A statistical mechanics framework for polymer chain scission, based on the concepts of distorted bond potential and asymptotic matching

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Abstract

to design increasingly tough, resilient, and fatigue-resistant elastomers and hydrogels, the relationship between controllable network parameters at the molecular level (bond type, non-uniform chain length, entanglement density, etc.) to macroscopic quantities that govern damage and failure must be established. Many of the most successful constitutive models for elastomers have been rooted in statistical mechanical treatments of polymer chains. Typically, such constitutive models have used variants of the freely jointed chain model with rigid links. However, since the free energy state of a polymer chain is dominated by enthalpic bond distortion effects as the chain approaches its rupture point, bond extensibility ought to be accounted for if the model is intended to capture chain rupture. To that end, a new bond potential is supplemented to the freely jointed chain model (as derived in the uFJC framework of Buche and Silberstein (2021) and Buche et al. (2022)), which we have extended to yield a tractable, closed-form model that is amenable to constitutive model development. Inspired by the asymptotically matched uFJC model response in both the low/intermediate chain force and high chain force regimes, a simple, quasi-polynomial bond potential energy function is derived. This bond potential exhibits harmonic behavior near the equilibrium state and anharmonic behavior for large bond stretches tending to a characteristic energy plateau (akin to the Lennard-Jones and Morse bond potentials). Using this bond potential, approximate yet highly-accurate analytical functions for bond stretch and chain force dependent upon chain stretch are established. Then, using this polymer chain model, a stochastic thermal fluctuation-driven chain rupture framework is developed. This framework is based upon a force-modified tilted bond potential that accounts for distortional bond potential energy, allowing for the derivation and subsequent calculation of the dissipated chain scission energy. The cases of rate-dependent and rate-independent scission are accounted for throughout the rupture framework. The impact of Kuhn segment number on chain rupture behavior is also investigated. The model is fit to single-chain mechanical response data collected from atomic force microscopy tensile tests for validation and to glean deeper insight into the molecular physics taking place. Due to their analytical nature, this polymer chain model and the associated rupture framework can be straightforwardly implemented in finite element models accounting for fracture and fatigue in polydisperse elastomer networks.

Keywords: asymptotic matching, statistical mechanics, chain extensibility, polymer chain scission, distorted bond potential, dissipated energy, fracture toughness

1. Introduction

Elastomers are materials composed of flexible entropic polymer chains oriented randomly, cross-linked together, and arranged in a network structure. Due to their resilience and ability to undergo large and

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recoverable deformations, elastomers have been used as components in traditional engineering applications, such as tires, belts, and sealers (Gent 2012). More recently, elastomers have emerged as ideal candidate materials for next-generation soft robotics components and biomedical devices (Zhalmuratova and Chung 2020). As elastomers with covalent cross-links become increasingly deformed, polymer chains begin to elongate, and bonds composing the backbone of these chains become stretched. Eventually, these bonds or the bonds of the cross-links rupture. These discrete rupture events collectively build up in the elastomer network and ultimately lead to macroscale failure of the bulk specimen. Additionally, these chain rupture events serve to dissipate energy imparted to the network, and enhance network toughness. This work will focus on rupture events impacting the chain backbone directly (and not the cross-links).

Understanding the fundamentals of energy dissipation, network toughness, and fracture mechanics in elastomers and gels has been an active area of research in recent years (Bai et al. 2019; Creton, 2017; Creton and Ciccotti 2016; Long and Hui 2016; Long et al. 2021; Zhao 2014; Zhao et al. 2021a). One overarching takeaway from this thrust of research is that the fracture energy of a soft elastomer network, \( \Gamma \), namely, the energy required to form new unit crack surface area in the bulk material, can be considered as the sum result of two contributions (Long and Hui, 2016; Long et al., 2021; Tanaka, 2007; Zhao, 2014; Zhao et al., 2021a). One

\[
\Gamma = \Gamma_0 + \Gamma_{\text{diss}},
\]

where \( \Gamma_0 \) is the intrinsic fracture energy and \( \Gamma_{\text{diss}} \) is the mechanical dissipation that takes place in a process zone surrounding the crack tip. Due to the random topology of the chain network, and the naturally occurring polydispersity of chain lengths that arises due to polymerization statistics, which can be thought of as network imperfections, chain rupture can occur in a delocalized manner in the elastomer (Itskov and Knyazeva 2016; Yang et al. 2019a). \( \Gamma_{\text{diss}} \) is generated from any dissipative phenomena that occurs during crack propagation, such as delocalized chain scission, molecular friction due to entanglements and chain pullout, viscoelasticity, poroelasticity, strain-induced crystallization, and polymer-filler interactions. The size of this process zone that is responsible for \( \Gamma_{\text{diss}} \) can range in length as different dissipation mechanisms become prominent. Various elastomer network characteristics govern how large \( \Gamma_{\text{diss}} \) is compared to \( \Gamma_0 \).

In ideal elastomer networks, \( \Gamma_{\text{diss}} \approx 0 \) and \( \Gamma/\Gamma_0 \approx 1 \), even with a small density of topological defects incorporated in the network (Lin et al., 2021). \( \Gamma_{\text{diss}} \approx 0 \) and \( \Gamma/\Gamma_0 \approx 1 \) also holds true for nearly unentangled networks, even with structural heterogeneities and topological defects present (Zheng et al., 2022). On the contrary, in entangled elastomer networks, \( \Gamma_{\text{diss}} > 0 \) and \( \Gamma/\Gamma_0 > 1 \), where the fracture toughness enhancement is postulated to originate from chain pullout and delocalized chain damage in a near-crack process zone (Kim et al., 2021; Zheng et al., 2022). In elastomer networks containing notable amounts of network imperfections from structural heterogeneities, topological defects, and even pre-existing cracks in the bulk material, \( \Gamma_{\text{diss}} > 0 \) and \( \Gamma/\Gamma_0 > 1 \) is also found to be the case (Lin et al., 2019; Yang et al., 2019a). Here, fracture toughness enhancement and elastic dissipation are believed to stem from delocalized chain scission (Liu et al., 2019; Yang et al., 2019a).

To reveal and better understand the complex molecular behavior of polymer chains in fractured, and more generally, damaged elastomers, mechanophores have been incorporated into elastomer networks to probe force-activated events originating at the chain level (Chen et al. 2021a; Simon and Craig, 2017; Stratigaki and Göstl 2020). Mechanophore motifs that alter their optical properties with respect to applied load – mechanochromophores and/or mechanofluorophores (hereafter referred to as luminescent mechanophores) – have emerged as the preferred tool to visualize such force-sensitive chain level behavior (Chen et al. 2021a; Göstl et al., 2017). Embedded luminescent mechanophores in elastomer networks have confirmed that chains located far from the crack surface (compared to the chain length) become ruptured during crack advance

\footnote{Different dissipation mechanisms contributing to \( \Gamma_{\text{diss}} \) can be further separated from one another and assumed to operate in different process zones. For instance, Lin et al. (2022) proposed a decoupling of highly entangled chain pullout and delocalized chain scission effects taking place in a “near-crack zone” from other bulk hysteretic dissipation effects which occur in a much larger process zone. The near-crack dissipation acting in the near-crack zone is \( \Gamma_{\text{diss}}^{\text{tip}} \), while the bulk hysteretic dissipation associated with the general process zone is \( \Gamma_{\text{diss}}^{\text{bulk}} \). \( \Gamma_{\text{diss}} \) is the sum result of these two dissipation contributions: \( \Gamma_{\text{diss}} = \Gamma_{\text{diss}}^{\text{tip}} + \Gamma_{\text{diss}}^{\text{bulk}} \). Slootman et al. (2022) has also proposed a similar mechanism governing bond scission in viscoelastic interpenetrating network elastomers.}
can be treated as a stochastic process driven by thermal oscillations (Arora et al., 2020, 2021; Guo and et al., 2021; Talamini et al., 2018). Alternatively, consistent with statistical thermodynamics, chain scission also be employed in a phase field fracture setting (Li and Bouklas, 2020; Mao and Anand, 2018; Mulderrig Mao et al., 2017b; Xiao et al., 2021; Zhao et al., 2021b). Another approach is to define a thermodynamically-value) (Arunachala et al., 2021; Buche and Silberstein, 2021; Dal and Kaliske, 2009; Lamont et al., 2021; resolve the statistics of chain rupture is to consider fully intact chains as automatically ruptured when their extensibility, i.e., the influence of extensible bonds are theoretically incorporated in the uFJC model of Buche and Silberstein (2021) and Buche et al. (2022) accounts for arbitrary bond extensibility, i.e., the influence of extensible bonds are theoretically incorporated in the uFJC model prior to any particularization of a governing bond potential energy function. Once the entropic and enthalpic contributions are defined, the statistics of rupture for a given population of chains can be studied. One way to resolve the statistics of chain rupture is to consider fully intact chains as automatically ruptured when their free energy or internal energy exceeds some rupture energy (or when their chain force exceeds its maximum per chain (FJC) model of Kuhn and Grün (1942) to account for the influence of bond extensibility. Inspired by this work, Mao et al. (2017b) took the Langevin-statistics based FJC Helmholtz free energy function, permitted bonds to vary in length, added an internal potential energy of bond stretching to the free energy, and heuristically forced the bond stretch to be the minimizer of this modified Helmholtz free energy. Bond extensibility can also be incorporated in a statistical mechanics-consistent extensible FJC model, as achieved recently by Buche and Silberstein (2021) and Buche et al. (2022) utilizing asymptotic matching. Notably, the uFJC model of Buche and Silberstein (2021) and Buche et al. (2022) accounts for arbitrary bond extensibility, i.e., the influence of extensible bonds are theoretically incorporated in the uFJC model prior to any particularization of a governing bond potential energy function. Once the entropic and enthalpic contributions are defined, the statistics of rupture for a given population of chains can be studied. One way to resolve the statistics of chain rupture is to consider fully intact chains as automatically ruptured when their free energy or internal energy exceeds some rupture energy (or when their chain force exceeds its maximum value) (Arunachala et al., 2021; Buche and Silberstein, 2021; Dal and Kaliske, 2009; Lamont et al., 2021; Mao et al., 2017b; Xiao et al., 2021; Zhao et al., 2021b). Another approach is to define a thermodynamically-consistent damage law (often dependent on the bond stretch) that accounts for network softening. This can also be employed in a phase field fracture setting (Li and Bouklas, 2020; Mao and Anand, 2018; Mulderrig et al., 2021; Talamini et al., 2018). Alternatively, consistent with statistical thermodynamics, chain scission can be treated as a stochastic process driven by thermal oscillations (Arora et al., 2020, 2021; Guo and
Strikingly, the extensible chain model used within the last two (more descriptive) treatments of chain rupture is, to date, solely the Mao et al. (2017b) phenomenologically modified FJC model. In other words, an extensible FJC model derived thoroughly upon statistical mechanics principles has yet to be embedded within either a damage law-based treatment or a stochastic treatment of chain rupture.

In this manuscript, we develop a framework to study polymer chain scission, where its novelty lies upon two key pillars: (i) an arbitrarily-extensible FJC model derived entirely through statistical mechanics that also respects the principles of statistical thermodynamics and asymptotic matching, and (ii) a probabilistic understanding of chain scission, starting from a consideration of thermal oscillations and rupture at the segment level, consistent with the principles of mechanochemistry. To address the first pillar, we extend the uFJC model from Buche and Silberstein (2021) and Buche et al. (2022) to yield an analytical form for the chain force and the Helmholtz free energy function (also seeking to connect to the prevalent phenomenological functional form proposed in Mao et al. (2017b)). Using the principles of asymptotic matching (as employed in the derivation of the uFJC model), a simple, anharmonic, quasi-polynomial potential energy function for a segment (or a bond) in a chain is derived. From this potential energy function, a highly-accurate approximate analytical form for segment stretch as a function of chain stretch is obtained. To address the second pillar, rate-dependent and rate-independent segment scission is treated as a stochastic, energy-activated process as captured via the force-modified tilted potential energy. Principles of scission physics as described in Wang et al. (2019) are evoked to derive the governing equations for rate-dependent and rate-independent dissipated chain scission energy. A functional form for the reference end-to-end chain distance is then derived that fully accounts for segment extensibility and chain length polydispersity. This proposed polymer chain rupture framework exhibits many beneficial properties; it is clearly based upon statistical mechanics principles accounting for bond extensibility, satisfies principles of statistical thermodynamics and asymptotic matching, accounts for scission originating from the molecular level of the bond, and provides a clear multiscale connection between the physics at the bond-level, segment-level, and chain-level. Ideally, the proposed chain rupture framework can be incorporated into future polymer damage and fracture models to gain insight into the complex nature of polymer network fracture toughness.

This manuscript is organized as follows: In Section 2, the fundamentals of the uFJC model from Buche and Silberstein (2021) and Buche et al. (2022) are reviewed. The uFJC model is then extended in Section 3 to ensure that an upscaled continuum model is defined in terms of tractable closed-form solutions. The analytical form for the chain force is determined in Section 3.1. The asymptotically-matched segment potential energy function is derived in Section 3.2.1 and Appendix A leading to the highly-accurate approximate analytical form for segment stretch as a function of chain stretch as derived in Section 3.2.2 and Appendix B. With the chain model complete, the chain rupture framework is developed in Section 4. Starting at the segment level in Section 4.1, the probability of rate-dependent and rate-independent segment scission is adopted from the principles of mechanochemistry, which consider segment scission as a stochastic process driven by thermal fluctuations and dependent upon the applied load to the segment. Governing equations for rate-dependent and rate-independent dissipated segment scission energy are then formulated. The segment scission framework is pushed up to the chain level via probabilistic considerations in Section 4.2. In Section 4.3 the functional form for the reference end-to-end chain distance dependent upon segment extensibility and segment number is derived through statistical mechanics considerations from Buche and Silberstein (2021). Verification and validation take place in Section 5. Section 5.1 presents the single chain model mechanical response. Implications of the chain scission framework are discussed in Section 5.2, and chain rupture behavior for short, intermediately-long, and long chains is investigated in Section 5.3. In Section 5.4 single chain mechanical response data generated from atomic force microscopy (AFM) tensile tests are used to validate the chain model. The chain rupture framework is called upon to uncover the level of dissipated energy and chain scission probability for the chains involved in the AFM tensile tests. Concluding remarks, improvements for future work, and implications for future research in elastomer fracture and fatigue modeling are highlighted in Section 6.
2. uFJC model review

Before defining a framework for the statistics of chain scission, the constitutive behavior of a single polymer chain must be specified. Since polymer chain rupture is an enthalpically dominated process [Lake and Thomas, 1967], the chain model must account for bond extensibility. The uFJC model has recently emerged as the first polymer chain model to intrinsically account for arbitrary segment extensibility within a statistical mechanics framework. In the following, a brief review of the uFJC model framework is provided as a means of establishing the proper context for the remainder of this work. This review (which will occupy the entirety of Section 2) is a summary of the most relevant results from Buche and Silberstein [2021] and Buche et al. [2022] (unless otherwise noted).

2.1. Statistical thermodynamics foundation

The uFJC is a freely jointed chain of \( \nu \) massless, flexible, and stretchable links, or Kuhn segments, connecting \( \nu + 1 \) point masses with mass \( m \) and momentum \( p \). The segment stretch \( \lambda_i \) is taken as the ratio of the segment length \( l_i \) with the equilibrium segment length \( l_i^{eq} \), \( \lambda_i = l_i / l_i^{eq} \). The energy state of each segment is described by the (arbitrary and non-particularized) segment potential \( U_i \), which inherently exhibits some characteristic segment potential energy scale \( E_i^{char} \) and segment stiffness \( k_i \), defined as

\[
k_i \equiv U_i''(l_i^{eq}) = \left. \frac{\partial^2 U_i(l_i)}{\partial l_i^2} \right|_{l_i = l_i^{eq}},
\]

where primes imply derivatives. Assuming fixed absolute temperature \( T \), a fixed inverse energy scale can be defined as \( \beta = 1/[k_B T] \) where \( k_B \) is the Boltzmann constant. Then, the nondimensional characteristic segment potential energy scale and nondimensional segment stiffness are respectively defined as \( \zeta_i^{char} \equiv \beta E_i^{char} \) and \( \kappa_i \equiv \beta(l_i^{eq})^2 k_i \). The single chain Hamiltonian of the uFJC model is

\[
H(\mathcal{P}) = \sum_{i=1}^{\nu+1} \frac{p_i^2}{2m} + \nu \sum_i U_i(l_i) = \sum_{i=1}^{\nu+1} \frac{p_i^2}{2m} + \nu \sum_i U_i(l_i),
\]

where \( \mathcal{P} \) is the phase space state of the chain. The single-segment isotensional configuration partition function is [Buche and Silberstein, 2020]

\[
Z_i(\xi_i) = \int_0^{2\pi} \int_0^\infty \int_0^{\xi_i^{eq}} e^{\beta f_i l_i^{eq} \cos \theta} e^{-\beta U_i(l_i)} dl_i d\theta, \tag{4}
\]

where \( f_i \) is the chain force, \( \xi_i = \beta f_i l_i^{eq} \) is its nondimensional counterpart, and \( \theta \) is the angle between the segment and the chain force. The chain isotensional configuration partition function is \( Z(\xi) = \left[Z_i(\xi_i)\right]^{\nu} \) [Fiasconaro and Falo, 2019]. The mechanical response of the chain \textit{vis-à-vis} the equilibrium chain stretch \( \lambda_i^{eq} \) is defined and provided [Buche and Silberstein, 2020] as

\[
\lambda_i^{eq}(\xi_i) = \lambda_i(\xi_i) \ast A_\nu = \frac{1}{\nu} \frac{\partial \ln(Z(\xi_i))}{\partial \xi_i} = \frac{\partial \ln(Z_i(\xi_i))}{\partial \xi_i} = \frac{r_i(\xi_i)}{\nu l_i^{eq}}, \tag{5}
\]

Here, \( r_i \) is the end-to-end chain distance, \( \lambda_i = r_i / r_i^{ref} \) is the chain stretch, \( r_i^{ref} \) is the reference end-to-end chain distance, and \( A_\nu = r_i^{ref}/[\nu l_i^{eq}] \) is the reference equilibrium chain stretch.

Obtaining an analytical form for \( \lambda_i^{eq} \) valid over all \( \xi_i \) regimes and intrinsically accounting for arbitrary segment extensibility (as governed by \( U_i(l_i) \)) is seemingly an impossible task. However, an analytical form is needed here for computational simplicity. To resolve this conundrum, asymptotic approximations for \( \lambda_i^{eq} \) are derived in the low-to-intermediate chain force regime and in the high chain force regime, both of which are valid only under steep segment potentials \( U_i(l_i) \). The segment potential is considered to be steep if it is deep and narrow, which is true when \( \zeta_i^{char} \) and \( \kappa_i \) are large (i.e., \( \zeta_i^{char}, \kappa_i \gg 1 \)). The asymptotic approximations for \( \lambda_i^{eq} \) are then combined via Prandtl’s method of asymptotic matching into a composite function valid for all \( \xi_i \). In the limit of sufficiently steep segment potentials, this asymptotically-matched equilibrium chain stretch function is further reduced into a particularly useful analytical form.
2.2. Low-to-intermediate chain force regime

For chain forces that are both low (i.e., \( \xi_c < 1 \)) and intermediate (i.e., \( 1 < \xi_c \ll \zeta_{\nu}^{\text{char}}, \kappa_{\nu} \)) and considering steep segment potentials \( (\zeta_{\nu}^{\text{char}}, \kappa_{\nu} \gg 1) \), Laplace’s method and various asymptotic considerations are employed to evaluate Eq. (4) to the following asymptotic relation:

\[
Z_{\nu}(\xi_c) \approx 4\pi \sqrt{l_{\nu}^{(\text{eq})} \xi_c} e^{\frac{\xi_c}{\kappa_{\nu}} \left[ 1 + \frac{\xi_c}{\tilde{\nu}} \coth(\xi_c) \right]},
\]

where \( 1/\tilde{\nu} \equiv 1 - u_{\nu}^{(\text{eq})}(1)/(2u_{\nu}^{(\text{eq})}(1)) \), \( u_{\nu}(x) \equiv \beta U_{\nu}(x^{\nu}) \) is the nondimensional segment potential, and \( x \) is a dummy variable (for now. Later on, \( x \) will be identified as the segment stretch \( \lambda_\nu \)). The corresponding asymptotic relation for the equilibrium chain stretch is

\[
\lambda_{\nu}^{\text{eq}}(\xi_c) \approx \mathcal{L}(\xi_c) + \frac{\xi_c}{\kappa_{\nu}} \left[ 1 + \frac{1 - \mathcal{L}(\xi_c) \coth(\xi_c)}{\tilde{\nu}} \right],
\]

where \( \mathcal{L}(y) = \coth y - \frac{1}{y} \) is the Langevin function.

2.3. High chain force regime

For high chain forces (i.e., \( \xi_c \approx \zeta_{\nu}^{\text{char}} \)) and with steep segment potentials \( (\zeta_{\nu}^{\text{char}}, \kappa_{\nu} \gg 1) \), asymptotic considerations are employed to simplify Eq. (4) to the following asymptotic relation:

\[
Z_{\nu}(\xi_c) \approx \frac{2\pi l_{\nu}^{(\text{eq})}^{3}}{\xi_c} \int_{0}^{\infty} e^{-u_{\nu}^{\text{tot}}(x)} x \, dx,
\]

where \( u_{\nu}^{\text{tot}} \) is the nondimensional total segment potential, defined as

\[
u_{\nu}^{\text{tot}}(x) \equiv u_{\nu}(x) - \xi_c x.
\]

The corresponding asymptotic relation for \( \lambda_{\nu}^{\text{eq}} \) is

\[
\lambda_{\nu}^{\text{eq}}(\xi_c) \approx \frac{\int_{0}^{\infty} e^{-u_{\nu}^{\text{tot}}(x)} x^2 \, dx}{\int_{0}^{\infty} e^{-u_{\nu}^{\text{tot}}(x)} x \, dx} - \frac{1}{\xi_c}.
\]

At this point, the implicit definition of the segment stretch \( \lambda_\nu \) as the minimizer of \( u_{\nu}^{\text{tot}} \) is introduced:

\[
\left. \frac{\partial}{\partial x} (u_{\nu}^{\text{tot}}(x)) \right|_{x = \lambda_\nu} = 0 \quad \Leftrightarrow \quad \xi_c = \xi_\nu \equiv \left. \frac{\partial u_{\nu}(x)}{\partial x} \right|_{x = \lambda_\nu} = \left. \frac{\partial u_{\nu}}{\partial \lambda_\nu} \right|_{\lambda_\nu = \lambda_\nu}.
\]

Here, \( \xi_\nu = \beta f_\nu l_{\nu}^{\text{eq}} \) is the nondimensional segment force, and \( f_\nu \) is its dimensional counterpart. Imposing the definition of \( \lambda_\nu \) and utilizing similar considerations from before, Eq. (10) simplifies to

\[
\lambda_{\nu}^{\text{eq}}(\xi_c) \approx \lambda_\nu(\xi_c) - \frac{1}{\xi_c}.
\]

2.4. Asymptotic matching for all forces

Utilizing Prandtl’s method of asymptotic matching [Powers and Sen 2015], a composite asymptotic relation for the equilibrium chain stretch is found that is applicable for all chain forces with steep segment potential \( (\zeta_{\nu}^{\text{char}}, \kappa_{\nu} \gg 1) \):

\[
\lambda_{\nu}^{\text{eq}}(\xi_c) \approx \mathcal{L}(\xi_c) + \frac{\xi_c}{\kappa_{\nu}} \left[ 1 + \frac{1 - \mathcal{L}(\xi_c) \coth(\xi_c)}{\tilde{\nu}} \right] + \lambda_\nu(\xi_c) - 1.
\]
When $\kappa_c$ is sufficiently large, causing the second term to become negligible, Eq. (13) can be simplified to a useful form
\[
\lambda_c^{eq}(\xi_c) = \mathcal{L}(\xi_c) + \lambda_c(\xi_c) - 1.
\]  
With $\lambda_c^{eq}$ in hand, the nondimensional Helmholtz free energy per segment, $\psi_{uw}$, is desired. Employing the Legendre transform, which is asymptotically valid in the thermodynamic limit of sufficiently long chains and appreciable chain forces (Buche and Silberstein, 2020), the Helmholtz free energy $\Psi_c$ is given as
\[
\Psi_c \approx r_c f_c(r_c) - \int r_c(f_c)df_c.
\]  
Substituting Eq. (14) in a nondimensional form of Eq. (15) and performing integration by parts leads to
\[
\psi_{uw}(\lambda_c^{eq}) = \xi_c(\lambda_c^{eq})\mathcal{L}(\xi_c(\lambda_c^{eq})) + \ln\left(\frac{\xi_c(\lambda_c^{eq})}{\sinh(\xi_c(\lambda_c^{eq}))}\right) + u_c(\lambda_c(\xi_c(\lambda_c^{eq}))),
\]  
where $\psi_{uw} = \beta\Psi_c/\nu$.

At this point, Buche and Silberstein (2021) and Buche et al. (2022) use numerics to determine $\xi_c$ from Eq. (14). However, this does not lend itself to a tractable closed-form model when the single chain model is upscaled to a continuum model. Ultimately, this limits the impact of the careful statistical mechanics analysis on the design of materials and resilient structures.

3. Extension of the uFJC model

To yield a tractable, closed-form continuum level model based upon the uFJC model, we extend the uFJC model by seeking an analytical form for $\xi_c(\lambda_c^{eq})$ and $\lambda_c(\lambda_c^{eq})$. Along the way, the principles of asymptotic matching and the use of highly accurate function approximations will be employed.

3.1. Analytical form for the chain force

The analytical form for $\xi_c(\lambda_c^{eq})$ is found by inverting Eq. (14)
\[
\lambda_c^{eq} = \mathcal{L}(\xi_c(\lambda_c^{eq})) + \lambda_c(\lambda_c^{eq}) - 1 = \mathcal{L}(\xi_c(\lambda_c^{eq})) + \lambda_c - 1,
\]  
$\xi_c(\lambda_c^{eq}) = \mathcal{L}^{-1}(\lambda_c^{eq} - \lambda_c + 1),$
\]  
where $\lambda_c$ is written with the understanding that $\lambda_c = \lambda_c(\lambda_c^{eq})$. Substituting Eq. (17) into Eq. (16) leads to a useful analytical form for $\psi_{uw}$
\[
\psi_{uw}(\lambda_c, \lambda_c^{eq}) = s_{uw}(\lambda_c, \lambda_c^{eq}) + u_c(\lambda_c),
\]  
\[
s_{uw}(\lambda_c, \lambda_c^{eq}) = |\lambda_c^{eq} - \lambda_c + 1|\mathcal{L}^{-1}(\lambda_c^{eq} - \lambda_c + 1) + \ln\left(\frac{\mathcal{L}^{-1}(\lambda_c^{eq} - \lambda_c + 1)}{\sinh(\mathcal{L}^{-1}(\lambda_c^{eq} - \lambda_c + 1))}\right),
\]  
\[
\psi_{uw}(\lambda_c, \lambda_c^{eq}) = |\lambda_c^{eq} - \lambda_c + 1|\mathcal{L}^{-1}(\lambda_c^{eq} - \lambda_c + 1) + \ln\left(\frac{\mathcal{L}^{-1}(\lambda_c^{eq} - \lambda_c + 1)}{\sinh(\mathcal{L}^{-1}(\lambda_c^{eq} - \lambda_c + 1))}\right) + u_c(\lambda_c).
\]  
where $s_{uw}$ is the nondimensional chain-level entropic contributions per segment, and $u_c$ is the nondimensional segment-level enthalpic contributions. Now, recall that the chain force $f_c$ can also be calculated with respect to the Helmholtz free energy $\Psi_c$ as
\[
f_c = \frac{\partial\Psi_c}{\partial r_c}.
\]  
Pushing Eq. (20) through a nondimensional form of Eq. (21) returns Eq. (17), thereby verifying the analytical form for $\xi_c(\lambda_c^{eq})$. 

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3.2. Asymptotically matched segment behavior

3.2.1. Segment potential function

In order for the nondimensional chain force function $\xi_c(\lambda_{eq}^c)$ as presented in Eq. (17) to truly be an analytical function of equilibrium chain stretch $\lambda_{eq}^c$, it is required that the segment stretch $\lambda_\nu$ also be an analytical function of $\lambda_{eq}^c$. The functional form of $\lambda_\nu$, defined as per Eq. (11), is dependent upon the complexity of the functional form of the segment potential $U_\nu(l_\nu)$ and its first derivative. Several functional forms of $U_\nu(l_\nu)$ have been proposed and utilized thus far in the literature, including the harmonic potential $U_{\nu}^{\text{har}}$ (Arunachala et al., 2021; Lamont et al., 2021; Li and Bouklas, 2020; Mao and Anand, 2018; Mao et al., 2017a; Mulderrig et al., 2021; Talamini et al., 2018), log-squared potential $U_{\nu}^{\ln2}$ (Arora et al., 2020, 2021; Lu et al., 2020; Mao et al., 2017b; Xiao et al., 2021), Lennard-Jones potential $U_{\nu}^{lj}$ (Feng et al., 2022; Jones, 1924; Lei et al., 2022; Yang et al., 2020; Zhao et al., 2021b), and Morse potential $U_{\nu}^{morse}$ (Buche and Silberstein, 2021; Dal and Kaliske, 2009; Guo and Zaïri, 2021; Lavoie et al., 2019; Morse, 1929):

$$U_{\nu}^{\text{har}}(l_\nu) = E_{\nu}^{\text{char}} \left[ \frac{k_\nu}{2 E_{\nu}^{\text{char}}} \left[ l_\nu - l_{eq}^\nu \right]^2 - 1 \right], \quad U_{\nu}^{\ln2}(l_\nu) = E_{\nu}^{\text{char}} \left[ \frac{1}{2} \frac{|l_{eq}^\nu|^2}{E_{\nu}^{\text{char}}} \ln \left( \frac{l_\nu}{l_{eq}^\nu} \right)^2 - 1 \right],$$

$$U_{\nu}^{lj}(l_\nu) = E_{\nu}^{\text{char}} \left[ \frac{|l_{eq}^\nu|^2}{l_\nu} \right]^{12} - 2 \left( \frac{|l_{eq}^\nu|}{l_\nu} \right)^6, \quad U_{\nu}^{\text{morse}}(l_\nu) = E_{\nu}^{\text{char}} \left[ \left[ 1 - e^{-a_\nu \left( l_\nu - l_{eq}^\nu \right)} \right]^2 - 1 \right], \quad (22)$$

where $a_\nu$ is the Morse parameter and is related to $E_{\nu}^{\text{char}}$ and $k_\nu$ via $k_\nu = 2a_\nu^2 E_{\nu}^{\text{char}}$. The nondimensional Morse parameter is defined as $a_{\nu} = |l_{eq}^\nu| a_\nu$. The nondimensional scaled segment potential $\pi_\nu$, and its (non-negative) shifted counterpart $\Pi_\nu$ are respectively defined as $\pi_\nu = u_\nu / c_{\nu}^{\text{char}}$ and $\Pi_\nu = \pi_\nu + 1$. The proposed segment potentials from Eq. (22) and Eq. (23) are graphically presented in Fig. 1 (in $\tilde{\nu}$ form).

The harmonic potential is the simplest and most commonly used potential to account for segment extensibility, and it approximately captures the general behavior of the other potentials in a neighborhood.
of small $\lambda_\nu$ about the equilibrium state. However, for large $\lambda_\nu$, segment potentials are expected to escape the harmonic potential energy well and exhibit anharmonic behavior. By definition, only the log-squared, Lennard-Jones, and Morse potentials capture this behavior. Additionally, for large $\lambda_\nu$, segment potentials are expected to ultimately escape to an energy plateau equal to $E_\nu^{char}$. Only the Lennard-Jones and Morse potentials capture this behavior. To retain all of the characteristics of the ideal segment potential, we desire to use either the Lennard-Jones or Morse potential in the model framework to yield an analytical form for $\lambda_\nu$.

Unfortunately, due to the squared-exponential term in the Morse potential and two-term polynomial form of the Lennard-Jones potential, it is mathematically impossible for each of these potentials to lead to an approximate analytical expression for $\lambda_\nu$ as a function of $\lambda_\nu^{eq}$ as per Eq. (11) and Eq. (17) (where the inverse Langevin function involved with $\xi_\nu$ is represented by some approximant). In order to overcome this obstacle, we seek to derive a simple, quasi-polynomial segment potential which generally captures the essential aforementioned characteristics exhibited by the Lennard-Jones and Morse potentials. This derivation will necessarily evoke the principle of asymptotic matching, consistent to and allowing for integration within the uFJC framework. Using this derived segment potential, an expression for $\lambda_\nu$ as a function of $\lambda_\nu^{eq}$ will be reached.

To begin, consider the behavior of $\lambda_\nu$ in the low-to-intermediate chain force state as compared to that in the high chain force state. For low and intermediate chain forces, $\lambda_\nu$ resides in a neighborhood about the equilibrium state ($\lambda_\nu \approx 1$). The Lennard-Jones and Morse segment potentials in this neighborhood can be considered to be approximated via the harmonic potential (as highlighted by the black dashed box in the lower left of Fig. 1)

$$\tilde{u}_\nu(\lambda_\nu) \approx \tilde{u}_\nu^{har}(\lambda_\nu) = \frac{1}{2} \frac{\kappa_\nu}{\zeta_\nu^{char}} [\lambda_\nu - 1]^2.$$  \hspace{1cm} (24)

For high chain forces, $\lambda_\nu$ is large ($\lambda_\nu \gg 1$), and the Lennard-Jones and Morse segment potentials have reached their energy plateau equal to $E_\nu^{har}$ (as highlighted by the black dashed box in the upper right of Fig. 1)

$$\tilde{u}_\nu(\lambda_\nu) \approx 1.$$  \hspace{1cm} (25)

When naively applying Prandtl’s method of asymptotic matching to the above low-to-intermediate chain force and high chain force segment potentials ([Powers and Sen] 2015), it is self-evident that an asymptotically-matched composite potential is prohibited. To go about creating a simple, quasi-polynomial, and asymptotically-matched composite potential using the fundamental building blocks available to us in Eq. (24) and Eq. (25), we define a modulation parameter $\mu_\nu = \mu_\nu(\lambda_\nu)$. $\mu_\nu$ is strictly a function of $\lambda_\nu$ with range $\mu_\nu \in [0, 1]$. $\mu_\nu(\lambda_\nu)$ is taken to be a monotonically-increasing function of $\lambda_\nu$. When $\mu_\nu = 0$, the composite potential directly returns the harmonic potential ($\tilde{u}_\nu(\lambda_\nu) = \frac{1}{2} \frac{\kappa_\nu}{\zeta_\nu^{har}} [\lambda_\nu - 1]^2$), and when $\mu_\nu = 1$, the composite potential directly returns the energy plateau $E_\nu^{char}$ ($\tilde{u}_\nu(\lambda_\nu) = 1$). Furthermore, $\mu_\nu \to 1$ faster than $\lambda_\nu \to \infty$, i.e., $\lim_{\lambda_\nu \to \infty} [ (1 - \mu_\nu) [\lambda_\nu - 1] ] = 0$. Finally, the overall composite potential $\tilde{u}_\nu(\mu_\nu, \lambda_\nu)$ is a monotonically-increasing function of $\lambda_\nu$ for $\lambda_\nu \geq 1$, as per Fig. 1. With all this taken into account, the low-to-intermediate chain force segment potential is modulated via $\mu_\nu$ as

$$\tilde{u}_\nu(\mu_\nu, \lambda_\nu) \approx [1 - \mu_\nu] \tilde{u}_\nu^{har}(\lambda_\nu) = [1 - \mu_\nu] \frac{1}{2} \frac{\kappa_\nu}{\zeta_\nu^{char}} [\lambda_\nu - 1]^2,$$  \hspace{1cm} (26)

and the high chain force segment potential is modulated via $\mu_\nu$ as

$$\tilde{u}_\nu(\mu_\nu, \lambda_\nu) \approx \mu_\nu^f,$$  \hspace{1cm} (27)

where $f$ and $g$ are integers. Now, we apply Prandtl’s method of asymptotic matching to the modulated low-to-intermediate chain force and high chain force segment potentials ([Powers and Sen] 2015), which involves satisfying

$$\lim_{\lambda_\nu \to \infty} [1 - \mu_\nu] \frac{1}{2} \frac{\kappa_\nu}{\zeta_\nu^{har}} [\lambda_\nu - 1]^2 = \lim_{\lambda_\nu \to 0} \mu_\nu^g = 0.$$  \hspace{1cm} (28)
From the above, \( f = 2 \) and \( g \neq 0 \) must hold true. In order to achieve the simplest composite function, we set \( g = 1 \). The composite potential is consequently written as

\[
\tilde{u}_\nu(\mu_\nu, \lambda_\nu) = [1 - \mu_\nu]^2 \frac{1}{2} \frac{\kappa_\nu}{\zeta_\nu^{\text{char}}} (\lambda_\nu - 1)^2 + \mu_\nu. \tag{29}
\]

All that remains to be satisfied is the condition that the composite potential is a monotonically-increasing function of \( \lambda_\nu \) for \( \lambda_\nu \geq 1 \):

\[
\frac{\partial}{\partial \lambda_\nu} [\tilde{u}_\nu(\mu_\nu, \lambda_\nu)] = \frac{\partial \tilde{u}_\nu}{\partial \mu_\nu} \frac{\partial \mu_\nu}{\partial \lambda_\nu} + \frac{\partial \tilde{u}_\nu}{\partial \lambda_\nu} \geq 0 \text{ for } \lambda_\nu \geq 1. \tag{30}
\]

Since it is assumed that \( \mu_\nu(\lambda_\nu) \) is a monotonically-increasing function of \( \lambda_\nu \), we seek to strongly satisfy the above by forcing the following equations to individually hold true

\[
\frac{\partial \tilde{u}_\nu}{\partial \lambda_\nu} = [1 - \mu_\nu]^2 \frac{\kappa_\nu}{\zeta_\nu^{\text{char}}} (\lambda_\nu - 1) \geq 0 \text{ for } \lambda_\nu \geq 1, \tag{31}
\]

\[
\frac{\partial \tilde{u}_\nu}{\partial \mu_\nu} = -[1 - \mu_\nu]^2 \frac{\kappa_\nu}{\zeta_\nu^{\text{char}}} (\lambda_\nu - 1)^2 + 1 \geq 0 \text{ for } \lambda_\nu \geq 1. \tag{32}
\]

Using the properties of \( \mu_\nu(\lambda_\nu) \), Eq. (31) automatically holds true. The satisfaction of Eq. (32), as detailed in Appendix A, yields the functional form for \( \mu_\nu = \mu_\nu(\lambda_\nu) \):

\[
\mu_\nu = \begin{cases} 
0, & \text{if } \lambda_\nu < \lambda_\nu^{\text{crit}} \\
1 - \frac{\zeta_\nu^{\text{char}}}{\kappa_\nu (\lambda_\nu - 1)^2}, & \text{if } \lambda_\nu \geq \lambda_\nu^{\text{crit}}
\end{cases} \tag{33}
\]

where \( \lambda_\nu^{\text{crit}} \equiv 1 + \sqrt{\frac{\zeta_\nu^{\text{char}}}{\kappa_\nu}} \) is called the critical segment stretch (and \( \lambda_\nu^{\text{crit}} \) is the corresponding critical equilibrium chain stretch). With this, the composite nondimensional scaled segment potential \( \pi_\nu \) can be written as a function of \( \lambda_\nu \)

\[
\pi_\nu(\lambda_\nu) = \begin{cases} 
\frac{1}{2} \frac{\kappa_\nu}{\zeta_\nu^{\text{char}}} (\lambda_\nu - 1)^2 - 1, & \text{if } \lambda_\nu < \lambda_\nu^{\text{crit}} \\
\frac{\kappa_\nu}{2 \zeta_\nu^{\text{char}}} (\lambda_\nu - 1)^2, & \text{if } \lambda_\nu \geq \lambda_\nu^{\text{crit}}
\end{cases} \tag{34}
\]

The composite nondimensional segment potential \( u_\nu \) is simply Eq. (34) multiplied by \( \zeta_\nu^{\text{char}} \). Using the functional forms for the modulation parameter in Eq. (33) and the segment potential (e.g., Eq. (34)), each presuppositional property of the modulation parameter \( \mu_\nu \) and the composite segment potential \( u_\nu \) can be trivially verified. Furthermore, it can also be verified that \( u_\nu \) is continuous up to the first derivative at \( \lambda_\nu = \lambda_\nu^{\text{crit}} \), i.e.,

\[
u(\lambda_\nu^{\text{crit}}) = -\frac{\zeta_\nu^{\text{char}}}{2} \text{ and } \frac{\partial u_\nu}{\partial \lambda_\nu} \bigg|_{\lambda_\nu=\lambda_\nu^{\text{crit}}} = \sqrt{\kappa_\nu \zeta_\nu^{\text{char}}}. \tag{35}
\]

The composite \( \pi_\nu \) is plotted alongside its Lennard-Jones and Morse potential counterparts in Fig. 2. From this figure, it is clear that the composite potential exhibits the desired characteristics of the Lennard-Jones and Morse potentials: harmonic behavior near the equilibrium state and anharmonic behavior for large \( \lambda_\nu \) tending to an energy plateau of \( E_\nu^{\text{char}} \). These desired characteristics are expressed purely as a consequence of the derivation undertaken here, without any consideration of the specific functional form of the Lennard-Jones and Morse potentials. Conveniently, the derivation results in a composite potential with a simple functional form, as per Eq. (34).

### 3.2.2. Segment stretch function

With the simple, quasi-polynomial composite segment potential in hand, a highly accurate approximated analytical relationship between segment stretch and equilibrium chain stretch can now be derived. Substituting the composite \( u_\nu \) (Eq. (34) multiplied by \( \zeta_\nu^{\text{char}} \)) into the definition of \( \lambda_\nu \) in Eq. (11) and simplifying
Figure 2: Lennard-Jones, Morse, and composite nondimensional scaled segment potentials $\vec{u}_\nu$ versus $\lambda_\nu$. The same $\zeta_{\nu}^{\text{char}}$ and $\kappa_\nu$ values are used here as in Fig. 1. The black dotted line denotes the critical segment stretch value $\lambda_{\nu}^{\text{crit}}$ for the composite segment potential.

leads to

$$\xi_c = \mathcal{L}^{-1}(\lambda_c^{eq} - \lambda_\nu + 1) = \frac{\partial u_\nu}{\partial \lambda_\nu} = \begin{cases} \kappa_\nu [\lambda_\nu - 1], & \text{if } \lambda_c^{eq} < (\lambda_c^{eq})^{\text{crit}} \\ \frac{\kappa_\nu^{\text{char}} - \kappa_\nu^{\text{char}}^2}{\kappa_\nu^{\text{char}}}, & \text{if } \lambda_c^{eq} \geq (\lambda_c^{eq})^{\text{crit}} \end{cases}.$$  \hspace{1cm} (36)

Note that $\lambda_c^{eq} < (\lambda_c^{eq})^{\text{crit}}$ corresponds one-to-one to the case when $\lambda_\nu < \lambda_\nu^{\text{crit}}$, and $\lambda_c^{eq} \geq (\lambda_c^{eq})^{\text{crit}}$ corresponds one-to-one to the case when $\lambda_\nu \geq \lambda_\nu^{\text{crit}}$. We now seek to employ an approximation for the inverse Langevin function in order to yield an approximate analytical solution. Two candidates stand out for the task: the Padé approximant \cite{Cohen1991}

$$\mathcal{L}^{-1}(y) \approx y \left( \frac{3 - y^2}{1 - y^2} \right),$$  \hspace{1cm} (37)

and the Bergström approximant \cite{Bergstrom2000}

$$\mathcal{L}^{-1}(y) \approx \frac{1}{\text{sgn}(y) - y}, \text{ for } 0.84136 < |y| < 1,$$  \hspace{1cm} (38)

where $\text{sgn}(y)$ is the sign function:

$$\text{sgn}(y) = \begin{cases} -1, & \text{if } y < 0 \\ 0, & \text{if } y = 0 \\ 1, & \text{if } y > 0 \end{cases}.$$  \hspace{1cm} (39)

Using the Padé approximant for the $\lambda_c^{eq} < (\lambda_c^{eq})^{\text{crit}}$ case and performing an appropriate cubic root analysis \cite{Zwillinger2002} leads to

$$\lambda_\nu = \lambda_\nu^{PSB}(\kappa_\nu; \lambda_c^{eq}),$$  \hspace{1cm} (40)
where the analytical form of $\lambda_{PS}^{eq}$ is provided in Appendix B. Likewise, using the Bergström approximant for the $\lambda_{eq}^{<} < (\lambda_{eq}^{eq})^{crit}$ case and performing an appropriate quadratic root analysis leads to

$$\lambda_{\nu} = \lambda_{BS}^{eq}(\kappa; \lambda_{eq}^{eq}),$$

(41)

where the analytical form of $\lambda_{BS}^{eq}$ is provided in Appendix B.

The top panel in Fig. 3 displays $\lambda_{PS}^{eq}$ and $\lambda_{BS}^{eq}$ in the domain $0 \leq \lambda_{eq}^{eq} < (\lambda_{eq}^{eq})^{crit}$, and the bottom panel displays the error of each approximation compared to $\lambda_{\nu}$, calculated using a highly accurate numerical solution for the inverse Langevin function. The bottom panel in Fig. 3 clearly shows that $\lambda_{PS}^{eq}$ is more accurate than $\lambda_{BS}^{eq}$ to the left of the black dashed line. On the contrary, $\lambda_{BS}^{eq}$ is more accurate than $\lambda_{PS}^{eq}$ to the right of the black dashed line. This black dashed line denotes $(\lambda_{eq}^{eq})^{PS}$, the equilibrium chain stretch value at which this crossover in numerical accuracy takes place (see Remarks 1 and 2 for more details).

Using the Bergström approximant for the $\lambda_{eq}^{eq} \geq (\lambda_{eq}^{eq})^{crit}$ case and performing an appropriate cubic root analysis (Zwillinger, 2002) leads to

$$\lambda_{\nu} = \lambda_{BS}^{eq}(\zeta_{\nu}; \kappa; \lambda_{eq}^{eq}),$$

(42)

where the analytical form of $\lambda_{BS}^{eq}$ is provided in Appendix B. Unfortunately, using the Padé approximant for the $\lambda_{eq}^{eq} \geq (\lambda_{eq}^{eq})^{crit}$ case results in a sixth-order polynomial in $\lambda_{\nu}$, which does not possess a general form for an analytical solution.
Considering all of this, the approximated analytical form of $\lambda_\nu$ as a function of $\lambda_{eq}^c$ is

$$
\lambda_\nu = \begin{cases} 
\lambda_{PB}^{PSB}(\kappa_\nu; \lambda_{eq}^c), & \text{if } \lambda_{eq}^c < (\lambda_{eq}^c)^{P2B} \\
\lambda_{PB}^{BSB}(\kappa_\nu; \lambda_{eq}^c), & \text{if } (\lambda_{eq}^c)^{P2B} \leq \lambda_{eq}^c < (\lambda_{eq}^c)^{crit} \\
\lambda_{BP}^{SP}(\kappa_{char}; \lambda_{eq}^c), & \text{if } \lambda_{eq}^c \geq (\lambda_{eq}^c)^{crit} 
\end{cases}
$$

Fig. 4 displays the approximated $\lambda_\nu$ function as per Eq. (43), $\lambda_\nu$ calculated using a highly accurate numerical solution for the inverse Langevin function, and the percent error of the approximation. This figure convincingly verifies that the approximated analytical $\lambda_\nu$ function is highly accurate with respect to the highly accurate numerical solution in the domain of physically-sensible $\lambda_{eq}^c$. 

In accordance with the uFJC model framework as introduced in Buche and Silberstein (2021) and Buche et al. (2022) (the reader is referred to the arguments detailed therein), $\lambda_\nu$ is implicitly defined to satisfy the equality between the chain force and the segment force, as per Eq. (11). This uFJC chain force satisfaction method differs from the condition that $\lambda_\nu$ be the minimizer of the chain Helmholtz free energy $\Psi_c$, as proposed by Mao et al. (2017b) and widely adopted in the literature since:

$$
\lambda_\nu = \text{arg min}_{\lambda_\nu \geq 1} \Psi_c(\lambda_\nu), \text{ where } \Psi_c(\lambda_\nu) = \Psi_c(\lambda_\nu, \lambda_c = \hat{\lambda}_c),
$$

where $\lambda_c = \hat{\lambda}_c$ is a given imposed chain stretch.

In an effort to compare the numerical results of the chain free energy minimization method to the uFJC chain force satisfaction method, $\lambda_\nu$ is calculated via both methods for increasingly steep segments, with the
latter method presented in the top panels in Fig. 5. The percent error of the $\lambda_v$ calculation from the chain free energy minimization method (with respect to the uFJC chain force satisfaction method) is provided in the bottom panels. In order to ensure an equal comparison between both $\lambda_v$ calculation methods, $\Psi_c$ involved in the chain free energy minimization method obeys $\text{Eq. (20)}$ multiplied by $\nu/\beta$. In addition, $\lambda_v$ is presented as a function of $\lambda^{eq}_v$, which normalizes the impact of chain segment number on the $\lambda_v$ calculations. $\lambda^{eq}_v$ is then further divided by $(\lambda^{eq}_v)^{crit}$ as a means of normalizing the impact of differing $(\lambda^{eq}_v)^{crit}$ values for segments with varying $\zeta^\text{char}_v$ and $\kappa_v$. As indicated by the bottom panels in Fig. 5 the chain free energy minimization method numerically complies quite well with the uFJC chain force satisfaction method for $\lambda^{eq}_v$ less than, equal to, and slightly greater than $(\lambda^{eq}_v)^{crit}$, i.e., for low and intermediate chain forces $\xi$. For extremely large $\lambda^{eq}_v$, i.e., for extremely high chain forces $\xi$, the chain free energy minimization method will numerically diverge from the uFJC chain force satisfaction method. This is implied by the trend in the percent error curves for increasing $\lambda^{eq}_v/(\lambda^{eq}_v)^{crit} \gg 1$.

Remark 1. The black dashed line in Fig. 3 denotes $(\lambda^{eq}_v)^{P2B}$, the equilibrium chain stretch value at which the Padé approximant $\lambda_v$ solution becomes less numerically accurate than the Bergström approximant $\lambda_v$ solution (hence $P2B$). Given $\text{Eq. (40)}$ and $\text{Eq. (41)}$, $(\lambda^{eq}_v)^{P2B}$ solely depends on $\kappa_v$. A curve fit analysis was used to determine the relationship between $(\lambda^{eq}_v)^{P2B}$ and $\kappa_v$:

$$\left(\lambda^{eq}_v\right)^{P2B} = \frac{1}{\kappa_v^2} + b,$$

where $n = 0.8187$ and $b = 0.6176.$  \hfill (45)

Remark 2. According to $\text{Eq. (38)}$, the Bergström approximant, as originally proposed, is only valid for $\lambda^{eq}_v - \nu_v + 1 \geq 0.84136$ (Bergström and Boyce 2000). $\lambda^{eq}_v$ values that exist at and to the right of the black dotted line in Fig. 3 correspond to the situation where $\lambda^{eq}_v - \nu_v + 1 \geq 0.84136$. However, for $\lambda^{eq}_v$ values that exist to the left of the black dotted line (where $\lambda^{eq}_v - \nu_v + 1 < 0.84136$) and to the right of the black dashed line (where $\lambda^{eq}_v > (\lambda^{eq}_v)^{P2B}$), $\lambda^{BSB}_v$ is highly accurate in this $\lambda^{eq}_v$ regime (even more accurate than $\lambda^{PSB}_v$ is). This can be visually confirmed in the bottom panel of Fig. 3. As a result, $\lambda^{BSB}_v$ is validated to be used in this $\lambda^{eq}_v$ regime (where $\lambda^{eq}_v > (\lambda^{eq}_v)^{P2B}$ and $\lambda^{eq}_v - \nu_v + 1 < 0.84136$ are true).

Figure 5: Comparison of segment stretches calculated via the uFJC chain force satisfaction method and the chain free energy minimization method. (a, top) Segment stretch $\lambda_v$ calculated via the uFJC chain force satisfaction method as a function of equilibrium chain stretch normalized by the critical equilibrium chain stretch, $\lambda^{eq}_v/(\lambda^{eq}_v)^{crit}$, for $\kappa_v = 1000$ and varying $\zeta^\text{char}_v$. (b, top) $\lambda_v$ calculated via the uFJC chain force satisfaction method as a function of $\lambda^{eq}_v/(\lambda^{eq}_v)^{crit}$, for $\zeta^\text{char}_v = 100$ and varying $\kappa_v$. (bottom) Percent error of $\lambda_v$ calculated via the chain free energy minimization method (with respect to $\lambda_v$ calculated via the uFJC chain force satisfaction method) as a function of $\lambda^{eq}_v/(\lambda^{eq}_v)^{crit}$. The sharp dips in these percent error curves take place where the $\lambda_v$ values calculated by the chain free energy minimization method cross over or under the $\lambda_v$ values calculated by the uFJC chain force satisfaction method.
Remark 3. Use of the approximated (and highly accurate) analytical form of $\lambda_\nu$ as a function of $\lambda_\nu^c$, as obtained in Eq. (43), allows one to avoid using numerics to computationally calculate the inverse relationship between $\lambda_\nu^c$ and $\lambda_\nu$. Furthermore, substituting Eq. (43) into Eq. (17) returns an approximated analytical form of $\xi_c$ as a function of $\lambda_\nu^c$ (where the inverse Langevin function present in Eq. (17) is represented by some approximant). This also allows one to avoid using the tools of numerics to computationally calculate the inverse relationship between $\lambda_\nu^c$ and $\xi_c$. Considering all of this, a tractable closed-form model emerges when the single chain model is upscaled to a continuum-level model. In this way, costly numerical inverse operations and/or minimization operations are replaced with efficient closed-form solutions in the computational implementation of this continuum model.

4. Single chain scission energetics and probabilistic considerations

With the single chain model established, a probabilistic description of single chain rupture can now be built upon the principles of mechanochemistry (Bell, 1978; Beyer and Clausen-Schaumann, 2005; Ribas-Arino and Marx, 2012; Zhurkov, 1965). To ultimately provide insight to fracture toughness at the network level, the energy released upon thermally-activated chain scission must be tracked in this framework (Wang et al., 2019). To close the loop in the statistical mechanics-based single chain framework accounting for rupture, the reference end-to-end chain distance is derived to be functionally dependent upon segment extensibility and segment number.

4.1. Segment scission energetics and probabilistic considerations

According to the principles of mechanochemistry, the segments along the backbone of a polymer chain are physically permitted to undergo thermally activated rupture with a probability dependent upon the externally applied force to the chain (Bell, 1978; Beyer and Clausen-Schaumann, 2005; Ribas-Arino and Marx, 2012; Zhurkov, 1965). Using these principles, a variety of rate-dependent bulk and interfacial polymer damage models have been developed (Chaudhury, 1999; Feng et al., 2022; Freund, 2014; Ghatak et al., 2000; Guo and Zaïri, 2021; Hui et al., 2004; Kothari et al., 2018; Lavoie et al., 2015, 2016; Lei et al., 2022; Lu et al., 2020; Tehrani and Sarvestani, 2017; Yang et al., 2020, 2019b). Notably, Yang et al. (2020) proposed a rate-dependent interfacial polymer damage model where the probability of bond dissociation is calculated using the force-dependent segment-level Gibbs free energy. In this current work, a segment-level rupture framework will be developed utilizing a force-distorted energy landscape. However, we impose the requirement that the segment explore this energy landscape only via its thermally-activated stretch state under a constantly-held externally applied chain force. Since the segment-level Gibbs free energy landscape can only be traversed via varying the applied chain force, a segment-level potential energy landscape dependent on a fixed applied chain force is instead used. This particular energy landscape choice is further substantiated by the fact that enthalpic segment distortion dominates over entropic contributions as the segments in a chain approach the state of rupture (Lake and Thomas, 1967; Wang et al., 2019). Probabilistic considerations will then be used as per Guo and Zaïri (2021) to develop a chain-level rupture framework.

In the absence of thermal vibrations, a segment in equilibrium must be supplied an activation energy equal to $E_{\nu}^{\text{bar}}$ in order to undergo rupture. However, this activation energy can be reduced upon the application of a force to the chain. The mechanochemical basis for this activation energy reduction can be found in the “tilting” or “distortion” of the segment potential energy landscape due to the externally applied chain force. This “tilted” segment potential is captured by the previously discussed nondimensional total segment potential in Eq. (9), following a Legendre transformation of the segment potential energy

$$u_{\nu}^{\text{tot}}(\hat{\xi}_\nu, \lambda_\nu) = u_\nu(\lambda_\nu) - \hat{\xi}_c \lambda_\nu,$$

where $\hat{\xi}_c$ is the particular force applied to the chain. Unlike earlier in this work, a hat overtop is used hereafter to signify quantities which are in the force controlled setting. The implicit definition of the segment stretch remains unchanged from before in Eq. (11) which implies that the application of chain force $\xi_c$ corresponds one-to-one to $\hat{\lambda}_\nu$. $\hat{\lambda}_\nu$ will be referred to as the applied (or particularized) segment stretch. The applied
(or particularized) equilibrium chain stretch $\dot{\lambda}_{eq}$ can be calculated from $\dot{\lambda}_v$ via inverting the $\lambda_v$ function in Eq. (43). The approximated analytical relationship between $\lambda_{eq}$ as a function of $\lambda_v$ is provided in Appendix C. For the sake of notational clarity (since there is a one-to-one relationship between $\xi_c$ and $\lambda_v$), $u_{tot}^{\nu}$ is equivalently written as $\dot{u}_{tot}^{\nu} \left( \dot{\lambda}_v, \lambda_v \right) = u_v \left( \lambda_v \right) - \xi_c \left( \dot{\lambda}_v \right) * \lambda_v$ (where the first argument of $\dot{u}_{tot}^{\nu}$ indicates the level of force-driven tilting imposed to $u_v$ - which transforms $u_v$ to $\dot{u}_{tot}^{\nu}$ - and the second argument specifies a particular state in the energy landscape of $\dot{u}_{tot}^{\nu}$).

Fig. 6 displays the energy landscape for the nondimensional scaled tilted segment potential $\hat{u}_{tot}^{\nu} = \dot{u}_{tot}^{\nu} / \xi_{char}^{\nu}$ for various states of $\xi_c$. The blue curve corresponds to $\dot{u}_{tot}^{\nu}$ for a segment in an undisturbed chain in a force-free state, i.e., $u_v$. Upon the application of $\xi_c$, $u_v$ transforms to $\dot{u}_{tot}^{\nu}$ via tilting the blue curve to a particular non-blue colored curve. Dots and squares correspond to the local minimum energy state and local maximum energy state of $\dot{u}_{tot}^{\nu}$, respectively, and the segment stretch corresponding to these two stationary points express the following form

$$\hat{\lambda}_{locmin} = \hat{\lambda}_v = 1 + \frac{\xi_c}{\kappa_v}, \quad \hat{\lambda}_{locmax} = 1 + \sqrt{\left[ \frac{\xi_{char}^{\nu}}{\kappa_v} \right]^2 \left[ \frac{1}{\xi_c} \right]}.$$

(47)

For the segment in an undisturbed, force-free chain, $\hat{\lambda}_{locmin} = 1$ and $\hat{\lambda}_{locmax} = \infty$ (hence why the blue square is not pictured in Fig. 6). Also, $\hat{\lambda}_{locmin} = \hat{\lambda}_{locmax} = \hat{\lambda}_{crit}^{\nu}$ (i.e., $\hat{\lambda}_v = \hat{\lambda}_{crit}^{\nu}$) occurs when $\xi_c = \sqrt{\kappa_v \xi_{char}^{\nu}} = \xi_{crit}^{\nu}$.

The activation energy barrier required for a segment to escape from the bottom of the potential energy well and undergo a scission reaction is simply the energy difference between an identically-colored square and dot pair (the difference between the local maximum and local minimum energy states of $\dot{u}_{tot}^{\nu}$). The nondimensional segment scission activation energy barrier thus obeys the following

$$\hat{\epsilon}_{sci}^{\nu} = \dot{u}_{tot}^{\nu} \left( \dot{\lambda}_v, \hat{\lambda}_{locmax} \right) - \dot{u}_{tot}^{\nu} \left( \dot{\lambda}_v, \hat{\lambda}_{locmin} \right).$$

(48)

The energy needed to overcome the activation energy barrier is supplied via segment-level thermal fluctuations. Considering a statistically significant number of segments, the rate-independent probability of segment scission $\hat{p}_{sci}^{\nu}$ and the rate-independent probability of segment survival $\hat{p}_{sur}^{\nu}$ are

$$\hat{p}_{sci}^{\nu} = \exp \left\{ -\hat{\epsilon}_{sci}^{\nu} \right\}, \quad \hat{p}_{sur}^{\nu,ext} = 1 - \hat{p}_{sci}^{\nu}.$$  

(49)

Clearly, when $\xi_c = \xi_{crit}^{\nu}$, then segment scission occurs automatically. The rate-dependent probability of segment survival $\rho_v$ follows an Arrhenius law (Freund 2009 Yang et al. 2020 2019b) and has an associated rate-dependent probability of segment scission $\gamma_v$

$$\frac{\dot{\rho}_v}{\rho_v} = -\omega_0 \hat{p}_{sci}^{\nu}, \quad \gamma_v = 1 - \rho_v \quad \Rightarrow \quad \frac{\dot{\gamma}_v}{1 - \gamma_v} = \omega_0 \hat{p}_{sci}^{\nu},$$

(50)

where the dot above implies a time derivative (i.e., a time rate-of-change) and $\omega_0$ is a microscopic frequency. This frequency is often interpreted as the natural frequency of atomic oscillation: $\omega_0 = (k_B T) / h \approx 10^{13} \text{ 1/sec}$, where $h$ is the Planck constant (Hänggi et al. 1990 Yang et al. 2020 2019b). However, different frequencies for $\omega_0$ have been proposed and investigated (Guo and Zauri 2021 Hänggi et al. 1990 Yang et al. 2020). For the rate-dependent scission framework, the segment lifetime decreases as the applied chain force increases.

The final quantity that remains to be ascertained is the amount of potential energy the segment releases upon scission. This energetic quantity is necessary to ultimately calculate the amount of energy dissipated within a polymer network due to chain rupture. Unfortunately, the tilted segment potential does not indicate whatsoever how much energy is released by the segment during a rupture event. To overcome this shortcoming, the conceptual schema provided in the formative work of Wang et al. (2019) is evoked.

First, Wang et al. (2019) identified the product of the force applied to the segment and the length of the segment as the distorted segment potential energy. More physically, the distorted segment potential
energy can be considered as the energy the segment stores due to its distortion under load, i.e., the work done by the applied load to the segment when assuming no thermal fluctuations. This energetic quantity is represented in nondimensional form as \( \tilde{u}_\nu^{\text{distort}} (\lambda_\nu) = \xi_c (\lambda_\nu) \ast \lambda_\nu \).

Then, Wang et al. (2019) proposed a reformulated tilted segment potential that captures both the reduction in segment scission activation energy upon applied force and the distorted segment potential energy. This reformulated tilted segment potential, \( \tilde{u}_\nu \), which we call the total distorted segment potential, is simply the sum of the original tilted segment potential and the distorted segment potential, and is provided in nondimensional form

\[
\tilde{u}_\nu (\lambda_\nu, \lambda_\nu) = \tilde{u}_\nu^{\text{tot}} (\lambda_\nu, \lambda_\nu) + \tilde{u}_\nu^{\text{distort}} (\lambda_\nu) = u_\nu (\lambda_\nu) - \xi_c (\lambda_\nu) \left[ \lambda_\nu - \lambda_\nu \right].
\]

More physically, the total distorted segment potential is the potential energy of the segment in the displacement controlled setting, plus the difference in work done by the load to the segment applied with and without thermal fluctuations. The implicit definition of the segment stretch using \( \tilde{u}_\nu \) also remains unchanged from before in Eq. (11). Figure 7 displays the energy landscape for the nondimensional scaled total distorted segment potential \( \tilde{u}_\nu = \tilde{u}_\nu / \xi_c^{\text{natur}} \) for various states of \( \xi_c \). Identically colored curves in both Fig. 6 and Fig. 7 correspond to identical states of \( \xi_c \). As in Fig. 6, dots and squares correspond to the energy state of the two stationarity points of \( \tilde{u}_\nu \), and the segment stretch of the stationary points of \( \tilde{u}_\nu \) are identical to those for \( \tilde{u}_\nu^{\text{tot}} \) in Eq. (47).
Clearly, $\hat{u}$ and squares represent the value of segment potential energy as the segment scission potential energy, and is provided in nondimensional form

$$u_{\nu}^{\text{sci}} = u_{\nu}(\lambda_{\nu}, \lambda_{\nu}^{\text{locmin}}) - u_{\nu}(1,1) = u_{\nu}(\lambda_{\nu}) + \zeta_{\nu}^{\text{char}}.$$  \hspace{1cm} (52)

When comparing the $u_{\nu}^{\text{tot}}$ curves in Fig. 6 to the $u_{\nu}$ curves in Fig. 7, two important takeaways can be made regarding the relationship between $u_{\nu}^{\text{tot}}$ and $u_{\nu}$. First, it is trivial to show that the activation energy barrier of segment scission for $u_{\nu}$ is (numerically) identical to that for $u_{\nu}^{\text{tot}}$. As a consequence, all of the segment scission probabilistics associated with $u_{\nu}$ are identical to the segment scission probabilistics calculated from $u_{\nu}^{\text{tot}}$. Second, $\hat{u}_{\nu}$ is clearly generated by translating $u_{\nu}^{\text{tot}}$ up in such a way so that its local minimum energy state is its intersection point with $u_{\nu}$, the potential energy curve for a segment in an undisturbed, force-free chain.

This last takeaway has serious implications on segment scission energetics, as displayed by Fig. 4 and as identified previously by Wang et al. [2019]: since a non-blue colored dot (the local minimum energy state of $\hat{u}_{\nu}$) always lies on the blue curve ($u_{\nu}$), then the stored potential energy in a distorted segment is simply the energy difference between a non-blue colored dot with the blue dot. If thermal fluctuations supply a segment the requisite energy to overcome its scission activation energy barrier, then the stored potential energy would be released upon the completion of the scission reaction. Wang et al. [2019] defined this stored segment potential energy as the segment scission potential energy, and is provided in nondimensional form

$$u_{\nu}^{\text{sci}} = \hat{u}_{\nu}(\lambda_{\nu}, \lambda_{\nu}^{\text{locmin}}) - \hat{u}_{\nu}(1,1) = \hat{u}_{\nu}(\lambda_{\nu}) + \zeta_{\nu}^{\text{char}}.$$  \hspace{1cm} (52)

Clearly, $u_{\nu}^{\text{sci}}$ is simply $u_{\nu}(\lambda_{\nu})$ shifted by $\zeta_{\nu}^{\text{char}}$. Considering this, the nondimensional segment scission
Figure 8: Segment scission energetics and probabilistics. Here, $\zeta_{\text{char}} = 100$ and $\kappa_{\nu} = 1000$, as per the composite segment potential displayed in Fig. 2. (top) Nondimensional scaled segment scission activation energy barrier $\hat{e}_{\text{sci}}$, nondimensional scaled segment scission energy $\hat{\varepsilon}_{\text{sci}}$, and rate-independent nondimensional scaled dissipated segment scission energy $\hat{\varepsilon}_{\text{diss}}$ as a function of applied segment stretch $\hat{\lambda}_{\nu}$ in the domain $1 \leq \hat{\lambda}_{\nu} \leq \lambda_{\nu}^{\text{crit}}$. (bottom) Rate-independent probability of segment scission $\hat{p}_{\text{sci}}$ and rate-independent probability of segment survival $\hat{p}_{\text{sur}}$ as a function of $\hat{\lambda}_{\nu}$ in the domain $1 \leq \hat{\lambda}_{\nu} \leq \lambda_{\nu}^{\text{crit}}$.

energy is then defined as the nondimensional per segment Helmholtz free energy under $\hat{\xi}_{\nu}$ shifted by $\zeta_{\text{char}}$

$$\hat{e}_{\nu} \equiv s_{\nu} \left( \hat{\lambda}_{\nu}, \hat{\lambda}_{\nu}^{eq} \right) + u_{\nu} \left( \hat{\lambda}_{\nu} \right) + \zeta_{\text{char}} \nu = \psi_{\nu} \left( \hat{\lambda}_{\nu}, \hat{\lambda}_{\nu}^{eq} \right) + \zeta_{\text{char}}. \quad (53)$$

Note that $\hat{e}_{\nu}^{\text{sci}}$ here is the energy released by a single segment as it ruptures. However, by considering a statistically significant number of segments, a nondimensional dissipated segment scission energy $\hat{\varepsilon}_{\nu}^{\text{diss}}$ can be defined. The rate-dependent $\hat{\varepsilon}_{\nu}^{\text{diss}}$ is defined via its time rate-of-change equation

$$\dot{\hat{\varepsilon}}_{\nu}^{\text{diss}} \equiv \dot{\hat{p}}_{\text{sci}}^{\text{diss}} \hat{e}_{\nu}^{\text{sci}}. \quad (54)$$

In an analogous way, the rate-independent $\hat{\varepsilon}_{\nu}^{\text{diss}}$ is defined via its applied segment stretch-based rate-of-change equation

$$\left( \hat{\varepsilon}_{\nu}^{\text{diss}} \right)' \equiv \left( \hat{p}_{\text{sci}}^{\text{diss}} \right)' \hat{e}_{\nu}^{\text{sci}}, \quad (55)$$

where derivatives are taken with respect to $\hat{\lambda}_{\nu}$. The analytical form of $\hat{\varepsilon}_{\nu}^{\text{sci}}$ and $(\hat{p}_{\text{sci}}^{\text{sci}})'$ can be found for $\hat{\lambda}_{\nu} \leq \lambda_{\nu}^{\text{crit}}$ (where $\dot{\xi}_{\nu} = \kappa_{\nu} [\hat{\lambda}_{\nu} - 1]$)

$$\hat{\varepsilon}_{\nu}^{\text{sci}} = \frac{1}{2} \kappa_{\nu} \left[ \hat{\lambda}_{\nu} - 1 \right]^2 - \frac{3}{2} \left[ \zeta_{\text{char}} \nu \right]^2 \kappa_{\nu} \left[ \hat{\lambda}_{\nu} - 1 \right]^2 + \zeta_{\text{char}}, \quad (56)$$

$$\left( \hat{p}_{\text{sci}}^{\text{sci}} \right)' = \hat{p}_{\text{sci}}^{\text{sci}} \left[ \frac{\left[ \zeta_{\text{char}} \nu \right]^2 \kappa_{\nu}}{\hat{\lambda}_{\nu} - 1} - \kappa_{\nu} [\hat{\lambda}_{\nu} - 1] \right]. \quad (57)$$
Eq. (55) can be rewritten as
\[
\left(\dot{\varepsilon}_{\nu}^{\text{diss}}\right)^{'} = \dot{p}_{\nu}^{\text{sci}} = \dot{p}_{\nu}^{\text{sci}} \left[ \sqrt{\frac{\zeta_{\nu} \lambda_{\nu}}{\kappa_{\nu} - 1}} - \kappa_{\nu} [\lambda_{\nu} - 1] \right] \varepsilon_{\nu}^{\text{sci}},
\]
(58)
where \(\dot{\varepsilon}_{\nu}^{\text{diss}} = 0\) at \(\dot{\lambda}_{\nu} = 1\). If irreversible segment scission is assumed to take place in the network, then \(\dot{p}_{\nu}^{\text{sci}} \geq 0\) and \(\left(\dot{\varepsilon}_{\nu}^{\text{diss}}\right)^{'} \geq 0\) must hold during deformation.

For segments in a chain between its undisturbed, force-free state and its critical state, Fig. 8 displays the evolution of \(\dot{p}_{\nu}^{\text{sci}}\), \(\dot{p}_{\nu}^{\text{sur}}\), and rate-independent \(\dot{\varepsilon}_{\nu}^{\text{diss}}\) in nondimensional scaled form (\(\varepsilon_{\nu}^{\text{sci}} = \dot{\varepsilon}_{\nu}^{\text{sci}} / \zeta_{\nu}, \varepsilon_{\nu}^{\text{sur}} = \dot{\varepsilon}_{\nu}^{\text{sur}} / \zeta_{\nu}\)). The associated rate-independent probabilities \(\dot{p}_{\nu}^{\text{sci}}\) and \(\dot{p}_{\nu}^{\text{sur}}\) are also displayed. The evolution of \(\dot{p}_{\nu}^{\text{sci}}\) in Fig. 8 confirms that the fundamental principle of the Bell (1978) model holds: an intrinsic activation energy barrier to thermally activated scission in the absence of external forces is reduced by an energetic term dependent upon the applied force. However, in contrast with the Bell (1978) model and in line with the findings in Yang et al. (2020), the activation energy barrier decreases in a nonlinear fashion upon an increase in applied force. This nonlinear relationship is accounted for in Eq. (56) where \(\lambda_{\nu} = 1 + \xi_{\lambda} / \xi_{\kappa}\).

The evolution of \(\dot{\varepsilon}_{\nu}^{\text{diss}}\) in Fig. 8 confirms that when \(\dot{p}_{\nu}^{\text{sci}}\) increases from 0 to 1, \(\dot{\varepsilon}_{\nu}^{\text{diss}}\) increases in a manner that simultaneously accounts for increasing \(\dot{\varepsilon}_{\nu}^{\text{sci}}\). At the critical chain state when \(\xi_{\nu} = \xi_{\nu}^{\text{crit}}, \dot{\varepsilon}_{\nu}^{\text{sci}} / \zeta_{\nu} = \dot{\varepsilon}_{\nu}^{\text{sci}} = \dot{\varepsilon}_{\nu}^{\text{sci}} / \zeta_{\nu}^{\text{char}}, \text{and} \dot{\varepsilon}_{\nu}^{\text{diss}} \equiv \dot{\varepsilon}_{\nu}^{\text{diss}} / \zeta_{\nu}^{\text{char}}\). As a matter of interpretation, recall that \(\dot{p}_{\nu}^{\text{sci}}, \dot{p}_{\nu}^{\text{sur}},\) and \(\dot{\varepsilon}_{\nu}^{\text{diss}}\) are intended to describe the probabilistic and energetic for a statistically large number of segments.

4.2. Chain-level scission energetics and probabilistic considerations

With the rate-dependent and rate-independent segment-level scission framework established, probabilistic considerations will now be used to establish a chain-level rupture framework. Chain rupture can take place when any one segment along its backbone ruptures. The rate-independent probability of chain survival \(\dot{p}_{\nu}^{\text{sur}}\) and the rate-independent probability of chain scission \(\dot{p}_{\nu}^{\text{sci}}\) are calculated as
\[
\dot{p}_{\nu}^{\text{sur}} = \frac{\dot{p}_{\nu}^{0}}{1 - \dot{p}_{\nu}^{\text{sur}}}, \quad \dot{p}_{\nu}^{\text{sci}} = 1 - \dot{p}_{\nu}^{\text{sur}}.
\]
(59)

The segment that becomes ruptured contributes an energy dissipation of \(\dot{\varepsilon}_{\nu}^{\text{sci}}\) (since thermal excitations supply the segment the activation energy \(\dot{\varepsilon}_{\nu}^{\text{sci}}\) needed to execute the rupture reaction). Meanwhile, after the segment rupture event takes place, the remaining \(\nu - 1\) intact segments in the ruptured chain will each traverse the undisturbed segment potential energy landscape back to the minimum energy state at equilibrium, since the ruptured chain is suddenly unable to bear load. Visually, an intact segment will slide down the blue curve from a non-blue colored dot to the blue dot in Fig. 7 as the chain ruptures at another location. As a result of this, each of the \(\nu - 1\) intact segments contributes an energy dissipation of \(\dot{\varepsilon}_{\nu}^{\text{sci}}\) as well. Therefore, the nondimensional chain scission energy is simply the nondimensional chain Helmholtz free energy at the moment of scission shifted by \(\nu \dot{\varepsilon}_{\nu}^{\text{char}}\)
\[
\tilde{\varepsilon}_{\nu}^{\text{sci}} = \nu \tilde{\varepsilon}_{\nu}^{\text{sci}} = \nu \left[ \tilde{\psi}_{\nu} \left( \dot{\lambda}_{\nu}^{-\nu} \right) + \tilde{\psi}_{\nu}^{\text{char}} \right] \dot{\lambda}_{\nu}^{-\nu}
\]
(60)

The nondimensional chain scission energy per segment, \(\tilde{\varepsilon}_{\nu}^{\text{sci}} / \nu\), is equivalent to the nondimensional segment scission energy
\[
\tilde{\varepsilon}_{\nu}^{\text{sci}} / \nu = \tilde{\varepsilon}_{\nu}^{\text{sci}} / \nu
\]
(61)

The rate-dependent probability of chain survival \(p_{\nu}\) is related to the rate-dependent probability of segment survival \(p_{\nu}\) as \(p_{\nu} = [p_{\nu}]^{\nu}\) (Yang et al., 2020). Considering this, the rate-dependent probability of chain survival \(p_{\nu}\) and rate-dependent probability of chain scission \(\gamma_{\nu}\) equal
\[
\frac{\dot{p}_{\nu}}{p_{\nu}} = -\nu \omega_{\nu} \dot{p}_{\nu}^{\text{sci}}, \quad \gamma_{\nu} = 1 - p_{\nu} \quad \Rightarrow \quad \dot{\gamma}_{\nu} = \frac{\dot{p}_{\nu}^{\text{sci}}}{1 - \gamma_{\nu}} = \nu \omega_{\nu} \dot{p}_{\nu}^{\text{sci}}.
\]
(62)
Analogous to the segment-level theory, the time rate-of-change equation for the rate-dependent nondimensional dissipated chain scission energy per segment \( \dot{\varepsilon}_{\text{sc}}^{\text{diss}} \) is defined as \( \text{Guo and Zarré} \ [2021] \)

\[
\dot{\varepsilon}_{\text{sc}}^{\text{diss}} = \dot{\varepsilon}_{\text{sc}}^{\text{sci}}.
\]  

(63)

The applied segment stretch-based rate-of-change for the rate-independent \( \dot{\varepsilon}_{\text{sc}}^{\text{diss}} \) is defined as

\[
(\dot{\varepsilon}_{\text{sc}}^{\text{diss}})' = (\dot{\rho}_{\text{sc}}^{\text{p}})' \xi_{\text{sc}}^{\text{p}}, \quad (\dot{\rho}_{\text{sc}}^{\text{p}})' = \nu[1 - \nu^{\text{sci}}]^{-1} (\dot{\rho}_{\text{sc}}^{\text{p}})',
\]

(64)

\[
(\dot{\varepsilon}_{\text{sc}}^{\text{diss}})' = \nu[1 - \nu^{\text{sci}}]^{-1} \rho_{\text{sc}}^{\text{p}} \left[ 1 + \frac{[\nu^{\text{char}}]^2}{\nu^{\text{sci}}} \frac{\kappa_{\nu}}{\nu^{\text{sci}} - 1} - \kappa_{\nu} (\lambda_{\nu} - 1) \right] \dot{\varepsilon}_{\text{sc}}^{\text{sci}},
\]

(65)

where \( \dot{\varepsilon}_{\text{sc}}^{\text{diss}} = 0 \) at \( \lambda_{\nu} = 1 \). If irreversible chain scission is assumed to take place in the polymer network, then \( (\dot{\rho}_{\text{sc}}^{\text{p}})' \geq 0 \) and \( (\dot{\varepsilon}_{\text{sc}}^{\text{diss}})' \geq 0 \) must hold during deformation.

**Remark 4.** Any arbitrary anharmonic segment potential is able to be directly utilized within the segment rupture and chain rupture formulation developed in this work. For instance, consider the Morse segment potential provided in [Eq. (23)]. Using the Morse potential, the local minimum and local maximum for the corresponding \( \dot{u}_{\nu} \) take the following functional forms

\[
\lambda_{\nu}^{\text{locmin}} = \lambda_{\nu} = 1 + \frac{1}{\alpha_{\nu}} \ln \left( \frac{2}{1 + \sqrt{1 - \frac{\xi_{\nu}^{\text{char}}}{\xi_{\nu}}}} \right), \quad \lambda_{\nu}^{\text{locmax}} = 1 + \frac{1}{\alpha_{\nu}} \ln \left( \frac{2}{1 - \sqrt{1 - \frac{\xi_{\nu}^{\text{char}}}{\xi_{\nu}}}} \right),
\]

(66)

where \( \alpha_{\nu} = \sqrt{\frac{\kappa_{\nu}}{\nu^{\text{char}}}} \). When \( \xi_{\nu} = 0 \), then \( \lambda_{\nu}^{\text{locmin}} = 1 \) and \( \lambda_{\nu}^{\text{locmax}} = \infty \), as expected. At the critical point where \( \lambda_{\nu}^{\text{crit}} = \lambda_{\nu}^{\text{locmin}} = \lambda_{\nu}^{\text{locmax}} \), it is found that \( \xi_{\nu}^{\text{crit}} = \sqrt{\frac{\nu^{\text{char}}}{\nu^{\text{sci}}}}, \lambda_{\nu}^{\text{crit}} = 1 + \ln(2)/\alpha_{\nu}, \dot{\varepsilon}_{\text{sc}}^{\text{sci}} = 0, \) and \( \dot{u}_{\nu} = \xi_{\nu}^{\text{char}}/4 \). The analytical form of \( \dot{\varepsilon}_{\nu}^{\text{sci}} \) and \( (\dot{\rho}_{\text{sc}}^{\text{p}})' \) can be found for \( \lambda_{\nu}^{\text{crit}} \leq \lambda_{\nu} \)

\[
\dot{\varepsilon}_{\nu}^{\text{sci}} = \xi_{\nu}^{\text{char}} \left[ 2e^{-\alpha_{\nu}[\lambda_{\nu} - 1]} - 1 \right] - \xi_{\nu}^{\text{crit}} \left[ 1 - \left[ 2e^{-\alpha_{\nu}[\lambda_{\nu} - 1]} - 1 \right]^2 \right] \left[ 1 - \frac{1}{\alpha_{\nu}} \ln \left( 1 - e^{-\alpha_{\nu}[\lambda_{\nu} - 1]} \right) - \lambda_{\nu} \right],
\]

(67)

\[
(\dot{\rho}_{\text{sc}}^{\text{p}})' = \rho_{\text{sc}}^{\text{p}} \left[ 2e^{-\alpha_{\nu}[\lambda_{\nu} - 1]} - 1 \right] - \xi_{\nu}^{\text{crit}} \left[ 4\alpha_{\nu} e^{-\alpha_{\nu}[\lambda_{\nu} - 1]} \left[ 2e^{-\alpha_{\nu}[\lambda_{\nu} - 1]} - 1 \right] \left[ 1 - \frac{1}{\alpha_{\nu}} \ln \left( 1 - e^{-\alpha_{\nu}[\lambda_{\nu} - 1]} \right) - \lambda_{\nu} \right] \right]
\]

(68)

where \( \dot{\varepsilon}_{\nu}^{\text{sci}} = \xi_{\nu}^{\text{char}} \) at \( \lambda_{\nu} = 1 \). From this point on, the remainder of the segment scission and chain scission formulation can be implemented for the Morse potential, with the caveat that the inverse relationship between \( \lambda_{\nu}^{\text{cri}} \) and \( \lambda_{\nu} \) must be calculated computationally. Do take stock of this caveat and its implications: as discussed in Remark 3, using numerics to calculate the inverse relationship between \( \lambda_{\nu}^{\text{cri}} \) and \( \lambda_{\nu} \) will ultimately prevent an upscaled continuum damage model to be cast in a tractable closed-form manner. On the contrary, and as implied by Remark 3, the segment rupture and chain rupture formulation developed in this work using the composite segment potential directly leads to a tractable closed-form continuum damage model. In the context of segment rupture and chain rupture, this is truly what sets the composite segment potential apart from other anharmonic segment potentials.

### 4.3. Chain scission informed equilibrium probability distribution considerations

With a description of the intact and ruptured chain configuration spaces at hand, a formalization of the equilibrium probability distribution for intact chains can now be undertaken\(^2\). Once again, the statistical mechanics theory derived in [Buche and Silberstein] [2021] is employed and briefly reviewed.

\(^2\) In this section, equilibrium refers to time-independent behavior of constituents in a statistical ensemble. This is in contrast to the use of the term equilibrium thus far in this manuscript, which has referred to the minimum potential energy state of a segment in an undisturbed, force-free chain.
The total configuration equilibrium probability for a chain to be either intact or ruptured is given by the following conservation law

\begin{equation}
1 = \int \cdots \int P_{eq}^{\text{intact}}(r_\nu)d^3r_\nu + \sum_{j=1}^{\nu} \int \cdots \int P_{eq}^{\text{rup}}(r_\nu)d^3r_\nu,
\end{equation}

where \( r_\nu \) is the end-to-end chain vector, \( \int \cdots \int d^3r_\nu \) denotes integration about all spatial chain configurations at equilibrium, \( P_{eq}^{\text{intact}}(r_\nu) \) is the intact chain configuration equilibrium probability distribution, and \( P_{eq}^{\text{rup}}(r_\nu) \) is the chain configuration equilibrium probability distribution for a chain ruptured via the \( j \)th segment. \(^3\) Multiplying the total configuration equilibrium probability in Eq. (69) by the total configuration equilibrium partition function \( Z_{eq}^{\text{tot}} \) leads to the following relationship

\begin{equation}
Z_{eq}^{\text{tot}} = \int \cdots \int Z^{\text{intact}}(r_\nu)d^3r_\nu + \sum_{j=1}^{\nu} \int \cdots \int Z^{\text{rup}}(r_\nu)d^3r_\nu,
\end{equation}

where \( Z^{\text{intact}}(r_\nu) \) is the intact chain configuration partition function and \( Z^{\text{rup}}(r_\nu) \) is the chain configuration partition function for a chain that has ruptured via the \( j \)th segment. Via the principle thermodynamic connection formula \( \beta \Psi_c(r_\nu) = -\ln(Z(r_\nu)) \), the net Helmholtz free energy change is defined solely for the \( j \)th segment undergoing rupture, provided in nondimensional form

\begin{equation}
\Delta \psi^{\text{rup}}_j \equiv -\ln \left( \frac{\int \cdots \int Z^{\text{rup}}(r_\nu)d^3r_\nu}{\int \cdots \int Z^{\text{intact}}(r_\nu)d^3r_\nu} \right).
\end{equation}

Using the above, \( Z_{eq}^{\text{tot}} \) and \( P_{eq}^{\text{intact}}(r_\nu) \) are respectively calculated as

\begin{equation}
Z_{eq}^{\text{tot}} = \left[ 1 + \sum_{j=1}^{\nu} e^{-\Delta \psi^{\text{rup}}_j} \right] \left[ \int \cdots \int Z^{\text{intact}}(r_\nu)d^3r_\nu \right],
\end{equation}

\begin{equation}
P_{eq}^{\text{intact}}(r_\nu) = \frac{Z^{\text{intact}}(r_\nu)}{Z_{eq}^{\text{tot}}} = \frac{Z^{\text{intact}}(r_\nu)}{1 + \sum_{j=1}^{\nu} e^{-\Delta \psi^{\text{rup}}_j} \left[ \int \cdots \int Z^{\text{intact}}(r_\nu)d^3r_\nu \right]}.
\end{equation}

At this point, \( \Delta \psi^{\text{rup}}_j \) is identified as the rate-independent nondimensional dissipated segment scission energy at the critical segment stretch \( \lambda_{\nu}^{\text{crit}} \). The integral of \( Z^{\text{intact}}(r_\nu) \) is taken over all chain configurations where chain survival is probable. In light of the chain scission framework established in Section 4.1 and Section 4.2 that integral is evaluated as

\begin{align}
\int \cdots \int Z^{\text{intact}}(r_\nu)d^3r_\nu &= 4\pi \int_{0}^{\lambda_{\nu}^{\text{crit}}} e^{-\nu \psi_c(I_\nu, r_\nu)} r_\nu^2 dr_\nu \\
&= 4\pi e^{\nu \psi_{\text{char}}(I_\nu)} [\nu I_\nu^{\text{eq}}]^3 \int_{0}^{\lambda_{\nu}^{\text{equiv}}} e^{-\nu [\psi_c(\lambda_\nu, \lambda_{\nu}^{\text{equiv}}) + \psi_{\text{char}}]} [\lambda_{\nu}^{\text{equiv}}] d\lambda_{\nu}^{\text{equiv}} = 4\pi e^{\nu \psi_{\text{char}}(I_\nu)} [\nu I_\nu^{\text{eq}}]^3 \mathcal{F}(3, \nu),
\end{align}

\begin{equation}
\mathcal{F}(n, \nu) \equiv \int_{0}^{\lambda_{\nu}^{\text{equiv}}} e^{-\nu [\psi_c(\lambda_\nu, \lambda_{\nu}^{\text{equiv}}) + \psi_{\text{char}}]} [\lambda_{\nu}^{\text{equiv}}]^{n-1} d\lambda_{\nu}^{\text{equiv}},
\end{equation}

\(^3\)According to Buche and Silberstein (2021), the following assumptions underlie the statistical mechanics theory derived up to this point: (i) Polymer chains are noninteracting and considered as members of a classical, canonical statistical mechanics ensemble; (ii) Local equilibrium is independently maintained in the phase space region associated with intact chains and the phase space region associated with ruptured chains, as per transition state theory; (iii) Any arbitrary segment along a polymer chain backbone may become ruptured; (iv) A chain is considered ruptured once only a single segment becomes ruptured; (v) The possibility of two chains ruptured at different segment locations cross-reforming together is neglected.
Figure 9: Comparison of reference equilibrium chain stretches calculated via the uFJC statistical mechanics framework and the inextensible Gaussian chain assumption. Here, $c_{nu}^{\text{bar}} = 100$ and $\kappa_n = 1000$, as per the composite segment potential displayed in Fig. 2. (top) Reference equilibrium chain stretch $A_\nu$ calculated via the uFJC statistical mechanics framework and the inextensible Gaussian chain assumption as a function of segment number $\nu$ in the domain $5 \leq \nu \leq 3125$. (bottom) Percent error between $A_\nu$ calculated via the uFJC statistical mechanics framework and the inextensible Gaussian chain assumption as a function of $\nu$ in the domain $5 \leq \nu \leq 3125$. The sharp dip and rise in the percent error curve takes place where $A_\nu$ calculated via the uFJC statistical mechanics framework crosses over $A_\nu$ calculated via the inextensible Gaussian chain assumption.

where $\lambda_{eq}^n$ is substituted in for $r_\nu$. Note that segment extensibility is functionally accounted for in the integral function $\mathcal{J}(n, \nu)$ as per the segment stretch function in Eq. (43). $Z_{eq}^{\text{tot}}$ and $P_{eq}^{\text{intact}}(r_\nu)$ can now be simplified

$$Z_{eq}^{\text{tot}} = \left[ 1 + \nu e^{-\hat{\varepsilon}_d(\lambda_{eq}^n)} \right] 4\pi e^{\hat{\mu}_n^{\text{bar}}} [\nu^2_{eq}]^3 \mathcal{J}(3, \nu), \quad (77)$$

$$P_{eq}^{\text{intact}}(r_\nu) = \frac{Z_{eq}^{\text{intact}}(r_\nu)}{1 + \nu e^{-\hat{\varepsilon}_d(\lambda_{eq}^n)}} 4\pi e^{\hat{\mu}_n^{\text{bar}}} [\nu^2_{eq}]^3 \mathcal{J}(3, \nu). \quad (78)$$

Using $P_{eq}^{\text{intact}}(r_\nu)$ and considering the chain configurations corresponding to probable chain survival, the root-mean-square end-to-end chain distance $r_{\nu}^{\text{rms}}$ is calculated as

$$\left( r_{\nu}^{\text{rms}} \right)^2 = \int \cdots \int r_\nu^2 P_{eq}^{\text{intact}}(r_\nu) d^3 r_\nu = [\nu^2_{eq}]^2 \left[ \frac{1}{1 + \nu e^{-\hat{\varepsilon}_d(\lambda_{eq}^n)}} \right] \mathcal{J}(5, \nu) \mathcal{J}(3, \nu), \quad (79)$$

$$r_{\nu}^{\text{rms}} = \nu^2_{eq} \sqrt{\left[ \frac{1}{1 + \nu e^{-\hat{\varepsilon}_d(\lambda_{eq}^n)}} \right] \mathcal{J}(5, \nu) \mathcal{J}(3, \nu)}. \quad (80)$$

Taking the root-mean-square end-to-end chain distance $r_{\nu}^{\text{rms}}$ as the reference end-to-end chain distance $r_{\nu}^{\text{ref}}$, the reference equilibrium chain stretch $A_\nu$ directly falls out from the above

$$A_\nu = \sqrt{\left[ \frac{1}{1 + \nu e^{-\hat{\varepsilon}_d(\lambda_{eq}^n)}} \right] \mathcal{J}(5, \nu) \mathcal{J}(3, \nu)}. \quad (81)$$
Segment extensibility is fundamentally incorporated in the statistical mechanics underpinning the \( A_v \) calculation. In the case of inextensible chains described via Gaussian statistics, then it can be shown that \( A_v = 1/\sqrt{\nu} \). \( A_v \) calculated via the uFJC-based approach and the inextensible Gaussian chain assumption for a range of segment numbers associated with short, intermediately-long, and long chains are presented in the top panel in Fig. 9. The percent error between the \( A_v \) calculations of the two approaches is provided in the bottom panel. For short chains, the inextensible Gaussian chain assumption poorly complies with the uFJC \( A_v \), with percent errors up to \( \approx 10\% \) for short chains. The percent error only improves slightly for intermediately-long and long chains, converging from above to \( \approx 0.1\% \). Since \( A_v \) is extensively used throughout the model in functions which capture the state of a chain, it is crucial for \( A_v \) to be precisely calculated.

Finally, as per Guo and Zaïri (2021), the reference segment stretch \( \Lambda_v^{ref} \) is taken as the ratio of the reference segment length \( l_v^{ref} \) with the equilibrium segment length \( l_v^{eq} \), \( \Lambda_v^{ref} = l_v^{ref} / l_v^{eq} \), and can be straightforwardly calculated as \( \Lambda_v^{ref} = \lambda_v \). Note that the quantity \( \lambda_v / \Lambda_v^{ref} = l_v / l_v^{ref} \) is the ratio of the segment length \( l_v \) with the reference segment length \( l_v^{ref} \), and may be considered as an alternate segment stretch measure for modeling use.

5. Results and discussion

At this point, the probabilistic description of single chain rupture is fully established. In light of the rupture framework, the mechanical response of the chain is presented and described. Then, implications of the chain scission framework in the context of polymer chain damage and fracture models are discussed. Chain rupture behavior for short, intermediately-long, and long chains is then investigated. Finally, model validation is achieved by fitting experimental single chain atomic force microscopy tensile test results to the uFJC framework with the composite segment potential. Using the fitted model, the dissipated energy and probability associated with chain scission are presented for each chain involved in the AFM tensile tests, providing deeper insight to the experimental results.
5.1. Single chain mechanical response

The mechanical response of a chain with segments obeying the composite potential is presented in Fig. 10. This figure presents the chain mechanical response only for states where chain survival is probable, i.e., for chain states inclusively between the undisturbed force-free state ($\lambda_{\nu}^{eq} = 0$) and the critical state ($\lambda_{\nu}^{eq} = (\lambda_{\nu}^{eq})^{crit}$). In Fig. 10a, $\zeta^{char}$ is held fixed while $\kappa_{\nu}$ is permitted to vary, and vice versa in Fig. 10b. In order to calculate the nondimensional force response, Eq. (43) was used with Eq. (17).

The nFJC composite potential chain mechanical response compares quite well with other extensible chain mechanical response results (Buche and Silberstein 2021, Li and Bouklas 2020, Mao et al. 2017b, Mulderrig et al. 2021). For low equilibrium chain stretch $\lambda_{\nu}^{eq}$ values, the chain mechanical response exhibits compliant, entropically-dominated behavior that is independent of $\zeta^{char}$ and $\kappa_{\nu}$. As the chain is stretched near its inextensible equilibrium contour length, $0.75 \leq \lambda_{\nu}^{eq} \leq 1$, segments begin to stretch, and enthalpic contributions begin to emerge. For increasing $\kappa_{\nu}$, these enthalpic contributions dominate more and more as $\lambda_{\nu}^{eq} \to 1$, and the chain becomes increasingly stiffer and stiffer. As the chain is stretched past its inextensible equilibrium contour length, $\lambda_{\nu}^{eq} > 1$, the chain mechanical response exhibits enthalpically-dominated stiffening behavior as the segments continue to stretch more and more. For increasing $\kappa_{\nu}$, $\zeta^{crit}$ increases while $\lambda^{crit}$ and $(\lambda_{\nu}^{eq})^{crit}$ decreases. Meanwhile, as $\zeta^{char}$ increases, $\lambda^{crit}$, $\lambda_{\nu}^{eq}$ and $\zeta^{crit}$ all increase. However, prior to the critical point, the chain mechanical response remains identical to the case with smaller $\zeta^{char}$.

5.2. Implications of the chain scission framework

In light of polymer chain damage and fracture modeling, two important implications can be highlighted from the chain scission framework developed in Section 4.2. First, this framework can account for the damage of polymer networks composed of chains with a polydispersity in segment number. The dependence of chain scission behavior with respect to segment number is further examined in Section 5.3. Second, this chain scission framework can now be directly incorporated in polymer chain damage and fracture models, such as
the Lake and Thomas theory of polymer network fracture [Lake and Thomas, 1967]. In these models, the criterion for chain scission and associated energy dissipation fall into one of several categories – an upper bound, a lower bound, or one of several intermediate limits – as follows:

1. **Upper bound of chain scission:** All of the segments in the chain are assumed to be identically stretched up to the point of dissociation before one of the segments becomes ruptured. The dissipated scission energy for a chain, \( \hat{\varepsilon}_c^{\text{diss}} / \beta \), is taken to be approximately equal to \( \nu \varepsilon_{\nu \text{char}} \). Clearly, this criterion neglects both thermal fluctuations and the reduction in scission activation energy under an increasing chain force. This criterion was first introduced by Lake and Thomas (1967), and has since been widely used (Arunachala et al., 2021; Lamont et al., 2021; Li and Bouklas, 2020; Mao and Anand, 2018; Mao et al., 2017b; Mulderrig et al., 2021; Talamini et al., 2018; Vernaerey et al., 2018). An exception to this implementation is found in Dal and Kaliske (2009), which considered a segment as a critical segment stretch of rupture \( \hat{\lambda} \). The chain is considered ruptured if \( \hat{\lambda} = \hat{\lambda}_c \), at which point one of the segments becomes ruptured (Buche and Silverstein, 2021; Dal and Kaliske, 2009; Tehrani and Sarvestani, 2017). Note that the point when the chain force equals the maximum segment force has been referred to in this work as the critical point, with nondimensional maximum segment force equal to \( \xi_{\text{crit}} \). For segments described by the Morse potential and the composite potential from this work, \( \hat{\varepsilon}_c^{\text{diss}} / \beta \) is taken to be approximately equal to \( \nu \varepsilon_{\nu \text{char}} / 4 \) and \( \nu \varepsilon_{\nu \text{char}} / 2 \), respectively. This criterion neglects the probabilistic nature thermal fluctuations and the reduction in scission activation energy under an increasing chain force.

2. **Lower bound of chain scission:** Considering the rapid time scale of thermal fluctuations, it is assumed that the chain becomes ruptured when the energy needed for a single segment to dissociate is imparted to the chain as a whole, \( \hat{\varepsilon}_c^{\text{diss}} / \beta \) is taken to be approximately equal to \( \varepsilon_{\nu \text{char}} \) (Lei et al., 2021, 2020). This criterion neglects both the probabilistic nature of thermal fluctuations and the reduction in scission activation energy under an increasing chain force.

3. **Chain scission at maximum segment force:** All of the segments in the chain are assumed to be identically stretched up to the point when the chain force equals the maximum segment force (as determined by the particular anharmonic segment potential in use), at which point one of the segments becomes ruptured (Buche and Silverstein, 2021; Dal and Kaliske, 2009; Tehrani and Sarvestani, 2017). The chain is considered ruptured if \( \hat{\lambda} = \hat{\lambda}_c \). For segments described by the Morse potential and the composite potential from this work, \( \hat{\varepsilon}_c^{\text{diss}} / \beta \) can be calculated via density functional theory (Beyer, 2000; Grandbois et al., 1999) or measured by single-chain atomic force microscopy tensile test results. Since \( \xi_{\text{crit}} \) is typically less than the maximum segment force \( \xi_{\text{crit}} \) from the prior criterion, \( \hat{\varepsilon}_c^{\text{diss}} / \beta \) for a chain obeying this criterion will be a positive energy value less than \( \hat{\varepsilon}_c^{\text{diss}} / \beta \) taken at \( \xi_{\text{crit}} \).

4. **Chain scission at a previously measured chain force of rupture:** As proscribed by Wang et al. (2019) and used in [Zhang and Hutchens, 2021], all of the segments in the chain are assumed to be identically stretched up to the point when the chain force equals a pre-defined force of rupture before one of the segments becomes ruptured. This dissipated energy of chain scission, \( \hat{\varepsilon}_c^{\text{diss}} / \beta \), is calculated as the work done to extend a polymer chain from a force-free equilibrium state up to this pre-calculated or pre-measured force of rupture \( \xi_{\text{crit}} \) (in nondimensional terms). \( \xi_{\text{crit}} \) can be calculated from the prior criterion. \( \hat{\varepsilon}_c^{\text{diss}} / \beta \) for a chain obeying this criterion will be a positive energy value less than \( \hat{\varepsilon}_c^{\text{diss}} / \beta \) taken at \( \xi_{\text{crit}} \).

5. **Thermally-driven stochastic force-activated chain scission:** Segment rupture is stochastically driven by thermal excitations supplying the energy needed to overcome a force-dependent activation energy barrier of scission. All such rate-dependent bulk and interfacial polymer damage models intrinsically incorporate these features to account for chain rupture. Recently, several models, including this work, have begun to incorporate the effects of segment extensibility in the rate-dependent damage model context (Feng et al., 2022; Guo and Za¨ıri, 2021; Li and Bouklas, 2020; Mao and Anand, 2018; Yang et al., 2020). Furthermore, only Guo and Za¨ıri (2021) and this work (in Eq. (63)) have defined a rate equation for chain scission energy dissipated upon rupture. Notably, this work also proposes a rate-independent polymer damage framework that fully complies with the assumptions underlying this criterion. \( \hat{\varepsilon}_c^{\text{diss}} / \beta \) for a chain obeying this criterion will be a positive energy value less than \( \hat{\varepsilon}_c^{\text{diss}} / \beta \) taken at the maximum segment force \( \xi_{\text{crit}} \) from the third criterion.

Excluding the last criterion, the above criteria are often implemented in computational models via calculating a critical segment stretch of rupture \( \lambda_{\text{sci}}^c \). The chain is considered ruptured if \( \hat{\lambda}_\nu \geq \lambda_{\text{sci}}^c \). The nondimensional dissipated chain scission energy is then calculated as \( \hat{\varepsilon}_c^{\text{diss}} = \nu \psi_{\text{char}} (\hat{\lambda}_\nu = \lambda_{\text{sci}}^c) \) or \( \hat{\varepsilon}_c^{\text{diss}} = \nu \psi_{\text{char}} (\hat{\lambda}_\nu = \lambda_{\text{sci}}^c) \). An exception to this implementation is found in [Dal and Kaliske, 2009], which considered a segment as ruptured when a numerical discontinuity arose in the \( \lambda_\nu \) calculation. Note that this numerical discontinuity arose only when \( \xi_c = \xi_{\text{sci}}^c \).
to rupture at smaller \( \hat{c} \) when any one segment along its backbone ruptures. However, even though it is favorable for longer chains to rupture at smaller \( \hat{c} \), this does not mean that longer chains will undergo rupture before shorter chains within a deformed polymer chain network as \( \hat{c} \) increases with increasing segment number, as expected. However, on a per-segment basis, \( \hat{c} \) at the critical state actually decreases as the number of segments in a chain increases, as shown in the top panel in Fig. 11a.

### 5.4. Comparison with experiments

Now that the theory underpinning the uFJC model with the composite segment potential is completely established, model validation via fitting single chain mechanical response data from AFM tensile tests is desired. These data also provide a depth of information that we will try to extract with our framework. Polymer chains composed of either single carbon-carbon bonds (C-C) or single silicon-oxygen bonds (Si-O) – two common backbone bonds found in many elastic polymer chains – are desired for model fitting. The characteristic bond potential energy scale \( E_{\text{char}} \) and equilibrium bond length \( l_{\text{eq}} \) for the C-C bond are experimentally found to be 370.3 kJ/mol (Luo, 2007) and 1.524 Å (Allen et al., 1987), respectively. Likewise, \( E_{\text{char}} \) and \( l_{\text{eq}} \) for the Si-O bond are experimentally found to be 444.0 kJ/mol (Wiberg et al., 2001) and 1.645 Å (Allen et al., 1987), respectively. These experimentally-derived bond parameter values are used within the uFJC model to fit AFM single chain force versus extension data. Note that the transition from
Figure 13: PVA single chain mechanical response, probability of chain scission, and dissipated chain scission energy from rate-dependent and rate-independent single chain AFM tensile test simulations. Each tensile test simulation initially begins in the undisturbed, force-free chain state. Tension is then applied to the chain up to the critical chain state. Several different loading rates are investigated. Fundamental segment and chain parameters are taken from the uFJC model fit presented in Fig. 12a. (top) Nondimensional chain force \( \xi_c \) as a function of equilibrium chain stretch \( \lambda_{eq}^c \), which produce identical curves for the rate-dependent and rate-independent cases. The experimental PVA single chain tensile test data from Fig. 5 in Hugel et al. (2001) is presented in nondimensional form here. The horizontal black dashed line is the reported maximum nondimensional chain force a single C-C bond can sustain as calculated from density functional theory calculations in Beyer (2000). (upper-middle) Segment stretch \( \lambda_\nu \) as a function of \( \lambda_{eq}^c \), which produce identical curves for the rate-dependent and rate-independent cases. (lower-middle) Rate-dependent and rate-independent probability of chain scission, \( \gamma_c \) and \( \hat{p}_{sci}^c \), respectively, as a function of \( \lambda_{eq}^c \). (bottom) Rate-dependent and rate-independent nondimensional scaled dissipated chain scission energy per segment \( \hat{\varepsilon}_{diss}^{sci} \) as a function of \( \lambda_{eq}^c \), along with the nondimensional scaled chain scission energy per segment \( \hat{\varepsilon}_{sci}^{sci} \) as a function of \( \lambda_{eq}^c \). The rate-dependent and rate-independent \( \hat{\varepsilon}_{diss}^{sci} \) are represented by the non-black colored curves.

the bond level to the segment level that necessarily takes place in the uFJC model fit follows the theory outlined in Appendix D. Through the model fit procedure, the number of bonds in a single segment \( \nu_b \), the number of segments in the chain \( \nu \), the nondimensional segment stiffness \( \kappa_\nu \), and the nondimensional characteristic segment potential energy scale \( \zeta_{\nu}^{char} \) are obtained. To comply with the physical makeup of a polymer chain, \( \nu_b \) and \( \nu \) are restricted to integer values. Using single polyvinylamine (PVA) chain mechanical response data from Hugel et al. (2001), \( \kappa_\nu = 912.2 \) and \( \zeta_{\nu}^{char} = 298.9 \) are found, along with \( \nu_b = 2 \) and \( \nu = 3347 \). Using single polydimethylsiloxane (PDMS) chain mechanical response data from Al-Maawali et al. (2001), \( \kappa_\nu = 3197.5 \) and \( \zeta_{\nu}^{char} = 537.6 \) are found, along with \( \nu_b = 3 \) and \( \nu = 120 \). Fig. 12 presents the AFM single chain tensile test force versus extension results along with the respective uFJC model fits. In order to yield these well-fit results, AFM tensile tests that forced the chain to its enthalpic-dominated response regime were sought after, which Hugel et al. (2001) and Al-Maawali et al. (2001) both provide. Do note that the PVA and PDMS chains here were pulled via an AFM tip until a detachment event occurred, where either the chain detached from the AFM tip, the chain detached from a fixed substrate, or a backbone bond ruptured in the chain.

To elucidate deeper insight into the molecular physics taking place in these single chain AFM tensile tests, rate-dependent and rate-independent single chain AFM tensile test calculations were undertaken using...
Figure 14: PDMS single chain mechanical response, probability of chain scission, and dissipated chain scission energy from rate-dependent and rate-independent single chain AFM tensile test simulations. Each tensile test simulation initially begins in the undisturbed, force-free chain state. Tension is then applied to the chain up to the critical chain state. Several different loading rates are investigated. Fundamental segment and chain parameters are taken from the uFJC model fit presented in Fig. 12b. (top) Nondimensional chain force $\xi_c$ as a function of equilibrium chain stretch $\lambda^{eq}_c$, which produce identical curves for the rate-dependent and rate-independent cases. The experimental PDMS single chain tensile test data from Fig. 3 in Al-Maawali et al. (2001) is presented in nondimensional form here. The horizontal black dashed line is the reported maximum nondimensional chain force a single Si-O bond can sustain as calculated from density functional theory calculations in Beyer (2000). (upper-middle) Segment stretch $\lambda_\nu$ as a function of $\lambda^{eq}_c$, which produce identical curves for the rate-dependent and rate-independent cases. (lower-middle) Rate-dependent and rate-independent probability of chain scission, $\gamma_c$ and $\hat{p}_{sci}^c$, respectively, as a function of $\lambda^{eq}_c$. (bottom) Rate-dependent and rate-independent nondimensional scaled dissipated chain scission energy per segment $\hat{\varepsilon}_{diss}^{cs\nu}$ as a function of $\lambda^{eq}_c$, along with the nondimensional scaled chain scission energy per segment $\hat{\varepsilon}^{cs\nu}$ as a function of $\lambda^{eq}_c$. $\hat{\varepsilon}_{diss}^{cs\nu} = \hat{\varepsilon}^{cs\nu}$ is represented by the black curve. The rate-dependent and rate-independent $\hat{\varepsilon}_{diss}^{cs\nu}$ are represented by the non-black colored curves.

Each uFJC model fit. The rate-dependent and rate-independent single PVA chain mechanical response, probability of chain scission $\gamma_c$ and $\hat{p}_{sci}^c$ (respectively), and nondimensional dissipated chain scission energy per segment $\hat{\varepsilon}_{diss}$ (provided in scaled form) are presented as a function of $\lambda^{eq}_c$ in Fig. 13. The PVA chain mechanical response from the AFM tensile test in Hugel et al. (2001) (as presented in Fig. 12a) is included in Fig. 13 in nondimensional form. Analogous single PDMS chain results are presented in Fig. 14. Several chain force loading rates $f_c$ are presented, and the chain is pulled up to the critical loading state as per the uFJC model fit. $f_c = 10^3 \text{nN/sec}$ is a typical AFM force loading rate for these single chain AFM tensile test experiments (Beyer 2000; Ribas-Arino and Marx 2012).

Comparison of the AFM tensile test data and the modeled scission probabilistics presented in the top and lower-middle panels of Fig. 13 and Fig. 14 strongly suggests that a backbone bond in the PVA or PDMS chains did not undergo scission at the moment of detachment. This corroborates the intuition of Hugel et al. (2001) and Al-Maawali et al. (2001): Hugel et al. (2001) assumed that covalent bonds between PVA chains and an epoxy-functionalized glass surface ruptured during the AFM tensile test, while Al-Maawali et al. (2001) asserted that PDMS chains detached from the AFM tip. Another chain scission-based comparison to make is with density functional theory: the black dashed line in the top panel in Fig. 13 and Fig. 14 corresponds to the maximum force that a C-C or Si-O bond can respectively withstand as determined via
the density functional theory calculations performed in Beyer (2000). The maximum bond force calculated in Beyer (2000) is analogous to the critical bond force in this work. The critical C-C bond force calculated from the model fit with the PVA chain from Hugel et al. (2001) corresponds quite well with maximum C-C bond force from Beyer (2000), but the critical Si-O bond force calculated from the model fit with the PDMS chain from Al-Maawali et al. (2001) is about double the maximum Si-O bond force from Beyer (2000).

The relationship between rate-dependent chain scission to rate-independent chain scission is clearly implied from the scission probabilities and dissipated chain scission energies presented in the lower-middle and bottom panels in Fig. 13 and Fig. 14. As \( \dot{f} \) increases larger and larger, the initiation of non-zero \( \gamma \) and non-zero \( \varepsilon_{\text{diss}} \) occurs at larger and larger \( \lambda_{\nu}^{eq} \), and the critical \( \varepsilon_{\text{diss}} \) increases in value. Essentially, as \( \dot{f} \) increases, rate-dependent \( \gamma \) and \( \varepsilon_{\text{diss}} \) curves gradually approach their rate-independent counterparts. In effect, this clearly implies that rate-independent chain scission is equivalent to the limiting case of rate-dependent chain scission under an infinitely-large \( \dot{f} \).

Finally, \( \varepsilon_{\text{diss}}/\beta \) at the critical chain state for both rate-dependent and rate-independent chain scission is well below the characteristic segment potential energy scale \( E_{\nu}^{\text{char}} \). According to the bottom panel in Fig. 13 for a rate-dependent PVA chain with typical AFM force loading rate of \( \dot{f} = 10 \text{ nN/sec} \) and for a rate-independent PVA chain, the critical \( \varepsilon_{\text{diss}} \) equals 0.196 \( \times \varepsilon_{\nu}^{\text{char}} \) and 0.335 \( \times \varepsilon_{\nu}^{\text{char}} \), respectively. The analogous values for a PDMS chain equal 0.264 \( \times \varepsilon_{\nu}^{\text{char}} \) and 0.399 \( \times \varepsilon_{\nu}^{\text{char}} \), respectively (as per the bottom panel in Fig. 14). This result complies with the findings of Wang et al. (2019). Do note that \( \gamma_{c} \), \( \dot{\varepsilon}_{\nu}^{c_{\text{eq}}} \), and \( \varepsilon_{\text{diss}}^{c_{\nu}} \) presented in Fig. 13 and Fig. 14 are statistical descriptions of an ensemble, while the experiments are obviously discrete events. If we truly consider an individual single chain in an AFM tensile test and find that the chain ruptures in this test at some \( \lambda_{\nu}^{eq} = \left( \lambda_{\nu}^{eq} \right)_{\text{sci}} \) corresponding to \( \lambda_{\nu} = \lambda_{\nu}^{sci} \), then the probability of chain scission will instantaneously jump from 0 to 1 at the moment of rupture. At the same time, \( \varepsilon_{\text{diss}}^{c_{\nu}} \) will instantaneously jump from \( \varepsilon_{\text{diss}}^{c_{\nu}} = 0 \) to \( \varepsilon_{\text{diss}}^{c_{\nu}} = \varepsilon_{\text{sci}}^{c_{\nu}} \left( \lambda_{\nu}^{sci} \right) \). Graphically speaking, \( \varepsilon_{\text{diss}}^{c_{\nu}} \) will jump from the zero line to the black curve at \( \lambda_{\nu} = \lambda_{\nu}^{sci} \) in the bottom panel of Fig. 13 and Fig. 14.

6. Conclusions

In this manuscript, we developed a chain rupture framework founded upon a freely-jointed chain model derived entirely via statistical mechanics principles accounting for arbitrary bond extensibility. An extended version of the uFJC model from Buche and Silberstein (2021) and Buche et al. (2022) was first formulated and utilized to establish the statistical mechanics and thermodynamics foundation for the model. Using the principles of asymptotic matching, a simple, anharmonic, quasi-polynomial segment potential energy function was derived and verified. This potential energy function permitted a highly-accurate approximate analytical function to be derived that relates the chain stretch to the segment stretch, which is of critical importance for efficient computations. By considering scission as a stochastic, load-dependent process driven by thermal oscillations, the probability of rate-dependent and rate-independent segment scission was formulated. By considering the physics of segment scission along the lines of Wang et al. (2019), the dissipated energy of rate-dependent and rate-independent segment scission was also formulated. This segment scission framework was then pushed up to the chain level using probabilistic principles. Implications from this scission framework over statistical mechanics considerations in Buche and Silberstein (2021) permitted for the reference end-to-end chain distance to be represented as a function of segment extensibility and segment number. The chain model was used to precisely fit single-chain mechanical response data from atomic force microscopy tensile tests, validating the efficacy of the chain model. The scission framework was then called upon to yield valuable insight over the molecular physics taking place in the polymer chains under the AFM tensile test protocol.

Taking this chain modeling framework as a point of departure, a number of research paths are evident. Finite element-based elastomer fracture and fatigue models can seamlessly implement the framework presented in this manuscript since the entire framework is cast in terms of straightforward, computationally-efficient analytical functions. An exciting challenge is to incorporate this rupture framework in phase field
fracture models simulating elastomers with a non-uniform distribution of chain length in order to explicitly capture delocalized chain rupture during fracture and fatigue. In addition to fracture and fatigue studies, nucleation and cavitation in elastomer networks can also be investigated. An outstanding challenge for a micromechanically-motivated continuum framework is the network-level representative micro-to-macro transition, which can also be motivated by discrete network calculations, as the bond potential derived here can be easily incorporated in coarse-grained molecular dynamics network calculations.

Clearly, the rupture framework as presented in this manuscript does not account for viscoelastic effects or for chain entanglements, which are increasingly important at the network level. Incorporating these effects to the rupture framework would certainly improve the model by adding a further dimension of relevant molecular physics to the theory. One could potentially go about adding viscoelasticity and chain entanglement effects from the fundamental statistical mechanics level via accounting for rate-dependent molecular friction force contributions to the chain. Alternatively, viscoelastic effects could be incorporated in a more statistical manner via the transient network theory developed by [Vernerey et al. 2017]. Note that in such a model, reversible bond dissociation must be distinguished from irreversible bond rupture, along the lines of [Lamont et al. 2021]. Meanwhile, chain entanglement effects could be incorporated at the chain level in a more phenomenological manner by modulating the bond force along the chain with respect to the presence of entanglements, relevant to the recent work of [Hassan et al. 2022]. Hassan et al. (2022) find that for short-chain elastomer networks, fracture toughness is independent of loading rate, but for long-chain elastomer networks above some critical loading rate, fracture toughness exhibits an inversely proportional relationship to loading rate. Hassan et al. (2022) postulate that for long chains at low loading rates, stresses caused by chains sliding relative to one another are negligible. As a result, the chain sustains tension evenly along its length, and the entire chain dissipates energy upon rupture, leading to high fracture toughness. However, for long chains at high loading rates, entanglements concentrate tension within a short portion of the chain, causing that high-tension region of the chain to rupture and dissipate energy while the rest of the chain remains relatively relaxed, thereby reducing fracture toughness. Incorporating this physical picture to the chain level in some phenomenological way would provide the means to study how chain entanglements impact delocalized chain rupture and fracture toughness in elastomer networks.

### Appendix A. Derivation of the modulation parameter $\mu_\nu(\lambda_\nu)$

From the derivation of the asymptotically matched segment potential, it is found that Eq. (32) must hold true:

$$\frac{\partial \tilde{u}_\nu}{\partial \mu_\nu} = -[1 - \mu_\nu] \frac{\kappa_\nu}{\zeta_{\nu}^{\text{char}}} [\lambda_\nu - 1]^2 + 1 \geq 0 \text{ for } \lambda_\nu \geq 1.$$  \hspace{1cm} (A.1)

To proceed, consider the satisfaction of the equality and the conditional separately, for $\lambda_\nu \geq 1$

(A) $\frac{\partial \tilde{u}_\nu}{\partial \mu_\nu} > 0 \implies -[1 - \mu_\nu] \frac{\kappa_\nu}{\zeta_{\nu}^{\text{char}}} [\lambda_\nu - 1]^2 + 1 > 0$, \hspace{1cm} (A.2)

(B) $\frac{\partial \tilde{u}_\nu}{\partial \mu_\nu} = 0 \implies -[1 - \mu_\nu] \frac{\kappa_\nu}{\zeta_{\nu}^{\text{char}}} [\lambda_\nu - 1]^2 + 1 = 0$. \hspace{1cm} (A.3)

Examining the above leads to the following conditions:

(A) $\frac{\partial \tilde{u}_\nu}{\partial \mu_\nu} > 0 \implies 1 - [1 - \mu_\nu][\kappa_\nu/\zeta_{\nu}^{\text{char}}][\lambda_\nu - 1]^2 > 0$. This is satisfied under the following:

(A1) $\mu_\nu > 1 - \zeta_{\nu}^{\text{char}} / [\kappa_\nu[\lambda_\nu - 1]^2]$. However, this does not set any strict regulation on the exact value of $\mu_\nu$, and is therefore mathematically unhelpful.

(A2) $1 - \mu_\nu < 0$. However, this violates the chain damage condition that $\mu_\nu \in [0, 1]$.

(A3) $\mu_\nu = 1$ or $\lambda_\nu = 1$, both of which imply that $1 > 0$.

(A4) $\mu_\nu = 0 \implies \kappa_\nu[\lambda_\nu - 1]^2/\zeta_{\nu}^{\text{char}} < 1$, which potentially holds true depending on the values of $\zeta_{\nu}^{\text{char}}$, $\kappa_\nu$, and $\lambda_\nu \geq 1$.  

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The above holds provided that \( \frac{\lambda}{\nu} \), which are each satisfied for physically-sensible \( \nu \). However, when \( \nu = \lambda^{\text{crit}} \), then \( \mu = 0 \).

Given this, an unambiguous definition of the modulation parameter \( \mu \) is provided

\[
\mu = \begin{cases} 
0, & \text{if } \nu < \nu^{\text{crit}} \\
1 - \frac{\nu^{\text{char}}}{\nu^{\text{crit}}}, & \text{if } \nu \geq \nu^{\text{crit}} \end{cases},
\]

(A.4)

where \( \nu^{\text{crit}} \equiv 1 + \sqrt{\frac{\nu^{\text{char}}}{\nu}} \) is called the critical segment stretch. This analysis is exactly analogous to that performed in Appendix E of Mulderrig et al. (2021).

Appendix B. Analytical form of the segment stretch function

Substituting the Padé approximant (Eq. (37)) for the \( \nu^{\text{eq}} < (\lambda^{eq})^{\text{crit}} \) case in (Eq. (36)) and performing an appropriate cubic root analysis (Zwillinger 2002) leads to

\[
\nu = \nu^{PSB}(\nu^{eq}; \nu^{eq}) = 2\sqrt{-\frac{\pi}{3}} \cos \left( \frac{1}{3} \arccos \left( \frac{3\tilde{\rho} - \sqrt{\frac{3}{\pi}}} {2} \right) - \frac{2\pi}{3} \right) - \frac{\tilde{\beta}}{3\tilde{\alpha}},
\]

(B.1)

where

\[
\tilde{\alpha} = 1, \quad \tilde{\beta} = -\left[ \frac{3[\kappa + 1] + \lambda_{c}^{eq} [2\kappa + 3]}{\kappa + 1} \right], \quad \tilde{\gamma} = \frac{2\kappa + \lambda_{c}^{eq} [4\kappa + 6 + \lambda_{c}^{eq} [\kappa + 3]]}{\kappa + 1},
\]

\[
\tilde{\delta} = 2 - \lambda_{c}^{eq} [2\kappa + \lambda_{c}^{eq} [\kappa + 3] + \lambda_{c}^{eq}]], \quad \tilde{\pi} = \frac{3\tilde{\alpha} - \tilde{\beta}^2}{3\tilde{\alpha}^2}, \quad \tilde{\rho} = \frac{2\tilde{\beta}^3 - 9\tilde{\alpha}\tilde{\beta}^2 + 27\tilde{\alpha}^2 \tilde{\delta}}{27\tilde{\alpha}^3}.
\]

The above holds provided that \( 4\tilde{\pi}^3 + 27\tilde{\rho}^2 < 0, 3\tilde{\alpha} - \tilde{\beta}^2 < 0 \), and

\[-1 < \frac{3\tilde{\rho} - \sqrt{\frac{3}{\pi}}} {2} < 1,
\]

which are each satisfied for physically-sensible \( \nu^{eq} \).

Using the Bergström approximant (Eq. (38)) for the \( \nu^{eq} < (\lambda^{eq})^{\text{crit}} \) case in (Eq. (36)) and performing an appropriate quadratic root analysis leads to

\[
\nu = \nu^{BSB}(\nu^{eq}; \nu^{eq}) = \frac{\lambda_{c}^{eq} + 1 + \sqrt{[\lambda_{c}^{eq}]^2 - 2\lambda_{c}^{eq} + 1 + \frac{4}{\nu^{eq}}}}{2},
\]

(B.2)

The above holds provided that \( [\lambda_{c}^{eq}]^2 - 2\lambda_{c}^{eq} + 1 + \frac{4}{\nu^{eq}} > 0 \), which is satisfied for physically-sensible \( \nu^{eq} \).

Using the Bergström approximant (Eq. (38)) for the \( \nu^{eq} > (\lambda^{eq})^{\text{crit}} \) case in (Eq. (36)) and performing an appropriate cubic root analysis (Zwillinger 2002) leads to

\[
\nu = \nu^{BS}(\nu^{eq}, \nu^{eq}) = 2\sqrt{-\frac{\tilde{P}}{3}} \cos \left( \frac{1}{3} \arccos \left( \frac{3\tilde{R} - \sqrt{\frac{3}{\tilde{P}}} } {2\tilde{P}} \right) - \frac{2\pi}{3} \right) - \frac{\tilde{B}}{3\tilde{A}},
\]

(B.3)

where

\[
\tilde{A} = 1, \quad \tilde{B} = -3, \quad \tilde{C} = 3 - \sqrt{\frac{[\nu^{eq}]^2}{\kappa^{eq}}}, \quad \tilde{\tilde{D}} = \sqrt{\frac{[\nu^{eq}]^2}{\kappa^{eq}}} \nu^{eq} - 1,
\]

\[
\tilde{\tilde{P}} = \frac{3A\tilde{C} - B^2}{3A^2}, \quad \tilde{\tilde{R}} = \frac{2B^3 - 9A\tilde{B}\tilde{C} + 27A^2 \tilde{D}}{27A^3}.
\]
Figure C.15: Equilibrium chain stretch evolution. Here, $\zeta_{\text{char}}^\nu = 100$ and $n_\nu = 1000$, as per the composite segment potential displayed in [Fig. 2]. The black dotted lines denote the critical segment stretch $\lambda_{\text{crit}}^\nu$ and the critical equilibrium chain stretch $(\lambda_{\text{eq}}^\nu)^{\text{crit}}$. (top) Equilibrium chain stretch $\lambda_{\text{eq}}^\nu$ as a function of segment stretch $\lambda_\nu$ as per the approximated analytical $\lambda_{\text{eq}}^\nu$ function from Eq. (C.5) along with $\lambda_{\text{eq}}^\nu$ calculated using a highly accurate numerical solution for the inverse Langevin function. (bottom) The percent error of the approximated analytical $\lambda_{\text{eq}}^\nu$ function in Eq. (C.5) relative to $\lambda_{\text{eq}}^\nu$ calculated using a highly accurate numerical solution for the inverse Langevin function.

The above holds provided that $4 \tilde{P}^3 + 27 \tilde{R}^2 < 0$, $3 \tilde{A} \tilde{C} - \tilde{B}^2 < 0$, and

$$-1 < \frac{3 \tilde{R}}{2 \tilde{P}} \sqrt{-\frac{3}{\tilde{P}}} < 1,$$

which are each satisfied for physically-sensible $\lambda_{\text{eq}}^\nu$.

A note regarding the superscript nomenclature: $P$ and $B$ indicate if the solution for $\lambda_\nu$ is derived using either the Padé approximant ($P$) or the Bergström approximant ($B$). $SB$ indicates if the solution for $\lambda_\nu$ is derived for the case where $\lambda_{\text{eq}}^\nu$ is less than its so-called critical value, $(\lambda_{\text{eq}}^\nu)^{\text{crit}}$, i.e., the segment is in a sub-critical ($SB$) state. $SP$ indicates if the solution for $\lambda_\nu$ is derived for the case where $\lambda_{\text{eq}}^\nu$ is greater than or equal to its so-called critical value, i.e., the segment is in a super-critical ($SP$) state.

Appendix C. Analytical form of the equilibrium chain stretch function

Recall that substituting the nondimensional composite segment potential into the definition of segment stretch and simplifying leads to

$$\mathcal{L}^{-1}(\lambda_{\text{eq}}^\nu - \lambda_\nu + 1) = \frac{\partial u_\nu}{\partial \lambda_\nu} = \begin{cases} \kappa_\nu [\lambda_\nu - 1], & \text{if } \lambda_\nu < \lambda_{\text{eq}}^{\text{crit}}, \\ \frac{\kappa_\nu [\lambda_\nu - 1]^2}{\kappa_{\nu\text{char}}^\nu}, & \text{if } \lambda_\nu \geq \lambda_{\text{eq}}^{\text{crit}}. \end{cases}$$  

(C.1)
where $\lambda_\nu^{\text{crit}} = 1 + \sqrt{\frac{c_{\text{crit}}}{\nu}}$. Using the Padé approximant for the $\lambda_\nu < \lambda_\nu^{P2B}$ case (where $\lambda_\nu^{P2B} = \lambda_\nu((\lambda_\nu^{eq})^{P2B})$) and performing an appropriate cubic root analysis leads to

$$\lambda_\nu^{eq} = 2 \sqrt{-\frac{\pi}{3}} \cos \left( \frac{1}{3} \arccos \left( \frac{3\bar{\rho}}{2\pi} \sqrt{1 - \frac{3}{\pi}} \right) - \frac{2\pi}{3} \right) - \frac{\bar{\beta}}{3\bar{\alpha}}, \quad \text{(C.2)}$$

with

$$\bar{\alpha} = 1, \quad \bar{\beta} = [\kappa_\nu + 3][1 - \lambda_\nu], \quad \bar{\gamma} = [2\kappa_\nu + 3][\lambda_\nu^2 - 2\lambda_\nu] + 2\kappa_\nu,$$

$$\bar{\delta} = [\kappa_\nu + 1][3\lambda_\nu^2 - \lambda_\nu^3] - 2[\kappa_\nu\lambda_\nu + 1], \quad \bar{\pi} = \frac{3\bar{\alpha}\bar{\gamma} - \bar{\beta}^2}{3\bar{\alpha}^2}, \quad \bar{\rho} = \frac{2\bar{\beta}^3 - 9\bar{\alpha}\bar{\beta}\bar{\gamma} + 27\bar{\alpha}^2\bar{\delta}}{27\bar{\alpha}^3}.$$  

The above holds provided that $4\bar{\pi}^3 + 27\bar{\rho}^2 < 0$, $3\bar{\alpha}\bar{\gamma} - \bar{\beta}^2 < 0$, and

$$-1 < \frac{3\bar{\rho}}{2\pi} \sqrt{-\frac{3}{\pi}} < 1,$$

which are each satisfied for physically-sensible $\lambda_\nu$. Using the Bergström approximant for the $\lambda_\nu^{P2B} \leq \lambda_\nu < \lambda_\nu^{eq}$ case and simplifying leads to

$$\lambda_\nu^{eq} = \lambda_\nu - \left[ \frac{1}{\kappa_\nu} \right] \left[ \frac{1}{\lambda_\nu - 1} \right], \quad \text{(C.3)}$$

where $\lambda_\nu > 1$ holds true here. Using the Bergström approximant for the $\lambda_\nu \geq \lambda_\nu^{crit}$ case and simplifying leads to

$$\lambda_\nu^{eq} = \lambda_\nu - \left[ \frac{\kappa_\nu}{(\kappa_\nu^{eq})^{2/3}} \right] [\lambda_\nu - 1]^3. \quad \text{(C.4)}$$

Considering all of this, the approximated analytical form of the equilibrium chain stretch as a function of segment stretch is

$$\lambda_\nu^{eq} = \begin{cases} 2 \sqrt{-\frac{\pi}{3}} \cos \left( \frac{1}{3} \arccos \left( \frac{3\bar{\rho}}{2\pi} \sqrt{1 - \frac{3}{\pi}} \right) - \frac{2\pi}{3} \right) - \frac{\bar{\beta}}{3\bar{\alpha}}, & \text{if } \lambda_\nu < \lambda_\nu^{P2B} \\ \lambda_\nu - \left[ \frac{1}{\kappa_\nu} \right] \left[ \frac{1}{\lambda_\nu - 1} \right], & \text{if } \lambda_\nu^{P2B} \leq \lambda_\nu < \lambda_\nu^{eq} \\ \lambda_\nu - \left[ \frac{\kappa_\nu}{(\kappa_\nu^{eq})^{2/3}} \right] [\lambda_\nu - 1]^3, & \text{if } \lambda_\nu \geq \lambda_\nu^{crit} \end{cases}, \quad \text{(C.5)}$$

with

$$\bar{\alpha} = 1, \quad \bar{\beta} = [\kappa_\nu + 3][1 - \lambda_\nu], \quad \bar{\gamma} = [2\kappa_\nu + 3][\lambda_\nu^2 - 2\lambda_\nu] + 2\kappa_\nu,$$

$$\bar{\delta} = [\kappa_\nu + 1][3\lambda_\nu^2 - \lambda_\nu^3] - 2[\kappa_\nu\lambda_\nu + 1], \quad \bar{\pi} = \frac{3\bar{\alpha}\bar{\gamma} - \bar{\beta}^2}{3\bar{\alpha}^2}, \quad \bar{\rho} = \frac{2\bar{\beta}^3 - 9\bar{\alpha}\bar{\beta}\bar{\gamma} + 27\bar{\alpha}^2\bar{\delta}}{27\bar{\alpha}^3}.$$  

Fig. C.15 displays the approximated equilibrium chain stretch function as per Eq. (C.5) the equilibrium chain stretch calculated using a highly accurate numerical solution for the inverse Langevin function, and the percent error between each of these functions. This figure convincingly verifies that the approximated analytical equilibrium chain stretch function is sufficiently accurate with respect to the highly accurate numerical solution in the domain of physically-sensible segment stretches.

As a matter of proper interpretation, Eq. (C.5) ought to be treated as the inverse segment stretch function given in Eq. (43).

**Appendix D. Bond-level theory**

To reconcile the transition from the segment level to the bond level, this Appendix section highlights the minor differences that arise for the bond-level theory for the single chain model and the rupture framework.
The transition from the segment level to the bond level is built upon the fact that each individual segment in the chain is identically composed of \(n_b\) bonds. Given this, then the product \([\nu]n_b\) is the number of bonds composing the entire polymer chain backbone, \(n_b\). The bond stretch is the ratio of the bond length \(l_b\) with the equilibrium bond length \(l_b^\text{eq}\), \(\lambda_b = l_b/l_b^\text{eq}\). The energy state of each bond is described by the bond potential, \(U_b\), which inherently exhibits some characteristic bond potential energy scale \(E_b^\text{char}\) and bond stiffness \(k_b\) defined as

\[
k_b \equiv U_b''(l_b^\text{eq}) = \left. \frac{\partial^2 U_b(l_b)}{\partial l_b^2} \right|_{l_b=l_b^\text{eq}}. \tag{D.1}
\]

The functional form for the bond potential analogously follows that for the segment potential as per \[\text{Eq. (22)}\] and \[\text{Eq. (23)}\] with the segment-level parameters \(l_b\), \(l_b^\text{eq}\), \(E_b^\text{char}\), and \(k_b\) respectively swapped for the bond-level parameters \(l_b\), \(l_b^\text{eq}\), \(E_b^\text{char}\), and \(k_b\)

\[
U_b^\text{bar}(l_b) = E_b^\text{char}\left[\frac{1}{2} \frac{k_b}{E_b^\text{char}} [l_b - l_b^\text{eq}]^2 - 1\right], \quad U_b^\text{har}(l_b) = E_b^\text{char}\left[\frac{1}{2} \frac{k_b}{E_b^\text{char}} \left[\ln\left(\frac{l_b}{l_b^\text{eq}}\right)\right]^2\right] - 1, \tag{D.2}
\]

\[
U_b^{\text{morse}}(l_b) = E_b^\text{char}\left[1 - e^{-a_b[l_b-l_b^\text{eq}]}\right]^2 \tag{D.3}
\]

where \(a_b\) is the Morse parameter and is related to \(E_b^\text{char}\) and \(k_b\) via \(k_b = 2a_b^2 E_b^\text{char}\). The composite bond potential is written as

\[
U_b(l_b) = \begin{cases} 
E_b^\text{char}\left[\frac{1}{2} \frac{k_b}{E_b^\text{char}} [l_b - l_b^\text{eq}]^2 - 1\right], & \text{if } l_b < l_b^{\text{crit}} = \frac{l_b^\text{eq}}{k_b}\alpha_{\text{crit}}, \\
\frac{l_b^\text{eq} - a_b k_b}{2k_b[l_b-l_b^\text{eq}]}^2, & \text{if } l_b \geq l_b^{\text{crit}}.
\end{cases} \tag{D.4}
\]

The nondimensional bond potential, nondimensional characteristic bond potential energy scale, and nondimensional bond stiffness are respectively defined as \(u_b \equiv \beta U_b\), \(\xi_b^\text{nondimensional} \equiv \beta E_b^\text{nondimensional}\), and \(k_b \equiv \beta [l_b^\text{eq}]^2 k_b\). The nondimensional Morse parameter is also defined as \(\alpha_b \equiv l_b^\text{eq}a_b\). The nondimensional scaled bond potential \(\pi_b\), and its (non-negative) shifted counterpart \(\tilde{\pi}_b\) are respectively defined as \(\pi_b \equiv u_b U_b\) and \(\tilde{\pi}_b \equiv \pi_b + 1\). The bond force is given in nondimensional terms as

\[
\xi_b = \frac{\partial u_b}{\partial \pi_b}. \tag{D.5}
\]

Segment-level length and energy measures multiplicatively scale with their bond-level counterparts by a factor of \(\nu_b\). Thus, segment length, equilibrium segment length, and segment potential are respectively defined as \(L_b = \nu_b l_b\), \(L_b^\text{eq} = \nu_b l_b^\text{eq}\), and \(U_b = \nu_b U_b\). As a corollary, the following relations are found to hold true

\[
\lambda_{\nu} = \lambda_b, \quad E_{\nu}^\text{char} = \nu_b E_b^\text{char}, \quad k_{\nu} = \frac{k_b}{\nu_b}, \quad u_{\nu} = \nu_b u_b, \quad E_{\nu}^\text{char} = \nu_b E_b^\text{char}, \quad \kappa_{\nu} = \nu_b \kappa_b, \tag{D.6}
\]

\[
\lambda_{\nu}^{\text{crit}} = \lambda_b^{\text{crit}}, \quad a_{\nu} = \frac{a_b}{\nu_b}, \quad \alpha_{\nu} = \alpha_b, \quad \pi_{\nu} = \pi_b, \quad \tilde{\pi}_{\nu} = \tilde{\pi}_b, \quad \xi_{\nu} = \nu_b \xi_b. \tag{D.7}
\]

Considering all of this, the nondimensional Helmholtz free energy per bond, \(\psi_{\text{nondimensional}}\), is given as

\[
\psi_{\nu}(\lambda_b, \lambda_b^\text{eq}) = s_{\nu}(\lambda_b, \lambda_b^\text{eq}) + u_b(\lambda_b), \tag{D.8}
\]

\[
s_{\nu}(\lambda_b, \lambda_b^\text{eq}) = \frac{1}{\nu_b} \left[\lambda_b^\text{eq} - \lambda_b + 1\right] L^{-1}(\lambda_b^\text{eq} - \lambda_b + 1) + \ln\left(\frac{L^{-1}(\lambda_b^\text{eq} - \lambda_b + 1) + 1}{\sinh(L^{-1}(\lambda_b^\text{eq} - \lambda_b + 1))}\right), \tag{D.9}
\]

\[
\psi_{\nu}(\lambda_b, \lambda_b^\text{eq}) = \frac{1}{\nu_b} \left[\lambda_b^\text{eq} - \lambda_b + 1\right] L^{-1}(\lambda_b^\text{eq} - \lambda_b + 1) + \ln\left(\frac{L^{-1}(\lambda_b^\text{eq} - \lambda_b + 1) + 1}{\sinh(L^{-1}(\lambda_b^\text{eq} - \lambda_b + 1))}\right) + u_b(\lambda_b), \tag{D.10}
\]

where \(s_{\nu}\) is the nondimensional chain-level entropic contributions per bond, \(u_b\) is the nondimensional bond-level enthalpic contributions, and \(\psi_{\nu\nu} = \nu_b \psi_{\nu\nu}\).
With $\lambda_b = \lambda_c$, then, by proxy, the functional form for $\lambda_c$ is provided by Eq. (43) As a result, the reference bond stretch $\Lambda_{b}^{ref} = \Lambda_{c}^{ref}$, where $\Lambda_{b}^{ref}$ is taken as the ratio of the reference bond length $l_{b}^{ref}$ with the equilibrium bond length $l_{b}^{eq}$, $\Lambda_{b}^{ref} = \frac{l_{b}^{ref}}{l_{b}^{eq}}$.

Finally, taking all of the bond-level formulation up to this point in consideration, a bond scission framework can be developed in a completely analogous manner to how the segment scission framework was developed in [Section 4.1]. Taking $\hat{\epsilon}_b^{sci}$ as the nondimensional bond scission activation energy barrier, then the rate-independent probability of bond scission $\hat{p}_b^{sci}$ and the rate-independent probability of chain scission $\hat{p}_c^{sci}$ are provided for a statistically significant number of bonds

$$\hat{p}_b^{sci} = \exp\{-\hat{\epsilon}_b^{sci}\}, \quad \hat{p}_c^{sci} = 1 - \hat{p}_b^{sci}. \quad (D.11)$$

The rate-dependent probability of bond survival $\rho_b$, and the rate-dependent probability of bond scission $\gamma_b$ are analogously defined

$$\dot{\rho}_b = -\omega_0\rho_b^{sci}, \quad \gamma_b = 1 - \rho_b \implies \dot{\gamma}_b = \omega_0\rho_b^{sci}. \quad (D.12)$$

The nondimensional bond scission energy is given as

$$\hat{\epsilon}_b^{sci} \equiv \hat{s}_b \left(\hat{\lambda}_b, \hat{\lambda}_c^{eq}\right) + \hat{u}_b \left(\hat{\lambda}_b\right) + \hat{\zeta}_b^{char} = \psi_{cb} \left(\hat{\lambda}_b, \hat{\lambda}_c^{eq}\right) + \hat{\zeta}_b^{char}. \quad (D.13)$$

The rate-dependent nondimensional dissipated bond scission energy $\hat{\epsilon}_b^{diss}$ is defined via its time rate-of-change equation

$$\hat{\epsilon}_b^{diss} = \dot{\hat{\epsilon}}_b^{sci}. \quad (D.14)$$

In an analogous way, the rate-independent $\hat{\epsilon}_b^{diss}$ is defined via its applied bond stretch-based rate-of-change equation

$$(\hat{\epsilon}_b^{diss})' = (\hat{\epsilon}_b^{sci})' \hat{\epsilon}_b^{sci}, \quad (D.15)$$

where derivatives are taken with respect to $\hat{\lambda}_b$. For $\hat{\lambda}_b \leq \lambda_b^{crit}$

$$\hat{\epsilon}_b^{sci} = \frac{1}{2}\kappa_b \left[\hat{\lambda}_b - 1\right]^2 - \frac{3}{2} \left[\kappa_b\right]^2 \kappa_b \left[\hat{\lambda}_b - 1\right] + \hat{\zeta}_b^{char}, \quad (D.16)$$

$$\left(\hat{\epsilon}_b^{sci}\right)' = \hat{\epsilon}_b^{sci} \left[\frac{\left[\hat{\lambda}_b - 1\right]^2 - \kappa_b\left[\hat{\lambda}_b - 1\right]}{\kappa_b} \right], \quad (D.17)$$

$$\left(\hat{\epsilon}_b^{diss}\right)' = \hat{\epsilon}_b^{sci} \left[\frac{\left[\hat{\lambda}_b - 1\right]^2 - \kappa_b\left[\hat{\lambda}_b - 1\right]}{\kappa_b} \right] \hat{\epsilon}_b^{sci}, \quad (D.18)$$

where $\hat{\epsilon}_b^{diss} = 0$ at $\hat{\lambda}_b = 1$. If irreversible bond scission is assumed to take place in the network, then $(\hat{\epsilon}_b^{sci})' \geq 0$ and $(\hat{\epsilon}_b^{diss})' \geq 0$ must hold during deformation. The rate-independent probability of segment scission $\hat{p}_\nu^{sci}$ and the rate-independent probability of segment survival $\hat{p}_\nu^{sur}$ are implied to be

$$\hat{p}_\nu^{sci} = \hat{p}_\nu^{sci}|_{\nu}, \quad \hat{p}_\nu^{sur} = 1 - \hat{p}_\nu^{sci}. \quad (D.19)$$

Via probabilistic considerations from [Guo and Zarrineh 2021], the rate-independent probability of chain survival $\hat{p}_c^{sur}$ and the rate-independent probability of chain scission $\hat{p}_c^{sci}$, are given

$$\hat{p}_c^{sur} = \hat{p}_c^{sur}|_{\nu}, \quad \hat{p}_c^{sci} = 1 - \hat{p}_c^{sur}. \quad (D.20)$$

The rate-dependent probability of chain survival $\rho_c$ is then related to $\rho_b$ via $\rho_c = \rho_b^{\nu}$. As a result, $\rho_c$ and its counterpart, the rate-dependent probability of chain scission $\gamma_c$, can be represented with respect to bond-level probabilistic quantities

$$\frac{\dot{\rho}_c}{\rho_c} = -n_b\omega_0\rho_b^{sci}, \quad \gamma_c = 1 - \rho_c \implies \dot{\gamma}_c = n_b\omega_0\rho_b^{sci}. \quad (D.21)$$
The time rate-of-change equation for the rate-dependent nondimensional dissipated chain scission energy per bond \( \dot{\hat{\varepsilon}}_{\text{diss} cb} \) is defined as (Guo and Zaïri, 2021)

\[
\dot{\hat{\varepsilon}}_{\text{diss} cb} \equiv \dot{\gamma} c \hat{\varepsilon}_{\text{sci} cb},
\]

(D.22)

The applied bond stretch-based rate-of-change for the rate-independent \( \hat{\varepsilon}_{\text{diss} cb} \) is defined as

\[
(\hat{\varepsilon}_{\text{diss} cb})' \equiv (\hat{\rho}_{\text{sci} cb})' \hat{\varepsilon}_{\text{sci} cb},
\]

\[
(\hat{\rho}_{\text{sci} cb})' = n_b [1 - \hat{\rho}_{\text{sci} b}]^{n_b-1} \hat{\rho}_{\text{sci} b} \left[ \frac{\left( \frac{\zeta_{\text{char}}}{\kappa_b} \right)^2 - \kappa_b [\hat{\lambda}_b - 1]}{\hat{\lambda}_b - 1} \right] \hat{\varepsilon}_{\text{sci} b},
\]

(D.23)

\[
(\hat{\varepsilon}_{\text{diss} cb})' = n_b [1 - \hat{\rho}_{\text{sci} b}]^{n_b-1} \hat{\rho}_{\text{sci} b} \left[ \frac{\left( \frac{\zeta_{\text{char}}}{\kappa_b} \right)^2 - \kappa_b [\hat{\lambda}_b - 1]}{\hat{\lambda}_b - 1} \right] \hat{\varepsilon}_{\text{sci} b},
\]

(D.24)

where \( \hat{\varepsilon}_{\text{diss} cb} = 0 \) at \( \hat{\lambda}_b = 1 \).

CRediT authorship contribution statement

**Jason Mulderrig:** Conceptualization, Methodology, Software, Formal analysis, Investigation, Writing - Original Draft, Writing - Review & Editing. **Brandon Talamini:** Conceptualization, Writing - Review & Editing. **Nikolaos Bouklas:** Conceptualization, Methodology, Resources, Writing - Review & Editing, Supervision.

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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