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Emergence of viscosity and dissipation via stochastic bonds

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ABSTRACT

"Viscosity is the most ubiquitous dissipative mechanical behavior" (Maugin, 1999). Despite its ubiquity, even for those systems where the mechanisms causing viscous and other forms of dissipation are known there are only a few quantitative models that extract the macroscopic rheological response from these microscopic mechanisms. One such mechanism is the stochastic breaking and forming of bonds which is present in polymer networks with transient cross-links, strong inter-layer bonding between graphene sheets, and sliding dry friction. In this paper we utilize a simple yet flexible model to show analytically how stochastic bonds can induce an array of rheological behaviors at the macroscale. We find that varying the bond interactions induces a Maxwell-type macroscopic material behavior with Newtonian viscosity, shear thinning, shear thickening, or solid like friction when subjected to shear at constant rates. When bond rupture is independent of the force applied, Newtonian viscosity is the predominant behavior. When bond breaking is accelerated by the applied force, a shear thinning response becomes most prevalent. Further connections of the macroscopic response to the interaction potential and rates of bonding and unbonding are illustrated through phase diagrams and analysis of limiting cases. Finally, we apply this model to polymer networks and to experimental data on "solid bridges" in polydisperse granular media. We imagine possible applications to material design through engineering bonds with specific interactions to bring about a desired macroscopic behavior.

1. Introduction

The rheology of both natural and man-made materials has long been an active field of study (Larson, 1999; Chen et al., 2010). Work has been done both at the continuum scale and the microscopic scale for a number of material systems including granular media (Goddard, 2014; Goddard and Kamrin, 2019), biological materials (Holzapfel et al., 2002), polymers (Knauss and Emri, 1981; Doi and Edwards, 1988; Reese and Govindjee, 1998) and hydrogels (Koetting et al., 2015) among many others (Crocker et al., 2000; Waigh, 2016; Edera et al., 2017). However, connecting macroscopic rheology to the microscopic features of a particular system remains a challenge because many different mechanisms can induce a particular macroscopic response, and scale bridging away from equilibrium remains notoriously difficult (Doi and Edwards, 1988; Oakley et al., 1998; Lee et al., 2013; Chaudhuri, 2017). In this paper, we explore precisely this connection in the context of stochastic formation and breaking of bonds on the microscopic scale. These stochastic bonds are shown to induce a wide range of macroscopic material behavior such as solid friction, viscous flow, and shear thinning and thickening viscoelastic response.

Stochastic breaking and formation of bonds is a feature of many mechanical processes/systems including polymer networks with transient cross-links (Smeulders and Govindjee, 1999; Broedersz et al., 2010; Vernerey et al., 2017), strong interlayer forces

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within graphene (Telling et al., 2003; Wen and Tadmor, 2019) and even muscle contraction (Huxley, 1957) and motor protein function (Tawada and Sekimoto, 1991). In the case of polymer networks, the breaking of transient cross-links allows the otherwise elastic network to flow under slow loading rates (Broedersz et al., 2010; Vernerey et al., 2017), while the reversibility of bonding allows many polymeric materials to be self-healing (Blaiszik et al., 2010). Additionally, stochastic unbonding plays a key role in explaining the enhanced or restricted diffusion of macromolecules embedded in transient networks (Sridhar et al., 2021), as well as rate dependent fracture in polymers (Hui et al., 2004; Yang et al., 2020; Song et al., 2021), fiber networks (Abhilash et al., 2012), and at polymer-glass interfaces (Chaudhury, 1999). Examples involving stochastic bonding and unbonding are not restricted to polymers, however. In Barel et al. (2010), the authors model contact between an Atomic Force Microscopy (AFM) cantilever and a crystalline surface using thermally activated bonds, and show how the temperature dependence of the bonding and unbonding rates explains the experimentally observed peak in the kinetic friction coefficient as a function of temperature.

The works mentioned above highlight the usefulness and success of analyzing stochastic bonding and unbonding to reveal the origin of complex mechanical behavior. These models, however, are either tailored to a specific system of interest, or they do not explore the full range of possible material behaviors which stochastic bonds are capable of producing. Our aim is to demonstrate how changing bond interactions (the potential) and rates of bonding and unbonding (the kinetics) can significantly alter how the system dissipates energy on the macroscopic scale. To achieve this aim, we focus on extending a relatively simple model (one originally proposed by Huxley (1957) and Schallamach (1963) independently to model muscle contraction and sliding friction between rubber and hard surfaces, respectively) to understand the impact of time dependent unbonding rates and complex bond interaction on the resulting macroscopic material behavior. In particular, we use tools from probability to provide (a) an explicit formula for computing the dissipation rate per bond in steady state as a function of the bond interaction and kinetic parameters for both force independent and force-dependent unbonding rates, (b) phase diagrams for macroscopic material behavior as a function of shear velocity (or shear rate) and bond stiffness for multiple, common interaction potentials, and (c) some general bounds on the dissipation rate for the limiting cases of high and low shear velocities. Finally, we apply this model to study dissipation in polymer networks with transient cross-links and "solid bridges" that arise in polydisperse granular media (Seiphoori et al., 2020). These examples highlight the fact that despite the model's simplicity, one can use it to model real systems. They are also broad in scope. Indeed, actin networks with transient cross-links are used by cells to perform vital functions (Broedersz et al., 2010) and transient cross-links are also an important toughening mechanism in polymer hydrogels (Vernerey et al., 2017). For its part, transient inter-grain bonds control the stability and strength of granular assemblies manifested in various geological, biological, and industrial systems. The microscopic physics of particle-particle interaction in such systems is not fully understood, and transferring models derived from particle-scale dynamics to macroscopic scales is far from implementation (Jerolmack and Daniels, 2019; Mueller et al., 2017).

To show how we proceed, we describe first the system of Huxley (1957) and Schallamach (1963), further adapted by Tawada and Sekimoto (1991), who used it to study "protein friction" between dynien and microtubules. In this model, elastic dynien heads are connected to a solid surface and can bond with a microtubule as it slides past (see Fig. 1(a)). Once bonded, the dynien elastically stores energy as it is stretched until the bond breaks and the energy is dissipated. Considering a system with *N* dynien heads, of which a fraction ρ_{on} are bonded at any given time, and remain bonded for time τ_{on} on average, one deduces that the dynien form bonds with frequency ρ_{on}/τ_{on} and the system (of dynein and microtubules) dissipates energy at a rate $\dot{D} = N \frac{\rho_{on}}{\tau_{qn}} \frac{1}{2} K(\tau_{on} V)^2$, where *K* is the elastic modulus of the dynien and *V* is the velocity of the microtubule. The result is a viscous-like material behavior which the authors termed "protein friction". As we will show, this simple model when generalized to include arbitrary bond interactions and force dependent bonding kinetics retains enough simplicity to allow for analytical results and enough flexibility to help elucidate the role of stochastic bonds in non-trivial systems.

The rest of this paper is organized as follows. We begin with a formal statement of the model of study (which we will refer to as the stochastic bond model) in Section 2.1, followed by a description of the mathematical result underlying our findings in Section 2.2. In Sections 3.1 and 3.2, we derive and discuss the connection between bond potential and macroscopic dissipation for force independent and force-dependent bond dissociation, respectively. Finally, Section 4 applies and connects the stochastic bond model to the aforementioned transient polymer networks and solid bridges, and we give some concluding remarks in Section 5.

2. Background

2.1. Description of the model

Consider two plates that lay parallel to each other (Fig. 1(a)). One plate is held fixed while the other is sheared past it at constant velocity V. A fixed number of bonding sites are distributed on the bottom plate. At a bonding site, a stochastic bond can form between the site and the opposite plate directly above. Once formed, bonds can stretch to resist shearing. Different bonds are taken to be independent, and bonds are assumed to be independent of their own bonding history. This means that the macroscopic behavior of a system composed of a large number of bonds is completely described by the behavior of a single bond. For this reason, the behavior and mechanics of a single bond will be the focus of our analysis, and the macroscopic system behavior will be extracted from averages of the behavior of a single bond.

The kinetic properties of the bonds are stochastic and are described by two probability densities. The time between an unbonding and the next bonding (the time spent unbonded) is given by the probability density $p_{off}(t_{off})$, and the time between a bonding and the next unbonding (the time spent bonded) by a density $p_{on}(t_{on})$. Throughout, $p_{off}(t_{off})$ will be taken to be an exponential distribution $p_{off}(t_{off}) := \kappa_{on} \exp(-\kappa_{on}t_{off})$ so that the rate of bond formation, κ_{on} , is always constant. On the other hand, the unbonding rate, $\kappa_{off}(t_{on})$, and hence the density of times spent bonded $p_{on}(t_{on})$, will in general depend on the bond interaction as well as the velocity

(or shear rate). The bonding and unbonding times will form inhomogeneous Poisson point processes (which becomes homogeneous in the case that $p_{on}(t_{on})$ is also exponential and $\kappa_{off} = \kappa_{on}$).

The energy stored in a bond is given by a bonding energy $\phi(x)$, which depends on the bond's length *x*. We make the following assumptions: (a) the energy only depends on the deviation from the natural length of the bond x_b (i.e., $\phi(x) = \phi(|x - x_b|)$), (b) both $x_b = 0$ and $\phi(0) = 0$ for simplicity, (c) bonds form at their natural length $x = x_b = 0$, and (d) bonds are stretched parallel to the two plates as a result of the shearing. Thus, if a bond lasts for time t_{on} , it stretched a distance Vt_{on} , and had energy $\phi(Vt_{on})$ at rupture. Dissiplation, then, arises due to the breaking of bonds as the energy stored is instantaneously released. We assume that dissiplated energy is lost to the environment and does not impact future bonding and unbonding events.

Further assumptions on the system will be made throughout the paper. Although some will be explained in more detail later, we will state these assumptions here to make them easy for the reader to find. Some of the assumptions simplify the analysis without much loss of detail, and could be dropped without need of further techniques beyond those given here. Others are more fundamental and cannot be discarded without requiring additional mathematical techniques.

As stated above, we assume a constant rate of bonding, κ_{on} . For many systems, this is not appropriate when, for example, bonds may form under some applied force (Lieou et al., 2013), or when the molecules forming the bond must travel some distance before bonding can occur (Stukalin et al., 2013). However, for the stochastic bond model presented here the distance between plates is assumed to remain fixed, and bonds always form at the same length (their natural length). Thus, a constant rate of bonding is justified. The methods presented in this paper are equipped to handle non-constant bonding rates in an analogous fashion to a non-constant rate of unbonding. All that is needed is an expression for the probability density of times spent unbonded $p_{off}(t_{off})$.

When we consider the case of force dependent unbonding, we assume that the force dependence is reasonably well approximated using the Bell model (see Section 3.2 for details). This greatly simplifies the computation of the density of times spent bonded, $p_{on}(t_{on})$, while still capturing qualitative details. As with the times spent unbonded, one can repeat the analysis presented here using a more complex and accurate model of the force dependence so long as it is possible to calculate $p_{on}(t_{on})$.

An implicit assumption of the stochastic bond model is the infinite extent of the two plates which ensures that the system converges to a steady state. Assuming the plates have finite length could, for example, lead to a changing number of total bonds in the system and hence invalidate the steady state assumption. However, the parallel plate geometry which we analyze here is not essential. All mathematical results are derived at the bond level, and are then applied to the system as a whole under the assumption that it has reached a steady state. It is equally possible to apply the same analysis as presented here to other geometries which lead to steady state (say two rotating disks) so long as the bonding energy and distributions of times spent bonded and unbonded are adjusted accordingly. We use this fact in our final example of solid bridges.

It is also worth noting that allowing for a distribution of bond lengths at the time of bonding (i.e., allowing bonds to form such that they immediately exert a force on the top plate either to the left or to the right with some probability) can lead to additional physics. Using a similar model, initial bond stretching has been shown to enhance or suppress diffusion of the moving plate (Sridhar et al., 2021). The primary focus of this paper is characterizing the possible viscous and friction like forces induced by the transient bonding, and so these effects will be ignored for now. However, in future work it would be interesting to study the stochastic bond model when both dissipative mechanisms are present.

2.2. Steady state dissipation rate

We now intend to articulate some of the basic tools of probability theory and give a heuristic argument for the equation relating the steady state dissipation rate of the model system to bonding energy and the bonding/unbonding rates (full proofs can be found in Appendix C). Let t_{off} and $\{t_{2i-1}\}_{i=1}^{\infty}$ be independent and identically distributed (iid) bonding times drawn from the distribution $p_{off}(t) = \kappa_{on} \exp(-\kappa_{on}t)$ and let t_{on} and $\{t_{2i}\}_{i=1}^{\infty}$ be iid unbonding times with distribution $p_{on}(t)$. The impact of bond interaction will enter through this unbonding time distribution as well as through the equation for the dissipation. Let $T_n := \sum_{i=1}^n t_n$ be the time of the *n*th event, and $T_0, t_0 := 0$. The collection of times $\{t_n\}_{n=0}^{\infty}$ describes the complete bonding hords at time $T_1 = t_1$. Then it waits time t_2 before unbonding again at time $T_2 = t_1 + t_2$. The remaining times in the sequence $\{T_n\}_{n=0}^{\infty}$ are labeled similarly.

The dissipation of a single bond after *n* events (i.e., after time T_n) is then given by

$$D_n = \sum_{i=1}^{\lfloor n/2 \rfloor} \phi(Vt_{2i}),$$

where $\lfloor x \rfloor$ is the largest integer less than *x*, as the dissipation only occurs during unbonding (even-indexed times). In order to investigate the dissipation after a given total time *T*, we introduce the random index $N_T := \inf\{n \mid T_n \ge T\}$ which is the index of the first time such that $T_n \ge T$. In other words, $N_T - 1$ is the total number of bondings and unbondings which have occurred by time *T*. With this definition, the dissipation due to a single bonding site after a time *T* is given by

$$D_T = \sum_{i=1}^{\lfloor (N_T - 1)/2 \rfloor} \phi(Vt_{2i}).$$

As mentioned previously, we are interested in the macroscopic behavior of a large number of bonds. For such systems, the total macroscopic dissipation is dominated by the average behavior of an individual bond: $D_T^{tot} \approx N \langle D_T \rangle$, where *N* is the number of bonds and $\langle \cdot \rangle$ denotes averaging over the distribution of the total bonding history $\{t_i\}_{i=0}^{\infty}$ of an individual bond (we will also use $\langle \cdot \rangle_{on}$ and



(b)

Fig. 1. (a) A sketch of the stochastic bonds model. Bonds form with a rate κ_{on} , are stretched by the shearing of the two plates, and break with rate $\kappa_{off}(t)$ causing the stored elastic energy to dissipate. (b) The first few times of a model trajectory of a single bond. Odd-indexed lowercase times t (e.g. $t_1, t_3, t_5, ...$) denote times spent unbonded (solid blue). Even-indexed lowercase times (e.g. $t_2, t_4, t_6, ...$) denote times spent bonded (dashed black). Capital T_n , denote the total time past after n bonding and unbonding events. For any given time T (shown in red), N_T is the trajectory dependent index such that N_T is the smallest n so that $T_n \ge T$.

 $\langle \cdot \rangle_{\text{off}}$ to denote the average with respect to the densities $p_{\text{on}}(t)$ and $p_{\text{off}}(t)$, respectively). We observe that the average dissipation of a single bond limits to a linear function of time, characteristic of a system tending to a non-equilibrium steady state with a constant dissipation rate per bond. Hence, we define the steady state dissipation rate of a single bond as

$$\dot{D}_{SS} := \lim_{T \to \infty} \frac{d}{dT} \langle D_T \rangle.$$
(1)

We will refer to this quantity as the steady state dissipation rate throughout. $N\dot{D}_{SS}$ can be viewed as the energy per unit time necessary to keep the macroscopic system in steady state. It is the behavior of \dot{D}_{SS} and its dependence on the velocity V which will later help us interpret the resulting macroscopic material behavior as a function of the bonding energy and kinetic rates.

Equation (1) alone is not suitable for deriving a connection between the steady state dissipation rate and the microscopic features of the model because the average defining $\langle D_T \rangle$ is over all possible bonding histories up until time *T*. Although not impossible, computing this average is a challenge even for simple unbonding distributions. In order to form a more workable equation, we first use a fact about differentiable functions: if $\lim_{t\to\infty} f'(t)$ exists then $\lim_{t\to\infty} f'(t) = \lim_{t\to\infty} \frac{f(t)}{t}$ (Lemma C.1). Thus,

$$\dot{D}_{SS} = \lim_{T \to \infty} \frac{\langle D_T \rangle}{T}.$$
(2)

Using tools from the theory of martingales in probability theory, we prove in Appendix C.3 that the right hand side of (2) limits to

$$\lim_{T \to \infty} \frac{\langle D_T \rangle}{T} = \frac{\langle \phi(Vt_{\rm on}) \rangle_{\rm on}}{\langle t_{\rm off} \rangle_{\rm off} + \langle t_{\rm on} \rangle_{\rm on}}.$$

Putting the two together shows that

$$\dot{D}_{ss} = \lim_{T \to \infty} \frac{\langle D_T \rangle}{T} = \frac{\langle \phi(V t_{\text{on}}) \rangle_{\text{on}}}{\langle t_{\text{off}} \rangle_{\text{off}} + \langle t_{\text{on}} \rangle_{\text{on}}}.$$
(3)

Equation (3) provides a more manageable means of computing the steady state dissipation rate as the averages on the right hand side correspond to individual bonding or unbonding events rather than the entire history. It tells us that the steady state dissipation rate is simply the average energy dissipated at a single bond rupture divided by the average length of time of a single bonding and unbonding cycle.

3. Results and discussion

In the following section we use Eq. (3) to explore the connection between the bond interaction potentials and bonding rates and the macroscopic dissipation of the system as a whole. First, we focus on the case when unbonding is independent of the applied force, where we are able to derive an equation for the average dissipation of a single bond as a function of time explicitly (including the transient behavior). Next, we incorporate force dependence through the so-called Bell model (Bell, 1978; Evans and Ritchie, 1997) and explore the limiting cases of low and high shear velocities.

3.1. Force independent unbonding

To begin, we first consider the case in which the unbonding rate is independent of the force on the bond. In this circumstance, the rate of unbonding is constant, and the lifetime of each bond is exponentially distributed, $p_{on}(t_{on}) = \kappa_{off} \exp(-\kappa_{off}t_{on})$. Using Eq. (3) it is straight forward to compute the steady state dissipation rate which arises from an arbitrary positive monomial interaction potential

$$\phi(x) = ax^p \quad (a, p > 0) \qquad \Rightarrow \qquad \dot{D}_{ss} = \frac{\langle a(t_{on}V)^p \rangle_{on}}{1/\kappa_{off} + 1/\kappa_{on}} = \frac{\kappa_{on}}{(\kappa_{off} + \kappa_{on})} \frac{\Gamma(p+1)}{\kappa_{per}^{p-1}} aV^p, \tag{4}$$

where $\Gamma(p+1)$ is the gamma function which evaluates to $\Gamma(p+1) = p!$ when *p* is a non-negative integer, although the equation holds for any *p* positive. Equation (4) extends to interactions consisting of polynomials in *x* with positive coefficients linearly. In the case of a spring interaction, $\phi(x) = \frac{1}{2}Kx^2$, the steady state dissipation rate is given by

$$\dot{D}_{ss} = \frac{\kappa_{\rm on}}{\kappa_{\rm off} + \kappa_{\rm on}} \frac{K}{\kappa_{\rm off}} V^2 = \rho_{\rm on} \tau_{\rm on} K V^2,$$

where $\rho_{on} = \kappa_{on}/(\kappa_{off} + \kappa_{on})$ is the average fraction of bonds which are bonded and $\tau_{on} = 1/\kappa_{off}$ is the average life time of a single bond. As this is the expected dissipation rate for a single bond, a large system consisting of *N* identical and independent bonds can be expected to reach a steady state dissipation rate of $N\rho_{on}\tau_{on}KV^2$, which is macroscopically characteristic of a Newtonian fluid, as the dissipation rate depends quadratically on the shear velocity. This is almost exactly the result derived by Tawada and Sekimoto (1991) (it is off by a factor of 2 as they have taken the average energy lost at the bond rupture to be $\frac{1}{2}k\langle t_{on}V\rangle_{on}^2$, i.e., the energy lost at the average length $\langle t_{on}V\rangle_{on}$ at rupture, versus $\langle \frac{1}{2}K(t_{on}V)^2\rangle_{on}$ which is the average energy of the bond at rupture) and Eq. (4) can be viewed as a generalization of their result to arbitrary polynomial bonding interactions.

Perhaps the most exciting feature of Eq. (4) is the direct link it provides between the bonding potential and the macroscopic dependence of the steady state dissipation rate on the velocity. As already mentioned, a linear spring-like bonding energy causes the macroscopic system to dissipate energy like a Newtonian fluid. Alternatively, an energy which is linear in the bond length causes the macroscopic system to exert constant force against the shearing, analogous to classical Coulomb friction. However, the behavior is not restricted to just these two potentials. Using $p = 1 + \alpha$ for $\alpha \in (0, 1)$, we achieve a shear thinning power law fluid with viscosity proportional to the shear rate to the power $\alpha - 1$ (i.e., $\eta \propto \dot{\gamma}^{\alpha-1}$), and p > 2 corresponds to shear thickening fluids. Thus, this model shows that only a minor change of the bond interactions can lead to a wide range of macroscopic behavior.

It is worth noting that it is also possible to derive an expression for the average dissipation $\langle D_T \rangle$ at all times for a monomial interaction potential $\phi(x) = ax^p$ assuming that all of the bonds are initially unbonded (see Appendix B)

$$\langle D_T \rangle = aV^p \bigg(\sum_{n=1}^{\infty} \frac{n \kappa_{\text{onf}}^{n+1} \kappa_{\text{off}}^n T^{2n+1+p} p! \exp(-\kappa_{\text{off}}T)}{(2n+1+p)!} {}_1F_1(n+1, 2n+2+p; \Delta\kappa T) + \sum_{n=1}^{\infty} \frac{n \kappa_{\text{off}}^n \kappa_{\text{on}}^n T^{2n+p} p! \exp(-\kappa_{\text{on}}T)}{(2n+p)!} {}_1F_1(n+p, 2n+1+p; -\Delta\kappa T) \bigg),$$
(5)

where $_{1}F_{1}(a,b;x) := \sum_{m=0}^{\infty} \frac{(a+m-1)!(b-1)!}{(b+m-1)!(a-1)!} \frac{x^{m}}{m!}$ is Kummer's confluent hypergeometric function (Abramowitz et al., 1988, chapter 13) and $\Delta \kappa = \kappa_{\text{off}} - \kappa_{\text{on}}$. When the two bonding rates are equal ($\kappa_{\text{on}} = \kappa_{\text{off}} =: \kappa$) and for the particular case of the spring interaction $\phi(x) = \frac{1}{2}Kx^{2}$ it reduces to

$$\left\langle D_T \right\rangle = \frac{1}{2} \frac{K V^2}{\kappa^2} \left(\kappa T - \beta(T) \right)$$

where the transient $\beta(T)$ is given by

$$\beta(T) = \frac{5}{2} - 2(1 + \kappa T) \exp(-\kappa T) - \frac{1}{2} \exp(-2\kappa T).$$

As a means of verification, we have conducted kinetic Monte Carlo (KMC) simulations of the stochastic bonding and unbonding process in order to compare the analytical result for the average dissipation per bond to averages of randomly generated trajectories (see Appendix A for details of the KMC simulations). This comparison is shown in Fig. 2(a) for various choices of rates and bonding potentials, and it is clear that there is good agreement between both methods.



Fig. 2. (a) A comparison of the exact expression for the average dissipation per particle assuming force independence as shown in Eq. (5) (lines) and an empirical average of 10,000 KMC simulations each (scattered points). The time axis is normalized by the expected time of one bonding and one unbonding event $\tau = \frac{1}{\kappa_{eff}} + \frac{1}{\kappa_{eff}}$, and the dissipation is normalized by the dissipation after time $T_{max} = 5\tau$ in steady state: $T_{max} D_{SS}$. The comparison shows excellent agreement over all choices of κ_{on} , κ_{off} , V, and $\phi(x)$ (simulation 1: $\kappa_{on} = 0.3$, $\kappa_{off} = 1.0$, V = 0.5, $\phi(x) = 2.4x^2$, simulation 2: $\kappa_{on} = 3.0$, $\kappa_{off} = 0.2$, V = 0.1, $\phi(x) = x^3$, simulation 3: $\kappa_{on} = 1.0$, $\kappa_{off} = 1.0$, V = 1.0, $\phi(x) = x^{1.5}/5$, simulation 4: $\kappa_{on} = 1.0$, $\kappa_{off} = 1.0$, V = 1.0, $\phi(x) = x^2/2$, simulation 5: $\kappa_{on} = 0.3$, $\kappa_{off} = 0.2$, V = 2.0, $\phi(x) = x^{0.3}$). (b) A comparison of the steady state dissipation rate versus normalized velocity for a system with Lennard-Jones interaction potential with depth *E*, constant width $\sigma = 1$, and force dependent unbonding. Scattered points denote the values obtained from kinetic Monte Carlo simulations (average dissipation is determined from line denote those obtained through the Eq. (11).

3.2. Force dependent unbonding

Next, we consider the case of force dependent bond dissociation. Including force dependence is a necessary step for accurately modeling many of the systems mentioned in the introduction (Chaudhury, 1999; Wei, 2014; Vernerey et al., 2018; Yang et al., 2020; Song et al., 2021). In Chaudhury (1999), Yang et al. (2020), and Song et al. (2021) the dependence of the dissociation rate on the applied force is assumed to be governed by the Bell model which we describe shortly (see also Bell (1978) and the introduction of Evans and Ritchie (1997)). A reaction rate equation describing the time dependent mean volume (or area) density of active bonds is then solved and utilized to study macroscopic material properties such as energy dissipated and damage evolution during rupture of an adhesive. In Vernerey et al. (2018), a similar reaction rate equation is solved, but instead the rate of bond dissociation is assumed to increase quadratically in the force. Finally, Wei (2014) makes use of the Bell model, but assumes the system remains near equilibrium so as to work directly with the Gibbs–Boltzmann distribution, and derives a traction-separation relation. Although more complex and accurate models for the force dependence of bond dissociation have been established following the reaction rate theory of Kramers (Kramers, 1940; Evans and Ritchie, 1997; Dudko et al., 2006; Freund, 2009) and the theory of first passage times (Szabo et al., 1980), we elect to use the Bell model since we are interested only in developing a qualitative understanding, and so we trade off accuracy for relative simplicity. However, it is worth noting that Eq. (3) is valid quite generally, only requiring a few assumptions on the probability densities $p_{on}(t_{on})$ and $p_{off}(t_{off})$, and it could be used to compute the steady state dissipation rate under any of these models for bond dissociation.

Under the Bell model, the rate of bond dissociation accelerates exponentially with the applied force. Symbolically,

$$\kappa_{\rm off}(F) = \kappa_{\rm off} \exp(a\beta F),$$

where *F* is the force exerted on the bond, *a* is the distance between the bond energy minimum and the transition state, and β is the inverse absolute temperature (Evans and Ritchie, 1997). Since the plates move at a constant relative velocity, it is useful to write the rate of unbonding as a function of the time spent bonded

$$\kappa_{\rm off}(t) = \kappa_{\rm off} \exp(\beta a F(V t)). \tag{6}$$

Using this equation, it is straightforward to derive the corresponding distribution of unbonding times. Denoting by S(t) the survival probability of bonds at time t (i.e., the fraction of bonds remaining at time t), S(t) is related to the unbonding rate through the ordinary differential equation

$$\frac{dS}{dt}(t) = -\kappa_{\rm off}(t)S(t). \tag{7}$$

Since S(t) is the probability that a bond survives longer than time t, 1 - S(t) is the probability that a bond breaks before time t, and the density of unbonding times can be found via (Durrett, 2019, Page 10)

$$p_{\rm on}(t) = -\frac{d}{dt}(1 - S(t)) = \kappa_{\rm off}(t)S(t).$$
(8)

Since all bonds are intact immediately after they form (i.e., S(0) = 1), Eq. (7) can be solved assuming $\kappa_{off}(t) \ge 0$ as

$$S(t) = \exp\left(-\int_0^t \kappa_{\rm off}(s)ds\right).$$

In the special case of $\kappa_{off}(t)$ given by (6), S(t) becomes

$$S(t) = \exp\left(-\int_0^t \kappa_{\text{off}} \exp(\beta a F(Vs)) ds\right).$$
(9)

Using Eqs. (8) and (9) shows that the density of times spent bonded is

$$p_{\rm on}(t) = \kappa_{\rm off} \exp\left(\beta a F(Vt)\right) \exp\left(-\kappa_{\rm off} \int_0^t \exp(\beta a F(Vs)) ds\right).$$
⁽¹⁰⁾

With this equation for the unbonding distribution we proceed as before with the force independent case. Equation (3) allows us to relate the steady state dissipation rate directly to the potential. The average dissipation from a single bond is

$$\langle D \rangle_{\rm on} = \int_0^\infty \phi(Vt) p_{\rm on}(t) d$$

and the average time spent bonded is

$$\langle t_{\rm on} \rangle_{\rm on} = \int_0^\infty t p_{\rm on}(t) dt$$

Therefore, after inserting Eq. (10) and integrating by parts, the steady state dissipation rate is given by

$$\dot{D}_{SS} = \frac{\int_0^\infty VF(Vt) \exp\left[-\kappa_{\text{off}} \int_0^t \exp(\beta aF(Vs))ds\right] dt}{\int_0^\infty \exp\left[-\kappa_{\text{off}} \int_0^t \exp(\beta aF(Vs))ds\right] dt + \frac{1}{\kappa_{\text{on}}}}.$$

In order to determine the impact of the many microscopic parameters of the model, it is helpful to rewrite this equation in terms of dimensionless quantities

$$\dot{d}_{SS} := \frac{\beta \dot{D}_{SS}}{\kappa_{\text{off}}} = \frac{\int_0^\infty f(ax) \exp\left[-\frac{1}{v} \int_0^x \exp(f(ay)) dy\right] dx}{\frac{1}{v} \int_0^\infty \exp\left[-\frac{1}{v} \int_0^x \exp(f(ay)) dy\right] dx + \frac{\kappa_{\text{off}}}{\kappa_{on}}},$$
(11)

where $f(ax) := a\beta F(ax)$ is the normalized force, x and y are unitless lengths, and $v := \frac{V}{a\kappa_{\text{off}}}$ is a normalized velocity. As in the force independent case, Eq. (11) allows us to directly relate the steady state dissipation rate to the interaction potential via the force f(ax). Fig. 2(b) compares the results of Eq. (11) to KMC simulations where the steady state dissipation rate is estimated through linear regression. It is clear that both the analytical values and those extracted from numerical simulations are in excellent agreement.

In order to better understand the relationship between d_{ss} and v, we investigate the quantity

$$P := \frac{d \log(\dot{d}_{SS})}{d \log(v)}$$

which we will refer to as the phase. This definition is motivated by the force independent case where we have shown that an interaction potential of the form $\phi(x) = ax^p$ induces a steady state dissipation rate $\dot{D}_{SS} = bV^p$ for some constant *b* independent of *V*. In this case, $\log(\dot{d}_{SS}) = p\log(v) + \log(c)$ for some *c* independent of *v*, so $P := \frac{d\log(d_{SS})}{d\log(v)} \equiv p$ is independent of *a* and the bonding rates. Moreover, the phase indicates the model's macroscopic behavior at a particular ($\frac{v(v)}{v}$) velocity v. For example, if $P(v_0) = 2$, the system behaves like a Newtonian fluid for $v \approx v_0$. If $P(v_0) \in (1,2)$ then the system behaves like a shear-thinning fluid. The plots shown in Fig. 3 depict the dependence of the phase on the normalized velocity and the normalized stiffness ($k = af'(0) = a^2\beta F'(0)$) of the interaction potential for three standard interatomic potentials: spring (harmonic), Lennard-Jones, and the soft Coulomb (see Fig. 5 for visuals and Appendix C.4 for the algebraic forms of these potentials). The diagrams reveal that these three potentials lead to qualitatively similar macroscopic behaviors. In each case, for fixed stiffness and (non-dimensional) shear velocity low enough, the system has a phase value of two, meaning that the system behaves like a Newtonian fluid. As the velocity increases, the value of the phase drops and the system behaves like a shear thinning fluid. For even higher shear velocities, the phase value hits one and then decreases below one.

The fact that each of these systems has a phase value of two for low velocities is directly connected to our analysis in the force independent case. To illustrate this point, Fig. 4 shows the same diagrams, but instead compares quadratic, cubic, and quartic interaction potentials. These plots contain a few differences not present for the previous interatomic potentials. In the limit of low shear velocities, the phase of the quadratic, cubic and quartic potential tend to two, three, and four, respectively. This occurs because at low velocities most bonds break before the bond can be stretched to the point that it feels a meaningful force, and thus the bonding kinetics closely approximate the force independent case. In the case of a Lennard-Jones and the soft Coulomb interactions, the low shear velocities also implies that most bonds are never stretched very far away from the local minimum at zero stretch. Both the Lennard-Jones and the soft Coulomb have lowest order quadratic approximations and hence behave like harmonic spring potentials at low velocities.

The previous diagrams intentionally cover many decades of dimensionless shear velocities in order to examine the full range of possible behavior. It is also worth examining shear rates and kinetic parameters which correspond to realistic systems and achievable experiments. Using the kinetic and bonding parameters listed in Barel et al. (2010) ($\kappa_{on} = \omega_{on} \exp(-E_{on}/k_BT)$ and $\kappa_{off} = \omega_{off} \exp(-E_{off}/k_BT)$ with $\omega_{on} = \omega_{off} = 10^{10} \text{ s}^{-1}$, $E_{on} = 0.05 \text{ eV}$, $E_{off} = 0.15 \text{ eV}$, and T = 300 K, and a = .25 nm, V = 10 - 10000 m

Journal of the Mechanics and Physics of Solids 158 (2022) 104660



Fig. 3. Plots of the phase *P* against normalized velocity *v* and normalized stiffness (k := af'(0)) for a harmonic spring, Lennard-Jones, and soft Coulomb potentials (algebraic forms of the potentials used are listed in Appendix C.4). For both the Lennard-Jones and the soft Coulomb potentials, the potential height, *E*, and the potential width, σ , were chosen so that $\frac{E}{\sigma^2} = K$ and the ratio of the *E* to σ remained fixed ($a\beta$ was taken to be one).



Fig. 4. Phase diagrams comparing the harmonic spring, cubic, and quartic potentials. Since f'(x) vanishes for the cubic and quartic potentials, stiffness here corresponds to the value of the first non-vanishing derivative of the normalized force $k = \frac{d^n}{dx^n} f(ax)\Big|_{x=0} = a^n f^{[n]}(0)$. In each case, $\lim_{v\to 0} P(v) = p$ where $\phi(x) \propto x^p$ as in the force independent case.



Fig. 5. Plots of the Lennard-Jones (a) and soft-Coulomb (b) potentials in blue. The red dashed line depicts the limiting height of the potential E, and the x-axis is scaled by the width of the potential σ .

nm/s) which were originally used to model sliding friction between a crystalline surface and an Atomic Force Microscope (AFM) tip, the resulting phase diagram is shown in Fig. 6 (larger scanning velocities are used to show where shear thinning begins). We see that the physical regime (circled in red in the phase diagram) corresponds with the low and mid-range shear rates mentioned previously. For potentials with quadratic approximations to their minimum, this corresponds to a Newtonian fluid at low shear rates which eventually becomes shear thinning at higher shear rates. Since most interaction potentials fit this criteria, this model predicts that in most systems, stochastic bonds will lead to a Newtonian fluid or a shear thinning fluid like response to applied shear. As a comparison, Fig. 6b shows the shear thinning behavior of the stochastic bond model together with three other standard shear thinning fluid models: the Eyring model, the Carreau model, and the limiting stress model (Mate and Carpick, 2019, Chapter 3).



Fig. 6. (a) Phase diagram for a system with a soft Coulomb interaction using kinetic and bonding parameters taken from Barel et al. (2010) (specifically $\kappa_{on} = \omega_{on} \exp(-E_{on}/k_BT)$ and $\kappa_{off} = \omega_{off} \exp(-E_{off}/k_BT)$ with $\omega_{on} = \omega_{off} = 10^{10} \text{ s}^{-1}$, $E_{on} = 0.05 \text{ eV}$, $E_{off} = 0.15 \text{ eV}$, and T = 300 K, and a = .25 nm, V = 10 - 10000 nm/s). The region corresponding to values near these are circled by the red ellipse. Except for near very large stiffness of the AFM tip, the phase is predominantly P = 2 signifying a Newtonian fluid behavior. (b) A comparison of the effective viscosity predicted for the stochastic bond model with three common shear thinning models: the Eyring model, the Carreau model, and the limiting stress model ($\eta_{Eyring} = 30.6 \text{ kPa s}$, $\dot{\gamma}_{Eyring} = 13400 \text{ s}^{-1}$, $\eta_{Carreau} = 30.8 \text{ kPa s}$, $\dot{\gamma}_{Carreau} = 12300 \text{ s}^{-1}$, $n_{Carreau} = 0.47$, $\eta_{limiting stress} = 30.7 \text{ kPa s}$, $\dot{\gamma}_{limiting stress} = 42800 \text{ s}^{-1}$). Kinetic and bonding parameters are the same as those used for the phase diagram. A spring interaction with K = 6 N/m, a distance h = 1 nm between the AFM tip and the crystalline surface, and a bond concentration of $c := N/\pi r^2 = 20/\pi (10)^2 \approx 0.064$ nm⁻² using the estimation of 20 bonds on the AFM tip (Barel et al., 2010) and an AFM tip with radius 10 nm (Mate and Carpick (2019) page 33). The effective viscosity is then $\eta = \frac{c \cdot hD_{SS}}{V}$ is the steady state stress and $\frac{V}{h}$ is the shear rate. All models have qualitatively similar behavior, but the Eyring model obtains the best fit to the viscosity given by the steady state dissipation rate equation.

3.2.1. Low shear velocity limit

We turn our attention to deriving approximations to the steady state dissipation rate in both the low and high shear rate limit. In the limit of low shear rates, the force dependence of the unbonding rate is dominated by the behavior of the potential near its minimum since bonds rupture due to thermal fluctuations (encoded in the intrinsic unbonding rate κ_{off}) before they can stretch far with high probability. Thus, for many interactions the behavior at low shear rates is well approximated by the behavior of a spring interaction with effective spring constant $K_{eff} = F'(0)$. In this case, by explicitly computing the integral in Eq. (10), we find that the unbonding distribution is a Gompertz distribution

$$p_{\rm on}(t) = \kappa_{\rm off} \exp(-\frac{\kappa_{\rm off}}{\omega} \exp(\omega t) + \omega t + \frac{\kappa_{\rm off}}{\omega}),\tag{12}$$

where $\omega = a\beta K_{\text{eff}}V$ is the scale parameter and $\kappa_{\text{off}}/\omega$ is the shape parameter. The mean time spent bonded is then

$$\langle t_{\rm on} \rangle_{\rm on} = \frac{1}{\omega} \exp(\frac{\kappa_{\rm off}}{\omega}) \int_{\frac{\kappa_{\rm off}}{\omega}}^{\infty} u^{-1} \exp(-u) du$$
(13)

and the average dissipation due to a single unbonding is proportional to the second moment

$$\langle D \rangle_{\rm on} = K_{\rm eff} V^2 \frac{\exp(\frac{\kappa_{\rm off}}{\omega})}{\omega^2} \int_1^\infty \frac{\log(u) \exp(-\kappa_{\rm off} u/\omega)}{u} du$$
(14)

(see Lenart (2014) Proposition 2). The functions

$$\int_{t}^{\infty} \frac{\exp(-u)}{u} du \tag{15}$$

and

$$\int_{1}^{\infty} \frac{\log(u) \exp(-tu)}{u} du \tag{16}$$

admit an expansion in powers of $\frac{1}{t}$ (see Appendix D for derivations). This allows us to investigate the limit as $V \to 0$ and $\kappa_{\text{off}}/\omega \to \infty$. Using these expansions for $\langle t_{\text{on}} \rangle_{\text{on}}$ and $\langle D \rangle$, and $\langle t_{\text{off}} \rangle_{\text{off}} = 1/\kappa_{\text{on}}$ gives

$$\dot{D}_{SS} = \frac{\rho_{\rm on} K_{\rm eff} V^2}{\kappa_{\rm off}} \left(1 - \frac{\omega}{\kappa_{\rm off}} (3 - \rho_{\rm on}) + \left(\frac{\omega}{\kappa_{\rm off}}\right)^2 (17 + \rho_{\rm on}^2 - 2\rho_{\rm on}) + \mathcal{O}(\omega^3) \right),\tag{17}$$

where $\rho_{on} = \kappa_{on}/(\kappa_{off} + \kappa_{on})$ is the force independent equilibrium fraction of active bonds. For $\omega \ll \kappa_{off}$ or $V \ll \frac{\kappa_{off}}{a\beta\kappa_{eff}}$, the steady state dissipation rate grows like V^2 , leading to a value of two for the phase. Higher order terms become relevant when $V \approx \frac{\kappa_{off}}{a\beta\kappa_{eff}}$ which explains why the yellow bands in Fig. 3 have a slope of negative one as this transition can also be written as

$$\log(v) = \log(\frac{V}{a\kappa_{\rm off}}) \approx -\log(a^2\beta K_{\rm eff}) = -\log(k_{\rm eff}).$$



Fig. 7. Theoretic densities of unbonding times as a function of normalized velocity of the top plate for a spring (a) with K = 1.0 and Lennard-Jones (b,c) interactions (E = 1.0, $\sigma = 10$). For the spring interaction, the probability density becomes highly peaked near zero and essentially vanishes for long times as $v \to \infty$ (legend of (a) applies here too). For the Lennard-Jones interaction, some fraction of bonds break rapidly, but the distribution tends to an exponential (as in the force independent case). The solid black line depicts an exponential distribution (the force independent distribution) for reference.

In the general case (i.e., bond interactions whose expansion about the minimum need not have a quadratic term), the force independent steady state dissipation rate gives the lowest order approximation in the force dependent case at low velocities. This can be seen by expanding the unbonding probability density and the interaction potential to the lowest order in V (here denoted by p). The resulting steady state dissipation rate is given by

$$\dot{D}_{SS} = \frac{\langle \phi(Vt_{\text{on}}) \rangle_{\text{on}}}{\langle t_{\text{on}} \rangle_{\text{on}} + \langle t_{\text{off}} \rangle_{\text{off}}} = \frac{\phi^{[p]}(0)(V/\kappa_{\text{off}})^p + \mathcal{O}(V^{p+1})}{\frac{1}{\kappa_{\text{off}}} + \frac{1}{\kappa_{\text{on}}} + \mathcal{O}(V)} = \frac{\rho_{\text{on}}}{\kappa_{\text{off}}^{p-1}} \phi^{[p]}(0)V^p + \mathcal{O}(V^{p+1}),$$

where $\phi^{[p]}(x)$ is the *p*th derivative of ϕ evaluated at *x* and $\mathcal{O}(V^{p+1})$ represents a term which goes to zero at least as fast as V^{p+1} as $V \to 0$. Moreover, examining the expansion for the unbonding probability density reveals that to lowest order, the unbonding density is an exponential (as in the force independent case) and the next order effect is to increase the probability of unbonding at short times $t < \frac{p}{\kappa_{\text{off}}}$ and reduce the probability of longer unbonding times $t > \frac{p}{\kappa_{\text{off}}}$ (for details see Appendix D.2).

3.2.2. High shear velocity limit

From the plots shown in Figs. 3 and 4 it is clear that in all cases the phase, and hence the strength of the dependence of the steady state dissipation rate on the shear rate, decreases dramatically as the shear rate increases for all values of the potential stiffness. However, there is a subtle difference between the behaviors of the steady state dissipation when the interaction potentials remain bounded for large separations versus when they become unbounded. In both cases, the large shear rates cause the bonds to experience a large force very quickly, accelerating bond dissociation. In the case of an unbounded interaction, all of the bonds dissociate rapidly. However, in the case of a bounded interaction, only some of the bonds dissociate rapidly, but the remainder are pulled to the plateau of the bonding potential. There, the force is greatly reduced and the unbonding distribution becomes approximately exponential as in the force independent limit. These two distinct behaviors are shown through the unbonding distributions of the spring (unbounded) and Lennard-Jones (bounded) in Fig. 7.

This manifests as distinctive behaviors for the steady state dissipation rate. Taking spring interaction with spring constant *K* as an example of an unbounded interaction, we can study the limiting behavior of the Gompertz distribution for $V \to \infty$ and $\kappa_{off}/\omega \to 0$. Using the result of Lenart (2014) (see proofs of corollaries one and two), we can expand the mean time bonded and the mean dissipation per bond to get an expansion for the steady state dissipation rate

$$\dot{D}_{SS} = \frac{\kappa_{\rm on}}{2Ka^2\beta^2} \left[\log(\frac{\omega}{\kappa_{\rm off}})^2 - \gamma_{\rm Euler}\log(\frac{\omega}{\kappa_{\rm off}}) + \gamma_{\rm Euler}^2 + \frac{\pi^2}{6} + o(1) \right],$$

where, $\gamma_{\text{Euler}} \approx 0.57722$ is the Euler–Mascheroni constant, and o(1) signifies a remainder going to zero as $\omega \to \infty$. This expansion parallels the work of Chaudhury (1999) who solved a reaction equation equivalent to Eq. (7) with unbonding rate given by the Bell model and a spring interaction (F = KVt), and found that the energy dissipated by the fracture of an adhesive at a polymer-glass interface is given by

$$G_{\rm el} = \frac{N}{2Ka^2\beta^2} \left[\log\left(\frac{\beta KVa}{n\kappa_{\rm off}}\right) \right]^2 = \frac{N}{2Ka^2\beta^2} \left[\log\left(\frac{\omega}{n\kappa_{\rm off}}\right) \right]^2.$$

This expression differs only by the prefactors of N, the total number of bonds, and κ_{on} since Chaudhury (1999) computes the total dissipated energy rather than the dissipation rate per bond, and a factor of n in the logarithm due to the fact that the polymers in the adhesives are described as having n links and hence n possible locations for rupture. Here, we have the benefit of an analytical expression for all the moments of the Gompertz distribution, thanks to the work of Lenart (2014), which allows us to expand the steady state dissipation rate per bond to higher orders. Given the parallels of the methodology, it may be possible to use the

techniques presented here to estimate the rate dependent fracture energy like the one calculated by Chaudhury (1999), but for different polymer bond energies.

Returning to our analysis, the fastest growing term grows like $\dot{D}_{SS} \propto \log(V^2)$ which becomes arbitrarily large in the limit of high velocities. However, in the case of an bounded potential $\phi(x) \leq \phi_{max}$, the steady state dissipation rate is also bounded as well,

$$\dot{D}_{SS} = \frac{\langle \phi(Vt_{\rm off}) \rangle}{\langle t_{\rm off} \rangle + \langle t_{\rm on} \rangle} \le \kappa_{\rm on} \phi_{\rm max}.$$

This explains why the phase tends to zero in all cases. In the case of the spring interaction, the largest term in \dot{D}_{SS} grows like $(\log(V))^2$ and hence when the dimensions are removed, $\dot{d}_{SS} \propto (\log(v))^2$ for large v. Thus $P = \frac{d}{d \log(v)} \log(\dot{d}_{SS}) \propto \frac{1}{\log(v)} \rightarrow 0$ as $v \rightarrow \infty$. Moreover, for the bounded potentials \dot{d}_{SS} is bounded. But if the phase P were larger than any $\alpha > 0$ for all v this would mean \dot{d}_{SS} would grow at least as fast as v^{α} and hence be unbounded: a contradiction. Thus, the phase must eventually tend to zero.

4. Applications to physical systems

4.1. Dynamic response and a connection to transient polymer networks.

Now we turn our focus to understanding the viscoelastic response of the stochastic bond model. To do this, we derive the system's response to an instantaneous displacement $\epsilon(t) = \epsilon H(t)$ where H(t) is the Heaviside step function

$$H(t) = \begin{cases} 0 & t < 0, \\ 1 & t \ge 0. \end{cases}$$

In other words, we derive the response to a stress relaxation experiment. Since the system experiences zero strain prior to time $t_0 = 0$, it will have had time to relax, and the probability of a bond being bonded at time $t_0 = 0$ is simply the equilibrium probability of being bonded

$$\rho_{\rm on} = \frac{\frac{1}{\kappa_{\rm off}}}{\frac{1}{\kappa_{\rm off}} + \frac{1}{\kappa_{\rm on}}}.$$

If a bond is not already bonded at time $t_0 = 0$, the instantaneous displacement will not have any effect and this bond will not contribute to the force on the top plate. If the bond is bonded, however, it will exert a force $F(\epsilon)$ against the displacement until it unbonds, after which it will no longer exert any force. Surviving bonds experience the force $F(\epsilon)$ and so their unbonding rate is accelerated to $\kappa(\epsilon) = \kappa_{\text{off}} \exp(a\beta F(\epsilon))$ giving an accelerated unbonding density

$$p_{\rm on}(t) = \kappa(\epsilon) \exp(-\kappa(\epsilon)t).$$

This means the fraction of bonds which existed at time $t_0 = 0$ and which are still intact by time t > 0 is $\exp(-\kappa(\epsilon)t)$. Thus, the average response of an individual bond to the instantaneous displacement is given by

$$\sigma(t) = \rho_{\rm on} F(\epsilon) \exp(-\kappa(\epsilon)t). \tag{18}$$

Equation (18) holds for any displacement ϵ . Fig. 8(a) shows Eq. (18) compared to the average force per bond in KMC simulations of an instantaneous displacement with 10,000 bonds.

Now, we use this result to derive the dynamic moduli, characterizing the system's response to small strains. To compute the dynamic moduli, we define a response function $G(t, \epsilon_M)$ which is dependent on the maximum strain ϵ_M as

$$G(t, \epsilon_M) := \frac{\rho_{\text{on}} F(\epsilon_M)}{\epsilon_M} \exp(-\kappa(\epsilon_M) t),$$

so that it is consistent with the theoretical response to a step displacement, i.e., for $\epsilon(t) = \epsilon_M H(t)$

$$\sigma(t) = \int_{-\infty}^{t} G(t-s,\epsilon_M) \dot{\epsilon}(s) ds.$$

We then write down the predicted response to the periodic driving $\epsilon(t) = \epsilon_M \sin(\omega t)$

$$\begin{aligned} \sigma(t) &= \int_{-\infty}^{t} G(t - s, \epsilon_M) \epsilon_M \omega \cos(\omega s) ds \\ &= \frac{\rho_{\text{on}} F(\epsilon_M) \omega^2 \kappa(\epsilon_M)}{(\omega^2 + \kappa(\epsilon_M)^2)} \sin(\omega t) + \frac{\rho_{\text{on}} F(\epsilon_M) \kappa(\epsilon_M) \omega}{(\omega^2 + \kappa(\epsilon_M)^2)} \cos(\omega t). \end{aligned}$$

Hence, the system has dynamic moduli

$$G'(\omega, \epsilon_M) = \frac{\rho_{\text{on}} F(\epsilon_M) \omega^2}{\epsilon_M \left(\omega^2 + \kappa(\epsilon_M)^2\right)}$$
(19)
$$G''(\omega, \epsilon_M) = \frac{\rho_{\text{on}} F(\epsilon_M) \omega \kappa(\epsilon_M)}{\epsilon_M \left(\omega^2 + \kappa(\epsilon_M)^2\right)},$$
(20)



Fig. 8. (a) A comparison of the predicted and simulated average response to relaxation tests at various strains. The analytic formula (Eq. (18)) is shown in the line, and the simulated data in the scattered markers. There is excellent agreement for all choices of strain ϵ . (b,c) A comparison of the predicted dynamic moduli and those observed from simulations of periodic driving over a range of frequencies. We use a soft Coulomb potential with energy height E = 1.0 and width $\sigma = 1.0$. (b) For small strains well within the linear regime of the interaction ($\epsilon = 0.08$ is plotted here), there is very good agreement with the predicted Maxwell model behavior. (c) For finite strains ($\epsilon = 2.0$ plotted), non-linearities cause the fit to lose its quantitative predictability. However, the response remains qualitatively similar.

which corresponds to the well studied Maxwell material with spring constant $E := \frac{\rho_{on}F(\epsilon_M)}{\epsilon_M}$ and relaxation time $\tau := \frac{1}{\kappa(\epsilon_M)}$. In the limit of infinitesimal strains $F(\epsilon_M)/\epsilon_M \to F'(0)$ and $\kappa(\epsilon_M) \to \kappa_{off}$, and hence a strain independent description can only be applied when the interaction is harmonic about its minimum (so that $\phi''(0) = F'(0) \neq 0$). Fig. 8b,c depicts a comparison of Eqs. (19) and (20) against the dynamic moduli gathered from KMC simulations of periodic driving. We find that at low strains Eqs. (19) and (20) accurately predict the response to periodic driving. However, for larger strains, there is disagreement. This is likely both due to nonlinear effects that large strains (and hence larger stresses) induce on the unbonding distribution, as well as due to the assumption that the amplitude of the driving (ϵ_1 in $\epsilon(t) = \epsilon_1 \sin(\omega t)$) should correspond to the maximum amplitude in the instantaneous displacement (ϵ_2 in $\epsilon(t) = \epsilon_2 H(t)$ and we assume that we should compare the case of $\epsilon_1 = \epsilon_2$).

Finally, it is worth mentioning two observations. The first is that a Maxwell material behavior is consistent with our previous analysis of the steady state behavior. When subjected to a constant strain rate, a Maxwell material is expected to flow as a Newtonian fluid. This is also the prediction of the steady state behavior for bonds with interactions admitting a harmonic expansion (which are also the bonds for which strain independent moduli can be defined). Thus the two findings are mutually compatible. Second, we note that the crossover point of G' and G'' marks the inverse relaxation time (set $G'(\omega) = G''(\omega)$ and solve to get $\omega = \kappa(\epsilon_M)$ in this case). Thus, the unbonding rate κ_{off} could be found experimentally by finding the crossover frequency in the limit of zero strain.

An exponential decay response is a common occurrence among polymer networks with transient cross-links (Long et al., 2013; Yang et al., 2015). Maxwell type material behavior has already been shown to be the limiting response of a continuum model for these networks in the limit of no permanent cross-links (i.e., only stochastic bonds with short average bonding and unbonding times) (Vernerey et al., 2017) and for ideal reversible polymer networks (Parada and Zhao, 2018). Moreover, in the regime of finite strains, the increase and flattening of the dynamic moduli prior to the crossover time is qualitatively similar to the behavior of biopolymer actin networks as described in Broedersz et al. (2010). Although the quantitative power law dependence of 1/2 shown in Broedersz et al. (2010) is not observed, this could be explained by the lack of long lasting bonds in the model we study here. Including long lasting bonds may improve the ability to model polymer networks, however our main focus is characterizing the dissipative rather than elastic behavior. Thus, it appears that the simplified model can indeed help elucidate the mechanical properties resulting from transient cross-links. Perhaps the connection between bonding interaction on the microscale and macroscopic material behavior could be of use for those seeking to engineer networks with desirable mechanical response.

4.2. Solid bridges in granular media

We conclude by applying the stochastic bond model to a study of "solid bridges" which arise in polydisperse granular media subject to transient hydrodynamic forces (Seiphoori et al., 2020). We use this model to predict the rate of energy dissipation due to the rupture of inter-particle bonds in geomaterials involved in various geophysical flow processes such as slow-moving landslides (e.g., Highland et al. (2008)). Many natural and industrial materials are composed of particles of various size and are subject to intermittent cycles of wetting and drying. As liquid evaporates from a polydisperse colloidal suspension, smaller particles (size \leq 5 µm) tend to condense within the shrinking capillary bridges between larger grains and the substrate or one grain to another. After full evaporation, smaller particles act as inter-grain bonds, giving rise to an effective cohesion. Such bonds, referred to as solid bridges, can form mechanically stable aggregates that resist subsequent rewetting and shear flow. Understanding the mechanical stability of aggregates composing such systems is essential for predicting their macroscopic mechanical and transport behavior. The collapse and erosion of natural soils results from disintegration of aggregates when inter-particle bonds are reduced (Barthes and Roose, 2002; Li et al., 2019).

Here we perform experiments by creating a bidisperse aggregate system composed of 20-µm and 3-µm particles, where smaller particles ring larger grains and connect them to the substrate through solid bridges. We then use an Atomic Force Microscope



Fig. 9. (a) Microscopic images of a 20 μm microsphere in a monodispersed and bidispersed solution which originally appeared in Seiphoori et al. (2020) Figure 2. Also included is an illustration of the AFM pull-off experiment. The tip of the AFM approaches and attaches to the 20 μm microsphere. The epoxy is allowed to solidify at which point the cantilever arm is retracted, pulling the 20 μm microsphere away from the substrate and the solid bridge in the particle assembly from a bidisperse solution. Similar illustrations originally appeared in Figure 5.B of the same article. These figures were published under the Creative Commons CC BY-NC-ND license. (b) Force versus displacement data for an adhesion, monodisperse, and bidisperse pull-off experiment.

(AFM) to measure the force required to pull a 20 μ m bead out off its solid bridge (see Appendix E for details). Fig. 9 shows both an illustration of the experiment as well as the resulting force versus displacement data from the pull-off experiment.

To model this experiment, we combine the interactions between the AFM tip and the microsphere and that between the substrate and the microsphere into a single force which we describe as a spring with spring constant K_{eff} . The solid bridge is modeled as a number of kinetic bonds (estimated around 30 from microscopic images) which we assume have a spring interaction with spring constant K_{bond} . These bonds are in series with the effective AFM/substrate spring force and so if there are *N* bonds in the solid bridge at a given time, the total spring constant of the whole system is $K_{\text{tot}} = \frac{NK_{\text{bond}}K_{\text{eff}}}{NK_{\text{bond}}+K_{\text{eff}}}$. Using the force versus displacement data shown in Fig. 9(b), we split the data up into seven sections defined by the seven

Using the force versus displacement data shown in Fig. 9(b), we split the data up into seven sections defined by the seven approximately linear and decreasing pieces. We interpret these linear pieces as periods of constant number of bonds in the solid bridge and the nonlinear portions of the plot as periods of bond formation or breaking. From each linear piece, we extract the slope as the observed spring constant for that section, labeled K_{obs}^i for i = 1, ..., 7. Then, we use these to fit the total number of bonds N_{tot} and the two spring constants, K_{eff} , K_{bond} as follows. For fixed values of N_{tot} and K_{eff} , we assume the first effective spring constant corresponds to all N_{tot} bonds formed (i.e., $N_1 := N_{tot}$), and so we use the equation

$$K_{\rm obs}^{1} = \frac{N_1 K_{\rm bond} K_{\rm eff}}{N_1 K_{\rm bond} + K_{\rm eff}}$$

to solve for K_{bond} . For the remaining effective spring constants K_{obs}^i , i = 2, ..., 7, we choose the integer N_i such that $N_i K_{\text{bond}} K_{\text{eff}} / (N_i K_{\text{bond}} + K_{\text{eff}})$ is closest to K_{obs}^i , which gives a best estimate for the number of surviving bonds during the portion of the experiment where K_{obs}^i is observed. The fit is then scored by summing the squares of the distance between the predicted and observed effective spring constants

$$G(N_{\text{tot}}, K_{\text{eff}}) = \sum_{i=1}^{7} \left(K_{\text{obs}}^{i} - \frac{N_i K_{\text{bond}} K_{\text{eff}}}{N_i K_{\text{bond}} + K_{\text{eff}}} \right)^2$$

and the best fit is chosen as the minimizer of this quantity. The best fit over the range $N_{tot} \in [1, 35] \cap \mathbb{Z}$ and $K_{eff} \in [0.03, 0.08]$ (N/m) is shown in Fig. 10(a). The observed spring constants and their uncertainty (computed using standard error prorogation through the least squares regression formula assuming 3% error in the force measurement (Seiphoori et al., 2020)) are shown in black and the allowable effective spring constants depicted by the red lines (i.e., those corresponding to integer number of bonds). The best fit model parameters are $N_{tot} = 25$, $K_{eff} = 68$ (nN/µm), $K_{bond} = 2$ (nN/µm). We put an upper bound on the number of bonds N_{tot} , because as N_{tot} increases the effective spring constants allowed become more dense to the point where any observed spring constant is approximated well. An upper bound on the number of bonds is necessary to avoid this erroneous overfitting. We choose 35 as a maximum so as to be consistent with our microscopic observations.

We now turn to using the predicted K_{bond} , K_{eff} , and N_i to estimate the kinetic parameters of the bonds. Using the N_i and the displacement data of the experiment, we can write the observed number of active bonds as a function of time N(t) which is piecewise constant during the periods of constant number of bonds, and linearly interpolating during periods when bonds are breaking or forming. The force on a single bond as a function of time is

$$F(t) = \frac{K_{\rm eff}K_{\rm bond}Vt}{N(t)K_{\rm bond} + K_{\rm eff}},$$



Fig. 10. (a) This plot shows the fit for the observed spring constants. The black crosses show the experimentally observed spring constants and the blue lines those corresponding to an integer number of bonds. Vertical black lines show the error in the observed spring constant assuming 3% error in force measurement (Seiphoori et al., 2020). The fit shown uses $N_{tot} = 25$, $K_{eff} = 68$ ($nN/\mu m$), $K_{bond} = 2$ ($nN/\mu m$). Note that bonding and unbonding often occurs many at a time. (b) A comparison of the observed number of active bonds taken from data and the empirical average over 100,000 KMC simulations of the pull-off experiment using the MLE parameters. The best fit rates are $\kappa_{on} = 3.47$ s⁻¹, $\kappa_{off} = 4.17$ s⁻¹, and $F_c = 1.99$ nN. (c) A KMC simulation of the pull-off experiment using the base of the cantilever arm. There is strong qualitative resemblance to the experimental data in shown in Fig. 9(b). (d) The empirical average of the same three quantities as a function of time using 100,000 KMC simulations.

where $V = 8.97 \,\mu\text{m/s}$ is the velocity of the base of the cantilever. To predict κ_{on} , κ_{off} , and the critical force $F_c := (a\beta)^{-1}$ at which unbonding is accelerated, we use maximum likelihood estimation, a standard method of parameter estimation in statistics (Rossi, 2018, p. 226). The maximum likelihood estimator (MLE) for the parameters κ_{on} , κ_{off} , and F_c is defined as follows. The likelihood function of κ_{on} , κ_{off} , and F_c is defined as the probability density of observing N(t) assuming the solid bridge model with these specific parameters

$$\ell(\kappa_{\text{on}}, \kappa_{\text{off}}, F_c) := p_{\text{SB}}(N(t) \mid \kappa_{\text{on}}, \kappa_{\text{off}}, F_c),$$

(see Appendix F for details in computing $p_{\text{SB}}(N(t) \mid \kappa_{\text{on}}, \kappa_{\text{off}}, F_c)$). The MLE is then the set of parameters which maximize the likelihood function

$$\hat{\kappa}_{\text{on}}, \hat{\kappa}_{\text{off}}, \hat{F}_c := \operatorname*{argmax}_{\kappa_{\text{on}}, \kappa_{\text{off}}, F_c} \ell(\kappa_{\text{on}}, \kappa_{\text{off}}, F_c).$$

In other words, the MLE is the set of parameters which is mostly likely to have brought about the observed data. Using the N(t) constructed from the solid bridge data, the MLE for the parameters is $\hat{\kappa}_{on} = 3.47 \text{ s}^{-1}$, $\hat{\kappa}_{off} = 4.17 \text{ s}^{-1}$, and $\hat{F}_c = 1.99 \text{ nN}$.

Using the estimated spring constants, number of bonds, kinetic properties, and critical force, we can use KMC simulations to generate force versus displacement plots mirroring the pull-off experiment (see Appendix A for details on the KMC simulations). We make one final assumption in generating simulated data. Since the microsphere forming the solid bridges between the 20 μ m particle and the substrate is 3 μ m in diameter, we assume that once the simulated bonds comprising the solid bridge are stretched beyond 3 μ m, broken bonds are no longer able to reform. An example simulation is plotted in Fig. 10(c). There is good qualitative agreement with the experimental data from Fig. 9(b). At early times, the force on the AFM cantilever is almost linear with small deviations due to unbonding. This is followed by a rapid flattening of the force on the cantilever, as well as a shortening of the length of each linear section as the number of active bonds drops below 10. Finally, there is a large discontinuous decreases in force as the last bonds break away. Using KMC simulations, we can also numerically estimate the number of active bonds, the force on the AFM cantilever, and the force on a single bond as a function of displacement averaged over many simulated experiments. These



Fig. 11. The effective potential energy for the solid bridge as a function of bond displacement and the unbonding probability density as a function of time spent bonded for a landslide velocity of (a) 10 μ m/s \approx .86 m/day and (b) 3 μ m/s \approx .26 m/day.

empirical averages are shown in Fig. 10(d). Additionally, the average number of active bonds is plotted in Fig. 10(b) along with the observed number of active bonds taken from the experimental data to show the goodness of fit of the MLE parameters. Some features of interest in the plot of empirical averages include an average peak force on the cantilever of around -20 nN which occurs at a displacement of -1.25 µm. In Fig. 10(c), the force on a single bond gradually increases until the final bond ruptures when it discontinuously jumps down to zero. The empirical average however, begins to slowly decrease after a displacement of 2 µm. This suggests that a significant number of simulated solid bridges ruptured on or after being pulled 2 µm. By this point, the magnitude of the force on a single bond is around 2.5 nN, and the rate of unbonding has accelerated by a factor of $\exp(F/F_c) = \exp(2.5/1.99) \approx 3.5$. One noticeable difference between the model and the experiment is the large non-linear increases in the force on the cantilever in the single simulation (Fig. 10(c)). This is likely due the fact that our model uses a constant rate of bonding. Since a newly reformed bond immediately experiences the force from the cantilever, a bonding rate which decreases with the magnitude of the applied force would likely be more appropriate. Additionally, the model supposes that each of the bonds are independent aside from their effect on the force felt. However, our fit for the number of active bonds at a given time N(t) suggests that multiple bonds break and reform together. A simple way one might try to model this is to group multiple bonds together as one effective bond which breaks and reforms as a group.

Finally, we use our model of the solid bridge rupture to give an estimate for the rate of energy dissipation due to solid bridges in the landslide example. Such systems may feature large grains or blocks of geomaterials moving under a steady state velocity (e.g., on the order of meter per day) (Highland et al., 2008) where the formation and rupture of transient bonds between the moving objects and the substrate (i.e., the hillslope or ground surface) is inevitable. While such cohesive bonds have a complex nature, the solid bridging and adhesion are likely the dominant microscopic mechanisms (Seiphoori et al., 2020). We approximate the dissipation due to the repeated rupture of such microscopic bonds using our steady state dissipation rate equation. Although originally formulated within the parallel plate geometry of the stochastic bond model, the derivation of the equation itself does not depend on this geometry. Instead, all that is necessary are repeated cycles of bonding and unbonding, an effective energy of the bonds, and the assumption that the system as a whole has converged to steady state.

Solid bridges form when a polydisperse system undergoes wetting and subsequent drying. Thus, we approximate $1/\kappa_{on}$ as the mean time between wetting and drying cycles (order of days or 10^5 s) and use an exponential distribution for the time spent unbonded, $p_{off}^{sb}(t_{off}) = \kappa_{on} \exp(-\kappa_{on}t_{off})$, as before. To approximate the distribution of times spent bonded, we use KMC simulations to compute an empirical cumulative distribution function (CDF). We run these simulations with a pulling velocity of $V = 10 \ \mu m/s$ or about 0.86 m/day which is our assumed average velocity of the larger particles sliding downhill. To write the approximation mathematically, suppose for each simulation, labeled i = 1, ..., M, that $\{t_i\}_{i=1}^M$ are the times at which the solid bridge breaks and does not reform. We approximate the empirical CDF as

$$\mathrm{CDF}^{\mathrm{sb}}(t) = \frac{\#\{i \mid t_i < t\}}{M}.$$

We then approximate this function with a cubic spline through 200 evaluation points, and differentiate the result to get an approximate probability density of times spent bonded, $p_{on}^{sb}(t_{on})$. In order to compute an effective potential for the solid bridge, $\phi^{sb}(x)$, we compute the average force on the solid bridge conditioned on the solid bridge still being formed and then numerically integrate to get a potential. The distribution of times spent bonded and the effective potential for the solid bridge is shown in Fig. 11(a). Plugging these quantities into the Eq. (3) gives

$$\dot{D}^{\rm sb} \approx \frac{3.46 \times 10^{-14}}{0.255 + 1/\kappa_{\rm on}} \frac{\rm J}{\rm s}$$

as the average rate of energy dissipation per particle which can form a solid bridge. When we plug in the order of magnitude estimate of $\kappa_{on} \approx 10^{-5} \text{ s}^{-1}$ we obtain $\dot{D}^{sb} \approx 3.5 \times 10^{-19}$ W. We can repeat the process with a slower pulling velocity of 3 μ m/s $\approx .26$

m/day to investigate the extent to which a slower flow velocity impacts the dissipation rate. The effective potential and unbonding distribution for $V = 3 \ \mu\text{m/s}$ is shown in Fig. 11(b). The resulting dissipation rate per bond is $\dot{D}^{\text{sb}} \approx \frac{2.20 \times 10^{-14}}{(0.738+1/\kappa_{\text{on}})}$ W or approximately 2.2×10^{-19} W using the order of magnitude estimate for κ_{on} . Despite using a velocity which is one third as fast, the dissipation rate per atom is only reduced to two thirds its value for $V = 10 \ \mu\text{m/s}$. Since we expect zero dissipation at zero velocity, this hints that there is a non-quadratic relationship between the velocity and the dissipation rate for this system.

5. Conclusion

We have shown that the stochastic formation and breaking of bonds is capable of producing a wide range of macroscopic material behavior in response to shear depending on the nature of the bond interaction and the bond kinetics. In particular, the model presented here offers an explanation for the occurrence of Newtonian viscosity and shear thinning rheology as most bond interactions in solids are locally quadratic about their minimum. Modifying this interaction gives a direct way to alter the macroscopic rheology and provides a means of designing materials with desired dissipative properties. The analytical formula for the steady state dissipation rate gives a rapid means of creating a phase diagram for a given interaction potential, which can also assist in the design process. Moreover, the model is readily extendable to more accurate models of force dependent unbonding (as well as time or force dependent bonding). Although we have studied the effects of force dependence under the Bell model, the same procedure may be followed to study other models of force or time dependent bond breaking and reforming, so long as one can obtain the rates of bonding and unbonding as a function of the time (i.e., $\kappa_{off}(t)$ and/or $\kappa_{on}(t)$). One such extension could incorporate a dependence of the unbonding rate on the normal force, which is an important feature of sliding friction. It may be possible to include this dependence within the force dependent unbonding rate. We have also presented applications of the stochastic bond model to both polymer networks and polydisperse granular media to highlight the model's utility despite its simplicity. Further work could reveal the full range of possible dissipative responses for these systems and others, such as interlayer forces in graphene or sliding friction between solids.

CRediT authorship contribution statement

Travis Leadbetter: Conception or design of the work, Acquisition, analysis, or interpretation of data for the work, Drafted the work and revised it critically for important intellectual content, Agree to be accountable for all aspects of the work in ensuring that questions related to the accuracy or integrity of any part of the work are appropriately investigated and resolved. **Ali Seiphoori:** Conception or design of the work, Acquisition, analysis, or interpretation of data for the work, Drafted the work and revised it critically for important intellectual content, Agree to be accountable for all aspects of the work in ensuring that questions related to the accuracy or integrity of any part of the work are appropriately investigated and resolved. **Celia Reina:** Conception or design of the work, Acquisition, analysis, or interpretation of data for the work, Drafted the work and revised it critically for important intellectual content, Agree to be accountable for all aspects of the work and revised it critically for important intellectual content, Agree to be accountable for all aspects of the work and revised it critically for important intellectual content, Agree to be accountable for all aspects of the work in ensuring that questions related to the accuracy or integrity of any part of the work are appropriately investigated and resolved. **Parshant K. Purohit:** Conception or design of the work, Acquisition, analysis, or interpretation of data for the work, Drafted the work and revised it critically for important intellectual content, Agree to be accountable for all aspects of the work and revised it critically for important intellectual content, Agree to be accountable for all aspects of the work and revised it critically for important intellectual content, Agree to be accountable for all aspects of the work and revised it critically for important intellectual content, Agree to be accountable for all aspects of the work in ensuring that questions related to the accuracy or integrity of any part of the work a

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Kinetic Monte Carlo simulations

Kinetic Monte Carlo algorithms are a standard technique to simulate transitions between discrete states when the transition rates are known in advance (Bortz et al., 1975; Gillespie, 1977; Prados et al., 1997). Here, we use a rejection free kinetic Monte Carlo (KMC) algorithm to model the bonding an unbonding within the stochastic bond model presented in Section 2.1. In all cases except the simulations of the granular solid bridges, every bonding site is independent and so systems of many bonding sites can be simulated by repeatedly simulating one bonding site.

To perform these simulations, it will be necessary to generate random times with a distribution given by the probability density

$$p_{\rm on}(t) = \kappa_{\rm off}(t) \exp\left(-\int_0^t \kappa_{\rm off}(s) ds\right),$$

from random numbers which are uniformly distributed on the unit interval. To do this, one must find an invertible function $U : (0,1) \rightarrow (0,\infty)$ such that if X is a random number uniformly distributed on the interval (0,1), then U(X) has a distribution given by $p_{on}(t)$. If t_{on} is a random time with density $p_{on}(t)$, then the density $p_{on}(t)$ is determined through the derivative of the probability that t_{on} is less that a given time t,

$$p_{\rm on}(t) = \frac{d}{dt} \mathbb{P}(t_{\rm on} < t).$$

Thus, if we select the function *U* such that $\mathbb{P}(U(X) < t) = \mathbb{P}(t_{on} < t)$, U(X) will have the correct distribution. Since $p_{on}(t) = 0$ for t < 0, we can integrate to get

$$\mathbb{P}(t_{\text{on}} < t) = \int_{0}^{t} p_{\text{on}}(s) ds$$

= $\int_{0}^{t} \kappa_{\text{off}}(s) \exp\left(-\int_{0}^{s} \kappa_{\text{off}}(u) du\right) ds$
= $\int_{0}^{t} -\frac{d}{ds} \exp\left(-\int_{0}^{s} \kappa_{\text{off}}(u) du\right) dt$
= $1 - \exp\left(-\int_{0}^{t} \kappa_{\text{off}}(s) ds\right).$

This means we want to pick U so that

$$\mathbb{P}(U(X) < t) = 1 - \exp\left(-\int_0^t \kappa_{\text{off}}(s) ds\right).$$

Since we assume U is invertible, U(X) < t if and only if $X < U^{-1}(t)$, and hence $\mathbb{P}(U(X) < t) = \mathbb{P}(X < U^{-1}(t))$. As X has a uniform distribution on (0, 1), $\mathbb{P}(X < x) = x$ for any $x \in (0, 1)$. This means $\mathbb{P}(U(X) < t) = \mathbb{P}(X < U^{-1}(t)) = U^{-1}(t)$ since $U^{-1}(t) \in (0, 1)$ by definition. Putting these facts together gives

$$U^{-1}(t) = \mathbb{P}(U(X) < t) = 1 - \exp\left(-\int_0^t \kappa_{\text{off}}(s)ds\right).$$

This determines U^{-1} as a function of t. To get the function U, we label $U^{-1}(t)$ as x and t as U(x) solve for U(x) which gives

$$\int_0^{U(x)} \kappa_{\rm off}(s) ds = \log\left(\frac{1}{1-x}\right).$$

By defining the utility function inverse_integral which given a positive number *y*, and a positive, continuous function $g : [0, \infty) \rightarrow (0, \infty)$ outputs

inverse_integral(y, g) =
$$G^{-1}(y)$$
 where $G(u) = \int_0^u g(s) ds$,

we can write

$$U(x) = \text{inverse_integral} \left(\log \left(\frac{1}{1-x} \right), \kappa_{\text{off}}(s) \right).$$

Since 1 - X also has a uniform distribution if X does, we may use instead

$$U(x) = \text{inverse_integral} \left(\log \left(\frac{1}{x} \right), \kappa_{\text{off}}(s) \right).$$

Hence, if *X* has a uniform distribution on (0, 1), t = U(X) defined this way has distribution $p_{on}(t)$.

Then, the code for a single bonding site simulation goes as follows

A	gorithm	1:	Single	Bond	KMC	Simulation
---	---------	----	--------	------	-----	------------

1 In	put: float tFinal, float kOn, function kOff;				
2 t ·	$\leftarrow 0.0$;				
3 times ← [];		<pre>/* initialize sequence of times */</pre>			
4 W	hile $t < tFinal$ do				
5	$u1 \leftarrow unif_random(0,1);$	/* generate two uniform random numbers in $[0,1]$ */			
6	$u2 \leftarrow unif_random(0,1);$				
7	$tOff \leftarrow \log(1/u1)/kOn$;	/* transform into a exponentially distributed time */			
8	$tOn \leftarrow inverse_integral(log(1/u2), kOff);$	/* transform into unbonding time */			
9	$t \leftarrow t + tOff;$				
10	Append t to times;				
11	$t \leftarrow t + tOn;$				
12	Append t to times;				
is end					
14 Output: times;					

Here, tFinal is the desired stopping time, kOn= κ_{on} is the bonding rate, and kOff= $\kappa_{off}(t)$ is the time dependent unbonding rate. The result is a collection of times at which each bonding and unbonding occurred, times = $\{T_i\}_{i=1}^N$, with $T_N > tFinal$ from which the steady state dissipation rate can be calculated using the formulas given in Section 2.2. Multiple bonds can be simulated by repeatedly generating independent trajectories.

In order to simulate the breaking of solid bridges, a slightly more complex algorithm is necessary since the bonds are no longer independent (the applied force depends on the number of attached bonds). Assuming that the base of the AFM cantilever moves with velocity V, that the interaction between the microsphere and the cantilever tip and substrate has a spring constant of K_{eff} , that each bond of the solid bridge has a spring constant K_{bond} , and that there are N(t) active bonds at time t, the force on an individual bond as a function of time is given by

$$F(t) = \frac{K_{\text{bond}} K_{\text{eff}} V t}{N(t) K_{\text{bond}} + K_{\text{eff}}}.$$
(A.1)

Since the number of active bonds is stochastic, we define the force as a function of time and N the number of active bonds F(t, N). The algorithm can be broken up into 4 steps: (1) store the equation for the sum of the rates of all possible transitions as a function of time, (2) randomly generate the time until the next bonding or unbonding event using the total rate, (3) randomly select whether the event is a bonding or an unbonding with the proper weighting, (4) update the simulation time and number of active bonds and repeat these steps until the terminating time.

We now go through steps in more detail. At a given step, the known quantities are the time T at the start of the step are the total number of bonds N_{tot} , and the number of active bonds N. The rate of unbonding as a function of time for each active bond is

$$\kappa_{\text{off}}(s) = \kappa_{\text{off}} \exp(a\beta F(T+s, N))$$

whereas the rate of bonding is simply κ_{on} . Thus the total rate starting at time *T*, defined as the sum of all the rates, is

$$\kappa_{\text{tot}}(s) = N \kappa_{\text{off}} \exp(a\beta F(T+s, N)) + (N_{\text{tot}} - N)\kappa_{\text{on}}$$

To get the time step, we generate a uniform random number in (0, 1), u, and find the Δt such that

$$\int_0^{\Delta t} \kappa_{\rm tot}(s) ds = \log(1/u)$$

(i.e., we compute $\Delta t \leftarrow \text{inverse_integral}(\log(1/u), \kappa_{\text{tot}})$). Finally, the next step is chosen to be a bonding with probability

$$p = \frac{(N_{\rm tot} - N)\kappa_{\rm on}\Delta t}{\int_0^{\Delta t} \kappa_{\rm tot}(s)ds}$$

or an unbonding with probability

1

$$-p = \frac{\int_0^{\Delta t} N \kappa_{\text{off}} \exp(a\beta F(t+s), N) ds}{\int_0^{\Delta t} \kappa_{\text{tot}}(s) ds}.$$

The algorithm is shown in Algorithm 2. Here, Ntot is the total number of bonds to be simulated, force is the force on an individual bond as a function of the total time passed and the current number of active bonds, and fCritical is $F_c = (a\beta)^{-1}$ as described in

Section 4.2. The output is the length of time between each event as in Algorithm 1 as well as a list of the number of active bonds at each step.

Algorithm 2: KMC simulation of a solid bridge pull-off experiment							
1 Input: Float tFinal, float kOn, function kOff, int Ntot, function force, float fCritical;							
2 t	<i>←</i> 0.0;						
3 N	factive \leftarrow Ntot;	<pre>/* start with all bonds bonded */</pre>					
4 times \leftarrow [t,];		<pre>/* initialize sequence of times */</pre>					
5 b	onds \leftarrow [Nactive,];	<pre>/* initialize sequence of bonds */</pre>					
6 W	while $t < tFinal$ do						
	<pre>/* generate two uniform random numbers in [0,1]</pre>	*/					
7	$u1 \leftarrow unif_random(0,1);$						
8	$u2 \leftarrow unif_random(0,1);$						
9	totalRate(s) \leftarrow Nactive kOff exp(force(s + t,Nactive)/fCritical) + (Ntot - Nactive) kOn ;						
10	$\Delta t \leftarrow inverse_integral(log(1/u1), totalRate);$						
11	kOffTotal $\leftarrow \int_0^{\Delta t}$ Nactive kOff exp(force(s + t, Nactive)/fCritical)ds;						
12	$kOnTotal \leftarrow \Delta t$ (Ntot - Nactive) $kOn;$						
13	if u2 < kOnTotal/(kOnTotal + kOffTotal) then						
14	$\Delta n \leftarrow +1;$						
15	else						
16	$\Delta n \leftarrow -1;$						
17	end						
18	$t \leftarrow t + \Delta t;$						
19	Nactive \leftarrow Nactive $+ \Delta n$;						
20	Append t to times;						
21	Append Nactive to bonds;						
22 end							
23 Output: times, bonds;							

Appendix B. Dissipation equation: force independent case

When the rate of unbonding is independent of the applied force it is possible to derive a closed form expression for the average dissipation as a function of time. The distributions of bonding time and unbonding times are both exponential

$$p_{\text{on}}(t) = \kappa_{\text{off}} \exp(-\kappa_{\text{off}} t)$$
$$p_{\text{off}}(t) = \kappa_{\text{on}} \exp(-\kappa_{\text{on}} t)$$

1.01

where $\kappa_{on} \neq \kappa_{off}$ in general. We fix an interaction $\phi(x) = ax^p$ for some a, p > 0 and we use the fact that the stopping time N_T is finite with probability one (proven in Appendix C) to write the average of D_T as the sum of the average of D_T when $N_T = n$ for $n = 0, 1, \dots$. We then split up the cases when N_T is even and when N_T is odd into two separate sums

$$\langle D_T \rangle = \left\langle \sum_{j=1}^{\lfloor (N_T - 1)/2 \rfloor} \phi(V t_{2j}) \right\rangle$$

= $\sum_{n=0}^{\infty} \sum_{j=1}^{\lfloor (n-1)/2 \rfloor} \langle \phi(V t_{2j}) \mathbb{1}_{N_T = n} \rangle$
= $\sum_{n=1}^{\infty} n \left(\langle \phi(V t_2) \mathbb{1}_{(N_T = 2n+1)} \rangle + \langle \phi(V t_2) \mathbb{1}_{(N_T = 2n+2)} \rangle \right).$ (B.1)

In the last line we have used the fact that for each $j = 1, 2, ..., \lfloor n/2 \rfloor$ the random variables $\phi(Vt_{2j})\mathbb{1}_{N_T=n}$ and $\phi(Vt_2)\mathbb{1}_{N_T=n}$ have the same distribution and hence the same expectation. Breaking up the sum in this way is a necessary step because N_T is also a random variable, and so specifying its value changes the random sum into a deterministic sum. Let $p_{on}^{[m]}(s)$ denote the density of the sum of *m* independent random times with density p_{on} (Durrett (2019) Theorem 2.1.16),

$$p_{\text{on}}^{[m]}(S) = \underbrace{p_{\text{on}} * \cdots * p_{\text{on}}}_{\text{m times}}(S),$$

where * denotes the convolution of two functions

$$f * g(x) = \int_{-\infty}^{\infty} f(y)g(x-y)dy.$$

Since $p_{on}(s) = \kappa_{off} \exp(-\kappa_{off} s)$ for $s \ge 0$ we can directly compute the convolution

$$p_{\text{on}}^{[2]}(S) = p_{\text{on}} * p_{\text{on}}(S) = \int_{-\infty}^{\infty} \kappa_{\text{off}} e^{-\kappa_{\text{off}} s} \kappa_{\text{off}} e^{-\kappa_{\text{off}}(S-s)} \mathbb{1}_{s \ge 0} \mathbb{1}_{S-s \ge 0} ds$$

$$= \kappa_{\text{off}}^2 \exp(-\kappa_{\text{off}} S) \int_{-\infty}^{\infty} \mathbb{1}_{s \ge 0} \mathbb{1}_{S-s \ge 0} ds$$
$$= \kappa_{\text{off}}^2 \exp(-\kappa_{\text{off}} S) \int_{0}^{S} ds$$
$$= \kappa_{\text{off}}^2 S \exp(-\kappa_{\text{off}} S).$$

Likewise, one can show by induction that $p_{\text{on}}^{[m]}(S) = \kappa_{\text{off}}^m S^{m-1} \exp(-\kappa_{\text{off}} S)/(m-1)!$. Define $p_{\text{off}}^{[m]}(s)$ analogously. Now, we want to determine the expectation of $\phi(Vt_2)\mathbb{1}_{(N_T=2n+1)}$. In order for N_T to be equal to 2n + 1 for a given trajectory, it must be the case that $T_{2n} < T$ and $T_{2n+1} \ge T$. Thus, the sum of the first *n* times spend unbonded and first *n* times spent bonded must add up to some S < T, and the final time spent unbonded t_{2n+1} must be greater than or equal to T - S. Finally, to compute the expectation, we need the first time spend bonded t_2 to be less that T (i.e., $t_2 < T$). Next, we need the sum of the remaining n - 1 times spent bonded, call it T_{on} (which has density $p_{\text{on}}^{[n-1]}(T_{\text{on}})$), to be less than $T - t_2$. We also need the sum of the other *n* times spent unbonded, call this sum T_{off} (which has density $p_{01}^{[n-1]}(T_{\text{on}})$), to be less than $T - t_2 - T_{\text{on}}$. Lastly, we need t_{2n+1} to be greater than $T - t_2 - T_{\text{on}} - T_{\text{off}}$. Summing up all of the possibilities with their respective probabilities and multiplying by $\phi(Vt_2)$ to measure its expectation then gives

$$\langle \phi(Vt_2)\mathbb{1}_{(N_T=2n+1)} \rangle = \int_0^T dt_2 \int_0^T dt_{\text{on}} \int_0^{T-t_2-T_{\text{on}}} \int_0^\infty dt_{2n+1} \phi(Vt_2) p_{\text{on}}(t_2) p_{\text{on}}^{[n-1]}(T_{\text{on}}) p_{\text{off}}^{[n]}(T_{\text{off}}) p_{\text{off}}(t_{2n+1}). \tag{B.2}$$

Writing out $\phi(Vt_2) = aV^p t_2^p$, writing out the densities, and carrying out the integration for t_{2n+1} and T_{off} gives

$$\begin{split} \langle \phi(Vt_2) \mathbbm{1}_{(N_T = 2n+1)} \rangle &= \int_0^T dt_2 \int_0^T dT_{\text{on}} \int_0^{T-t_2 - T_{\text{on}}} a(Vt_2)^p \kappa_{\text{off}} e^{-\kappa_{\text{off}} t_2} \frac{\kappa_{\text{off}}^{n-1} T_{\text{on}}^{n-2} e^{-\kappa_{\text{off}} T_{\text{on}}}}{(n-2)!} \frac{\kappa_{\text{on}}^n T_{\text{off}}^{n-1} e^{-\kappa_{\text{on}} T_{\text{off}}}}{(n-1)!} e^{-\kappa_{\text{on}} T_{\text{off}}} \\ &= \frac{aV^p \kappa_{\text{off}}^n \kappa_{\text{on}}^n e^{-\kappa_{\text{on}} T}}{(n-2)!(n-1)!} \int_0^T dt_2 t_2^p e^{-\Delta \kappa t_2} \int_0^{T-t_2} dT_{\text{on}} T_{\text{on}}^{n-2} e^{-\Delta \kappa T_{\text{on}}} \int_0^{T-t_2 - T_{\text{on}}} dT_{\text{off}} T_{\text{off}}^{n-1} \\ &= \frac{aV^p \kappa_{\text{off}}^n \kappa_{\text{on}}^n e^{-\kappa_{\text{on}} T}}{(n-2)!n!} \int_0^T dt_2 t_2^p e^{-\Delta \kappa t_2} \int_0^{T-t_2} dT_{\text{on}} T_{\text{on}}^{n-2} (T-t_2 - T_{\text{on}})^n e^{-\Delta \kappa T_{\text{on}}}, \end{split}$$

where $\Delta \kappa = \kappa_{\text{off}} - \kappa_{\text{on}}$. We are left with an integral of the form

$$\int_0^x u^m (x-u)^n \exp(-ku) du$$

where $u = T_{on}$, $x = T - t_2$, and $k = \Delta \kappa$. We use the fact that the exponential admits an everywhere absolutely convergent Taylor series to expand and integrate term by term. After doing so, repeatedly integrating by parts yields the identity

$$\int_0^x u^m (x-u)^n \exp(-ku) du = \sum_{l=0}^\infty \frac{(-k)^l}{l!} \int_0^x u^{m+l} (x-u)^n du = \sum_{l=0}^\infty \frac{(-k)^l n! (m+l)! x^{m+n+l+1}}{l! (m+n+l+1)!}$$

We apply the equation twice to get

$$\langle \phi(Vt_2) \mathbb{1}_{(N_T = 2n+1)} \rangle = \frac{aV^p \kappa_{\text{off}}^n \kappa_{\text{on}}^n e^{-\kappa_{\text{on}}T}}{n!(n-2)!} \sum_{l=0}^{\infty} \sum_{k=0}^{\infty} \frac{(-\Delta \kappa)^{l+k} n!(n-2+k)!(p+l)! T^{2n+p+l+k}}{k!l!(2n+l+k+p)!}$$

Next, we rewrite the sums in terms of m = l + k and $k \le m$,

$$\begin{split} \langle \phi(Vt_2)\mathbb{1}_{(N_T=2n+1)} \rangle &= \frac{aV^p \kappa_{\text{off}}^n \kappa_{\text{on}}^n T^{2n+p} e^{-\kappa_{\text{on}} T}}{(n-2)!} \sum_{m=0}^{\infty} \sum_{k=0}^m \frac{(-\Delta\kappa T)^m (n-2+k)! (p+m-k)!}{k! (m-k)! (2n+m+p)!} \\ &= \frac{aV^p \kappa_{\text{off}}^n \kappa_{\text{on}}^n T^{2n+p} e^{-\kappa_{\text{on}} T}}{(n-2)!} \sum_{m=0}^{\infty} \frac{(-\Delta\kappa T)^m}{(2n+m+p)!} \sum_{k=0}^m \frac{(n-2+k)! (p+m-k)!}{k! (m-k)!} \end{split}$$

And finally, we apply a combinatorial identity $\sum_{k=0}^{m} \frac{(q+k)!}{k!} \frac{(p+m-k)!}{(m-k)!} = \frac{p!q!}{m!} \frac{(p+q+m+1)!}{(p+q+1)!}$ to the rightmost sum (set q = n-2) and rewrite the result in terms of a hypergeometric function

$$\begin{split} \langle \phi(Vt_2) \mathbbm{1}_{(N_T = 2n+1)} \rangle &= a V^p \kappa_{\text{off}}^n \kappa_{\text{on}}^n p! T^{2n+p} e^{-\kappa_{\text{on}} T} \sum_{m=0}^{\infty} \frac{(-\Delta \kappa T)^m}{(2n+m+p)!} \frac{(n+p+m-1)!}{m!(n+p-1)!} \\ &= \frac{a V^p \kappa_{\text{off}}^n \kappa_{\text{on}}^n p! T^{2n+p} e^{-\kappa_{\text{on}} T}}{(2n+p)!} {}_1 F_1(n+p,2n+1+p;-\Delta \kappa T), \end{split}$$

which is the equation we state in Eq. (5). For reference, the definition of the hypergeometric function is

$${}_{1}F_{1}(a,b;z) = \sum_{m=0}^{\infty} \frac{(a+m-1)!(b-1)!}{(a-1)!(b+m-1)!} \frac{z^{m}}{m!}.$$

This gives the formula for n > 1. It is straight forward to show that this formula also holds for n = 1 after removing the integration with respect to the variable T_{on} in Eq. (B.2). Following almost the exact same steps, one can also compute the expectation of $\phi(Vt_2)\mathbb{1}_{(N_T=2n+2)}$ as

$$\begin{split} &= \frac{aV^{p}\kappa_{\mathrm{on}}^{n+1}\kappa_{\mathrm{off}}^{n}e^{-\kappa_{\mathrm{off}}T}}{n!(n-2)!} \int_{0}^{T} dT_{\mathrm{off}} T_{\mathrm{off}}^{n}e^{\Delta\kappa T_{\mathrm{off}}} \int_{0}^{T-T_{\mathrm{off}}} dT_{\mathrm{on}} T_{\mathrm{on}}^{n-2} \int_{0}^{T-T_{\mathrm{off}}-T_{\mathrm{on}}} dt_{2} t_{2}^{p}} \\ &= \frac{aV^{p}\kappa_{\mathrm{on}}^{n+1}\kappa_{\mathrm{off}}^{n}e^{-\kappa_{\mathrm{off}}T}}{n!(n-2)!(p+1)} \int_{0}^{T} dT_{\mathrm{off}} T_{\mathrm{off}}^{n}e^{\Delta\kappa T_{\mathrm{off}}} \int_{0}^{T-T_{\mathrm{off}}} dT_{\mathrm{on}} T_{\mathrm{on}}^{n-2} (T-T_{\mathrm{off}}-T_{\mathrm{on}})^{p+1} \\ &= \frac{aV^{p}\kappa_{\mathrm{on}}^{n+1}\kappa_{\mathrm{off}}^{n}p!e^{-\kappa_{\mathrm{off}}T}}{n!(n+p)!} \int_{0}^{T} dT_{\mathrm{off}} T_{\mathrm{off}}^{n} (T-T_{\mathrm{off}})^{n+p}e^{\Delta\kappa T_{\mathrm{off}}} \\ &= \frac{aV^{p}\kappa_{\mathrm{on}}^{n+1}\kappa_{\mathrm{off}}^{n}p!e^{-\kappa_{\mathrm{off}}T}}{n!(n+p)!} \sum_{l=0}^{\infty} \frac{\Delta\kappa^{l}(n+p)!(n+l)!T^{2n+p+l+1}}{l!(2n+p+l+1)!} \\ &= \frac{aV^{p}\kappa_{\mathrm{on}}^{n+1}\kappa_{\mathrm{off}}^{n}p!T^{2n+1+p}e^{-\kappa_{\mathrm{off}}T}}{(2n+p+1)!} {}_{1}F_{1}(n+1,2n+2+p;\Delta\kappa T). \end{split}$$

Plugging these two results into Eq. (B.1) gives Eq. (5).

Appendix C. Proofs for steady state dissipation equation

C.1. Limit of a differentiable function of time

Lemma C.1. Let $f : [0, \infty) \to \mathbb{R}$ be a continuously differentiable function such that $\lim_{t\to\infty} f'(t) = C < \infty$ exists and is finite. Then $\lim_{t\to\infty} f'(t) = C = \lim_{t\to\infty} \frac{f(t)}{t}$.

Proof. Fix $\epsilon > 0$, and choose $t_0 \ge 0$ large enough such that $|f'(t) - C| < \epsilon/3$ for all $t \ge t_0$. Next, choose $t_1 > t_0$ such that $|\frac{f(t_0)}{t_1}| < \epsilon/3$ and $|\frac{Ct_0}{t_1}| < \epsilon/3$. Then, for all $t \ge t_1$ one has

$$\begin{aligned} |\frac{f(t)}{t} - C| &= |\frac{1}{t} \left(f(t_0) + \int_{t_0}^t f'(s) ds \right) - C| \\ &\leq |\frac{f(t_0)}{t}| + |\frac{1}{t} \int_{t_0}^t f'(s) ds - C| \\ &< \frac{\epsilon}{3} + \frac{1}{t} \int_{t_0}^t |f'(s) - C| ds + |\frac{1}{t} \int_{t_0}^t C ds - C| \\ &< \frac{2\epsilon}{3} + |C\frac{t_0}{t}| \\ &< \epsilon. \end{aligned}$$

Since ϵ was arbitrary, $\lim_{t\to\infty} \frac{f(t)}{t} = C$.

C.2. Mathematical background on probability and martingales

The theory of martingales is a core topic within the broader theory of probability. Like in the theory of sequences of numbers in mathematical analysis, martingale theory is a theory of sequences of random variables with "a martingale" being a sequence which is constant on average. Martingales often have nice convergence properties, a fact that we take advantage of in the proof of the equation for the steady state dissipation rate. We only give details necessary for a conceptual understanding of the proof in the following section. Durrett (2019), Chapter 4 gives a full introduction to the theory of martingales.

Rather than give the technical definition of a martingale, we give an illustrative example which will suit our purposes. Let $\{\xi_i\}_{i=1}^{\infty}$ be a sequence of random numbers. Often, one will assume that each of the ξ_i are independent of each other and have the same distribution, but that need not be the case. Next, let $\{X_i\}_{i=1}^{\infty}$ be a sequence of functions where X_i depends on the first *i* random numbers ξ_1, \ldots, ξ_i , i.e., $X_i = X_i(\xi_1, \ldots, \xi_i)$. The sequence $\{X_i\}_{i=1}^{\infty}$ is a martingale with respect to the random numbers $\{\xi_i\}_{i=1}^{\infty}$ if the absolute value of each X_i has finite expectation with respect to the randomness of the sequence $\{\xi_i\}_{i=1}^{\infty}$, i.e., $\langle |X_i(\xi_1, \ldots, \xi_i)| \rangle < \infty$ for each *i*, and if the conditional expectation of X_i given that we know ξ_1, \ldots, ξ_{i-1} is X_{i-1} , i.e.,

$$\langle X_i(\xi_1,\ldots,\xi_i) \mid \xi_1,\ldots,\xi_{i-1} \rangle = X_{i-1}.$$

This last condition can be thought of as saying our best guess as to the value of X_i given that we know ξ_1, \ldots, ξ_{i-1} is X_{i-1} , the previous function in the sequence. Note that if we know ξ_1, \ldots, ξ_{i-1} , the value of $X_{i-1} = X_{i-1}(\xi_1, \ldots, \xi_{i-1})$ is deterministic rather than random. If $\{X_i\}_{i=1}^{\infty}$ is a martingale, the "tower property" of conditional expectations (Durrett, 2019, Theorem 4.1.13), for any j < i ensures that

$$\langle X_i \mid \xi_1, \dots, \xi_j \rangle = X_j,$$

and

 $\langle X_i \rangle = \langle X_i \rangle,$

hence the analogy to sequences which are constant. In the following section, the bonding and unbonding times $\{t_i\}_{i=1}^{\infty}$ will play the role of the $\{\xi_i\}_{i=1}^{\infty}$, and a centered dissipation (the dissipation minus its expected value) $\{\tilde{D}_n\}_{n=1}^{\infty}$ will play the role of the $\{X_i\}_{i=1}^{\infty}$.

C.3. Proof of the steady state dissipation rate equation

Here, we prove Eq. (3) using tools from the theory of martingales. Recall the definitions of $\{t_{2i-1}\}_{i=1}^{\infty}, \{t_{2i}\}_{i=1}^{\infty}, \{T_n\}_{n=1}^{\infty}, N_T, D_n,$ and D_T from the text, where the times spent bonded $\{t_{2i}\}_{i=1}^{\infty}$ may be distributed with an arbitrary rate of unbonding $\kappa_{\text{off}}(t)$ (i.e., $p_{\text{on}}(t) = \kappa_{\text{off}}(t) \exp(-\int_0^t \kappa_{\text{off}}(s) ds)$). We also define the random variable

$$\tilde{D}_n = D_n - \lfloor n/2 \rfloor \langle \phi(Vt_{\text{on}}) \rangle_{\text{or}}$$

for $n \ge 1$ and $\tilde{D}_0 = 0$ which is a recentering so that $\langle \tilde{D}_n \rangle = 0$ for all *n*. We know that $\langle t_{\text{off}} \rangle_{\text{off}} = \frac{1}{\kappa_{\text{on}}} < \infty$, but we also assume that $\langle t_{\text{on}} \rangle_{\text{on}} < \infty$ and $\langle \phi(Vt_{\text{on}}) \rangle_{\text{on}} < \infty$ (i.e., that the average time spent bonded is finite and the average energy stored in a bond when it breaks is also finite). We first check that \tilde{D}_n is a martingale with respect to the sequence of times $\{t_i\}_{i=1}^{\infty}$. First,

$$\left\langle \left| \tilde{D}_n \right| \right\rangle = \left\langle \left| \sum_{i=1}^{\lfloor n/2 \rfloor} \phi(Vt_{2i}) - \lfloor n/2 \rfloor \left\langle \phi(Vt_{\text{on}}) \right\rangle_{\text{on}} \right| \right\rangle < n \left\langle \phi(Vt_{\text{on}}) \right\rangle_{\text{on}} < \infty,$$

so the finite expectation condition is satisfied. For *n* odd, n = 2j + 1, $\tilde{D}_{2j+1} = \tilde{D}_{2j}$ so we know that when we take the conditional expectation

$$\langle \tilde{D}_n \mid t_1, \dots, t_{n-1} \rangle = \langle \tilde{D}_{2j+1} \mid t_1, \dots, t_{2j} \rangle = \langle \tilde{D}_{2j} \mid t_1, \dots, t_{2j} \rangle = \tilde{D}_{2j} = \tilde{D}_{n-1}$$

yields the desired result (example 4.1.3 of Durrett (2019) allows us to remove the conditional expectation since \tilde{D}_{2j} is completely determined by t_1, \ldots, t_{2j}). Likewise, when *n* is even, n = 2j, we have

$$\begin{split} \langle \tilde{D}_{n} \mid t_{1}, \dots, t_{n-1} \rangle &= \left\langle \sum_{i=1}^{j} \phi(Vt_{2i}) - j \langle \phi(Vt_{on}) \rangle_{on} \middle| t_{1}, \dots, t_{2j-1} \right\rangle \\ &= \left\langle \sum_{i=1}^{j-1} \phi(Vt_{2i}) - (j-1) \langle \phi(Vt_{on}) \rangle_{on} + \phi(Vt_{2j}) - \langle \phi(Vt_{on}) \rangle_{on} \middle| t_{1}, \dots, t_{2j-1} \right\rangle \\ &= \langle \tilde{D}_{2j-1} \mid t_{1}, \dots, t_{2j-1} \rangle + \langle \phi(Vt_{2j}) \mid t_{1}, \dots, t_{2j-1} \rangle - \langle \phi(Vt_{on}) \rangle_{on} \\ &= \tilde{D}_{n-1} \end{split}$$

since t_{2j} is independent of t_1, \ldots, t_{2j-1} and so the conditional expectation is equal to the regular expectation (example 4.1.4 in Durrett (2019)). Thus, $\{\tilde{D}_n\}_{n=1}^{\infty}$ is a martingale with respect to the times $\{t_i\}_{i=1}^{\infty}$.

The goal of the next step is to show that $\langle \tilde{D}_{N_T} \rangle = 0$ for every T. For every $T \ge 0$, N_T is finite with probability one. To see this, fix a $T \ge 0$, and we will consider the probability that N_T is larger than some given n for n large (i.e., $\mathbb{P}(N_T > n)$). Assume that $\langle t_{on} \rangle_{on}$ and $\langle t_{off} \rangle_{off}$ are not zero. In this case, there is a length of time s > 0 and a $p \in (0, 1)$ such that the sum $t_{on} + t_{off}$ is greater than s with probability p, i.e., $\mathbb{P}(t_{on} + t_{off} > s) = p$. Let m = [T/s] ([x] is defined as the smallest integer larger than x) so that $m \ge T$. Let n > 2m and consider pairs of bonding and unbonding time $t_{2i-1} + t_{2i}$ for $1 \le i \le \lfloor n/2 \rfloor$. If at least m such pairs obey $t_{2i-1} + t_{2i} > s$, then $T_n = \sum_{i=1}^n t_i \ge ms \ge T$ and hence $N_T \le n$. But this means that for n > 2m, the probability that $N_T > n$ is bounded above by the probability that there are less than m such times that $t_{2i-1} + t_{2i} > s$. That is

$$\mathbb{P}(N_T > n) \le \mathbb{P}\left(\#\left\{i \mid 1 \le i \le \lfloor n/2 \rfloor, t_{2i-1} + t_{2i} > s\right\} < m\right)$$

Since $\mathbb{P}(t_{2i-1} + t_{2i} > s) = p$, $\mathbb{P}(t_{2i-1} + t_{2i} \le s) = 1 - p$, and each pair is independent, the right hand side can be computed by referring to a binomial distribution with $\lfloor n/2 \rfloor$ trials and probability p of success. The right hand side is then the probability of having less than m successes, so

$$\mathbb{P}\Big(\#\{i \mid 1 \le i \le \lfloor n/2 \rfloor, \ t_{2i-1} + t_{2i} > s\} < m\Big) = \sum_{j=0}^{m-1} \binom{\lfloor n/2 \rfloor}{j} p^j (1-p)^{\lfloor n/2 \rfloor - j}$$

Using p < 1, $\binom{\lfloor n/2 \rfloor}{j} \le (\lfloor n/2 \rfloor)^j \le (n/2)^m$, $(1-p)^{\lfloor n/2 \rfloor - j} \le (1-p)^{n/2-m}$, and m < n/2 gives a more useful bound for the right hand side

$$\sum_{j=0}^{m-1} \binom{\lfloor n/2 \rfloor}{j} p^j (1-p)^{\lfloor n/2 \rfloor - j} \le \sum_{j=0}^{m-1} \left(\frac{n}{2}\right)^m (1-p)^{n/2 - m} \le \left(\frac{n}{2}\right)^{m+1} (1-p)^{n/2 - m}$$

This shows that the probability that $N_T > n$ decays exponentially once *n* is large enough. Now, we need a technical lemma to show that the rapid decay in $\mathbb{P}(N_T > n)$ ensures that N_T has finite expectation.

Lemma C.2. Let N be a random variable taking values in the non-negative integers including possibly infinity, $N \in 0, 1, 2, ..., \infty$. Let p_n be the probability that N > n. If $\sum_{n=0}^{\infty} p_n < \infty$, then $\langle N \rangle < \infty$ and $\langle N \rangle = \sum_{n=0}^{\infty} p_n$.

Proof. First, it must be the case that the probability that $N = \infty$ is zero. To see this, assume the opposite. If $\mathbb{P}(N = \infty) = q > 0$ for some q, the $p_n \ge q$ for each n. But this means the sequence $\{p_n\}_{n=0}^{\infty}$ could not be summable, a contradiction. Since $\mathbb{P}(N_T = \infty) = 0$, we can write

$$\langle N\rangle = \sum_{n=0}^{\infty} n \mathbb{P}(N=n)$$

Writing $n\mathbb{P}(N_T = n) = \sum_{i=1}^n \mathbb{P}(N_T = n)$ gives

$$\langle N_T \rangle = \sum_{n=0}^{\infty} \sum_{j=1}^{n} \mathbb{P}(N=n).$$

Every term in the summand is positive, so we may rearrange the order without changing the result. We exchange the order as follows. We ignore the n = 0 term since it is an empty sum. For the remaining n, we arrange the summands so that as written, we sum over the columns

$$\sum_{n=0}^{\infty} \sum_{j=1}^{n} \mathbb{P}(N=n) = \sum \begin{pmatrix} \mathbb{P}(N=1) & \mathbb{P}(N=2) & \mathbb{P}(N=3) & \cdots \\ & \mathbb{P}(N=2) & \mathbb{P}(N=3) & \cdots \\ & & \mathbb{P}(N=3) & \cdots \\ & & & \ddots \end{pmatrix}.$$

By summing over the rows instead, one gets

$$\sum_{n=0}^{\infty}\sum_{j=1}^{n}\mathbb{P}(N=n)=\sum_{n=0}^{\infty}\sum_{j=n+1}^{\infty}\mathbb{P}(N=j)=\sum_{n=0}^{\infty}p_n,$$

and hence $\langle N \rangle = \sum_{n=0}^{\infty} p_n$. \Box Returning to the proof that N_T is finite, we compute $\sum_{n=0}^{\infty} \mathbb{P}(N_T > n)$.

$$\begin{split} \sum_{n=0}^{\infty} \mathbb{P}(N_T > n) &= \sum_{n=0}^{2m} \mathbb{P}(N_T > n) + \sum_{2m+1}^{\infty} \mathbb{P}(N_T > n) \\ &\leq 2m + 1 + \sum_{n=0}^{\infty} \left(\frac{n}{2}\right)^{m+1} \frac{(\sqrt{(1-p)})^n}{(1-p)^m}, \end{split}$$

where we exchanged $\mathbb{P}(N_T > n)$ for the bound we derived when n > 2m and extended the sum to zero. Factoring out the terms which do not depend on n in the sum on the second line leaves a sum of the form $\sum_{n=0}^{\infty} n^{m+1} x^n$ with $x = \sqrt{(1-p)} < 1$. It is well known that $\sum_{n=0}^{\infty} x^n = 1/(1-x)$ for |x| < 1. For such x, the sum on the right converges absolutely and the function on the left is infinitely differentiable and it's derivatives are all continuous. Differentiating and then multiplying by x term by term on the left and on the right gives the equality

$$\sum_{n=0}^{\infty} nx^n = x \frac{d}{dx} \frac{1}{1-x},$$

with the right hand side being an infinitely differentiable function for all |x| < 1 since both x and 1/(1-x) are. We repeatedly apply the operation $\left(x\frac{d}{dx}\right)$ to both sides a total of m+1 times to get

$$\sum_{n=0}^{\infty} n^{m+1} x^n = \left(x \frac{d}{dx} \right)^{m+1} \frac{1}{1-x}.$$
(C.1)

The right hand side is still infinitely differentiable for |x| < 1 and hence continuous for such x and so evaluating at $x = \sqrt{(1-p)} < 1$ yields a finite result. Plugging Eq. (C.1) into the bound for $\sum_{n=0}^{\infty} \mathbb{P}(N_T > n)$ yields

$$\sum_{n=0}^{\infty} \mathbb{P}(N_T > n) \le 2\ m+1 + \frac{1}{2^{m+1}(1-p)^m} \left[\left(x \frac{d}{dx} \right)^{m+1} \frac{1}{1-x} \right]_{x=\sqrt{1-p}} < \infty.$$

Thus, $\langle N_T \rangle < \infty$ which means that $N_T < \infty$ with probability one. N_T is a so-called stopping time (i.e., the set of trajectories where $N_T = n$ only depends on the first *n* times t_1, \ldots, t_n), so for each $n \ge 0$, $N_T \land n$ is also a stopping time (where $a \land b = \min(a, b)$). Since $\mathbb{P}(N_T \wedge n \leq n) = 1$ and every martingale is a submartingale (essentially by definition, see Durrett (2019) page 188), we can apply Theorem 4.4.1 of Durrett (2019) to conclude that

$$\langle \tilde{D}_0 \rangle \le \langle \tilde{D}_{N_T \wedge n} \rangle \le \langle \tilde{D}_n \rangle.$$

Since the left and right hand terms are zero, $\langle \tilde{D}_{N_T \wedge n} \rangle = 0$ for every *n*. Finally, since N_T is finite with probability one, $\tilde{D}_{N_T \wedge n} \rightarrow \tilde{D}_{N_T \wedge n}$ as $n \to \infty$ with probability one. Moreover, the definition of \tilde{D}_n consists of the difference of two terms which are monotonic in n, we can apply the monotone convergence theorem (Rudin, 1986, 1.26) to conclude

$$\lim_{n \to \infty} \langle \tilde{D}_{N_T \wedge n} \rangle = \langle \lim_{n \to \infty} \tilde{D}_{N_T \wedge n} \rangle = \langle \tilde{D}_{N_T} \rangle.$$

The left hand side is a sequence of zeros, so its limit is zero. Thus, $0 = \langle \tilde{D}_{N_T} \rangle$. Since T was arbitrary, this holds for all $T \ge 0$.

Now we examine what this means for
$$\langle D_T \rangle$$
. First, since $\langle D_{N_T} \rangle = 0$ we know that

$$\langle D_{N_T} \rangle = \Big\langle \sum_{j=1}^{\lfloor N_T/2 \rfloor} \phi(Vt_{2j}) \Big\rangle = \langle \lfloor N_T/2 \rfloor \rangle \langle \phi(Vt_{\text{on}}) \rangle_{\text{on}}.$$

When N_T is odd, $D_T = D_{N_T-1} = D_{N_T}$. When N_T is even, $D_T = D_{N_T} - \phi(Vt_{N_T})$. This means we have the bounds

$$\left(\frac{\langle N_T \rangle}{2} - 1\right) \langle \phi(Vt_{\text{on}}) \rangle_{\text{on}} - \langle \phi(Vt_{N_T}) \rangle \le \langle D_T \rangle \le \frac{\langle N_T \rangle}{2} \langle \phi(Vt_{\text{on}}) \rangle \tag{C.2}$$

since $n/2 - 1 \le \lfloor n/2 \rfloor \le n/2$ for all n.

In the next step, we repeat the process, but instead derive bounds for $\langle N_T \rangle$ using *T*. It is easier to work with the sums of pairs of bonding and unbonding times, $t_{2i-1} + t_{2i}$ rather than the times individually. Let $s_i = t_{2i-1} + t_{2i}$ for $i \ge 1$, let $S_n = \sum_{i=1}^n s_i$, and finally let $M_T = \inf\{n \mid S_n \ge T\}$. Note that by definition $N_T = 2M_T$ or $2M_T - 1$. Thus, M_T is also finite with probability one. By the same argument as above, $\tilde{S}_n = S_n - n\langle s_1 \rangle$ is a martingale with respect to the times $\{s_i\}_{i=1}^{\infty}$, and is also the difference of two monotone sequences in *n*. Hence, we can also conclude that

$$0 = \lim_{n \to \infty} \langle \tilde{S}_{M_T \wedge n} \rangle = \langle \lim_{n \to \infty} \tilde{S}_{M_T \wedge n} \rangle = \langle \tilde{S}_{M_T} \rangle,$$

and so

$$\langle S_{M_T} \rangle = \langle M_T \rangle \langle s_1 \rangle$$

By the definition of M_T , $T \le S_{M_T} \le T + s_{M_T}$, which means we have the bounds (upon replacing $\langle s_1 \rangle = \langle t_1 + t_2 \rangle$),

$$\frac{T}{\langle t_1 + t_2 \rangle} \le \langle M_T \rangle \le \frac{T + \langle s_{M_I} \rangle}{\langle t_1 + t_2 \rangle}.$$
(C.3)

Using, $2M_T - 1 \le N_T \le 2M_T$, and substituting (C.3) into (C.2) gives

$$\left(\frac{T}{\langle t_1 + t_2 \rangle} - \frac{3}{2}\right) \langle \phi(Vt_{\text{on}}) \rangle_{\text{on}} - \langle \phi(Vt_{N_T}) \rangle \leq \langle D_T \rangle \leq \frac{T + \langle s_{M_T} \rangle}{\langle t_1 + t_2 \rangle} \langle \phi(Vt_{\text{on}}) \rangle_{\text{on}}.$$

Since $\langle \phi(Vt_{on}) \rangle_{on} < \infty$, dividing by *T*, replacing $\langle t_1 + t_2 \rangle = \langle t_{off} \rangle_{off} + \langle t_{on} \rangle_{on}$, and taking the limit as $T \to \infty$ shows that

$$\lim_{T \to \infty} \frac{\langle D_T \rangle}{T} = \frac{\langle \phi(Vt_{\rm on}) \rangle_{\rm on}}{\langle t_{\rm off} \rangle_{\rm off} + \langle t_{\rm on} \rangle_{\rm on}}$$

assuming that $\frac{\langle \phi(Vt_{N_T}) \rangle}{T}$ and $\frac{\langle s_{M_T} \rangle}{T}$ both limit to zero. This assumption amounts to assuming that the average dissipation due to the last unbonding and the average length of time of the last bonding and unbonding pair do not grow to be arbitrarily large as $T \to \infty$.

C.4. Algebraic form of the interaction potentials

Below are the algebraic forms of the potentials used to create the phase diagrams in Fig. 3. The potentials differ from standard presentations as they have been centered on x = 0 and $\phi(x) = 0$ in all cases. Spring potential:

$$\phi(x;K) = \frac{1}{2}Kx^2$$

Lennard-Jones potential:

$$\phi(x; E, \sigma) = E\left[\left(\frac{1}{(x/\sigma) + 1}\right)^{12} - 2\left(\frac{1}{(x/\sigma) + 1}\right)^{6}\right] + E$$

Soft Coulomb potential:

$$\phi(x; E, \sigma) = \frac{-E}{\sqrt{1 + (x/\sigma)^2}} + E$$

Appendix D. Integral expansions for low velocities

D.1. Gompertz integrals

We are interested in deriving the expansions of Eqs. (15) and (16). First, we note that (15) is a special case of the incomplete gamma function $\Gamma(n, z)$

$$\Gamma(n,t) = \int_{t}^{\infty} u^{n-1} \exp(-u) du$$

which for our case we will only consider for t > 0. By integrating by parts, one gets the identity

$$\begin{split} \Gamma(1-n,t) &= \int_t^\infty \frac{\exp(-u)}{u^n} du \\ &= \frac{\exp(-t)}{t^n} - \int_t^\infty \frac{n\exp(-u)}{u^{n+1}} du \\ &= \frac{\exp(-t)}{t^n} - n\Gamma(-n,t) \end{split}$$

for $n \ge 0$. We also have the bound for $t \ge 1$

$$\Gamma(-n,t) = \int_{t}^{\infty} \frac{\exp(-u)}{u^{n+1}} du \le \int_{t}^{\infty} \frac{\exp(-u)}{t^{n+1}} du = \frac{\exp(-t)}{t^{n+1}}.$$
(D.1)

By applying the identity recursively, we get ()

$$\begin{split} \Gamma(1-n,t) &= \frac{\exp(-t)}{t^n} - n\Gamma(-n,t) \\ &= \frac{\exp(-t)}{t^n} - n\frac{\exp(-t)}{t^{n+1}} + n(n+1)\Gamma(-n-1,t) \\ &= \dots \\ &= \frac{\exp(-t)}{t^n} \left[\sum_{m=0}^N \frac{(n-1+m)!}{(n-1)!} \frac{(-1)^m}{t^m} \right] + \frac{(-1)^{N+1}(n+N)!}{n!} \Gamma(-n-N,t) \\ &= \frac{\exp(-t)}{t^n} \left[\sum_{m=0}^N \frac{(n-1+m)!}{(n-1)!} \frac{(-1)^m}{t^m} + \mathcal{O}\left(\frac{1}{t^{N+1}}\right) \right], \end{split}$$

where in the last line we have used the bound (D.1). This holds for any N > 0 and $t \ge 1$ and gives the expansion for Eq. (15) by taking n = 1.

To derive an expansion for (16), first change variables v = ut

$$\int_{1}^{\infty} \log(u) \frac{\exp(-ut)}{u} du = \int_{t}^{\infty} \log(v) \frac{\exp(-v)}{v} dv - \log(t) \int_{t}^{\infty} \frac{\exp(-v)}{v} dv.$$
(D.2)

The second term on the right is $log(t)\Gamma(0,t)$ for which we have an expansion. For the first term on the right, define

$$I(n,t) := \int_t^\infty \log(v) \frac{\exp(-v)}{v^n} dv$$

for $n \ge 1$. Integrating by parts shows that

$$I(n,t) = \log(t)\frac{\exp(-t)}{t^n} + \int_t^\infty \left(\frac{1}{v^{n+1}} - \frac{n\log(v)}{v^{n+1}}\right) \exp(-v)dv$$

= $\log(t)\frac{\exp(-t)}{t^n} + \Gamma(-n,t) - nI(n+1,t).$ (D.3)

The function $g_n(v) = \frac{\log(v)}{v^n}$ has negative derivative for $v \ge e$,

$$g'_n(v) = \frac{1}{v^{n+1}} - \frac{n\log(v)}{v^{n+1}} = \frac{1 - n\log(v)}{v^{n+1}},$$

and so $\frac{\log(v)}{v^n}$ is non-increasing on for $v \ge e$. Thus, for $t \ge e$ we have the bound

$$I(n,t) = \int_t^\infty \log(v) \frac{\exp(-v)}{v^n} dv \le \int_t^\infty \frac{\log(t) \exp(-v)}{t^n} = \frac{\log(t) \exp(-t)}{t^n}$$

As before, we use the recursion formula to write

$$I(1,t) = \frac{\log(t)\exp(-t)}{t} + \Gamma(-1,t) - I(2,t)$$

$$= \frac{\log(t)\exp(-t)}{t} + \Gamma(-1,t) - \frac{\log(t)\exp(-t)}{t^2} - \Gamma(-2,t) + 2I(3,t)$$

$$= \dots$$

$$= \log(t)\frac{\exp(-t)}{t}\sum_{n=0}^{N} \left[\frac{(-1)^n n!}{t^n}\right] + \sum_{n=0}^{N} \left[(-1)^n n! \Gamma(-1-n,t)\right] + (-1)^{N+1}(N+1)! I(N+2,t), \quad (D.4)$$

.

for any $N \ge 1$. The remainder term

$$R(N+1,t) = (-1)^{N+1}(N+1)!I(N+2,t)$$

obeys the bound

$$|R(N+1,t)| \le (N+1)! \log(t) \frac{\exp(-t)}{t^{N+2}}.$$

The factorial term suggests blow up in the expansion for *t* near one. However, using Sterling's upper bound $n! \le n^{n+1/2}e^{-n+1}$ with n = N + 1, we see that

$$|R(N+1,t)| \le \log(t) \exp(-t - N) \left(\frac{N+1}{t}\right)^{N+2},$$

so that the rate of decay of the polynomial depends on $\frac{N+1}{t}$ rather than $\frac{1}{t}$ alone. Since we only need to take a few terms, the convergence is still of order $\mathcal{O}(\exp(-t)t^{-(N+1)})$ since $\log(t)/t = \mathcal{O}(1)$.

Finally, we first note that the terms in the first sum of Eq. (D.4) cancel with the terms in the expansion of $\log(t)\Gamma(0, t)$, which is the second term of Eq. (D.2). Thus, we can ignore this first sum in the expansion of I(1, t) and the $\log(t)\Gamma(0, t)$ term when we expand $\int_{1}^{\infty} \frac{\log(u) \exp(-ut)}{u}$. Writing out this expansion to order $\exp(-t)t^{-5}$

$$\int_{1}^{\infty} \log(u) \frac{\exp(-ut)}{u} du = \int_{t}^{\infty} \frac{\log(u) \exp(-u)}{t} - \log(t) \Gamma(0, t)$$
$$= \sum_{n=0}^{5} (-1)^{n} n! \Gamma(-1 - n, t) + \mathcal{O}(\exp(-t)t^{-6})$$

$$\begin{split} \Gamma(-1,t) &= \frac{\exp(-t)}{t^2} \left[1 - \frac{2}{t} + \frac{6}{t^2} - \frac{24}{t^3} + \mathcal{O}\left(\frac{1}{t^4}\right) \right] \\ \Gamma(-2,t) &= \frac{\exp(-t)}{t^3} \left[1 - \frac{3}{t} + \frac{12}{t^2} + \mathcal{O}\left(\frac{1}{t^3}\right) \right] \\ \Gamma(-3,t) &= \frac{\exp(-t)}{t^4} \left[1 - \frac{4}{t} + \mathcal{O}\left(\frac{1}{t^2}\right) \right] \\ \Gamma(-4,t) &= \frac{\exp(-t)}{t^5} \left[1 + \mathcal{O}\left(\frac{1}{t}\right) \right] \\ \Gamma(-5,t) &= \mathcal{O}\left(\frac{\exp(-t)}{t^6}\right) \end{split}$$

$$\int_{1}^{\infty} \log(u) \frac{\exp(-ut)}{u} du = \frac{\exp(-t)}{t^2} \left[1 - \frac{3}{t} + \frac{17}{t^2} - \frac{50}{t^3} \right] + \mathcal{O}\left(\frac{\exp(-t)}{t^6}\right).$$

As stated in the text, we can use Proposition 2 of Lenart (2014) to find the mean time and dissipation in Eqs. (13) and (14) using the expansion for $t = \frac{\kappa_{\text{off}}}{\omega}$ large

$$\langle t_{\rm on} \rangle_{\rm on} = \frac{1}{\omega} \exp(\frac{\kappa_{\rm off}}{\omega}) \int_{\frac{\kappa_{\rm off}}{\omega}}^{\infty} u^{-1} \exp(-u) du$$
$$= \frac{1}{\kappa_{\rm off}} \left[1 - \frac{\omega}{\kappa_{\rm off}} + 2\left(\frac{\omega}{\kappa_{\rm off}}\right)^2 - 6\left(\frac{\omega}{\kappa_{\rm off}}\right)^3 \right] + \mathcal{O}(\omega^{-4})$$

$$\langle D \rangle_{\rm on} = K_{\rm eff} V^2 \frac{\exp(\frac{\kappa_{\rm off}}{\omega})}{\omega^2} \int_1^\infty \frac{\log(u) \exp(-\kappa_{\rm off} u/\omega)}{u} du = \frac{K_{\rm eff} V^2}{\kappa_{\rm off}^2} \left[1 - 3\left(\frac{\omega}{\kappa_{\rm off}}\right) + 17\left(\frac{\omega}{\kappa_{\rm off}}\right)^2 - 50\left(\frac{\omega}{\kappa_{\rm off}}\right)^3 \right] + \mathcal{O}(\omega^{-4}).$$

Finally, using $\langle t_{\text{off}} \rangle_{\text{off}} = \frac{1}{\kappa_{\text{on}}}$ and plugging in the expansion for Eq. (3) shows

$$\dot{D}_{SS} = \frac{\langle D \rangle_{\text{on}}}{\langle t_{\text{on}} \rangle_{\text{on}} + \langle t_{\text{off}} \rangle_{\text{off}}} = \frac{\rho_{\text{on}} K_{\text{eff}} V^2}{\kappa_{\text{off}}} \left[1 - (3 - \rho_{\text{on}}) \frac{\omega}{\kappa_{\text{off}}} + (17 - 2\rho_{\text{on}} + \rho_{\text{on}}^2) \left(\frac{\omega}{\kappa_{\text{off}}}\right)^2 \right] + \mathcal{O}(\omega^{-3})$$

J

D.2. Expanding the probability density of times spent bonded as a function of shear velocity

The unbonding density as a function of the velocity (assuming the Bell model) is given by

$$p_{\rm on}(t;V) = \kappa_{\rm off} \exp\left(a\beta F(Vt) - \kappa_{\rm off} \int_0^t \exp\left(a\beta F(Vs)\right) ds\right).$$

Expanding the force and the integral shows that

$$p_{\rm on}(t;V) = \tilde{\kappa}_{\rm off} \exp(-\tilde{\kappa}_{\rm off} t) \exp\left[a\beta F'(0)t\left(1-\frac{\tilde{\kappa}_{\rm off} t}{2}\right)V + a\beta\left(F''(0)t^2(1-\frac{\tilde{\kappa}_{\rm off} t}{3}) - a\beta F'(0)^2\tilde{\kappa}_{\rm off}\frac{t^3}{3}\right)\frac{V^2}{2} + \mathcal{O}(V^3)\right],$$

where $\tilde{\kappa}_{off} = \kappa_{off} \exp(a\beta F(0))$ is the effective force independent unbonding rate. From this, we see the zeroth order term mirrors the force independent case

 $p_{\rm on}(t; V) \approx \tilde{\kappa}_{\rm off} \exp(-\tilde{\kappa}_{\rm off} t)$

with force independent unbonding rate $\tilde{\kappa}_{off}$. The next order effect

$$p_{\rm on}(t; V) \approx \tilde{\kappa}_{\rm off} \exp(-\tilde{\kappa}_{\rm off} t) \exp\left[a\beta F'(0)t\left(1 - \frac{\tilde{\kappa}_{\rm off} t}{2}\right)V\right]$$

increases the probability of unbonding at times $t < \frac{2}{\tilde{\kappa}_{\text{off}}}$ and decrease the probability of being bonded for longer times $t > \frac{2}{\tilde{\kappa}_{\text{off}}}$. When the interaction expands as $\phi(x) = cx^p + dx^{p+1} + \mathcal{O}(x^{p+2})$ for some c, d > 0 and $p \ge 3$, then

$$\int_0^t F(Vs)^2 ds = \mathcal{O}(V^{2(p-1)}) = \mathcal{O}(V^{p+1})$$

as $V \to 0$ (since $2(p-1) \ge p+1$ for $p \ge 3$). This means that

$$\begin{split} p_{\text{on}}(t;V) &= \kappa_{\text{off}} \exp\left(a\beta F(Vt) - \kappa_{\text{off}} \int_{0}^{t} \exp(a\beta F(Vs))ds\right) \\ &= \kappa_{\text{off}} \exp(-\kappa_{\text{off}}t) \exp\left(a\beta c p(Vt)^{p-1} + a\beta d(p+1)(Vt)^{p} - a\beta \kappa_{\text{off}} ct(Vt)^{p-1} - a\beta \kappa_{\text{off}} dt(Vt)^{p} + \mathcal{O}(V^{p+1})\right) \\ &= \kappa_{\text{off}} \exp(-\kappa_{\text{off}}t) \exp\left(a\beta ct^{p-1} \left(p - \kappa_{\text{off}}t\right) V^{p-1} + a\beta dt^{p} \left(p+1 - \kappa_{\text{off}}t\right) V^{p} + \mathcal{O}(V^{p+1})\right). \end{split}$$

Again, the zeroth order effect is the same as the force independent case and the next order effect increases the probability of bonding for $t < \frac{p}{\kappa_{\text{off}}}$ and decreases it for $t > \frac{p}{\kappa_{\text{off}}}$.

Appendix E. Formation of solid bridges and AFM pull-off experiment

To create the bidisperse colloidal systems, first aqueous suspensions of silica microspheres (Corpuscular Inc., NY, USA) with mean diameter of 20 and 3 μ m (particle density, $\rho = 2.65$ g/cm³) were diluted in deionized water (Milli-Q Reagent Water System, Millipore, MA, USA) and mixed. Using a high precision pipette, colloidal droplets (approximately 0.1 μ L) were placed on a borosilicate glass coverslip (Fisher Scientific, NH, USA; thickness varying from 0.13 to 0.17 mm) and then air-dried under laboratory conditions (RH =0.50 \pm 0.05, T=22 °C). To encourage the formation of widely dispersed, isolated aggregates after evaporation, the coverslip surface was pre-treated by using O₂-plasma (SCE-108 Barrel Asher, Anatech USA, CA, USA) under a radio frequency (RF) power of 50 W for a duration of 15 s under chamber pressure of 300 m Torr. By creating isolated aggregates, we were able to perform AFM pull-off experiments on a single 20- μ m particle bound to the substrate through solid bridges formed by 3 μ m particles. The deposits were placed in a vacuum chamber (500 m Torr) prior to pull-off experiments to minimize the adhesion due to humidity. Under such circumstances, the interparticle bonds are credibly governed by van der Waals attractive forces.

The pull-off force was measured by modifying the contact mode of an AFM Asylum MFP-3D unit (Asylum Research, CA, USA), where the force spectroscopy data were obtained using the IGOR PRO program (WaveMetrics, OR, USA). Soft contact mode cantilevers made of silicon nitride (NanoAndMore Co., CA, USA), 250-350 µm long with spring constant of 0.03-0.08 N/m, and Al backside coating, were used to cover the range of measured forces. The exact spring constant value of each cantilever was determined using the thermal calibration method prior to experiments. Devcon 5-Minute Epoxy (Devcon Co., MA, USA) was then prepared according to the manufacturer's instructions directly on a coverslip strip and flattened to form a thin film. The apex of the cantilever was approached to the film until contact with the epoxy surface was observed. The cantilever was then pulled up immediately to prevent an excessive amount of epoxy due to capillary action. After depositing a small bead of epoxy, the apex of the cantilever was moved on top and pushed onto the target 20-µm particle. The epoxy was then allowed to cure for 15 min and solidify. The experiment was performed by lifting the cantilever, while deflection data were recorded. The scan rate (loading/unloading rate) was 0.50 Hz in all experiments. The setpoint, or zero deflection position in the non-contact regime was set to the zero-voltage position for all force curves. Following the detachment of a single 20-µm particle from the substrate in a monodisperse system, we corrected the cantilever stiffness using thermal calibration data and measured the adhesion force between the particle and the substrate with values found in the range of 4 ± 2 nN for several spots on the substrate. The adhesion force between the bare AFM apex and the 20- μ m particles surface was measured to be in the range of 2 \pm 1 nN. The AFM measurements were carried out in the quasi-static regime, where the force curve should be completely determined by the elastic modulus of the cantilever. The thermal calibration we performed indicated a dissipation factor in the range of 2.1-3.2%, confirming that dissipation was negligible compared to measured forces.

Appendix F. Maximum likelihood estimation of solid bridge kinetic parameters

As described in Section 4.2, we are interested in finding the kinetic parameters κ_{on} , κ_{off} , and F_c which maximize the likelihood of observing the experimentally observed active bonds as a function of time, N(t), assuming the stochastic bond model for the solid bridge. Mathematically, we want to find

$$\hat{\kappa}_{\text{on}}, \hat{\kappa}_{\text{off}}, \hat{F}_c = \underset{\kappa_{\text{on}}, \kappa_{\text{off}}, F_c}{\operatorname{argmax}} \, \ell(\kappa_{\text{on}}, \kappa_{\text{off}}, F_c) = \underset{\kappa_{\text{on}}, \kappa_{\text{off}}, F_c}{\operatorname{argmax}} \, p_{\text{SB}}(N(t) \mid \kappa_{\text{on}}, \kappa_{\text{off}}, F_c)$$



Fig. F.12. (a) A figure depicting how the force versus displacement data from the pull-off experiment is split up into seven pieces (labeled as $N_i(t)$) each containing a linear portion (lighter color) which we interpret as periods of constant number of bonds, and non-linear portions (darker colors) which we interpret as periods of bonding and unbonding. The dashed black lines represent the extracted slopes which determine the observed, effective spring constants K_{Obs}^i . (b) The number of surviving bonds N(t) split up into seven pieces $N_i(t)$ based on the linear sections of the data. The coloring matches the plot (a).

where ℓ is the likelihood function and $p_{SB}(N(t) | \kappa_{on}, \kappa_{off}, F_c)$ is the probability density of observing N(t) given the solid bridge model with kinetic parameters κ_{on} , κ_{off} , and F_c . For notational simplicity, the conditioning on the parameters will be suppressed in what follows.

N(t) consists of seven section corresponding to the seven linear sections of the experimental data (Fig. F.12(a)). Label as $N_i(t)$ the section which starts off as a constant value N_i as defined in the text, and ends at the start of the section which is the constant value N_{i+1} ($N_7(t)$ ends just before the breaking of the epoxy). For each i = 1, ..., 6, let T_i be the starting time for $N_i(t)$, let t_i be the length of time that $N_i(t)$ remains constant (the length of time that the force versus displacement data is linear) and let Δt_i be the length of time that $N_i(t)$ is linearly interpolating (the length of time that the force versus displacement data is nonlinear before the next linear section). For i = 7, we can define T_7 and t_7 in the same way but there is no corresponding Δt_7 . Also let $\Delta N_i = N_{i+1} - N_i$ be the number of bonds that form (or break if the value is negative) between section i and i + 1.

We break up $p_{SB}(N(t))$ into the probability of each of the section $N_i(t)$ as follows. We may first think of this density as the density for the trajectory which first follows $N_1(t)$ from T_1 to T_2 , and then $N_2(t)$ from T_2 to T_3 and so on. The goal is to split the probability density into a product of the density of each of these pieces. However, the sections are not completely independent since, for example, $N_1(T_2)$ must equal $N_2(T_2)$ since they both give the value of the $N(T_2) = N_2$. From the definition of conditional probability, the probability density of following $N_1(t)$ and then $N_2(t)$ is equal to the probability density of following $N_1(t)$ times the probability density of following $N_2(t)$ conditioned on the fact that the trajectory first followed $N_1(t)$. Symbolically,

$$p_{\rm SB}(N_1(t), N_2(t)) = p_{\rm SB}(N_1(t))p_{\rm SB}(N_2(t) \mid N_1(t))$$

Since we have assumed that bonding trajectories are independent of their own past, the density for $N_2(t)$ depends only on $N_1(t)$ through their overlapping value at $N_1(T_2) = N_2(T_2) = N_2$. Thus, we know that

$$p_{\rm SB}(N_2(t) \mid N_1(t)) = p_{\rm SB}(N_2(t) \mid N_2(T_2) = N_2).$$

Likewise, when we consider the whole trajectory, we can repeatedly apply the same logic to conclude that

$$p_{\rm SB}(N(t)) = p_{\rm SB}(N_1(t)) \prod_{i=2}^7 p_{\rm SB}(N_i(t) \mid N_i(T_i) = N_i).$$

In order to determine $p_{SB}(N_i(t) | N_i(T_i) = N_i)$, we need to know the probability that none of the bonds change for the correct amount of time (that is t_i) and that when a bond does change, the right event (i.e. a bond or unbonding) occurs. For this we use the following technical lemma.

Lemma F.1. Let $m \ge 2$ and suppose that at a given time T, there are m possible events labeled i = 1, ..., m which can occur independently of each other. Suppose further that each occurs with rate $\kappa_i(t) \ge \kappa_{min} > 0$ for some minimum rate κ_{min} so that if one begins watching at time T, the probability density of observing event i at time t_i is given by

$$p_i(t_i) = \kappa_i(T+t_i) \exp\left(-\int_T^{T+t_i} \kappa_i(s) ds\right)$$

for each *i*. Under these assumptions, probability density that the first event observed after time T is event *j*, and that this event occurs at time *t* is

$$\kappa_j(T+t)\exp\left(-\int_T^{T+t}\left(\sum_{i=1}^m\kappa_i(s)\right)ds\right).$$

Proof. We assume that T = 0 for simplicity as the result for general *T* is just obtained by translating time. Let *j* be the first event observed. This event happens at time *t* if and only if $t_j = t$ and $t_i > t$ for all $i \neq j$. Since the events are independent, the probability density of this event is given by

$$p_j(t)\prod_{i\neq j}\mathbb{P}(t_i>t),$$

where $\mathbb{P}(t_i > t)$ is the probability that $t_i > t$. For each *i*, we know that

$$\mathbb{P}(t_i > t) = \int_t^\infty p_i(s) ds.$$

Substituting in the definition for $p_i(s)$, rewriting the integrand as a total derivative, and integrating gives

$$\mathbb{P}(t_i > t) = \int_t^\infty \kappa_i(s) \exp\left(-\int_0^s \kappa_i(u)du\right) ds$$

= $\int_t^\infty -\frac{d}{ds} \exp\left(-\int_0^s \kappa_i(u)du\right) ds$
= $\exp\left(-\int_0^t \kappa_i(s)ds\right) - \exp\left(-\int_0^\infty \kappa_i(s)ds\right)$
= $\exp\left(-\int_0^t \kappa_i(s)ds\right),$

since the term $\exp(-\int_0^\infty -\kappa_i(s)ds) = 0$ as we assumed that $\kappa_i(s) \ge \kappa_{\min} > 0$. Noting that

$$p_j(t) = \kappa_j(t) \exp\left(-\int_0^t \kappa_j(s) ds\right)$$

gives the desired result. \Box

We apply this lemma by noting that at any given time during the pull-off experiment, there are N_{tot} possible events which could occur, and each of these events is independent of the others except through their contribution to the total number of active bonds which impacts the force acting on each bond. Since we are interested in the probability density of a section conditioned on knowing the number of active bonds at the start of that section, the dependence between the events is negated and we can apply this lemma.

For example, we compute $p_{\text{SB}}(N_4(t) \mid N_4(T_4) = N_4)$. Section $N_4(t)$ begins at $T_4 = 0.0933$ s when there are an estimated $N_4(T_4) = 19$ bonds (see Fig. F.12(b)). These bonds last for $t_4 = 0.0527$ and bonds start breaking at time $T_4 + t_4 = 0.1460$ and continue to break for time $\Delta t_4 = 0.0078$ s until $N_5 = 14$ bonds are active. Since Lemma F.1 only applies to single events and in this case 5 bonds break, we break up $p_{\text{SB}}(N_4(t) \mid N_4(T_4) = N_4)$ by assuming that it is well approximated by the density that the first bond breaks after time t_4 and the remaining bonds break at equal intervals of the remaining Δt_4 (i.e., one more breaks after time $\frac{\Delta t_4}{\Delta N_4 - 1}$ where one has been subtracted to account for the first bond breaking). Using the lemma, the density for the first bond breaking is given by

$$N_4 \kappa_{\text{off}} \exp(F(T_4 + t_4, N_4)/F_c) \exp\left(-\int_{T_4}^{T_4 + t_4} (N_{\text{tot}} - N_4)\kappa_{\text{on}} + N_4 \kappa_{\text{off}} \exp(F(s, N_4)/F_c)ds\right)$$

where we have multiplied by the number of active bonds, N_4 , since any of these bonds could have broken at time $T_4 + t_4$. Calling $\delta t_4 := \frac{\Delta t_4}{\Delta N_4 - 1}$, the density for the next time is

$$(N_4 - 1)\kappa_{\rm off} \exp(F(T_4 + t_4 + \delta t_4, N_4 - 1)/F_c) \exp\left(-\int_{T_4 + t_4}^{T_4 + t_4 + \delta t_4} (N_{\rm tot} - N_4 + 1)\kappa_{\rm on} + (N_4 - 1)\kappa_{\rm off} \exp(F(s, N_4 - 1)/F_c)ds\right),$$

since there are now $N_4 - 1$ active bonds and one more broke. The densities for the unbonding of the remaining six bonds are computed in the same way. By taking the product of them all we get the density $p_{SB}(N_4(t) | N_4(T_4) = N_4)$,

$$p_{\rm SB}(N_4(t) \mid N_4(T_4) = N_4) = N_4 \kappa_{\rm off} \exp\left(F(T_4 + t_4, N_4)/F_c\right) \exp\left(-\int_{T_4}^{T_4 + t_4} (N_{\rm tot} - N_4)\kappa_{\rm on} + N_4 \kappa_{\rm off} \exp\left(F(s, N_4)/F_c\right)ds\right) \\ \times \prod_{l=1}^7 \left[(N_4 - l)\kappa_{\rm off} \exp\left(F(T_4 + t_4 + l\delta t_4, N_4 - l)/F_c\right) + \sum_{l=1}^7 \left[(N_4 - l)\kappa_{\rm off} \exp\left(F(T_4 + t_4 + l\delta t_4, N_4 - l)/F_c\right) + \sum_{l=1}^7 \left[(N_4 - l)\kappa_{\rm off} \exp\left(F(T_4 + t_4 + l\delta t_4, N_4 - l)/F_c\right) + \sum_{l=1}^7 \left[(N_4 - l)\kappa_{\rm off} \exp\left(F(T_4 + t_4 + l\delta t_4, N_4 - l)/F_c\right) + \sum_{l=1}^7 \left[(N_4 - l)\kappa_{\rm off} \exp\left(F(T_4 + t_4 + l\delta t_4, N_4 - l)/F_c\right) + \sum_{l=1}^7 \left[(N_4 - l)\kappa_{\rm off} \exp\left(F(T_4 + t_4 + l\delta t_4, N_4 - l)/F_c\right) + \sum_{l=1}^7 \left[(N_4 - l)\kappa_{\rm off} \exp\left(F(T_4 + t_4 + l\delta t_4, N_4 - l)/F_c\right) + \sum_{l=1}^7 \left[(N_4 - l)\kappa_{\rm off} \exp\left(F(T_4 + t_4 + l\delta t_4, N_4 - l)/F_c\right) + \sum_{l=1}^7 \left[(N_4 - l)\kappa_{\rm off} \exp\left(F(T_4 + t_4 + l\delta t_4, N_4 - l)/F_c\right) + \sum_{l=1}^7 \left[(N_4 - l)\kappa_{\rm off} \exp\left(F(T_4 + t_4 + l\delta t_4, N_4 - l)/F_c\right) + \sum_{l=1}^7 \left[(N_4 - l)\kappa_{\rm off} \exp\left(F(T_4 + t_4 + l\delta t_4, N_4 - l)/F_c\right) + \sum_{l=1}^7 \left[(N_4 - l)\kappa_{\rm off} \exp\left(F(T_4 + t_4 + l\delta t_4, N_4 - l)/F_c\right) + \sum_{l=1}^7 \left[(N_4 - l)\kappa_{\rm off} \exp\left(F(T_4 + t_4 + l\delta t_4, N_4 - l)/F_c\right) + \sum_{l=1}^7 \left[(N_4 - l)\kappa_{\rm off} \exp\left(F(T_4 + t_4 + l\delta t_4, N_4 - l)/F_c\right) + \sum_{l=1}^7 \left[(N_4 - l)\kappa_{\rm off} \exp\left(F(T_4 + t_4 + l\delta t_4, N_4 - l)/F_c\right) + \sum_{l=1}^7 \left[(N_4 - l)\kappa_{\rm off} \exp\left(F(T_4 + t_4 + l\delta t_4, N_4 - l)/F_c\right) + \sum_{l=1}^7 \left[(N_4 - l)\kappa_{\rm off} \exp\left(F(T_4 + t_4 + l\delta t_4, N_4 - l)/F_c\right) + \sum_{l=1}^7 \left[(N_4 - l)\kappa_{\rm off} \exp\left(F(T_4 + t_4 + l\delta t_4, N_4 - l)/F_c\right) + \sum_{l=1}^7 \left[(N_4 - l)\kappa_{\rm off} \exp\left(F(T_4 + t_4 + l\delta t_4, N_4 - l)/F_c\right) + \sum_{l=1}^7 \left[(N_4 - l)\kappa_{\rm off} \exp\left(F(T_4 + t_4 + l\delta t_4, N_4 - l)/F_c\right) + \sum_{l=1}^7 \left[(N_4 - l)\kappa_{\rm off} \exp\left(F(T_4 + t_4 + l\delta t_4, N_4 - l)/F_c\right) + \sum_{l=1}^7 \left[(N_4 - l)\kappa_{\rm off} \exp\left(F(T_4 + t_4 + l\delta t_4, N_4 - l)/F_c\right) + \sum_{l=1}^7 \left[(N_4 - l)\kappa_{\rm off} \exp\left(F(T_4 + t_4 + l\delta t_4, N_4 - l)/F_c\right) + \sum_{l=1}^7 \left[(N_4 - l)\kappa_{\rm off} \exp\left(F(T_4 + t_4 + l\delta t_4, N_4 - l)/F_c\right) + \sum_{l=1}^7 \left[(N_4 - l)\kappa_{\rm off} \exp\left(F(T_4 + t_4 + l\delta t_4, N_4 - l)/F_c\right) + \sum_{l=1}^7 \left[(N_4 - l)\kappa_$$

We compute the densities for the remaining pieces in this way, and form the whole density by taking the product of all of the pieces. The MLE is determined by taking the maximum of this density with respect to the parameters κ_{on} , κ_{off} , and F_c using a standard conjugate gradient method. In practice, the logarithm of the probability density is maximized rather than the probability density itself since this yields the same MLE and there is better convergence given the exponential factors and the number of products making up the total density. As mentioned in the text, the MLE for the solid bridge parameters was found to be $\kappa_{on} = 3.47 \text{ s}^{-1}$, $\kappa_{off} = 4.17 \text{ s}^{-1}$, and $F_c = 1.99 \text{ nN}$.

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