \phi} \log \left( e^{\phi t \Delta x_u/k_BT} - \frac{\Delta x_u \phi \log u}{k_BT N_f \alpha_u} \right)
$$

The first unfolding transition increases with loading rate, since the system has less time to unfold. The average load at which the polymer undergoes its first unfolding transition can be found by solving Eq. 3.4, yielding

$$
F_{\text{first,load}} = \frac{k_BT}{\Delta x_u \phi} \log \left( 1 + \frac{\Delta x_u \phi}{k_BT N_f \alpha_u} \right)
$$

Examining Eq. 3.7, the dependence on the loading rate is approximately linear for low rates, but is logarithmic for higher rates. This crossover in behavior occurs when $\phi x \approx k_BT N_f \alpha_u / \Delta x_u = 2.88$ fN/s. To study the displacement-controlled case, the end of the polymer chain is extended according to $x = vt$. The time between events is given by:

$$
\int_t^{t+\Delta t} N_f \alpha_u \exp \left[ \frac{\Delta x_u}{p} \left( \frac{1}{4} \left( 1 - \frac{vt}{L_c} \right)^{-2} - \frac{1}{4} + \frac{vt}{L_c} \right) \right] dt = -\log u
$$

For all numerical calculations, we use the constants given in Table 3.1, which were fitted by Rief et al. (1997a) for titin, a protein exhibiting a sawtooth load-displacement curve.

### 3.1.1 Response under increasing load

The load-displacement behavior of such polymers may be calculated for load-controlled and displacement-controlled situations. For the load-controlled situation, the applied load is increased linearly with time, $F = \phi t$. Finding the time until the next unfolding event $\Delta t$ requires the solution to the following integral:

$$
\int_t^{t+\Delta t} N_f \alpha_u \exp \left( \frac{\phi t \Delta x_u}{k_BT} \right) dt = -\log u
$$

By integrating Eq. 3.5, the time to the next unfolding event is:

$$
\Delta t = -t + \frac{k_BT}{\Delta x_u \phi} \log \left( e^{\phi t \Delta x_u/k_BT} - \frac{\Delta x_u \phi \log u}{k_BT N_f \alpha_u} \right)
$$

The first unfolding transition increases with loading rate, since the system has less time to unfold. The average load at which the polymer undergoes its first unfolding transition can be found by solving Eq. 3.4, yielding

$$
F_{\text{first,load}} = \frac{k_BT}{\Delta x_u \phi} \log \left( 1 + \frac{\Delta x_u \phi}{k_BT N_f \alpha_u} \right)
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Examining Eq. 3.7, the dependence on the loading rate is approximately linear for low rates, but is logarithmic for higher rates. This crossover in behavior occurs when $\phi x \approx k_BT N_f \alpha_u / \Delta x_u = 2.88$ fN/s. To study the displacement-controlled case, the end of the polymer chain is extended according to $x = vt$. The time between events is given by:

$$
\int_t^{t+\Delta t} N_f \alpha_u \exp \left[ \frac{\Delta x_u}{p} \left( \frac{1}{4} \left( 1 - \frac{vt}{L_c} \right)^{-2} - \frac{1}{4} + \frac{vt}{L_c} \right) \right] dt = -\log u
$$
The nonlinearity of the entropic force, Eq. 3.2, complicates the solution of Eq. 3.8. Using a bisection method, the average load at first unfolding may be calculated numerically, as shown in Fig. 3.3. The displacement-controlled process exhibits crossover behavior similar to the load-controlled case. Although the irreversible limit is studied here, the transition is expected to exist even if the reverse reaction is allowed. The refolding kinetics will, however, change the nature of the slow velocity state and position of the crossover point.

One possible simplification is to assume that the unfolding event will occur at a small displacement compared to the contour length of the polymer. In this case, $x \ll L_c$, and the polymer will act as a Hookean spring. Eq. 3.2 may be linearized to the form $F_{wlc} = 3k_BT_\Delta x / 2pL_c$ and Eq. 3.8 may be used to calculate the average force for the first unfolding event:

$$F_{\text{first,disp}} = \frac{k_BT}{\Delta x_u} \log \left( 1 + \frac{3v}{2N_f\alpha_uP} \right)$$

(3.9)

which will have a crossover point at $v_x \approx 2N_f\alpha_uP/L_c/3\Delta x_u$, about 5.25pm/s. This is a very small velocity, even relative to the typical strain rates in single-molecule tests. For instance, the pulling rates used in the experiments of Rief et al. (1997b) ranged between 10-500 nm/s.

For large velocities, the force at first unfolding may be written as:

$$F_{\text{first,disp}} = \frac{k_BT}{\Delta x_u} \left[ \log v + \log \left( \frac{3\Delta x_u}{2N_f\alpha_uP} \right) \right]$$

(3.10)

The time dependent response of nacre under compression was examined by Menig et al. (2000). The average strength was found to increase with increasing loading rate. This is qualitatively consistent with this model. The present analysis also suggests that the strength, as well as the stiffness, will increase under an increase in temperature.

### 3.1.2 Energy dispersion

By solving Eq. 3.6 and Eq. 3.8 numerically for $\Delta t$ using bisection, the location of unfolding events on the load-displacement curve for particular realizations may be calculated numeri-
Figure 3.4: Typical load-displacement curves under load-controlled conditions. The loading rates used were $\phi = 1 \, \text{pN/s}$ for the solid curve, and $\phi = 10^{-3} \, \text{pN/s}$ for the dashed curve.

Figure 3.5: Typical load-displacement curves for isolated chain under displacement-controlled loading. Two simulations on either side of the transition are shown here. The dashed line corresponds to a simulation performed with $v = 10^{-2} \, \text{nm/s}$, while the solid line corresponds to a simulation with $v = 10^3 \, \text{nm/s}$.
The random variates \( u \) were generated using the Mersenne Twister algorithm (Matsumoto and Nishimura, 1998). The intermediate points are interpolated using Eq. 3.2. Typical load-displacement curves are shown in Fig. 3.4 and Fig. 3.5. For displacement-controlled loading, the work done during loading and unloading is compared for the deformation of a single polymer up to a maximum extension of \( x_{\text{max}} = 140 \) nm. The work done during loading \( W \) may be defined as the area under the load-displacement curve.

\[
W = \int_0^{x_{\text{max}}} Fdx
\]  

(3.11)

The work dissipated during the unfolding events, \( \Delta W = W - W_{\text{unloading}} \), is another important quantity. The fractional work lost is calculated as \( \Delta W/W \). As shown in Fig. 3.6, this quantity is quite significant in the case of polymer, reaching 70% at high strain rates. Similarly to the unfolding transition, there is an apparent logarithmic dependence on the loading rate. The energy dispersed drops significantly for velocities smaller than \( v_t \). This may be compared to the concept of internal friction, as studied in dislocation plasticity. The response of a crystal to a periodic applied stress can be calculated, considering that the crystal contained a network of dislocations. By considering dislocations to act like damped, vibrating springs, the relative loss per cycle, \( \Delta W/W \), may be calculated as a function of the forcing frequency (Granato and Lücke, 1956). The maximum relative loss per cycle is about one, on the order of the energy dispersed by the polymer bundle.

### 3.1.3 Discussion

The current study suggests the importance of experimentally determining thermodynamic and kinetic data for the relevant biomolecules in structural biomaterials. In the literature, these parameters have been fit to numerical simulations of Eq. 3.1 using a fixed time-step Monte Carlo scheme (FTSMC) (Rief et al., 1997a,b; Qi et al., 2006). In this technique, using Eq. 3.1, the probability \( P_u(t)dt \) for observing an unfolding event in some finite time \( dt \) is calculated. The simulation
proceeds by choosing random numbers to determine if an unfolding event occurs in a particular time step $dt$. The load-displacement curves from this method may be compared to experiments to extract the relevant phenomenological parameters, $\Delta x_u$ and $\alpha_u$. This is a somewhat clumsy procedure.

The present analysis may be used to extract kinetic data from such experiments without requiring a fit to such FTSMC simulations. By rearranging Eq. 3.8, it is possible to derive an expression for the loading rate $v$ as a function of the average displacement at first unfolding, $x_0$.

$$v = \int_0^{x_0} N_f \alpha_u \exp \left[ \frac{\Delta x_u}{p} \left( \frac{1 - \frac{x}{L_c}}{\frac{L_c}{4}} - \frac{1}{4} \right) \right] dx$$  \hspace{1cm} (3.12)

By performing a nonlinear fit of experimental data to Eq. 3.12, the kinetic parameters $\Delta x_u$ and $\alpha_u$ may be determined. Using the published data points in Rief et al. (1997b) yields $\Delta x_u = 0.3$ nm and $\alpha_u = 1 \times 10^{-5}$ s$^{-1}$, in fair agreement with the fits to FTSMC in the literature. The treatment of arrays of polymers is more difficult: this is the subject of the two remaining sections in this chapter.

### 3.2 The kinetic Monte Carlo method

In order to analyze statistical problems using computer simulations, a variety of techniques using random sampling have been developed. These algorithms are generically known as Monte Carlo methods (Metropolis and Ulam, 1949). They have been adapted to study many classical problems in materials science. An important subset of these algorithms simulates dynamic phenomena, using Poisson statistics (Fichthorn and Weinberg, 1991). This approach has come to be known as kinetic Monte Carlo (KMC). If the system may be modeled as existing in one of many discrete states, the rate at which the system transforms from one state to another may be calculated using transition-state theory.

There are several algorithms that are consistent with Poisson statistics, including the previously mentioned FTSMC method. However, each of these algorithms has limitations. For instance, one of the computational difficulties with FTSMC is that the algorithm requires that at most one event will occur during a single time step. An accurate simulation would require a very small value of the time step.

Another technique that allows for the size of the time step to vary is to calculate tentative reaction times for all possible reactions, then choose the identity of the reaction based on the shortest reaction time. This technique was developed by Gillespie (1976) and is known as the first-reaction method or Gillespie algorithm. The suitability of an algorithm to model a particular problem depends on the computational expense of calculating the transition rates. In this case, the first-reaction method is not efficient; under an increasing load, all reaction times must be recalculated at every time step. Instead, the algorithm of Jansen (1995) was chosen to model the extension of ensembles of polymers with sacrificial bonds.

The reasoning behind this KMC algorithm may be illustrated by considering a generic system, originally in some state $\alpha$. The probability at which the system leaves the state $\alpha$ and enters a state $\beta$ between $t$ and $t + dt$ is defined to be $\omega_{\beta \alpha}(t) dt$. The probability that the system will leave the state $\alpha$ and enter any state is defined to be the cumulative transition probability, $S_{\alpha}(t) dt = \sum_{\beta} \omega_{\beta \alpha}(t) dt$, where the sum is over all states accessible from $\alpha$.  

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Taking discrete time steps \( \delta \) such that \( t = n \delta \), the probability with which the system leaves the state \( \alpha \) and enters the state \( \beta \) at time step \( n \) is:

\[
\omega_{\beta \alpha}^n = \delta \omega_{\beta \alpha}(n\delta)
\]  

(3.13)

Similarly, the discrete cumulative transition probability is set as \( S_{\alpha}^N = \delta S_{\alpha}(n\delta) \). The probability \( R_{\alpha}^N \) that the reaction will occur at the \( N \)th time step is given by the product of the probability that the system will transition at time step \( N \) with the probability that it did not in the previous \( N-1 \) time steps.

\[
R_{\alpha}^N = S_{\alpha}^N \prod_{i=1}^{N-1} (1 - S_{\alpha}^i) = \delta S_{\alpha}(N \delta) \prod_{i=1}^{N-1} (1 - \delta S_{\alpha}(i \delta))
\]  

(3.14)

In the limit that \( \delta \to 0 \), \( R_{\alpha}^N \) may be written as

\[
R_{\alpha}^N = \delta S_{\alpha}(N \delta) \prod_{i=1}^{N-1} \exp(-\delta S_{\alpha}(i \delta))
\]  

\[
= \delta S_{\alpha}(N \delta) \exp\left(-\sum_{i=1}^{N-1} \delta S_{\alpha}(i \delta)\right)
\]  

(3.15)

(3.16)

For large values of \( N \), the summation in Eq. 3.16 may be rewritten as a continuous integral. In this limit, the probability that the transition will occur between the time \( t_0 = (N-1)\delta \) and \( N\delta \) is \( R_{\alpha}(t_0) = R_{\alpha}^N \), such that

\[
R_{\alpha}(t_0) = S_{\alpha}(t_0) \exp\left(-\int_{t_0}^{t_0} S_{\alpha}(t)dt\right)
\]  

(3.17)

where the continuous version of the summation has been taken. In order to generate a time consistent with staying in this state, it is necessary to find \( P_{\alpha}(t) \), the probability that the transition has not occurred at a time \( t \):

\[
P_{\alpha}(t) = 1 - \int_{t_0}^{t} dt' R_{\alpha}(t') = 1 - \exp\left(-\int_{t_0}^{t} S_{\alpha}(t')dt'\right)|_{t_0=0}
\]  

(3.18)

By combining Eq. 3.17 and Eq. 3.18, the simple relationship \( R_{\alpha}(t) = S_{\alpha}(t)P_{\alpha}(t) \) is seen to hold. It is interesting to note that \( P_{\alpha}(t) \) satisfies a differential law similar to exponential decay, where the rate at which the probability of remaining in that state decays proportionally to the probability of being in the state \( \alpha \).

\[
\frac{dP_{\alpha}(t)}{dt} = S_{\alpha}(t)P_{\alpha}(t)
\]  

(3.19)

A random time consistent with staying in the state \( \alpha \) may be found by choosing a uniform variate \( u \in (0, 1] \), then solving

\[
P_{\alpha}(t) = u
\]  

(3.20)

Now that the time until the next reaction is known, it is possible to choose the next reaction consistent with the time-dependent reaction rates. Consider the probability that a particular reaction \( \alpha \to \beta \) occurs. Using similar arguments, the probability density \( R_{\beta \alpha}(t) \) that the \( \alpha \to \beta \) reaction occurs between time \( t \) and \( t + dt \) is:

\[
R_{\beta \alpha}(t)dt = \omega_{\beta \alpha}(t)P_{\beta \alpha}(t)dt
\]  

(3.21)
The probability $P_{\beta \alpha}(t)dt$ that the $\alpha \rightarrow \beta$ reaction has not occurred before time $t$ is:

$$P_{\beta \alpha}(t) = \exp \left( - \int_0^t S_{\beta \alpha}(t')dt' \right)$$

(3.22)

The probability that the reaction to a particular state $\beta$ occurs is the first to occur between time $t$ and $t + dt$ may be written as a product of two probabilities: the probability that a $\alpha \rightarrow \beta$ reaction occurs between time $t$ and $t + dt$, multiplied by the probability that no other reaction has occurred before this time. This may be written as:

$$\tilde{R}_{\beta \alpha}(t)dt = \left[ R_{\beta \alpha}(t) \right] \left[ \prod_{\gamma \neq \alpha, \beta} P_{\gamma \alpha}(t) \right] dt$$

(3.23)

Combining Eqs. 3.21 and 3.23 shows that the probability that a particular reaction will occur first is proportional to the rate of the reaction:

$$\tilde{R}_{\beta \alpha}(t)dt = \omega_{\beta \alpha}(t) \left[ \prod_{\gamma \neq \alpha} P_{\gamma \alpha}(t) \right] dt$$

(3.24)

So, to develop a KMC algorithm consistent with Poisson statistics, it is necessary to choose the time until the next reaction to be consistent with Eq. 3.20, and the identity of the next reaction according to Eq. 3.24. The steps in the present KMC algorithm are:

1. Generate a random variate $u \in (0, 1]$
2. Determine the time until the next event based on solving the equation $u = P_{\alpha}(t_{next})$
3. Generate a list of cumulative reaction rates $S_{\beta \alpha}(t_{next}) = \sum_{\gamma=1}^\beta \omega_{\gamma \alpha}(t_{next})$
4. Generate a random variate $u' \in (0, 1]$
5. Choose which reaction occurs by finding the $\beta$ that satisfies $S_{\beta-1, \alpha}(t_{next}) < u'S_{\alpha}(t_{next}) \leq S_{\beta \alpha}(t_{next})$

### 3.3 Nonlinear fiber-bundle model

A simple way to study the many-chain model is to treat the load sharing according to a mean-field approximation, and to ignore interactions between the polymers. Although this model does not incorporate spatial correlations, it is still possible to model the effects of the nonlinear elastic constant on the macroscopic behavior. The dynamic behavior of this model is treated using the KMC method developed in 3.2.

#### 3.3.1 Implementation of KMC algorithm

It is possible to incorporate structural randomness into the simulation in several ways. The current study takes the initial contour lengths of the polymers to be random. The initial contour length of the $i$th chain is drawn from a uniform distribution $L_i = [0, L_0]$. The rate at which the
Figure 3.7: Schematic diagram of fiber bundle model. The circles on the chain represent modules that may unfold discretely. The polymer may be strained under load-controlled (specified $F$) or displacement-controlled (specified $x$) conditions.

The $i$th chain has an unfolding event is given by $N_i \omega_i(F_i)$, where $N_i$ is the number of folded domains on the $i$th polymer and $F_i$ is the applied force on that polymer. Under displacement controlled conditions, $x(t) = vt$. The unfolding rate for the $i$th chain may be calculated similarly to Eq. 3.1

$$\omega_{u,i}(t) = \alpha_u \exp \left( \frac{F_{wle}(x(t), L_i) \Delta x_u}{k_B T} \right)$$  \hspace{1cm} (3.25)

In the present formulation of KMC, it is more convenient to calculate the next displacement for an event, rather than time. Combining with Eq. 3.18, the next event may be found by numerically solving:

$$u = P_u(x_{next}) = \exp \left( - \int_0^{x_{next}/v} \sum_i \omega_{u,i}(t') dt' \right)$$  \hspace{1cm} (3.26)

Eq. 3.26 may be solved using bisection. The extension until the next event is bounded, as $0 < x_{next} < \min(L_i)$. Some care must be taken while implementing this step in a numerical simulation. In particular, the integral on the right-hand side can be very large, exceeding the limits of double precision variables. This is because the force diverges as the displacement approaches the contour length of the polymer. In order to avoid this problem, a multiple precision arithmetic library may be used. For load-controlled conditions, the total external force increases at a fixed rate.

$$F_{ext} = \phi t = \sum_i F_{wle}(x, L)$$  \hspace{1cm} (3.27)

To find the next event time, is possible to simultaneously solve Eq. 3.26 and Eq. 3.27 numerically. In order to further simplify the numerical algorithm, an additional simplification may be made. First,

$$\frac{dt}{dx} = \phi^{-1} \sum_i \frac{dF_{wle}(x)}{dx} = \frac{k_B T}{p \phi} \sum_i \left( \frac{1}{L_i} + \frac{L_i^2}{2(L_i - x)} \right)$$  \hspace{1cm} (3.28)

So, for a load-controlled experiment, the next event may be chosen as:

$$u = \exp \left( - \int_0^{x_{next}} \sum_i N_{u,i} \alpha_u \exp \left( \frac{F_{wle}(x, L_i) \Delta x_u}{k_B T} \right) \frac{dt}{dx} dx \right)$$  \hspace{1cm} (3.29)
Eq. 3.29 may again be solved using bisection, noting that $0 < x_{\text{next}} < \min(L_i)$. Choosing the unfolding event is the same for both cases. The cumulative rate list is generated as:

$$
S_{\beta\alpha}(x_{\text{next}}) = \sum_i \beta N_{u,i} \alpha_u \exp \left( \frac{F_{\text{wlc}}(x, L_i) \Delta x_u}{k_B T} \right) \tag{3.30}
$$

Performing an unfolding event extends the contour length of the chain $\beta$, $L_\beta \rightarrow L_\beta + \Delta L$. When the last domain has unfolded, there are multiple possible behaviors. If the polymers are taken to be unbreakable, they remain in the simulation and provide a remnant elastic response. Another possibility is that the polymer will fail according to an unfolding rate law similar to Eq. 3.1.

The KMC algorithm may be summarized as follows:

1. Initialize initial lengths $L_i \in (0, L_{\text{max}}]$

2. Generate a random variate $u \in (0, 1]$

3. Determine the time until the next event by solving either Eq. 3.26 (displacement controlled behavior) or Eq. 3.29 (load controlled behavior).

4. Generate a list of cumulative rates $S_{\beta\alpha}(t_{\text{next}}) = \sum_i \omega_i(t_{\text{next}})$

5. Generate a random variate $u' \in (0, 1]$

6. Choose which reaction occurs by finding the $\beta$ that satisfies $S_{\beta-1,\alpha}(x_{\text{next}}) < u'S_{\alpha}(x_{\text{next}}) \leq S_{\beta\alpha}(x_{\text{next}})$

7. If unfolded domains remain, return to Step 2.

The instantaneous elastic constant at the extension $x_f$ is given by the derivative of the force constant:

$$
k_{\text{eff}}(x_f) = \frac{dF}{dx} \bigg|_{x=x_f} = \sum_i \frac{k_B T}{p} \left[ \frac{1}{2L_i} \left( 1 - \frac{x}{L_i} \right)^{-3} + \frac{1}{L_i} \right] \tag{3.31}
$$

### 3.3.2 Infinitely strong polymers

In the limit that the polymers do not break, plastic deformation may only occur through the unfolding of the discrete domains. To this end, simulations were performed with FBM of $10^3$ chains, each with $n_f = 7$. The initial lengths were taken from a uniform distribution between $L_c = [0, L_0]$ nm. Although it may be more realistic to use a Gaussian or Weibull distribution, the uniform distribution was chosen since it contains only one parameter. Typical stress-strain data for the displacement-controlled case is shown in 3.8. There is a very strong rate dependence. For higher loading rates, the rate of hardening increases. By performing numerical experiments, some trends may be extracted from the dynamic FBM. The spring constant tends to decrease during the extension. By performing a best fit between the displacement of the first unfolding event and 140 nm, the hardening rate may be estimated as a function of loading rate. By averaging the results of 100 trials at each velocity, a nearly logarithmic relationship for the slope of the hardening region $m_{h,d}$ may be found,

$$
m_{h,d}[\mu N/m] = 0.29 + 0.031 \ln(v[\text{nm/s}]) \tag{3.32}
$$
Figure 3.8: Typical results of displacement-controlled KMC simulations of FBM. Panel 3.8a depicts the load-displacement behavior for different values of the pulling velocity, $v$. The corresponding effective spring constants are shown in Panel 3.8b. In these simulations, $N = 1000$. 
Figure 3.9:  Slope of the hardening region for various values of loading rate for displacement-controlled deformation (Panel 3.9a) and load-controlled deformation (Panel 3.9b). Data points are the average of 100 trials, with $N = 100$. The error bars are one standard deviation.
The results of the numerical simulation are shown in Fig. 3.9. The error bars on this plot are calculated by taking the standard deviation of the slopes for the 100 trials.

The load-controlled simulations are performed at controlled values of $\phi/N^0_{\text{chains}}$. Qualitatively, the load-displacement behavior is quite similar, as seen in Fig. 3.10. For smaller values of the loading rate, the amount of softening is also smaller. Similarly to the displacement-controlled simulations, the average slope of the hardening may also be calculated as a function of $\phi/N^0_{\text{chains}}$. The smoothness of the deformation, however, is strongly related to the deformation rates. For faster deformations, the load-displacement curve becomes increasingly jerky. Again, a logarithmic dependence of the hardening may be found:

$$m_{h,l}[\mu N/m] = 0.36 + 0.026 \ln(\phi/N^0_{\text{chains}}[\mu N/s])$$  \hspace{1cm} (3.33)

3.3.3 Polymer failure

An alternate physical situation may be considered in which the polymers are allowed to fail as well as break sacrificial bonds. In the case that the polymer fails, it is necessary to define kinetic parameters for the failure event. There have not been experimental measurements of these parameters, so in these simulations, the polymer is assumed to fail immediately after the final domain unfolds.

Taking the initial number of chains to be $N^0_{\text{chains}}$, the load-controlled simulations are performed at controlled values of $\phi/N^0_{\text{chains}}$. Qualitatively, the load-displacement behavior is quite similar, as seen in Fig. 3.9. For sufficiently small values of the loading rate, the bundle does not appreciably soften. Similarly to the displacement-controlled simulations, the average slope of the hardening may also be calculated as a function of $\phi/N^0_{\text{chains}}$. The smoothness of the deformation, however, is strongly related to the deformation rates.

Representative load-displacement curves are plotted in Fig. 3.11. These curves are very similar to those generated for infinitely strong polymers. The more striking consequences of polymer failure come from considering the strengths of the polymer bundles. The strengths are not uniform, but instead follow a distribution that depends on the rate at which the bundle is deformed. To this end, bundles of 50 polymers were stressed until failure. Each polymer was taken to have 10 domains. $10^3$ trials were performed to find the distribution of strengths. The results are plotted in Fig. 3.12.

Under load-controlled conditions, the stress on each polymer will increase as plastic events occur. This will increase the stress on each polymer, causing correlations between plastic events. By analogy with dislocation plasticity, the size distributions of plastic events may be analyzed using a scaling function analysis.

3.3.4 Distribution of plastic events

The distributions of time between plastic events were found to follow a power law, as shown in Fig. 3.13. Based on this observation, a scaling hypothesis may be made for $n(a,t)da.dt$, the number of plastic events where the extension to the next event falls between $a$ and $a + da$ and the time to the next event falls between $t$ and $t + dt$. The ansatz is

$$\lambda n(a,t) = n(\lambda^\alpha a, \lambda^\nu t)$$ \hspace{1cm} (3.34)
Figure 3.10: Typical results of load-controlled KMC simulations of FBM. Panel 3.10a depicts the load-displacement behavior for different values of the normalized pulling rate, $\phi/N_{chains}$. The corresponding effective spring constants are shown in Panel 3.10b.
Figure 3.11: Typical results of load-controlled bundles that are allowed to progress to failure. After the last unfolding event occurs, the polymer is removed from the simulation.

Figure 3.12: Distributions of failure strengths of fiber bundle models, allowing for polymer failure. These failure strengths are normalized by the average failure strength for that velocity, $\langle \sigma \rangle$. 
where \( \lambda \) is an arbitrary constant, and \( \alpha \) and \( \zeta \) are the critical exponents of this transition. In particular, by taking \( \lambda = t^{-1/\zeta} \), it may be shown that

\[
t^{-1/\zeta}n(a,t) = n(t^{-\alpha/\zeta}a,1)
\]  

(3.35)

This expression is a function only of \( t^{-\alpha/\zeta}a \). In other words, all data should collapse onto the same curve, if plotted in terms of this parameter. Since Eq. 3.34 is chosen such that it reflects scaling-law behavior in the time between plastic events and the size of the jump, it is possible to calculate functions \( \tilde{n}(a) \) and \( \tilde{n}(l) \) from this analysis:

\[
\tilde{n}(l) = \int_0^\infty \lambda n(l,a)da
\]  

(3.36)

\[
\tilde{n}(a) = \int_0^\infty \lambda n(l,a)dl
\]  

(3.37)

The functions \( \tilde{n}(a) \) and \( \tilde{n}(l) \) are power laws. It is possible to demonstrate this by using the scaling ansatz, then explicitly performing the integration. 

\[
\tilde{n}(l) = \lambda^{-1} \int_0^\infty n(\lambda^\alpha l, \lambda^\zeta a)da
\]  

(3.38)

Choosing \( \lambda = l^{1/\alpha} \):

\[
\tilde{n}(l) = l^{1/\alpha} \int_0^\infty n(1, l^{-\zeta/\alpha}a)da
\]  

(3.39)

By performing the substitution \( x = l^{-\zeta/\alpha}a, dx = l^{-\zeta/\alpha}da \), a power law is found:

\[
\tilde{n}(l) = l^{(1+\zeta)/\alpha} \int_0^\infty n(1,x)dx
\]  

(3.40)

with \( x = l^{-\zeta/\alpha}a \) and \( dx = l^{-\zeta/\alpha}da \). The other exponent may be calculated similarly:

\[
\tilde{n}(a) = a^{(1+\alpha)/\zeta} \int_0^\infty n(y,1)dy
\]  

(3.41)
Figure 3.14: Scaling form of plastic size events of a nonlinear fiber bundle. These events are characterized by $t$, the time to the next failure event and $x$, the displacement associated with that event. The color key denotes the value of $x$ in nm corresponding to the event. This plot was performed using the values $\alpha = 0.35$ and $\zeta = 0.35$.

The scaling ansatz proposed is therefore consistent with the scaling laws observed in the simulation. Typically, these exponents are found by fitting the curve by hand. In the spirit of Bhattacharjee and Seno (2001), a measure of the quality of fit can be introduced. Since the analytical scaling law is not known, it is not possible to calculate the quality of the fit using a typical least-squares approach. The following measure is introduced:

$$P_b = \frac{1}{N_{over}} \sum_j |\mathcal{E} \left( n(t_j^{-\alpha/\zeta}a_j, 1) \right) - t_j^{-1/\zeta}n(a_j, t_j) |$$

where $\mathcal{E}$ is a spline function that interpolates a continuous distribution, given a set of $a_j$ and $t_j$, and $N_{over}$ is the total number of pairs. By minimizing $P_b$ with respect to $\alpha$ and $\delta$, the exponents may be fit. $n(a, t)$ was approximated by performing 100 simulations, and binning each plastic event according to the corresponding values of $a$ and $t$. As seen in Fig. 3.14, smaller events appear to show signs of collapse. The larger events appear more distributed, and do not.

3.3.5 Discussion

The method developed in this section is only a first step to understanding the overall mechanical properties of the composite. The results of the current analysis cannot be directly applied to actual materials, since real polymers are linked in a complicated network structure. During plastic deformation, unfolding events will occur on many different chains. Because an unfolding event locally changes the elastic modulus of the network, the mean-field approximation is broken. This is important because related models going beyond the mean-field approximation (the RFM and the local-load sharing FBM) may exhibit non-trivial size dependence. In these models, weak regions may arise that concentrate stress. Because different scaling laws apply to these two different situations, it is possible that the mean-field model considered here will not yield the same physical laws as real systems.
The effect of the connectivity on the elastic response of network structures has been modeled using techniques such as the eight-chain model (Arruda and Boyce, 1993). In this way, the response from the WLC model may be related to a nonlinear elastic model (Ogden et al., 2006), such as the Gent equation (Gent, 1996) or the Mooney-Rivlin model (Mooney, 1940; Rivlin, 1948). In principle, the KMC algorithm presented here may be similarly modified to take spatial variation into account. This is more difficult than the mean-field problem addressed in this section. As an example, consider a cubic array of $N_c \times N_c \times N_c$ nodes, connected by polymer chains. Connect the chains along the cube diagonals. The system is put under a uniform strain state, and the nodes are allowed to move around until no forces act on them. Consider each polymer chain to have some number of folded states, unfolding with a rate determined by Eq. 3.25. In order to calculate $P_\alpha$, it is necessary to solve $3 \times N_c^3$ nonlinear equations at every integration step. This causes the calculation of the cumulative rates to become computationally expensive. Although this calculation is feasible, it also motivates a desire to study models with simplified dynamics, as described in the next chapter.
Chapter 4

Quasi-static models of fracture

Errors, like straws, upon the surface flow; he who would search for pearls must dive below.

– John Dryden

As shown in Chapter 3, heterogeneous microscopic properties affect the dynamics of the failure process. However, the KMC model was not easily extended beyond the mean-field approximation. Although they may be generalized to higher dimensions, it is computationally expensive to do so. As a result, effects such as crack trapping or crack deflection cannot be understood with such a model. To this end, a set of quasistatic models were developed that could study both size effects and spatial correlations in failure. These models incorporate Hookean springs and assume adiabatic, critically damped dynamics.

4.1 Random-fuse models of nacre

The mechanical properties of materials such as nacre may be treated with quasistatic theories of composites. Nacre’s brick and mortar structure is inherently discrete, and so should be modeled according to a discrete model. The properties of nacre are spatially inhomogeneous: for instance, platelets have a distribution of sizes and thicknesses. Such a model should also exhibit hysteresis: like the dynamic FBM, it should be able to accumulate damage due to plastic deformation.

The random-fuse model is said to be quasi-brittle: it incorporates some toughening mechanisms due to distributed damage. However, it does not include other toughening mechanisms that have been proven to be important in natural composites, such as bridging (Koester et al., 2008). In the spirit of the continuous damage random-fuse model (CDRFM) studied by Zapperi et al. (1997), a quasistatic model is introduced to study the contributions to toughening from the organic adhesive. Before considering the properties of failure in this model, it is first necessary to show connections between the microscopic properties of nacre and the lattice model.

4.1.1 Equivalence between spring lattice and shear-lag model

Consider the limit where the blocks are unbreakable but are allowed to move relative to each other. If the blocks are also infinitely stiff, only their relative position is important, and they may
Shear springs (modulus $G_p$)
Mineral platelet (infinite modulus)

Figure 4.1: Schematic of 2-d lattice model of nacre. The tablets are of length $L$ and thickness $t$. The thickness of the organic adhesive is $w$.

be treated as points. The force on each point corresponds to the force on the block. Practically, this corresponds to a random fuse model on a tilted square array. Let’s compare this with the elastic modulus of a spring array. Let the platelets have depth $d$, thickness $t$ and length $L$. The platelets overlap by some length $\eta L$, as illustrated in Fig. 4.1. The springs are taken to have a spring constant $k$ and a width $w$. Consider deforming the spring array under a uniform shear strain of $\Delta x/w$. The definition of the shear modulus is the shear stress divided by the shear strain,

$$G_p = \frac{k\Delta x/(\eta L d)}{\Delta x/w} = \frac{kw}{\eta L d}$$

which defines the shear modulus of the composite $G_p$ in terms of the spring constant $k$. It is similarly possible to calculate the external stress $\sigma$ needed to deform the array based on the force balance on a single block in tension:

$$\sigma = \frac{F}{d(w+t)} = \frac{k\Delta x}{d(w+t)}$$

Substituting the expression for the elastic modulus of the composite, Eq. 4.1,

$$\sigma = \frac{G_p\eta L^2}{w(w+t)} \epsilon = \frac{G_p \Phi \rho^2 \eta}{1 - \Phi} \epsilon$$

where we have further noted that in our model the volume fraction of mineral is $\Phi = t/(w+t)$ and the blocks have an aspect ratio $\rho = L/t$. So, the shear-lag model of Gao (2006) in the limit of infinite mineral stiffness has the same elastic properties as a spring block model with $\eta = 1/2$.

### 4.1.2 Diluted RFM

Prior studies have calculated the toughness of the RFM under strong disorder as a function of both crack size and system size (Alava et al., 2008). It was found that there is a crossover in the fracture behavior for sufficiently large systems. Large systems fail according to scaling laws consistent with fracture mechanics: the strength of a system with a flaw depends on the size of that
flaw. Small systems, however, are “notch-tolerant,” and are independent of the size of the flaw. In other words, there is a transition observed in the toughness of RFMs depending on the crack size.

This may be understood similarly to the Gao criterion, discussed in Sec. 2.1.2. Under a certain critical size, the inhomogeneities already present in the material will weaken the material. Under this size, the material is notch-intolerant, and the strength of the sample will be determined by the random nature of the material. One simple way to incorporate disorder into an RFM is to constrain all springs to share the same fracture strength and modulus, but consider that only a fraction $p$ of the bonds are initially occupied. In the limit that $p$ is close to 1, this is known as the diluted RFM, since there is only a small number of initially empty bonds.

The strength of the diluted model was calculated by Duxbury et al. (1987). They claimed that, similarly to cracks in brittle materials, the strength of the RFM is determined by the size of a critical flaw. This defect must contain a critical number of broken bonds, $n_c$. For a $\sqrt{N} \times \sqrt{N}$ square lattice, this was found to be

$$n_c \approx \frac{\ln N}{\ln(1 - p)}$$

(4.4)

This criterion has consequences for materials that may be described by shear-lag theory. Considering bricks with length $L$, and a total system size of $L_{sys} = L\sqrt{N}$, it is possible to calculate the size of a critical defect relative to the length of the block.

$$\frac{a_c}{L} \approx \frac{2\ln L - \ln(L_{sys})}{\ln(1 - p)}$$

(4.5)

According to (Gao et al., 2003), the criterion for notch tolerance is set when the fracture strength of a half-cracked sample is equal to the intrinsic strength of the material. This sets the maximum system size $L_{nt}$ for which the sample is notch-tolerant. The strength of a half-cracked sample may be calculated by setting $a_c/L_{sys} = 1/2$,

$$\frac{1}{2} \approx \frac{L}{L_{nt}} \cdot \frac{2\ln L - \ln(L_{nt})}{\ln(1 - p)}$$

(4.6)

This may be rearranged into the form

$$p \approx 1 - \exp \left( -4 \frac{L}{L_{nt}} \ln \left( \frac{L_{nt}}{L} \right) \right)$$

(4.7)

Increasing the level of randomness increases the size of the cracks to which the material is notch insensitive. However, it also decreases the strength of the system. This simple calculation predicts that notch-tolerance is a property that is inherently dependent on the statistical distributions of the microscopic properties. This suggests the importance of understanding the effect of distributions on other toughening mechanisms in nacre. This is explored in the following sections.

4.1.3 Modified CDRFM

As described in Section 2.1.3, the CDRFM was initially developed as a way to model plastic deformation in heterogeneous materials. The elements are plastic in the sense that if one fails, it is replaced with another fuse with a different spring constant. However, this microscopic plastic law does not reflect the microscopic response of the organic adhesive.
Considering the results of the KMC model described in Chapter 3, a microscopic plasticity law should be chosen that replicates the load-controlled response of the polymer. This is necessary because the blocks relax to a position in which they experience no force, even if the external boundary condition is displacement controlled. Because the FBM exhibited hardening, the CDRFM may be modified to have a yield strength that increases after each failure event. This behavior is illustrated schematically in Fig. 4.2

Estimates of the parameters may be extracted from the dynamic FBM. Some approximations are made to simplify the lattice model. First, the elastic response is assumed to be linear. Second, damage is incorporated discretely: the spring constant is reduced by a constant factor at every failure event. In the continuum limit, this is equivalent to the spring constant decreasing exponentially.

More formally, the algorithm may be described as follows. The $i$th spring is characterized by an initial stiffness $k_i^0$ and an initial threshold $F_{th,i}^0$. The spring network is expanded at a fixed rate and the force on each spring is calculated to be $F_{s,i}$. The next spring to yield is selected by finding the minimum $F_{th,i} - F_{s,i}$. After the $n$th yield event, the stiffness is reduced to be $k_i(n) = a^n k_i^0$, and the failure threshold is increased to be $F_{th,i}(n) = F_{th,i}^0 + b$. For displacement-controlled loading conditions, the spring array will be subjected to a displacement $vt$, where $v$ is the externally imposed loading rate and $t$ is the simulation time. The time to the breakage event can then be calculated from the force required to rupture that spring: $F_{th,i}/vk_i$. If this value is smaller than the current simulation time, the spring breakage event is taken to be part of a larger plastic event including multiple springs. If this value is larger than the current simulation time, the displacement is increased to $F_{th,i}/k_i$ and the process repeats.

**Spatial extent of damage**

In order to understand how fracture processes are affected by the local microscopic laws, it is important to understand how damage spreads during deformation. In particular, it is important to understand under what conditions damage localizes into a well-defined crack. This is done by considering the deformation of $32 \times 32$ element lattices, using $F_{th} = 1$, $k = 1$ and $a = 0.9$. The amount of hardening was calculated for different values of $b$.

The progressive yielding of the springs may be visualized with a contour plot of the number of yield events experienced by the different springs. This is plotted for different, representative
simulation times in Fig. 4.3. Inspection of this plot reveals there are two types of steady state. Without hardening, the steady state is localized to a 1-d band, while with hardening, damage is spread out over the entire 2-d sample. Comparing the evolution of the microscopic plasticity laws, the hardening law tends to spread the damage compared to the model without hardening. In other words, the plastic instability can be suppressed by manipulating the hardening law.

Recalling the results of the dynamic FBM studied in Chapter 3, it was observed that an FBM stressed at higher loading rates will increase the hardening rate. If the springs in the lattice model follow this viscoplastic behavior, a higher loading rate will lead to more uniform damage across the material. To quantify this effect, some statistics of the deformation process may be taken. One measure of the localization is to see how many times a particular spring deforms. If the deformation is uniform throughout the sample, all springs will deform the same number of times. If the deformation is localized, only a few springs will fail many times.

This inspires the definition of the following measure: let $N_e$ be the number of single deformation events during some time-frame of interest. Let $n_{e;i}$ be the number of times that a deformation occurs on the $i$th spring. If there are $N$ total springs, the parameter $Z$ can be defined as follows:

$$Z = \frac{1}{N} \sum \frac{(n_{e;i} - \langle n_e \rangle)^2}{\langle n_e \rangle}^{1/2}$$

where $\langle n_e \rangle$ is the mean number of times that the springs have failed. The measure $Z$ is therefore the standard deviation of the number of failures of each spring, normalized by the mean number of times each spring has failed. In the case of uniform deformation, all springs will be damaged equally and $Z \rightarrow 0$. This measure will therefore be positive, where $Z = 0$ corresponds to uniform deformation. It is important to note that $Z = 0$ does not necessarily correspond to uncorrelated deformation events, but to a limit where all elements deform at once. In the case that one spring bears all of the damage, $Z \rightarrow \sqrt{N}$. As the damage is distributed over multiple springs, $Z < \sqrt{N}$ during these simulations.

The rate at which the system approaches the steady state is of particular interest. The evolution of the system as a function of simulation time is plotted in Fig. 4.4. Larger values of the hardening parameter $b$ increase the rate at which the system approaches the steady state. The case of $b = 0$ is special: it appears to asymptote to a non-zero value, corresponding to a localized crack.

The effects of localized deformation are also observed in the distribution of plastic events. In this model, spring deformation events can occur discretely: because of local variations in elastic modulus and spring failure strength, not all springs will be damaged at the same time. To quantify this effect, the distribution of plastic events has been calculated for different levels of the microscopic hardening rate. The simulation is allowed to undergo 2500 simulation steps. Data is extracted from the next 2500 steps, and averaged over 8 simulation runs. An apparently power-law distribution was measured for the number of springs involved in a particular plastic event. This is suggestive of a scale-free critical state. Very different behavior is expected for $b = 0$ from $b > 0$ because of the difference in the dimension of the steady-state. These avalanche distributions are plotted in Fig. 4.5.

**Effect of mineral bridges**

The previous sections discussed a model in which the interaction between platelets grows stronger during deformation. Alternative mechanisms have also been proposed that do not sat-
Figure 4.3: Time evolution of damage in fuse model. A contour plot of the number of times a particular spring has failed is plotted for a simulation applying a uniform tensile strain in the $x$ axis. Panel 4.3a illustrates a time sequence for damage with no microscopic hardening, where Panel 4.3b illustrates a time sequence with hardening. $A$ and $D$ represent the deformation in the elastic region, $B$ and $E$ represent the initial deformation of the array and $C$ and $F$ depict the deformation at longer times. Qualitatively, damage is localized to a small 2-d region in the first model, while it is spread over the entire sample in the second model.
Figure 4.4: The damage measure $Z$ is plotted as a function of simulation time for various levels of the hardening $b$. Larger values of the hardening spread deformation more uniformly through the system.

Figure 4.5: Distribution of plastic events during the deformation of a CDRFM with hardening. There is an apparent power law distribution for the CDRFM with no hardening.
isfy this criterion. Mineral bridges, for example, have been suggested to fail progressively and interact less strongly over the course of the deformation (Meyers et al., 2007).

In principle, if the shear load is borne by the mineral bridges, the behavior may also be described by a CDRFM with an appropriate microscopic plasticity law. The bridges are assumed to fail at the theoretical strength of the aragonite, \( \sigma_{th} \). The spring constant may be calculated from the definition of the shear modulus. The force required to break a bridge is proportional to the thickness of the bridge. The spring constant of a bridge may be directly calculated from the elastic modulus. If there are \( N_b \) bridges between the platelets, the yield force will be \( N_b F_0 \). A linear Hooke’s law can then be used to describe the elastic response of the bridge, so the spring constant is simply \( N_b k_0 \).

This case is not as interesting as the biopolymer picture considered in the previous sections. Mineral bridge networks will soften under deformation: after each failure, the yield strength of each element would be smaller, making it more likely to fail again. This will lead to similar behavior exhibited by the classical, quasi-brittle RFM.

4.2 Models of fiber pull-out

The lattice models described in Section 4.1 do not incorporate the effects of extrinsic toughening mechanisms, such as crack bridging or grain pull-out. However, because these mechanisms include interactions from many elements, it may still be thought of as a statistical process. In particular, for long cracks, nontrivial size effects are expected. In other words, the work of separation is not anticipated to scale linearly with the number of bridging elements engaged in a particular crack. In this spirit, a very simple quasi-static model of a fiber composite can be developed to understand how random property distributions affect pull-out in a single crack.

Traditional analyses of fiber pull-out has been performed under the key assumption that friction is a smooth process. In other words, the motion of the fibers are uniform. Further, the calculation is performed under displacement-controlled conditions, where the redistribution of load is considered to be unimportant.

However, this frictional interaction may be very complicated. For instance, in fiber composites, fibers have been observed to have a stick-slip interaction when being pulled out of the matrix. By comparing this behavior to that of earthquakes, a simple model can be generated that contains some features of fiber pull-out. In particular, an estimate of the bridging traction can be performed.

4.2.1 Smooth pull out processes

By considering the mechanism of frictional pull-out, it is possible to calculate the work needed to pull out a fiber of length \( L_0 \) under the assumption that the fibers move uniformly. In this type of simplistic analysis, the interactions between fibers are ignored. The fibers are treated as if they are connected by rigid elements, so all fibers experience identical forces during the entire pull-out process. If the interfacial shear stress is taken to be uniform over the entire sample, the force required to overcome friction is \( 2\pi r x \tau_i^* \), for a fiber of radius \( r \), an embedded length of \( x \), and frictional force \( \tau_i^* \):

\[
W = \int_0^{L_0} (2\pi r x \tau_i^*) dx = \pi r L_0^2 \tau_i^*
\]  

(4.9)
This is known as the Cottrell-Kelly pull-out work (Cottrell, 1964; Kelly and Tyson, 1965). Although more sophisticated micromechanical analyses have been performed that take into account the effects of different slip types for an isolated fiber, such analyses still assume that the fibers move uniformly (Tsai and Kim, 1996).

4.2.2 Stick-slip friction

Because only a finite number of bridges can be engaged at a particular time, it is likely that statistical effects will arise. In the case of biological materials such as bone, nacre and antler, the number of bridges can number into the thousands or higher, depending on the level of hierarchy involved. The bridging fibers are assumed to be parallel. The equation of motion of the \( i \)th fiber is given by

\[
m \ddot{X}_j = k_c (X_{j+1} - 2X_j + X_{j-1}) - k_p X_j - F_f (v + \dot{X}_j) \quad (4.10)
\]

where \( m \) is the mass of the fiber, and \( X_j \) is the displacement of the \( j \)th fiber. Each fiber is connected to its nearest neighbors with a spring \( k_c \), and to a plate with a spring \( k_p \). \( F_f (v) \) describes the velocity-dependent frictional force. In other words, this model for fiber pull-out may be mapped directly onto the BK model for earthquakes introduced in Eq. 2.13.

The algorithm used in this section is based off the Olami-Federer-Christensen (OFC) cellular automaton model (Olami et al., 1992). The OFC model considers a square array of blocks, where the initial displacements to be chosen randomly. This corresponds to randomly setting \( f_{ij} \), the initial force on the block at position \( i \) and \( j \). After the force on a block reaches a threshold force \( F_{th} \) picked from some distribution, it will slip and relax to a position with zero force. It redistributes the force to the nearest neighbors with indexes \( n, m \) according to the rule:

\[
f_{ij} \rightarrow 0 \quad (4.11)
\]

\[
f_{nm} \rightarrow f_{nm} + \alpha f_{ij} \quad (4.12)
\]

where \( \alpha \) is an elastic ratio defined as

\[
\alpha = \frac{k_c}{4k_c + k_p} \quad (4.13)
\]
The main parameters of interest are different from those considered during the study of earthquakes. In fact, the main engineering parameter is that of the average force necessary to move the entire block array. This may be simply calculated as $F_{\text{depinning}} = \sum f_{i,j}$; the rationale is that the sum of the forces on all the individual blocks is the total force on the surface. This may be plotted as a function of the elastic ratio $\alpha$. The system begins from a uniform random distribution, and is run $10^4$ simulation steps. $F_{\text{depinning}}$ is then averaged over the next $10^4$ steps. This is plotted in Fig. 4.7, and demonstrates that the pinning force decreases with $\alpha$. In other words, as the coupling spring $k_p$ increases in stiffness, the pinning force increases as well. It is important to notice that this model for elastic coupling is somewhat artificial: in elastic systems, it is unlikely that load will be redistributed only to nearest neighbors. However, some features of this model are robust to this detail. For instance, avalanche behavior will arise even if the elastic coupling between blocks is completely non-local (Ding and Lu, 1993).

4.3 Properties of single crystal aragonite

The connection between the mechanical properties of aragonite and the microstructure of nacre proposed by Gao et al. (2003) may be checked using ab initio techniques. Considering Eq. 2.8, an estimate for the size of the tablets depends on the elastic constant $E_m$, the theoretical strength $\sigma_{th}$, and the surface energy $\gamma$. In spite of the limited success ab initio methods has had predicting mechanical properties, it has been successfully been used to predict the anisotropic elastic constants as well as the ideal strength, the stress at which an infinite, defect-free crystal undergoes an elastic instability. The ideal strength is an upper limit for the theoretical strength, associated with a cleavage fracture. The ideal strength has been calculated using ab initio techniques for a wide range of materials, such as tungsten, molybdenum (Krenn et al., 2002), iron (Clatterbuck et al., 2002) and intermetallics (Li et al., 2004a).

Some properties of aragonite may be calculated using ab initio techniques. The mineral component of nacre is aragonite, an orthorhombic phase of Ca(CO$_3$), belonging to space group $Pmnc$. It
has a fairly complicated unit cell, with 10 atoms in the primitive cell. Using density functional theory (DFT) based electronic structure total energy techniques, the equilibrium crystal structure may be calculated computationally, using the Vienna Ab-initio Simulation Package (VASP) (Kresse and Furthmüller, 1996). Calculations were performed under the Local Density Approximation (Perdew and Zunger, 1981) using ultra-soft pseudopotentials (Vanderbilt, 1990; Kresse and Hafner, 1994).

The minimum energy configuration may be calculated by using the conjugate gradient algorithm to optimize the lattice constants and internal degrees of freedom. Atomic positions were relaxed so that the forces are within $10^{-6}$ eV/Å. The lattice constants are tabulated in Table 4.1, comparable to other DFT studies of aragonite (Medeiros et al., 2006) as well as experimental measurements (Balmain et al., 1999).

### 4.3.1 Anisotropic elastic constants

Because aragonite has a orthorhombic symmetry, it is elastically anisotropic. Its stiffness tensor $C$ has 9 nonzero elements.

$$
\begin{pmatrix}
    c_{11} & c_{12} & c_{13} & 0 & 0 & 0 \\
    c_{12} & c_{22} & c_{23} & 0 & 0 & 0 \\
    c_{13} & c_{23} & c_{33} & 0 & 0 & 0 \\
    0 & 0 & 0 & c_{44} & 0 & 0 \\
    0 & 0 & 0 & 0 & c_{55} & 0 \\
    0 & 0 & 0 & 0 & 0 & c_{66}
\end{pmatrix}
$$

(4.14)

where the Voigt notation is used. Hooke’s law may be written as

$$
\sigma_{ij} = c_{ijkl}\epsilon_{kl}.
$$

(4.15)

The anisotropic elastic constants of aragonite may be calculated by considering small perturbations to the strain. The contribution to the energy of the system may be calculated through the work done on an infinitesimal element

$$
dw = \sigma_{ij}d\epsilon_{ij} = c_{ijkl}\epsilon_{kl}d\epsilon_{ij}
$$

(4.16)

Integrating, the elastic energy of a crystal in strain state $\epsilon$ is given by

$$
F_V = \frac{F_0}{V_0} + \frac{1}{2}c_{ijkl}\epsilon_{ij}\epsilon_{kl}
$$

(4.17)
Table 4.1: Computed structural constants of aragonite.

<table>
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<th>LDA</th>
<th>Literature</th>
<th>% difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a)</td>
<td>5.506</td>
<td>5.743</td>
<td>-1.2%</td>
</tr>
<tr>
<td>(b)</td>
<td>4.881</td>
<td>4.962</td>
<td>-1.6%</td>
</tr>
<tr>
<td>(c)</td>
<td>7.808</td>
<td>7.969</td>
<td>-2.0%</td>
</tr>
</tbody>
</table>

Table 4.2: Computed elastic constants of aragonite.

<table>
<thead>
<tr>
<th></th>
<th>LDA</th>
<th>Literature</th>
<th>% difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>(C_{11})</td>
<td>208 GPa</td>
<td>171.1</td>
<td>21.6%</td>
</tr>
<tr>
<td>(C_{22})</td>
<td>127</td>
<td>110.1</td>
<td>15.3%</td>
</tr>
<tr>
<td>(C_{33})</td>
<td>115</td>
<td>98.4</td>
<td>16.9%</td>
</tr>
<tr>
<td>(C_{44})</td>
<td>45</td>
<td>39.3</td>
<td>14.5%</td>
</tr>
<tr>
<td>(C_{55})</td>
<td>27</td>
<td>24.2</td>
<td>11.6%</td>
</tr>
<tr>
<td>(C_{66})</td>
<td>47</td>
<td>40.2</td>
<td>16.9%</td>
</tr>
<tr>
<td>(C_{12})</td>
<td>73</td>
<td>60.3</td>
<td>21.1%</td>
</tr>
<tr>
<td>(C_{13})</td>
<td>44</td>
<td>27.8</td>
<td>58.3%</td>
</tr>
<tr>
<td>(C_{23})</td>
<td>68</td>
<td>41.9</td>
<td>62.3%</td>
</tr>
</tbody>
</table>

The explicit form for the change in elastic energy for a general deformation \(\eta\) may now be written:

\[
\delta U = \frac{C_{11}\epsilon_{11}^2}{2} + 2c_{66}\epsilon_{12}^2 + 2c_{55}\epsilon_{13}^2 + c_{12}\epsilon_{11}\epsilon_{22} + \frac{c_{22}\epsilon_{22}^2}{2} + 2c_{44}\epsilon_{23}^2 + c_{13}\epsilon_{11}\epsilon_{33} + c_{23}\epsilon_{22}\epsilon_{33} + \frac{c_{33}\epsilon_{33}^2}{2}
\]  

(4.18)

By independently varying the different strain parameters, the elastic constants may be calculated. Since there are 9 unknown elastic constants, the energies must be calculated along 9 independent strain paths. The elastic moduli are tabulated in Table 4.2, and compared with values from the literature. The agreement is very good, suggesting that future studies will be able to calculate both the ideal strength and the surface energies from first principles.
Chapter 5

Models of microstructural evolution

Everything’s got a moral, if only you can find it.

- Lewis Carroll

5.1 Rayleigh instability in hollow-core dislocations

The energy of a hollow-core dislocation may be separated into surface, elastic, and chemical components. Following Frank (1951) and Cahn (1957), the free energy of a cylindrically symmetric hollow-core dislocation may be represented by a functional that depends on the radius, \( R(z) \),

\[
F[R(z)] = \int_0^L dz \left\{ 2\pi \gamma R \left[ 1 + \left( \frac{\partial R}{\partial z} \right)^2 \right]^{1/2} - A \log R - \pi f R^2 \right\}, \tag{5.1}
\]

where \( \gamma \) is the surface energy and \( -f \) is taken to be the volumetric free energy of formation of the void. The \( A \log R \) term corresponds to the elastic energy relieved from the presence of the void. The value of \( A \) depends on the character of the dislocation: \( A = G b^2 / 4\pi (1-\nu) \) for edge dislocations and \( A = G b^2 / 4\pi \) for screw dislocations. \( G \) and \( \nu \) are the shear modulus and Poisson’s ratio of the matrix, and \( b \) is the length of the Burgers’ vector of the dislocation. Formally, the system must be finite in size: otherwise, the elastic energy of the system diverges. For computational simplicity, the matrix is considered to be a cylinder of radius \( R_{\text{mat}} \), centered around the hollow-core dislocation.

Frank (1951) considered Eq. 5.1 in the limit of isotropic surface energy, and set \( f = 0 \). Under these conditions, the energy per unit length of a cylinder radius \( R \) is given by

\[
F_L(R) = 2\pi \gamma R - A \log R \tag{5.2}
\]

If mass is not conserved, the free energy is minimized for dislocations of a critical radius, \( R^* = A / 2\pi \gamma \). This prediction for the equilibrium size of a hollow-core dislocation is known as Frank’s radius.

5.1.1 Thermodynamic analysis

Consider a single, initially cylindrical hollow-core dislocation with radius \( R_0 \). Using Eq. 5.1, it is possible to calculate the increase in free energy from a sinusoidal perturbation with wavelength
Choosing fluctuations that conserve mass, the radius is chosen to be a function of $z$ in the form
\[ R(z, t) = R_1 + \delta(t) \cos(2\pi z / \lambda) \] (5.3)
where $\delta(t)$ is taken to be small compared to $R_0$. The value of $R_1$ is set by a mass conservation condition. The volume of the perturbed cylinder is taken to be equal to that of the unperturbed cylinder for a single period of the sinusoid.

\[ V_{\text{unperturbed}} = V_{\text{perturbed}} \] (5.4)
\[ \pi R_0^2 \lambda = \pi \int_0^\Lambda [R_1 + \delta(t) \cos(2\pi z / \lambda)]^2 dz \] (5.5)

Eq. 5.5 sets the constraint on $R_1$ that $R_0^2 - R_1^2 = \delta^2 / 2$. Following Cahn (1979), $\gamma$ is taken to be anisotropic in the direction of the dislocation line. The geometry of the system remains axisymmetric, and $\gamma$ is a function only of the angle $\phi = \partial R / \partial z$. $\gamma$ may be expanded about $\phi$ as
\[ \gamma(\phi) = \gamma_0 + \phi \gamma' + \frac{1}{2} \phi^2 \gamma'' + O(\phi^3), \] (5.6)
where $\gamma' = \partial \gamma / \partial \phi$ and $\gamma'' = \partial^2 \gamma / \partial \phi^2$. $\Delta F$ may be calculated by combining Eq. 5.1, Eq. 5.3 and Eq. 5.6. Keeping only terms of order $\delta^2$,
\[ \Delta F = \left[ \frac{A \lambda^2}{2R_0^2} - \frac{\pi \gamma \lambda}{2R_0} + \frac{2\pi^3 R_0 \gamma}{\lambda} + \frac{2\pi^3 R_0 \gamma''}{\lambda} \right] \delta^2. \] (5.7)

A hollow-core dislocation is unstable to perturbations that cause the free energy to decrease relative to $F_{\text{perfect}}$. The condition $\Delta F < 0$ is true for values of $\lambda$ which satisfy:
\[ \lambda > 2(\pi R_0)^{3/2} \sqrt{\frac{\gamma_0 + \gamma''}{\pi R_0 \gamma_0 - A}}. \] (5.8)

In the limit that $R^* \rightarrow 0$ and $\gamma'' \rightarrow 0$, this expression reduces to the classical Rayleigh (1878) condition, $\lambda > \lambda_{\text{isotropic}}^{\text{min}} = 2\pi R_0$. The form of Eq. 5.8 suggests that it is useful to define a scaling parameter $S$,
\[ S = \sqrt{\frac{1 + \gamma'' / \gamma_0}{1 - 2R^* / R_0}} \] (5.9)

which contains contributions from both surface-energy anisotropy as well as elastic energy from the dislocation. Fig. 5.1 explores the relationship between these two parameters, plotting $S$ for different values of $\gamma'' / \gamma_0$ over a range of $R_0 / R^*$.

Using this definition, it is easy to show that there is a minimum unstable wavelength $\lambda_{\text{min}} = \lambda_{\text{isotropic}}^{\text{min}} S$. A cylindrical hollow-core dislocation will be unstable to perturbations with wavelength $\lambda > \lambda_{\text{min}}$. Conversely, perturbations with wavelength shorter than the minimum wavelength will decay.

### 5.1.2 Kinetic analysis

The main result of the thermodynamic analysis is an expression for $\lambda_{\text{min}}$, the minimum allowed wavelength for Rayleigh break-up. It is not a prediction for the observed periodicity of the instability. This is a difficult problem, which would require direct simulation of the microstructure. To
Figure 5.1: Dependence of the scaling parameter \( S \) on surface-energy anisotropy and dislocation strength. For isotropic surface energies, the scaling factor approaches unity if \( R_0 \gg R^* \).

make this problem tractable for theoretical analysis, an analysis is proposed that considers only the \textit{onset} of the perturbation. The fastest-growing mode at initiation is most likely to be the periodicity of the final pore array (Nichols and Mullins, 1965b). For this calculation, the perturbation is assumed to be self-similar: \( \delta(t) \propto \exp(\Lambda t) \). It is therefore sufficient to calculate

\[
\frac{\dot{\delta}}{\delta} \equiv \frac{1}{\delta} \frac{\partial}{\partial t} \delta = \Lambda
\]

for different mechanisms of mass transport. In particular, surface-diffusion and volume-diffusion controlled systems are considered. This amplification factor, \( \dot{\delta}/\delta \), will be positive for wavelengths larger than the minimum wavelength, and negative otherwise. A mode will grow unstably if it is of a sufficiently large wavelength, and will shrink if smaller. The fastest-growing mode will maximize \( \dot{\delta}/\delta \).

**Chemical potential and modified Gibbs-Thompson equation**

In order to determine the driving force for diffusion, a chemical potential for vacancies at the surface of the hollow-core dislocation must be defined. Similarly to the phase-field method, the potential can be related to the appropriate first variation of Eq. 5.1. The cross-sectional area \( A_x \) must be conserved in order for mass to be conserved, leading to the definition

\[
\mu = \frac{\delta F}{\delta A_x} = \frac{\delta R}{\delta A_x} \frac{\delta F}{\delta R}
\]

The interpretation of this potential is that for a small change in the local cross sectional area, from \( A_x \) to \( \delta A_x \), there is a change in the free energy

\[
\delta F = \int \mu \delta A_x dz
\]

To evaluate \( \mu \), the variational derivative is found using the formula

\[
\frac{\delta F}{\delta R} = \frac{\partial F}{\partial R} - \nabla \frac{\delta F}{\delta R}
\]

50
In the one-dimensional problem considered here, $\nabla \approx \frac{\partial}{\partial z}$. For a circular cross-section, $A_x = \pi R^2$ and so $(\delta R/\delta A_x) = (\partial A_x/\partial R)^{-1} = (2\pi R)^{-1}$.

$$\mu = \frac{1}{2\pi R} \left\{ 2\pi \gamma \left[ 1 + \left( \frac{\partial R}{\partial z} \right)^2 \right]^{1/2} - \frac{A}{R} - 2\pi f R - \frac{\partial R}{\partial z} \frac{2\pi R}{2\pi R^2} \left[ 1 + \left( \frac{\partial R}{\partial z} \right)^2 \right]^{1/2} \right\}$$ (5.14)

For infinitesimal perturbations, only terms of first order in $\partial R/\partial z$ must be retained. The linearized potential is then:

$$\mu = \frac{\gamma_0}{R} - \left( \gamma_0 + \gamma'' \right) \frac{\partial^2 R}{\partial z^2} - \frac{A}{2\pi R^2} - f$$ (5.15)

This form of the chemical potential has consequences for the Gibbs-Thompson effect. The local solubility must also be affected by surface-energy anisotropy and strain energy. To quantitatively calculate this effect, an additional assumption is made, that vacancies do not interact elastically either with the dislocation strain field or with each other. It is also necessary to choose a reference state for the enrichment in solubility. This is taken to be a cylindrical hollow-core dislocation with radius $R_{\text{ref}}$. The difference in chemical potential between the reference state and the system with an arbitrary profile $R(z)$ is:

$$\Delta \mu = \mu(R, dR/dz) - \mu(R_{\text{ref}}, 0) = \frac{\Omega \gamma_0}{R} - \Omega \left( \gamma_0 + \gamma'' \right) \frac{\partial^2 R}{\partial z^2} - \frac{\Omega A}{2\pi R^2} \frac{\Omega R_{\text{ref}}}{R_{\text{ref}}} + \frac{\Omega A}{2\pi R^2_{\text{ref}}}(5.16)$$

where $\Omega$ is the molar volume of the vacancy. The transfer of $dn$ moles of material from the reference state to the system of interest causes an increase in free energy

$$dG = \Delta \mu dn.$$ (5.17)

Eq. 5.17 is true locally: it is valid at every point $z$. The free energy change may then be defined as:

$$\Delta \mu = \mathcal{G}_B(R, dR/dz) - \mathcal{G}_B(R_{\text{ref}}, 0) = k_B T \log \frac{a_B(R, dR/dz)}{a_B(R_{\text{ref}}, 0)}$$ (5.18)

where $\mathcal{G}_B(R, dR/dz)$ is the partial molar free energy and $a_B(R, dR/dz)$ is the activity of the vacancy. In the dilute-solution limit, $a_B = \gamma_0 c_B$. According to Henry’s law, the activity coefficient is independent of concentration and so:

$$\Delta \mu = k_B T \log \frac{c_B(R, dR/dz)}{c_B(R_{\text{ref}}, 0)}$$ (5.19)

After solving for $c_B(R, dR/dz)$ and linearizing:

$$c_B(R, dR/dz) = c_B(R_{\text{ref}}, 0) \exp \frac{\Delta \mu}{k_B T} \approx c_B(R_{\text{ref}}, 0) \left( 1 + \frac{\Delta \mu}{k_B T} \right)$$ (5.20)

Defining the local enrichment to be $\Delta c = c_B(R, dR/dz) - c_B(R_{\text{ref}}, 0),$

$$\Delta c = \frac{c_B(R_{\text{ref}}, 0) \Omega}{k_B T} \left( \frac{\gamma_0}{R} - \left( \gamma_0 + \gamma'' \right) \frac{\partial^2 R}{\partial z^2} - \frac{R^*}{R} + \frac{R^*}{R_{\text{ref}}} \right)$$ (5.21)

If the reference state is chosen to be sufficiently large, the final terms of Eq. 5.21 vanish. In the case that $R \ll R_{\text{ref}} \ll R_{\text{mat}}, c_B(R_{\text{ref}}, 0)$ approaches $\alpha_0$, the equilibrium concentration at a flat
interface, in the absence of dislocations. For this choice of reference state, the modified form of the Gibbs-Thompson relationship is:

\[
\Delta c = \frac{c_0}{k_B T} \left( \frac{\gamma_0}{R} - \left( \frac{\gamma_0 + \gamma''}{\gamma_0} \right) \frac{\partial^2 R}{\partial z^2} - \gamma_0 \frac{R^*}{R^2} \right) \tag{5.22}
\]

In the limit of surface-energy isotropy and in the absence of a dislocation, Eq. 5.22 reduces to the classical Gibbs-Thompson equation.

Surface diffusion

Mullins (1957) proposed a general expression for the normal velocity of the surface \( \partial n / \partial t \) due to surface diffusion

\[
\frac{\partial n}{\partial t} = \frac{D_s N_s \nabla^2 \mu}{k_B T} \tag{5.23}
\]

where \( D_s \) is the surface diffusion coefficient, and the \( \nabla_s \) is the surface Laplacian. A combination of Eq. 5.15 and Eq. 5.23 may be used to determine the evolution of the infinitesimally perturbed cylinder described by Eq. 5.3. Keeping only terms of order \( \delta \), the chemical potential is

\[
\mu = \frac{\gamma_0}{R_0} - \frac{\gamma_0 \delta \cos \omega z}{R_0^2} + \left( \frac{\gamma_0 + \gamma''}{\gamma_0} \right) \omega^2 \delta \cos \omega z - \frac{A}{2\pi R_0^2} + \frac{A\delta \cos \omega z}{\pi R_0^3} - f \tag{5.24}
\]

where \( \omega = 2\pi/\lambda \). For small perturbations, \( s \approx z \), and the surface Laplacian becomes \( \nabla_s^2 = (\partial^2 / \partial z^2) \). The velocity of the surface is then given by

\[
\frac{\partial n}{\partial t} = B \omega^2 \left( \frac{1}{R_0^2} \frac{\gamma_0}{R_0} - \omega^2 \left( \frac{\gamma_0 + \gamma''}{\gamma_0} \right) - \gamma_0 \frac{2R^*}{R_0^3} \right) \delta \cos \omega z \tag{5.25}
\]

where \( B = (D_s N_s \Omega) / (k_B T) \). Another expression for the surface velocity may be found by differentiating Eq. 5.3 with respect to time.

\[
\frac{\partial n}{\partial t} = \frac{\partial R}{\partial t} = \dot{\delta} \cos \omega z \tag{5.26}
\]

By comparing Eq. 5.25 and 5.26, an expression for the amplification factor \( \dot{\delta} / \delta \) may be found to be

\[
\frac{\dot{\delta}}{\delta} = B \omega^2 \left( \frac{1}{R_0^2} \frac{\gamma_0}{R_0} - \omega^2 \left( \frac{\gamma_0 + \gamma''}{\gamma_0} \right) - \gamma_0 \frac{2R^*}{R_0^3} \right). \tag{5.27}
\]

Volume diffusion

When volume diffusion governs the Rayleigh instability, the amplification factor may be found by solving Fick's Laws using Eq. 5.22 as a boundary condition. Considering a perturbed hollow-core dislocation with profile described by Eq. 5.3, the change in solubility at the surface of the dislocation is:

\[
\Delta c = \frac{c_0 \gamma_0}{k_B T} \left( \frac{1}{R_0} - \frac{\delta \cos \omega z}{R_0^2} + \left( \frac{\gamma''}{\gamma_0} \right) \omega^2 \delta \cos \omega z - \frac{R^*}{R_0^3} \left( 2R^* \delta \cos \omega z - \frac{R^*}{R_0^3} \right) \right) \tag{5.28}
\]
to first order in $\delta$. The steady-state concentration must satisfy Laplace’s equation, $\nabla^2 c = 0$. For the case of cylindrical symmetry, the general solution is:

$$\Delta c = \{A' I_0(\omega r) + B' K_0(\omega r)\} \{C \sin \omega z + D \cos \omega z\} + E$$  \hspace{1cm} (5.29)

where $I_0(z)$ is the modified Bessel function of the first kind of order 0, $K_0(z)$ is the modified Bessel function of the second kind of order 0, and $A'$, $B'$, $C$, and $E$ are constants set by the boundary conditions. To determine the value of these constants, multiple distinct situations that can be analyzed. Two situations are “external” volume diffusion, where volume diffusion through the matrix is the dominant transport mechanism, and “internal” volume diffusion, where volume diffusion in the hollow-core dislocation is dominant.

Under normal conditions, the core of a hollow-core dislocation is empty, and so internal volume diffusion is not physically meaningful. However, this case is applicable to the more general situation, where the core is filled with an arbitrary phase. This is the case if a second-phase cylindrical precipitate is formed on a dislocation. A formal treatment of this microstructure is more difficult than the current one of a hollow-core dislocation: in particular, elastic effects from the interface complicate the analysis. However, if the mismatch is not large, it should have the similar generic behavior to the present case.

In the case of external volume diffusion, it is necessary to consider the vacancy concentration outside of the cylinder. $I_0(\omega r)$ diverges as $z \to \infty$, forcing $A' = 0$. Since the perturbation chosen is proportional to $\cos \omega z$, $C = 0$. Then, only two parameters are free, and the concentration is set by the equation:

$$\Delta c = B'' K_0(\omega r) \cos \omega z + E$$  \hspace{1cm} (5.30)

The modified Gibbs-Thompson equation sets the value of this equation at the cylinder surface, $r = R$. By comparison to Eq. 5.28, the constants may be set as:

$$B'' = \frac{1}{K_0(\omega R_0)} c_0 \frac{\gamma_0}{k_B T} \left(-\frac{1}{R_0^2} + \left(1 + \frac{\gamma''}{\gamma_0}\right) \omega^2 + \frac{R^*}{R_0^3} \right) \delta$$  \hspace{1cm} (5.31)

$$E = \frac{c_0 \Omega \gamma_0}{k_B T} \left(\frac{1}{R_0} - \frac{R^*}{R_0^2}\right)$$  \hspace{1cm} (5.32)

so the solution for the concentration field for all space is:

$$\Delta c = \frac{c_0 \Omega \gamma_0}{k_B T} \left[\left(1 + \frac{\gamma''}{\gamma_0}\right) \omega^2 - \frac{1}{R_0^2} + \frac{2R^*}{R_0^3}\right] K_0(\omega r) \delta \cos \omega z + \frac{1}{R_0} - \frac{R^*}{R_0^2} \right]$$  \hspace{1cm} (5.33)

Assuming that growth is diffusion limited, the rate at which vacancies are transported to the surface of the hollow-core dislocation will determine the rate at which the perturbation grows. Using Fick’s first law, which relates mass flux to concentration gradients, the vacancy flux into the dislocation may be calculated. The radial component of the vacancy flux, evaluated at the surface of the hollow-core dislocation, is

$$J_r = \left(-D \frac{\partial c}{\partial r}\right)_{r=R_0+\delta \cos \omega}$$  \hspace{1cm} (5.34)

where $D$ is the lattice diffusion coefficient. The normal velocity of the surface is proportional to $J_r$.

$$\frac{dn}{dt} = \frac{dr}{dt} = \Omega J = \frac{D \Omega^2 c_0 \gamma_0}{k_B T} \left(\frac{1}{R_0^2} - \frac{2R^*}{R_0^3} - (1 + \frac{\gamma''}{\gamma_0}) \omega^2\right) K_1(\omega r) \delta \cos \omega z$$  \hspace{1cm} (5.35)
where the fact that \((d/dz)K_0(z) = K_1(z)\) has been used. By comparing this expression to Eq. 5.26, the amplification factor \(\delta/\delta\) may be identified as:

\[
\frac{\delta}{\delta} = \frac{D\Omega^2c_0\gamma_0\omega(1 - 2R^*/R_0)}{k_BT} \left( \frac{1}{R_0^2} - \frac{1 + \gamma''/\gamma_0}{2R_0^*} \omega^2 \right) \frac{K_1(\omega R_0)}{K_0(\omega R_0)}
\]  

(5.36)

The case of internal volume diffusion requires the solution of a different diffusion problem, determining the concentration profile inside of the hollow-core dislocation. In this case, the curvature and the driving force both have the opposite sign as the case of external volume diffusion. The boundary conditions to the diffusion equation also change. Even though Eq. 5.29 still defines the general solution, the values of the constants \(A', B', C,\) and \(E\) are different. Because \(K_0(z)\) diverges as \(z \to 0\), the constraint \(B' = 0\) must be imposed to keep the solution finite at the origin. Since the perturbation chosen is proportional to \(\cos \omega z\), \(C = 0\). Again, there are only two free parameters, and the concentration profile may be calculated to be

\[
\Delta c = -\frac{c_0\Omega\gamma_0}{k_BT} \left\{ \left( 1 + \frac{\gamma''}{\gamma_0} \right) \omega^2 - \frac{1}{R_0^2} + \frac{2R^*}{R_0^*} \right\} \frac{I_1(\omega r)}{I_0(\omega R_0)} \delta \cos \omega z + \left( 1 - \frac{R^*}{R_0^*} \right)
\]

(5.37)

By noting that the normal velocity is now \(-\Omega J,\)

\[
\frac{\partial n}{\partial t} = \frac{dr}{dt} = -\Omega J = \frac{D\Omega^2c_0\gamma_0\omega}{k_BT} \left( \frac{1}{R_0^2} - \frac{1 + \gamma''}{2R_0^*} \omega^2 \right) \frac{I_1(\omega r)}{I_0(\omega R_0)} \delta \cos \omega z
\]

(5.38)

By again comparing the expression for the surface velocity to Eq. 5.26, the amplification factor \(\delta/\delta\) may be calculated:

\[
\frac{\delta}{\delta} = \frac{D\Omega^2c_0\gamma_0\omega(1 - 2R^*/R_0)}{k_BT} \left( \frac{1}{R_0^2} - \frac{1 + \gamma''/\gamma_0}{2R_0^*} \omega^2 \right) \frac{I_1(\omega R_0)}{I_0(\omega R_0)}
\]

(5.39)

**Comparison of diffusion mechanisms**

The rates at which different modes grow or shrink were calculated for three different mass transport mechanisms: surface diffusion, volume diffusion in the matrix, and volume diffusion in the dislocation. The goal of this analysis is to understand how the different mechanisms tend to affect the microscopic observations. If a hollow-core dislocation undergoing a Rayleigh instability ultimately forms a regular array of pores on a dislocation, one hope is to be able to experimentally determine which diffusion mechanism was active during the breakup.

As previously mentioned, the fastest-growing wavelength at the onset of breakdown is assumed to be the microscopically observed periodicity of the Rayleigh instability. There are problems with this assumption. The assumption of self-similarity breaks down: growth modes will not remain sinusoidal, and these non-linear effects will effect the evolution of the microstructure. The finite length of the defect will also affect the kinetics. As analyzed in the context of blunting of field-emitter cathodes, breakup initiates from the end Nichols and Mullins (1965a). However, the present study only seeks to qualitatively understand which contributions will affect the breakup.

The fastest-growing wavelength \(\lambda_{max}\) is defined as the wavelength that initially maximizes \(\delta/\delta\). It must satisfy the condition:

\[
\frac{\partial \delta}{\partial \lambda} \bigg|_{\lambda=\lambda_{max}} = 0
\]

(5.40)
Figure 5.2: Dependence of fastest-growing wavelength on critical radius for an isotropic system. This dependence depends on the active transport mechanism. The fastest-growing wavelength of systems governed by volume diffusion outside of the hollow core is notably larger than that of systems governed by volume diffusion inside the hollow core or by surface diffusion.

For surface diffusion, an analytic expression may be found. By differentiating Eq. 5.27, it is found that \( \frac{\delta}{\delta} \) is maximized at the wavelength

\[
\lambda_{\text{max, surf}} = \frac{2\pi}{\omega_{\text{min, surf}}} = 2\pi R_0 \sqrt{\frac{2(1 + \gamma''/\gamma_0)}{1 - 2R^*/R_0}}, = \sqrt{2}\lambda_{\text{min}}
\]  

(5.41)

For volume diffusion, the presence of the Bessel functions make it necessary to use numerical methods. The fastest-growing modes as a function of critical radius are plotted in Fig. 5.2. For all three mechanisms, the fastest-growing wavelength diverges as the hollow-core dislocation radius approaches the critical radius. This is because in all expressions \( \frac{\delta}{\delta} = 0 \) at \( R_0 = 2R^* \). So, the minimum wavelength for Rayleigh decomposition according to the kinetic analyses is consistent with the thermodynamic prediction.

Surface-energy anisotropy has a consistent effect on the fastest-growing wavelength. If \( \gamma''/\gamma_0 < -1 \), the three expressions for \( \frac{\delta}{\delta} \) become monotonic. There should be no minimum for this case. This is illustrated in Fig. 5.3. The effect of anisotropy is roughly the same for the three transport mechanisms: decreasing values of \( \gamma''/\gamma_0 \) decrease the minimum wavelength of Rayleigh instability.

5.1.3 Relationship of theory to experimental observations

Frank’s radius may be be calculated to be less than 1 nm for dislocations in GaN. Frank’s radius is smaller than \( R_0 \approx 5 \) nm, the radii of experimentally observed hollow-core dislocations (Northrup, 2006). Because of this discrepancy, it has been suggested that hollow-core dislocations in GaN are the result of the growth process (Cherns et al., 1997).

Hollow-core dislocations are nonequilibrium structures that should be susceptible to microstructural evolution. The experimental observation by Pailloux et al. (2005) of a Rayleigh-like instability in thin-film GaN is consistent with this point of view. These bamboo structures have been reported
to have an observed wavelength of $\lambda = 10 - 50$ nm, smaller than the classical minimum Rayleigh wavelength of $2\pi R_0$. The present theory can be used to understand this observation.

By inspection of Eq. 5.8, the minimum wavelength is affected both by elastic terms and surface energy terms. Since the elastic terms can only increase the minimum wavelength, it is likely that this effect is due to surface energy anisotropy. This is consistent with the observation that bamboo structures in GaN are faceted. Of course, kinetic effects such as nonlinear terms in the kinetics will also play a role in the observed wavelengths.

This theory may be used to suggest how nanowires containing a dislocation may be stabilized. By doping heavily deformed sapphire with Ti, Nakamura et al. (2003) created arrays of Ti wires by allowing Ti to segregate to the dislocation cores and precipitate. This situation is very similar to the present case of the hollow-core dislocation, and may be treated with the current theory. The Frank radius may be calculated to be $2R^* \approx 1.13$ nm for $\frac{1}{3}[11\bar{2}0]$ for perfect edge dislocations in the $\alpha$-alumina system, using the following values from literature: $\gamma = 1.04 / \text{m}^2$, $G = 150$ GPa, $\nu = 0.24$, and $b = 0.476$ nm. This is on the same order as the experimentally observed wire sizes, and so this observation is again consistent with the present theory. If these wires were larger than the critical radius, they would be expected to be unstable upon thermal annealing. However, if the rate of breakup is slow, the Rayleigh instability may not be observable in experimental samples.

### 5.2 Coarsening of hollow-core dislocations

In the previous section, the presence of the dislocation was shown to affect the stability of a hollow-core dislocation to the Rayleigh instability, compared to the evolution of a cylindrical pore. The modified chemical potential derived in Sec. 5.1.2 has other consequences: it will also affect other capillary-driven instabilities. In particular, the driving force to coarsening is altered. This may be illustrated by considering the growth rate of an ensemble of parallel hollow-core dislocations with an initially nonuniform size distribution. Eq. 5.11 can be used to calculate the potential of
Figure 5.4: Chemical potential of point defects at the surface of the dislocation core as a function of dislocation radius. The chemical potential is normalized by $\Omega \gamma / 2R^*$. There is a maximum when the particle radius is twice the Frank radius.

point defects about the $i$th dislocation,

$$\mu_i = -\frac{A \Omega}{2\pi R_i^2} + \gamma \Omega \frac{R_i}{R^*} \left( -\frac{R_i^2}{R_i^2} + \frac{R_i^2}{R^2} \right)$$

(5.42)

where the $i$th dislocation has radius $R_i$. This potential is plotted in Fig. 5.4. Eq. 5.42 illustrates that the local growth rate is affected by the presence of the dislocation. If all hollow-core dislocations are able to exchange mass with each other, the growth rate of a particular dislocation will depend on the sizes of the other dislocations. Under a mean-field assumption, the driving force for the growth of the $i$th wire is driven by the difference of the chemical potential of the particular wire with the average chemical potential, $\Delta \mu = \bar{\mu} - \mu$. The average chemical potential of the system is given by $\bar{\mu} = \sum_j \mu_j$. It is important to note that even though a local particle growth law may be calculated, and continuity is observed, a LSW-style analysis is not valid. The effects of the dislocation becomes less important as rods grow in size. The existence of an internal length scale ensures that the asymptotic state does not exist, since spatial self-similarity cannot be observed in during coarsening.

It possible to determine some tendencies of this ensemble of hollow-core dislocations. Consider a distribution where the largest dislocation has a diameter smaller than $2R^*$. The slope of the potential is positive for all of the dislocations in the ensemble. This means that dislocations larger than the critical radius will have a positive chemical potential difference, and will tend to shrink. The interpretation of Eq. 5.42 is that there will be inverse coarsening when the largest dislocation has a diameter smaller than $2R^*$. Therefore, if the ensemble of hollow-core dislocations is sufficiently small, the system will tend to focus the dislocation sizes.

This limit for thermodynamic stability is different from Frank’s radius. This is because the boundary conditions considered for coarsening are different from the situation studied by Frank (1951). Frank considered the case that the mass of a particular wire is allowed to fluctuate, while the mass of the ensemble of wires is fixed to be constant in the coarsening problem.
5.3 Initiation of pore coarsening

The ultimate conclusion of a hollow-core dislocation undergoing a Rayleigh instability is the formation of an array of pores on a dislocation line. If the pores are large enough that the elastic effects are again ignored, and mass transport is assumed to be due only to the nearest neighbors, these pores will coarsen according to the linear bubble model (Hunderi et al., 1979; Vinals and Mullins, 1998). This section considers the onset of coarsening of an array of nearly equally sized pores. This problem is analogous to the Rayleigh stability problem.

5.3.1 Thermodynamic analysis

Consider a linear array of pores connected by a dislocation line, as shown in Fig. 5.5. Assume that coarsening is diffusion limited, and only diffusion through the dislocation is significant. An analysis may be done analogously to the Rayleigh-stability argument. If the centers of the pores have spacing \( d \), radius fluctuations of the following form are considered:

\[
\rho_i = \rho_1 + \delta \cos(2\pi id/\lambda)
\]  

\( \lambda \) is the periodicity of the perturbation, and volume conservation sets the value of \( \rho_1 \). Define the number of pores in one period, \( N_p = \lambda/d \). The total pore volume for the perturbed case over a single period is then:

\[
V_{\text{perturbed}} = \sum_i \frac{4\pi}{3}\rho_i^3 = N_p \left( \frac{4\pi}{3}\rho_1^3 + 4\pi \rho_1 \delta \sum_i \cos(2\pi id/\lambda) + 4\pi \rho_1 \delta^2 \sum_i \cos^2(2\pi id/\lambda) \right)
\]

Performing the summation:

\[
V_{\text{perturbed}} = N_p \frac{4\pi}{3}\rho_1^3 + 2\pi \rho_1 N_p \delta^2
\]

To leading order in \( \delta \), by setting \( V_{\text{unperturbed}} = V_{\text{perturbed}} \), \( \rho_1 = \rho_0 - (1/2\rho_0)\delta^2 \). The change in energy of the coarsening system is \( \Delta F = F_{\text{perturbed}} - F_{\text{perfect}} \) may be calculated to be:

\[
\Delta F = \gamma \sum_i 4\pi \rho_i^2 - \gamma N_p 4\pi \rho_0^2
\]

which is \( \Delta F = -2\pi \gamma N_p \delta^2 \) to leading order in \( \delta \). This change in surface energy is always negative, irrespective of the wavelength. So, unlike the Rayleigh problem considered earlier, there is no minimum wavelength.

5.3.2 Kinetic analysis

If mass transport occurs only through the dislocations, the concentration gradient along each dislocation is linear. From mass conservation, the volume of the \( i \)th pore is:

\[
\frac{dV_i}{dt} = J_{i-1} \pi r_0^2 + J_{i+1} \pi r_0^2
\]

58
Figure 5.5: Diagram of a simple geometry for pores coarsening on a dislocation line. Each pore is taken to be spherical with radius $\rho_i$ and is separated from its neighbors by a center-to-center distance $d$.

where the dislocation has a core radius $r_0$ and only contributions from the $i-1$ and $i+1$ pores are considered. In the absence of strain effects, the Gibbs-Thompson equation sets the solubility of each pore:

$$c_i = c_0 \exp \frac{2\Omega \gamma}{k_B T \rho_i} \approx c_0 \left(1 + \Gamma/\rho_i\right)$$  \hspace{1cm} (5.48)

where $\Gamma$ is the classical capillary length. This leads to the rate equation:

$$\frac{d\rho_i}{dt} = \frac{\pi \gamma_0^2}{4 \rho_i^2} D c_0 \Gamma \left(\frac{\rho_i^{-1} - \rho_{i-1}^{-1}}{d - \rho_i - \rho_{i-1}} + \frac{\rho_i^{-1} - \rho_{i+1}^{-1}}{d - \rho_i - \rho_{i+1}}\right)$$  \hspace{1cm} (5.49)

In the limit of zero volume fraction, this may be expressed as follows:

$$\frac{d\rho_i}{dt} = \frac{\pi \gamma_0^2}{4 \rho_i^2} D c_0 \Gamma \frac{1}{d} \left(\rho_i^{-1} - 2\rho_i^{-1} + \rho_{i+1}^{-1}\right)$$  \hspace{1cm} (5.50)

Again, consider perturbations of the form in Eq. 5.43. To leading order in $\delta$,

$$\frac{d\rho_i}{dt} = \frac{\pi \gamma_0^2}{4 \rho_i^2} D c_0 \Gamma \left(1 - \cos \frac{2\pi}{N_p}\right) \cos \frac{2\pi i}{N_p} \delta$$  \hspace{1cm} (5.51)

Solving for the usual amplification factor, $\dot{\delta}/\delta$,

$$\frac{\dot{\delta}}{\delta} = \frac{\pi \gamma_0^2}{4 \rho_i^2} D c_0 \Gamma \left(\cos \frac{2\pi}{N_p} - 1\right)$$  \hspace{1cm} (5.52)

The interpretation of Eq. 5.52 is that the short wavelength modes are favored. This amplification factor is maximized for $N_p = 2$, where pores alternately grow and shrink. This is consistent with the thermodynamic result that there is no minimum wavelength.
Chapter 6

Closing remarks

The truth is rarely pure and never simple.

— Oscar Wilde

Two types of strain-mediated instabilities were studied in this thesis. In Chapters 3 and 4, statistical mechanics techniques were used to study the fracture of heterogeneous systems. In Chapter 5, the evolution of a model microstructure due to instabilities from surface energy was considered. The role of strain energy is very different for the two examples studied. While strain is the driving force for fracture in composites, it tends to stabilize the capillary instability in hollow-core dislocations.

6.1 Deformation of nacre

The toughening mechanisms in nacre were considered using both quasi-static and time-dependent treatments. Because of the statistical nature of the models studied, size effects are naturally expected to arise. The deformation of nacre-like materials was studied using kinetic Monte Carlo techniques and direct integration in the adiabatic limit. The biopolymer was analyzed using a two state model for the deformation of a class of biopolymers under the rare event limit assuming irreversible kinetics. An algorithm was presented that allows calculation of the mechanical properties under various loading conditions. Analytical results for the force at first unfolding were found in the limit that unfolding is irreversible. The energy dispersed during unfolding is calculated to be a large fraction of the work needed to extend the system. This model was further extended to ensembles of polymer chains.

In some sense, the microscopic disorder is a way to characterize the fracture toughness of the system. These models may be slightly modified to other natural materials. Bone, for instance, also has a hierarchical structure that involves toughening mechanisms on many length scales. Similarly to lustrin A in nacre, the matrix proteins osteopontin (Fantner et al., 2007) and dentin matrix protein 1 (Adams et al., 2008) have been suggested to exhibit the same behavior. There are two important possible extensions to this model. First, the assumption of irreversible kinetics may be relaxed by incorporating refolding events. Further, the bundle geometry may be extended to more realistic configurations.
6.2 Structural stability of hollow-core dislocations

The susceptibility of the hollow-core dislocation to the Rayleigh instability and coarsening was studied, focusing on only leading-order effects. By assuming a self-similar evolution, analytical expressions were derived that determined a critical radius for the stability of hollow-core dislocations. A parameter $S(\gamma''/\gamma_0, R^*/R_0)$ was identified that summarizes the interplay between surface-energy anisotropy and strain energy. By analogy to precipitate formation, this suggests a path for the fabrication of a stable nanowire array.

However, a more detailed calculation would need to treat both the interface and the point defects more carefully. In a precipitate, the interface may be coherent, affecting the strain energy of the system. Point defects will also interact elastically, in principle changing the Gibbs-Thompson equation. Further, the transport equations used are simplistic: they are only true for the simple case of vacancy self-diffusion in a metal.

In order to deal with the case of diffusion in a ceramic, diffusion currents of multiple species must be considered. Since the various point defects have different charges associated with them, these currents will be strongly coupled. Likewise, the interfaces may develop a local space charge. This causes point defects to tend to arrange themselves to minimize the total energy of the system.

However, even by including these physical effects, the linear stability analysis cannot give a complete understanding of the behavior. For instance, it is not obvious if the growth of the Rayleigh instability is bounded. In other words, it is not clear if an unstable hollow-core dislocation will eventually pinch-off. Further, the finite size of real dislocations may play an important role in the ultimate break up of the rods. To study these aspects of Eq. 5.23, it is possible to consider the full evolution equation:

$$\frac{\partial n}{\partial t} = \frac{D_s N_s \Omega}{k_B T} \nabla^2 \left\{ \frac{2\pi \gamma \left[ 1 + \left( \frac{\partial R}{\partial z} \right)^2 \right] - R \left( \frac{\partial^2 R}{\partial z^2} \right) - A}{1 + \left( \frac{\partial R}{\partial z} \right)^2} \right\}$$

(6.1)

By solving this equation numerically, it should be possible to determine the time evolution of the hollow-core dislocation. This equation of motion is consistent with existing theories: in the limit that $A = 0$, this equation is identical to that considered by Nichols and Mullins (1965a).
Bibliography


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