A MICROMECHANICAL PLATFORM TO STUDY NONLINEAR BEHAVIOR OF ELASTOMERIC MATERIALS

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ABSTRACT

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Cross-linked polymers demonstrate nonlinear behavior under large deformations with inelastic features such as the Mullins effect, permanent set, deformation-induced anisotropy, and progressive stress softening. While several constitutive models are developed to take into account each of those features individually, there are only a few models which can consider damage accumulation in cross-linked elastomers that occur due to multiple parallel factors.

Here, a new modular platform is presented to integrate different inelastic mechanisms into one generalized constitutive model. The concept of network decomposition is the keystone of the proposed platform. Based on this concept, the polymer network is considered as a combination of parallel networks, each responsible for the specific inelastic response. The energy of each network is calculated through the concept of the unit sphere. Consequently, the polymer matrix total strain energy can be estimated by summation of the free energy of the sub-networks in all directions. Therefore, a three-dimensional (3D) polymer matrix can be decomposed to unidirectional sub-network elements uniformly distributed over a unit micro-sphere, which hosts a simplified 1D inelastic mechanism. The network models can be substituted, upgraded, or removed without influencing the integrity of the framework. In order to improve the accuracy of the proposed framework, the theory of elastomer elasticity has been revisited. Next, different micro-mechanical models are developed to describe the nature of Mullins effect, permanent set, deformation-induced anisotropy, and necking instability in highly cross-linked elastomeric gels based on different concepts.

First, the popular assumptions that influence computational accuracy and simplicity of the proposed framework are examined. In modeling polymeric systems, two competing factors determine the type of material model that should be used in the simulation: computational cost and accuracy. Optimizing the trade-off between these two factors determines the minimum requirements of the model. The proposed modular platform enables us to select the networks based on this tradeoff. Furthermore, network models are designed to return strain energy; the scale-transition will be based on a micro-sphere concept, and the Non-Gaussian entropic behavior is assumed for polymer chains. The non-gaussian theory is often approximated by the Kuhn-Grün (KG) distribution function, which is derived from the first-order approximation of the complex Rayleigh's exact Fourier integral distribution. The KG function is widely accepted in polymer physics, where the non-Gaussian theory is often used to describe the energy of the chains with various flexibility ratios. However, the KG function is shown to be relevant only for long chains and becomes extremely inaccurate for chains with fewer than 40 segments. In order to overcome this shortcoming, a novel modification of non-Gaussian theory using the inverse Langevin function is developed to provide a family of approximation functions for non-Gaussian theory with different degrees of accuracy. In addition, a set of simple and accurate approximation of the inverse Langevin function is proposed to further improve the accuracy of the energy of a 1D polymer chain.

Next, two constitutive models are developed to understand and describe the mechanical behavior of double network hydrogel (DN gel) based on statistical micro-mechanics of interpenetrating polymer networks. In the first model, the nonlinear behavior of the DN gels is attributed to the existence of pre-damage in the first network due to swelling during the polymerization process. In the second model, DN gels behavior is divided into three parts including pre-necking, necking, and hardening. The first network is dominant in the response of the gel in the pre-necking stage. The breakage of the first network to smaller network fractions (clusters) induces the stress softening observed in this stage. The disentanglement of the second network chains from broken first network chains and long chains in the second network are also considered as main contributors to the response of gels in necking and hardening stages, respectively. The contribution of clusters decreases during the necking as the second network starts hardening. The numerical results of the developed models are validated and compared by uni-axial cyclic tensile experimental data of DN gels. Finally, a finite-element implementation of the proposed model is presented to simulate the initiation and propagation of necking instability. Copyright by VAHID MOROVATI 2020 "This dissertation is dedicated to my wife, **Fatemeh**, for her unconditional support and love through all these years,

also to my respectful parents and parents-in-law for always believing in me."

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CHAPTER 1

INTRODUCTION

1.1 Motivation

Elastomeric materials can be found in a broad range of products, ranging from bio-medical devices to tires and hoses. Elastomers have a high extensibility with nonlinear elastic behavior, high-energy absorption ability, dynamic damping capacity, and low cost of manufacturing. These characteristics make them an ideal option for different engineering applications. In addition, the mechanical performance of these materials can be significantly enhanced by different strategies like synthesizing multi-network elastomers or addition of fillers such as carbon black, silica, and Nano particles. The elastomer behavior is non-linear and very complicated due to high stretch-ability, nearly incompressibility, permanent damage, and time-temperature dependent behavior. Although recent advances in the process and characterization of the elastomers have led to significant improvements in their properties, our understanding of the load transfer mechanism within them has remained sparse and inconclusive. Availability of an accurate constitutive model to predict behavior of elastomers under different loading conditions is significantly important in the design procedure.

Mechanical properties of rubber-like elastomers were studied intensively during the last century [6, 7, 8, 9, 10, 11, 12, 13, 14]. The behavior of elastomers in cyclic deformation including uni-axial tension, compression and shear tests shows many complex and interesting features. Fig. 1.1-a shows a typical stress-stretch behavior of filled rubbers under uni-axial loading. In a uni-axial tension, a considerable stress-softening is observed between loading and unloading. The amount of this softening reduces in the subsequent cycle until it reaches a stabilized value, generally referred as Hysteresis. Simplification of the constitutive behavior of elastomers is a regular practice in current modeling approaches. In elastomers, the hysteresis is considerably smaller in second and subsequent deformation cycles and thus, it is often considered as zero [15, 16]. Thus, the loading and reloading are assumed to be identical and the hysteresis is eliminated from the obtained experimental results (See Fig. 1.1d). In this case, the unloading curve provides a good estimation of the reloading response of the softened material, and the difference between the load and the unload curves in the first cycle is called idealized Mullins effect [17, 18, 19, 20, 21]. Recent experimental studies showed that tensile cycles in one direction do not cause the Mullins effect in the perpendicular direction [22, 23, 24]. When the Mullins effect in tension is already present, compressive stretches weaken the stress in other directions [25]. Accordingly, the anisotropy of the Mullins effect highly depends on the deformation in other directions [26]. This work specifically focuses on developing a platform to predict the idealized Mullins effect, strain-induced anisotropy and permanent set by neglecting the hysteresis. The modular nature of the proposed platform, however, allows us to later add new inelastic features to the predicted response such as hysteresis and strain-induced crystallization.

Experimental evidence of the Mullins effect, permanent set, and deformation-induced anisotropy suggest that all three of them can be considered as permanent damage mechanisms in elastomers [27, 23, 10]. Permanent damage has been investigated by several constitutive models [28, 22, 23, 29]. Two main categories of proposed concepts contain phenomenological and micro-mechanically motivated models. Some material parameters with no physical interpretations are used in phenomenological approaches, which should usually be defined by a fitting procedure. Micro-mechanically motivated models are proposed to provide a better understanding of mechanical behavior of Mullins effect by the interpreting physical nature of the phenomenon. These models use various concepts including the breakage of chains between the rubber and the fillers, slipping of molecules, cluster's rupture of fillers, chain disentanglement, and more complex composite structure formations [30, 23, 31].

2



Figure 1.1. (a) A schematical stress-stretch behavior of the rubber-like elastomers under a uni-axial tension test. Inelastic effects (Mullins effect, permanent set, and hysteresis) (b) Cyclic tension test in transverse direction of previous elongation. Inelastic effects (Deformation induced anisotropy) (c-d) The idealized modifications of the constitutive behavior of elastomers by excluding permanent set and hysteresis.

1.1.1 Micro-mechanical Platform

This study proposes a modular platform based on a constitutive model. The model describes a polymer matrix mechanics through a basis initiated from molecular physics, and implements it in a multi-scale model. The accuracy improvement of the platform is two-folds, (i) enhancing the polymer physics theory used in the platform and (ii) increasing the number of modules to consider different phenomena. Therefore, the framework consists of modules and several theories with different accuracy levels. Each module can be added from existing models to consider a specific inelastic phenomenon. The modules can be substituted, upgraded, or removed without influencing the integrity of the framework. Modules are derived to calculate the contribution of the

sub-network in the total strain energy. The entropic and enthalpic total energy can be considered for polymer chains. Scale transition is performed based on the assumption of uniform spatial distribution through a micro-sphere 3D generalization. The micro-sphere scale transition simplifies the complex 3D problem to a 1D integration of a simple rheological representation of damage for each spatial directions. Micro-sphere scale transition provides a simplified technique to model permanent stress softening in the material, which can consider the deformation-induced damage and permanent set as its byproducts.

1.2 Outline of the Present Work

This dissertation presents a general platform to predict the nonlinear behavior of elastomeric materials with a desired trade off between the accuracy of the model and computational cost of its numerical implementation. The trade-off is achieved through a micro-mechanical platform, which enables us to choose different phenomena to be added to the model with adjustable accuracy of the single polymer physics theory. The current study is divided into six chapters, a short summary of which is presented in the following.

- Chapter 2 reviews the **Non-Gaussian theory** of polymer physics. Different theories are compared with the exact distribution of random walk problem in terms of the chain endto-end distribution function, free energy, and entropic force. Finally, a new family of accurate approximation of the Non-Gaussian probability distribution function (PDF), entropic force, and the strain energy of a single chain are subsequently developed to describe the mechanics of a polymer chain.
- Chapter 3 presents a novel approach which can provide a family of approximation functions for inverse Langevin function (ILF) with different degrees of accuracy. This chapter starts with a current practice of estimation for the ILF and continues with the general properties of this function. At the end, three simple procedures are presented, which can take current approximation functions with an asymptotic behavior and enhance

them by the addition of a power series of their induced error. The accuracy/complexity trade-off for the family of ILF approximations, generated by the proposed approaches, is compared against those of other approaches to show the advantage of the proposed model.

- Chapter 4 proposes a **micro-mechanical model** to characterize the constitutive behavior of multinetwork elastomers in a quasi-static large deformation. In particular, we focused on describing the permanent damage in double-network (DN) elastomers under large deformations. Irreversible chain detachment and decomposition of the first network are explored as the underlying reasons for the nonlinear inelastic phenomenon. The proposed model is able to predict the nonlinear damage mechanism based on the microstructure of the matrix. The model is validated with uni-axial loading and unloading experiments of DN elastomers.
- Chapter 5 presents a constitutive model to understand and describe the mechanical behavior and **necking instability** of DN elastomers based on statistical micro-mechanics of interpenetrating polymer networks. Here, DN elastomers behavior is divided into three parts including pre-necking, necking, and hardening. The constitutive model for the first, interaction, and the second network is derived. Each of these networks is the main contributor in the pre-necking, necking, and hardening stages, respectively. Furthermore, a finite-element implementation of the proposed model is presented to simulate the initiation and propagation of the necking instability. Finally, the numerical results of the proposed model are validated and compared by uni-axial cyclic tensile experimental data of DN elastomers.
- Chapter 6 concludes the findings of the study presented in this dissertation. Possible future works extended from the current investigation are also discussed in this chapter.

CHAPTER 2

MODELING OF ELASTOMERS

The constitutive modelling of elastomers involves nonlinear continuum mechanical quantities, which describe the behavior of materials undergoing a large deformation. Thus, a basic foundation on continuum mechanics, including fundamental geometric mappings and basic stress measures of a solid body undergoing large deformations, is briefly discussed in this chapter. For a comprehensive description and understanding of the topic, the reader can refer to continuum mechanics reference materials such as [32], [33].

2.1 Some Notes on Continuum Mechanics

In continuum mechanics theory, it is assumed that an object fully occupies the space by its substances. Physical properties of a solid or fluid medium are related through mathematical tensors measures. These measures are independent of their observed coordinate system in general. However, they can be represented in different coordinate systems. In this section, the relation of various mechanical measurements are briefly reviewed.

2.1.1 Deformation gradient

A continuum body B_{t_0} in a 3D Euclidean space at time t_0 is shown in Fig. 2.1, in which any arbitrary point P_0 with respect to an arbitrary basis can be represented by $X \in \mathbb{E}^3$. As the body deforms in the space, the medium occupies its current configuration at B_t . Given that the geometrical mapping of body from B_{t_0} to B_t is one to one, any point from initial configuration, P_0 , uniquely maps to its new configuration coordinate, P, with an arbitrary basis of $x \in \mathbb{E}^3$.

The geometrical mapping of the regions of body from current configuration B_{t_0} to the reference configurations B_t in any arbitrary coordinate system, e^i (i = 1, 2, 3), can represent the position of point P and P_0 by

$$\boldsymbol{x} = \hat{\boldsymbol{x}}(\theta^{1}, \theta^{2}, \theta^{3}, t), \quad \boldsymbol{X} = \hat{\boldsymbol{X}}(\theta^{1}, \theta^{2}, \theta^{3}) = \hat{\boldsymbol{x}}(\theta^{1}, \theta^{2}, \theta^{3}, t_{0}). \quad i = 1, 2, 3, \quad (2.1)$$

Therefore, the displacement vector, \boldsymbol{u} , of point P can be written as

$$\boldsymbol{u} = \hat{\boldsymbol{u}}(\theta^1, \theta^2, \theta^3, t) = \boldsymbol{x} - \boldsymbol{X}$$
(2.2)



Figure 2.1. Deformation and motion of a continuum body.

Given an Euclidean space with a set of orthonormal (Cartesian) basis vectors, say e_i (i = 1, 2, 3), one can express each point of the body as

$$X = X^{i} e_{i}, \quad X^{j} = X \cdot e_{j}, \qquad j = 1, 2, 3,$$

$$u = u^{i} e_{i}, \quad u^{j} = u \cdot e_{j}, \qquad j = 1, 2, 3, \qquad (2.3)$$

$$x = x^{i} e_{i}, \quad x^{j} = x \cdot e_{j} = X^{j} + u^{j}, \qquad j = 1, 2, 3,$$

where the Einstein notation, summation over repeated indices, is applied. Deformation can be

related to the tangent vectors of the coordinate lines in each of the configurations. Tangent vectors of sufficiently differentiable X and x can be written as

$$\boldsymbol{G}_{i} = \frac{\partial \boldsymbol{X}}{\partial \theta^{i}} =, \qquad \boldsymbol{g}_{i} = \frac{\partial \boldsymbol{x}}{\partial \theta^{i}}, \quad i = 1, 2, 3,$$
(2.4)

The relative motion of an arbitrary point with respect to its adjacent point can be calculated in a direction a through the directional derivative as

$$\frac{d}{ds}\hat{\boldsymbol{x}}\left(\boldsymbol{X}+s\boldsymbol{a},t\right)\Big|_{s=0} = \lim_{\Delta s \to 0} \frac{\hat{\boldsymbol{x}}\left(\boldsymbol{X}+\Delta s\boldsymbol{a},t\right)-\hat{\boldsymbol{x}}\left(\boldsymbol{X},t\right)}{\Delta s} = \left(\operatorname{Grad}\boldsymbol{x}\right)\boldsymbol{a}.$$
(2.5)

Therefore, second order deformation gradient tensor, (Grad \boldsymbol{x}), can be written by a linear mapping of vector \boldsymbol{a} into vector $\frac{d}{ds}\hat{\boldsymbol{x}}(\boldsymbol{X} + s\boldsymbol{a}, t)\Big|_{s=0}$ as

$$\mathbf{F} = \text{Grad} \, \boldsymbol{x} = \frac{d\hat{\boldsymbol{x}}}{d\boldsymbol{X}}.$$
(2.6)

where, $d\mathbf{X}$ is a infinitesimal element before deformation and $d\hat{\mathbf{x}}$ is the same element on the body after deformation. This tensor play a pivotal role in deformation kinematics, which can describe the relative motion of material elements during deformation. Therefore, one has the relation of infinitesimal element in reference and current configurations as

$$d\boldsymbol{x} = \mathbf{F}d\boldsymbol{X}, \quad d\boldsymbol{X} = \mathbf{F}^{-1}d\boldsymbol{x}. \tag{2.7}$$

Moreover, the change of volume and surface elements can be related to deformation gradient tensor thorough these relations. To this end, a volume in the reference configuration of three non-coplanar vector, dX_1 , dX_2 and dX_3 , can be defined as

$$dV_0 = [d\boldsymbol{X}_1 d\boldsymbol{X}_2 d\boldsymbol{X}_3] = (d\boldsymbol{X}_1 \times d\boldsymbol{X}_2) \cdot d\boldsymbol{X}_3.$$
(2.8)

Using Eq. 2.7, each of these vectors deforms in the current configuration to

$$d\boldsymbol{x}_1 = \mathbf{F}d\boldsymbol{X}_1, \quad d\boldsymbol{x}_2 = \mathbf{F}d\boldsymbol{X}_2, \quad d\boldsymbol{x}_3 = \mathbf{F}d\boldsymbol{X}_3. \tag{2.9}$$

Thus, the volume of the element in the current configuration can be written as

$$dV = \left[d\boldsymbol{x}_1 d\boldsymbol{x}_2 d\boldsymbol{x}_3 \right] = \left(d\boldsymbol{x}_1 \times d\boldsymbol{x}_2 \right) \cdot d\boldsymbol{x}_3 = J dV_0,$$

where

$$J = \frac{dV}{dV_0} = \left| \mathbf{F}_{.j}^i \right| = \det \mathbf{F} > 0.$$
(2.10)

In addition, by defining the surface element of reference and current state as $d\mathbf{A}_0 = d\mathbf{X}_1 \times d\mathbf{X}_2$ and $d\mathbf{A} = d\mathbf{x}_1 \times d\mathbf{x}_2$, the relation of the surface areas can be calculated by substituting Eq. 2.9 into $dV_0 = JdV$ as

$$d\boldsymbol{A} = J\mathbf{F}^{-T}d\boldsymbol{A}_0. \tag{2.11}$$

where dA = |dA| and $dA_0 = |dA_0|$ are the surface areas in the current and reference configuration, respectively. An element length in reference and current states can be calculated similarly as

$$\|d\boldsymbol{x}\|^{2} = d\boldsymbol{x} \cdot d\boldsymbol{x} = d\boldsymbol{X} \left(\mathbf{F}^{\mathrm{T}} \mathbf{F}\right) d\boldsymbol{X} = d\boldsymbol{X} \mathbf{C} d\boldsymbol{X},$$
$$\|d\boldsymbol{X}\|^{2} = d\boldsymbol{X} \cdot d\boldsymbol{X} = d\boldsymbol{x} \left(\mathbf{F}^{-\mathrm{T}} \mathbf{F}^{-1}\right) d\boldsymbol{x} = d\boldsymbol{x} \mathbf{b}^{-1} d\boldsymbol{x},$$
(2.12)

where $\mathbf{C} = \mathbf{F}^{\mathrm{T}}\mathbf{F}$ and $\mathbf{b} = \mathbf{F}\mathbf{F}^{\mathrm{T}}$ are the right and left Cauchy-Green tensors, respectively. The change in the length of a linear element, the stretch of a material element, defined as the ratio of the deformed to the referenced length of the material element. Deformation changes the length of an element $d\mathbf{X}$ in direction \mathbf{N} in initial state to $d\mathbf{x}$ in direction \mathbf{n} in the current state as

$$\lambda(\mathbf{N}) = \frac{dx}{dX} = \sqrt{\frac{\|d\mathbf{x}\|^2}{\|d\mathbf{X}\|^2}} = \sqrt{\frac{dX\mathbf{N}\mathbf{C}\mathbf{N}dX}{dX^2}}$$
$$= (\mathbf{N}\mathbf{C}\mathbf{N})^{\frac{1}{2}}, \qquad (2.13)$$

and

$$\lambda(\boldsymbol{n}) = (\boldsymbol{n}\mathbf{b}^{-1}\boldsymbol{n})^{-\frac{1}{2}}.$$
(2.14)

Another measure of the change in element length during deformation can be written as

$$\|d\boldsymbol{x}\|^2 - \|d\boldsymbol{X}\|^2 = 2d\boldsymbol{X}\mathbf{E}d\boldsymbol{X}$$
$$= 2d\boldsymbol{x}\mathbf{E}d\boldsymbol{x}$$
(2.15)

where $\mathbf{E} = \frac{1}{2} (\mathbf{C} - \mathbf{I}) = \frac{1}{2} (\mathbf{F}^{\mathrm{T}} \mathbf{F} - \mathbf{I})$ called the Green-Lagrange strain tensor and $\mathbf{e} = \frac{1}{2} (\mathbf{I} - \mathbf{b}^{-1}) = \frac{1}{2} (\mathbf{I} - \mathbf{F}^{-\mathrm{T}} \mathbf{F}^{-1})$ is Almansi strain tensor.

2.1.2 Deformation rate

The material velocity gradient can be defined similar to the deformation gradient by

$$\mathbf{L} = \operatorname{Grad} \dot{\boldsymbol{x}} = \frac{\partial}{\partial \boldsymbol{X}} \left[\frac{\partial \boldsymbol{x}(\boldsymbol{X}, t)}{\partial t} \right] = \frac{\partial}{\partial t} \left(\frac{\partial \boldsymbol{x}}{\partial \boldsymbol{X}} \right) = \dot{\mathbf{F}}.$$
 (2.16)

The spatial velocity gradient, derivative of a spatial velocity field v with respect to the current configuration, can be written as

$$\mathbf{l} = \operatorname{grad} \dot{\boldsymbol{x}} = \frac{\partial \boldsymbol{v}}{\partial \boldsymbol{X}} \frac{\partial \boldsymbol{X}}{\partial \boldsymbol{x}} = \dot{\mathbf{F}} \mathbf{F}^{-1}.$$
 (2.17)

The spatial gradient of velocity can be decomposed to a symmetric part $\mathbf{d} = \frac{1}{2} (\mathbf{l} + \mathbf{l}^{\mathrm{T}})$ and a skew-symmetric part $\mathbf{w} = -\mathbf{w}^{\mathrm{T}} = \frac{1}{2} (\mathbf{l} - \mathbf{l}^{\mathrm{T}})$. The symmetric part is called deformation rate

$$\mathbf{d} = \frac{1}{2} \left(\mathbf{l} + \mathbf{l}^{\mathrm{T}} \right) = \frac{1}{2} \left(\dot{\mathbf{F}} \mathbf{F}^{-1} + \mathbf{F}^{-\mathrm{T}} \dot{\mathbf{F}}^{\mathrm{T}} \right) = \frac{1}{2} \mathbf{F}^{-\mathrm{T}} \dot{\mathbf{C}} \mathbf{F}^{-1}.$$
 (2.18)

In addition, the skew+symmetric part is referred to spin (vorticity) tensor

$$\mathbf{w} = -\mathbf{w}^{\mathrm{T}} = \frac{1}{2}(\mathbf{l} - \mathbf{l}^{\mathrm{T}}) = \frac{1}{2} \Big(\dot{\mathbf{F}} \mathbf{F}^{-1} - \mathbf{F}^{-\mathrm{T}} \dot{\mathbf{F}}^{\mathrm{T}} \Big).$$
(2.19)

The rate of Green-Lagrange strain tensor E can be written as

$$\dot{\mathbf{E}} = \frac{1}{2}\dot{\mathbf{C}} = \frac{1}{2}\mathbf{F}^{\mathrm{T}}\mathbf{dF}.$$
(2.20)

The rate of the volume change can be calculated by the time derivative of the determinant of the deformation gradient as

$$\dot{J} = \frac{\partial \det \mathbf{F}}{\partial t} = J \operatorname{tr} \mathbf{d}$$
 (2.21)

2.1.3 Stress measures

The stress is defined by traction force vector dF_s per unit of area (see Fig. 2.2), which is defined as the neighbouring continuum points of the body dA. The stress in each arbitrary point P_0 and Pin reference and its counterpart in the current configuration is defined based on infinitesimal areas dA and da around them with the unit vectors of N and n normal to them, respectively. Thus, the relation of the traction force and stress can be written as

$$dF_s = T dA = t da, \qquad (2.22)$$

where the vectors T and t are the traction force in reference and deformed configurations, respectively. Therefore, second-order tensors σ and P can be expressed based on the Cauchy's stress

theorem as



Figure 2.2. Continuum medium with a surface element and corresponding force vectors.

$$\boldsymbol{t} = \boldsymbol{\sigma}\boldsymbol{n} \quad \boldsymbol{T} = \boldsymbol{P}\boldsymbol{N},\tag{2.23}$$

where σ represents the Cauchy stress tensor related to force on the body surface in the current configuration and P is the first Piola-Kirchhoff stress second-order tensor defined based on the surface area in initial configuration. The first Piola-Kirchhoff stress and Cauchy stress tensor can be related through the Nanson's formula 2.11 and 2.23 as

$$d\mathbf{F} = \mathbf{t}dA = \boldsymbol{\sigma}d\mathbf{A} = J\boldsymbol{\sigma}\mathbf{F}^{-\mathrm{T}}d\mathbf{a}.$$
 (2.24)

The second Piola-Kirchhoff stress tensors S can be calculated by pulling-back the force vector df_s in the current state to the reference configuration. Similarly, another spatial stress measure, the Kirchhoff stress tensor τ , can be calculated and converted to other measures as the following set of equations

$$\mathbf{P} = J\boldsymbol{\sigma}\mathbf{F}^{-\mathrm{T}} = \tau\mathbf{F}^{-\mathrm{T}} = \mathbf{F}\mathbf{S}, \quad \mathbf{S} = J\mathbf{F}^{-1}\boldsymbol{\sigma}\mathbf{F}^{-\mathrm{T}}, \quad \boldsymbol{\tau} = J\boldsymbol{\sigma}$$
(2.25)

Note that nominal/first Piola-Kirchhoff stress is not a symmetric tensor due to its two-point coordinate systems.

2.1.4 Balance principles

For a body B with volume V, mass M, and boundary surface A in the current state, the rate of change of the linear momentum is directly proportional to the force applied on the body, which can be defined by

$$\int_{M} \boldsymbol{v} dM = \int_{V} \rho \dot{\boldsymbol{x}} dV,$$

where ρ is the density and $v = \dot{x}$ is the velocity vector of a particle. The momentum can be calculated by summation of a body force and a surface force as

$$\frac{d}{dt} \int_{V} \rho \dot{\boldsymbol{x}} dV = \int_{V} \boldsymbol{f} dV + \int_{A} \boldsymbol{t} dA.$$
(2.26)

The surface forces can be obtained through the Cauchy theorem (2.23) and divergence theorem

$$\int_{A} \boldsymbol{t} dA = \int_{A} \boldsymbol{\sigma} \boldsymbol{n} dA = \int_{V} \operatorname{div} \boldsymbol{\sigma} dV.$$
(2.27)

By substituting Eq. 2.27 into Eq. 2.26, the balance equation is then

$$\int_{V} \left(\operatorname{div} \boldsymbol{\sigma} + \boldsymbol{f} - \rho \ddot{\boldsymbol{x}} \right) dV = 0.$$
(2.28)

For any arbitrary point of the body, one can rewrite Eq. 2.28 as

$$\operatorname{div} \boldsymbol{\sigma} + \boldsymbol{f} = \rho \boldsymbol{\ddot{x}} \ . \tag{2.29}$$

In order to calculate the balance of mechanical energy, one can multiply Eq. 2.29 with the velocity vector v as

$$\boldsymbol{v} \cdot \operatorname{div} \boldsymbol{\sigma} + \boldsymbol{v} \cdot \boldsymbol{f} = \rho \boldsymbol{v} \cdot \ddot{\boldsymbol{x}}. \tag{2.30}$$

Eq. 2.30 can be further simplified considering symmetry of the Cauchy stress tensor as

$$\boldsymbol{v} \cdot \operatorname{div} \boldsymbol{\sigma} = \operatorname{div} (\boldsymbol{v} \boldsymbol{\sigma}) - \boldsymbol{\sigma} : \operatorname{grad} \boldsymbol{v} = \operatorname{div} (\boldsymbol{v} \boldsymbol{\sigma}) - \boldsymbol{\sigma} : \mathbf{d},$$
 (2.31)

which gives

$$\operatorname{div}(\boldsymbol{v}\boldsymbol{\sigma}) - \boldsymbol{\sigma} : \mathbf{d} + \boldsymbol{v} \cdot \boldsymbol{f} = \rho \frac{d}{dt} \left(\frac{1}{2} \boldsymbol{v} \cdot \boldsymbol{v} \right).$$
(2.32)

Integrating Eq. 2.32 over the volume of the body and considering Eq. 2.27 yield to

$$\frac{d}{dt} \int_{M} \left(\frac{1}{2} \boldsymbol{v} \cdot \boldsymbol{v} \right) \, dM + \int_{V} (\boldsymbol{\sigma} : \mathbf{d}) \, dV = \int_{A} (\boldsymbol{v} \cdot \boldsymbol{t}) \, dA + \int_{V} (\boldsymbol{v} \cdot \boldsymbol{f}) \, dV. \tag{2.33}$$

The balance of mechanical energy can be rewritten by taking into account the physical meaning of each term in the Eq. 2.33 as

$$\dot{K} + \mathcal{W} = \mathcal{P},$$
 (2.34)

where \mathcal{P} , \dot{K} , and \mathcal{W} refer to the power of external forces, the stress power, and the changes in the kinetic energy, respectively. The power of external forces can be written as

$$\mathcal{P} = \int_{A} (\boldsymbol{v} \cdot \boldsymbol{t}) \, dA + \int_{V} (\boldsymbol{v} \cdot \boldsymbol{f}) \, dV.$$
(2.35)

The kinetic energy and the stress power of the system is then formulated by

$$K = \int_{V} \left(\rho \frac{1}{2} \boldsymbol{v} \cdot \boldsymbol{v} \right) dV,$$

$$\mathcal{W} = \int_{V} (\boldsymbol{\sigma} : \mathbf{d}) dV.$$
 (2.36)

Note that the stress power can be calculated through other strain-stress measures and each of the stress measures σ , P, and S are conjugate with deformation measures d, $\dot{\mathbf{F}}$, and $\dot{\mathbf{E}}$, respectively. For instance, the stress power can be calculated using the first Piola-Kirchhoff stress and deforma-

tion gradient as

$$\mathcal{W} = \int_{V_0} \left(\mathbf{P} : \dot{\mathbf{F}} \right) dV_0 = \int_V J^{-1} \left(\mathbf{P} : \dot{\mathbf{F}} \right) dV.$$
(2.37)

Thus, the stress power can also be obtained from

$$\left(\mathbf{P}:\dot{\mathbf{F}}\right) = (\boldsymbol{\sigma}:\mathbf{d}) = \left(\mathbf{S}:\dot{\mathbf{E}}\right) = \left(\mathbf{S}:\frac{1}{2}\dot{\mathbf{C}}\right).$$
 (2.38)

In addition, the total energy dissipation due to the deformation \mathcal{D} can be obtained

$$\mathcal{D} = \mathcal{W} - \int_{V_0} \dot{\Psi} \, dV_0 \tag{2.39}$$

where $\dot{\Psi}$ refers to the rate of stored energy per unit volume in the reference state.

2.2 Thermo-elasticity

The relations between mechanical and thermal energy is called thermo-elasticity, which can be derived using the first and second laws of thermodynamics. The 1^{st} law of thermodynamics is the conservation of energy, which is formulated as

$$dU = dQ + dW. (2.40)$$

where dU, dQ, and dW are the changes in the internal energy of the system, the heat absorbed by the system, and the work done on the system. The U and W can be expressed as

$$U = \int_{V} \rho \mathcal{U} \, dV, \quad \mathcal{W} = \frac{dW}{dt} \tag{2.41}$$

where \mathcal{U} is the internal energy density. According to the second law, the changes in the entropy of a reversible process (elastic deformation), dS at absolute temperature T is formulated as

$$dS = \frac{dQ}{T}.$$
(2.42)

Moreover, the change in the Helmholtz energy \mathfrak{A} is defined as

$$d\mathfrak{A} = dU - SdT - TdS. \tag{2.43}$$

At a constant temperature, the change in Helmholtz energy is equal to the change in the work done on the system $dW = d\mathfrak{A}$. In the small displacement dl of solid-like structures, dW due to force fcan be written by

$$dW = f dl - p_h dV, \tag{2.44}$$

where p_h and dV denote the hydro-static pressure and the volume change. In the case of incompressible material like elastomers, dV can be neglected. So, the force of an isothermal process can be obtained using Eq. 2.43 and Eq. 2.44 as

$$f = \frac{dU}{dl} - T\frac{dS}{dl}.$$
(2.45)

The first part of Eq. 2.45 represents the energetic interactions of a single molecule or the volume change of the body [11]. However, experimental evidences suggest that the contribution of energetic force in the total force is negligible in moderate and large deformations of elastomers. Thus, the force of the system can be approximated only by entropy component as

$$f = -T\frac{dS}{dl}.$$
(2.46)

For an entropic material, the Helmholtz free energy required to perturb the entropy of the system is

$$d\mathfrak{A} = -TdS. \tag{2.47}$$

2.3 Thermodynamic Consistency

According to the second law of thermodynamic that is used in continuum mechanics, elastic energy of the system mainly increases due to the decrease in entropy, which is known as Clausius-Duhem inequality

$$\mathcal{D} \ge 0. \tag{2.48}$$

The constitutive model is thermodynamically consistent if and only if Clausius-Duhem inequality is satisfied on all points of body at any time. In other words, the energy balance should be satisfied during a thermodynamical deformation process. The energy balance can be rewritten by substituting Eq. 2.40 to Eq. 2.34 as

$$\dot{K} - P = \frac{d}{dt} (U - Q) = \dot{U} - \dot{Q},$$
 (2.49)

where the thermal power \dot{Q} is defined as

$$\dot{Q} = \int_{V} \rho \mathcal{Q} \, dV - \int_{A} \rho \boldsymbol{q} \cdot \boldsymbol{n} \, dA.$$
(2.50)

In Eq. 2.50 , Q and q are the transferred heat and the surface heat flux per unit of mass, respectively. Moreover, Eq. 2.49 can be rewritten as

$$\boldsymbol{\sigma} : \mathbf{l} = \rho \mathcal{U} - \rho \mathcal{Q} + \operatorname{div} \boldsymbol{q}. \tag{2.51}$$

Therefore, Clausius-Duhem inequality can be obtained by

$$\rho \mathcal{D} = \rho T \dot{\mathcal{S}} - (\rho \mathcal{Q} - \operatorname{div} \boldsymbol{q}) \ge 0, \qquad (2.52)$$

where S is the entropy density. Clausius-Duhem inequality can be further simplified by substitution of the energy balance law (2.51) and mass conservation ($\rho_0 = J\rho$) as

$$\mathcal{D} = T\dot{\mathcal{S}} - \left(\dot{\mathcal{U}} - \frac{1}{\rho_0}\boldsymbol{P} : \dot{\mathbf{F}}\right) \ge 0.$$
(2.53)

considering the stored energy density per unit of reference volume $\Psi = \hat{\Psi}(\mathbf{F}, T, \mathbf{\Omega})$ as a function of set of internal variables $\mathbf{\Omega}$. In most of the constitutive models, the internal variables have been adopted to describe the history dependent dissipative effects. Note that all the quantities of the Clausius-Duhem inequality, such as S, q, and \mathbf{P} should be functions of internal variables. For a more comprehensive review of thermo-elasticity, the reader is referred to [34, 35]. Substituting the Helmholtz free energy $\Psi = \rho_0 (\mathcal{U} - TS)$ into Eq. 2.53 results in

$$\rho J \mathcal{D} = -\dot{\Psi} - \rho J \mathcal{S} \dot{T} + \boldsymbol{P} : \dot{\mathbf{F}} \ge 0$$
(2.54)

where $\dot{\Psi}(\mathbf{F}, T, \mathbf{\Omega})$ can be obtained as

$$\dot{\Psi} = \frac{\partial \Psi}{\partial \mathbf{F}} : \dot{\mathbf{F}} + \frac{\partial \Psi}{\partial T} \dot{T} + \frac{\partial \Psi}{\partial \Omega} \cdot \dot{\mathbf{\Omega}}.$$
(2.55)

Eq. 2.54 can be rewritten considering Eq. 2.55 as

$$\rho J \mathcal{D} = -\frac{\partial \Psi}{\partial T} \dot{T} - \frac{\partial \Psi}{\partial \Omega} \cdot \dot{\mathbf{\Omega}} - \rho J \mathcal{S} \dot{T} + \left(\mathbf{P} - \frac{\partial \Psi}{\partial \mathbf{F}} \right) : \dot{\mathbf{F}} \ge 0.$$
(2.56)

Eq. 2.56 can be further simplified for the case of isothermal process and considering a physical expression for the first Piola-Kirchhoff stress $P = \frac{\partial \Psi}{\partial \mathbf{F}}$, which leads to an inequality of internal energy dissipation \mathcal{D} as

$$-\frac{\partial\Psi}{\partial\Omega}\cdot\dot{\mathbf{\Omega}}\geq0.$$
(2.57)

This inequality must always be satisfied over the body during deformation.

2.4 Incompressible Materials

Resistance of most of elastomers to change volume known as incompressibility condition should be considered in the constitutive modelling. Therefore, the internal energy function of an incompressible material is modified by

$$\Psi = \hat{\Psi} \left(\mathbf{F}, T, \mathbf{\Omega} \right) - p(J-1), \tag{2.58}$$

where $J = \det \mathbf{F} = \frac{dV}{dV_0} = 1$ is the incompressibility constraint and p is a Lagrange multiplier to satisfy the boundary conditions. The rate of the strain energy function Ψ is

$$\dot{\Psi} = \left(\frac{\partial \Psi\left(\mathbf{F}, T, \mathbf{\Omega}\right)}{\partial \mathbf{F}} - p\mathbf{F}^{-T}\right) : \dot{\mathbf{F}},$$
(2.59)

where the incompressibility condition is considered as the volume remains constant, $\dot{V} = \dot{J} = 0$. Substituting Eq. 2.59 to Eq. 2.39, one has

$$\left(\int_{V_0} \mathbf{P} dV_0 - \int_{V_0} \left(\partial_{\mathbf{F}} \hat{\Psi}\left(\mathbf{F}, T, \mathbf{\Omega}\right) - p\mathbf{F}^{-T}\right) \, dV_0\right) : \dot{\mathbf{F}} \ge 0.$$
(2.60)

Eq. 2.61 should be held for every deformation rate, $\dot{\mathbf{F}}$, which leads to

$$\mathbf{P} = \frac{\partial \hat{\Psi} \left(\mathbf{F}, T, \mathbf{\Omega} \right)}{\partial \mathbf{F}} - p \mathbf{F}^{-T}, \qquad (2.61)$$

This equation is valid for the case of

- Incompressible hyperelastic material
- Negligible contribution of internal energy in deformation
- Isothermal deformation
- Moderate and large range of deformation

CHAPTER 3

IMPROVED APPROXIMATIONS OF NON-GAUSSIAN PROBABILITY, FORCE, AND ENERGY OF A SINGLE POLYMER CHAIN

3.1 Introduction

In computational simulations of polymeric systems, two competing factors determine the type of the material model that should be used in the simulation; computational cost (i.e. the simulation time) and the accuracy. Optimizing the trade-off between these two factors determines the minimum requirements of the model. In mechanics of polymers, the excessive computational costs of accurate models prevents them from being used in large-scale simulations. Here, our goal is to propose a family of effective approximation functions with different range of accuracy and complexity that can address the existing trade-off problem.

In polymer physics, micro-mechanical constitutive models are mostly derived from the non-Gaussian statistical distribution of a randomly jointed molecular chain [36, 37, 38, 39]. In these models, the elasticity of the chains is induced from the changes in the probability of chain end-toend distance, r, in the course of deformation, and thus the change of the chain entropy [11]. The PDF of a perfectly flexible chain with fixed end positions P(r) can be calculated using a solution that is first proposed to solve the random flights problem [40, 41, 42]. The concept was later used in several theoretical and experimental studies to describe the properties of dilute polymer solutions. In dilute solutions, the isolation of polymer molecules allows characterization of individual molecules. A strong correlation was found between the number of segments of a chain, n, and its end-to-end distance, r given by $r \propto \sqrt{n}$ [11]. This correlation later became the basis to consider P(r) similar to that of a random-flight problem.

In most statistical polymer models, the stress-strain relation for the polymer matrix originates from molecular description of deformation of single chains. The first attempt in understanding behaviour of polymers was based on a statistical approach to derive entropic conformation of a polymer chain, which was independently proposed by Kuhn [40] and Guth and Mark [43]. Both theories successfully derived the Gaussian PDF estimation of a polymer chain from its entropy [44]. However, it can be shown that Gaussian statistics are exact only for the polymer chains with infinite length or very small deformation. Later, Kuhn and Grün proposed the inverse Langevin approximation for 'freely jointed chain' (FJC) to address the effect of finite chain length in the network, and reached to pioneer model for single chain statistics in large deformation. The popular Kuhn-Grün (KG) model describes the statistical probability of existence of an unconstrained single chain with an entirely random orientation in space [45]. Beside simplicity, the relevance of the assumption has motivated the majority of models ever since to use the KG function to estimate non-Gaussian PDF [38, 46, 47, 48]. This estimation is the first order approximation of the Rayleigh's exact Fourier integral distribution function [49], and can describe the finite extensibility of the polymer chains even at large strains. This model is widely accepted in the field of rubber elasticity due to its accuracy to captures the ultimate strain of polymer network [50, 37, 51]. In polymer physics, most constitutive models of the polymer matrix such as 3-chain [52], 4-chain [53], 8chain [37], the full-network models [11, 54], and the micro-macro unit sphere models [55] are based on the KG approximations of non-Gaussian theory, which generally includes the inverse Langevin function [11]. However, different studies in the literature examined its relatively large error for the short chains [11, 39].

As it shown in the literature, Gaussian distribution, energy and entropic force have very good agreement with theory of rubber elasticity and experimental evidences in small deformations. As deformation increases this theory cannot predict the behavior of elastomeric material with limited extensibility accordingly. In order to overcome this shortcoming, the non-Gaussian theory of rubber elasticity proposed to improve the theory for deformations near the failure of the material. The

complexity some of these theories leads to extensive application of KG theory in different area of polymer physics as a simple alternative of non-Gaussian theory. Despite the fact that KG theory is only valid for long chains, there are several studies that used this theory with less than 20 segments chains [55, 51, 29]. Arruda and Boyce (1993) [37] proposed their outstanding 8-chain model using KG theory, which is validated against experimental data assuming the chains length as low as 8. The Full network model [54] that considers the spatial uniform distribution used the KG model by chains with only 2.8 segments (the relative error of entropic force for chain with 3 segments will be shown in section 3.4, which is reach to more than 100% , Fig. 3.7).

Despite its wide acceptance, KG estimation is only valid for sufficiently large chains $(n \gg 40)$ [56, 44, 50]. While KG shows good graphical agreement with Rayleigh's exact distribution in low extensibility[56], it yields significant errors in the large extensibility (see Fig.3.1a). Moreover, for long chains, KG approximation becomes strongly inaccurate as $\frac{r}{nl} \rightarrow 1$ as the probability approaches to zero. Figure 3.1-a shows that the relative errors of a short chain and a long chain almost is the same unlike the most stated in the literature [56]. In polymer physics, the strain energy of a chain W, which is correlated with $W \propto \ln (P(r, n))$), is used more often than the P(r), and thus is the subject of interest. In Fig.3.1-d, we have plotted the relative errors in approximating Wby using KG PDF. As it can be in this figure, the maximum relative error of KG energy function is about 25% for the chain with 8 segments. However, the maximum relative error of KG energy function can reach to as much as 100% for the chain with 3 segments. It is evident that the relative error for short chains are much higher than that of long chains. To address this problem, Jerningan and Flory [56] introduced a new approximation, referred to as 'amended Kuhn-Grün' (A-KG), by adding an extra multiplicative term to the KG function. Due to its complexity, A-KG model were used in very few studies such as the work of Elias-Zuniga and Beatty [46].

Currently, almost all statistical models of chain elasticity are based on the KG PDF. Accordingly, the entropic force resulted from KG are the function of one parameter only; namely the extensibility ratio, $t = \frac{r}{L}$ where r is the end-to-end distance of a chain, L = nl the contour length. However, studies suggest that the entropic force resulted from PDFs are influenced by two param-


Figure 3.1. Comparison between Exact and KG (a-b) distribution functions and strain energies (c-d) for chains with n = 8 and 64 and their relative errors.

eters, namely t and n. To date, most constitutive models suffer from the large errors induced by the KG function in predicting the PDF, force or energy in the case of short chains. So far, there is no other feasible approximation of PDF that can also capture the behavior of the short chains.

Here, we developed an approach to derive a family of approximations for the PDF, force and strain energy of polymer chains. Such an approximation model is particularly relevant in constitutive models of polymer chains that use the ILF $\mathcal{L}^{-1}(\frac{r}{nl})$ to describe the entropic force of a chain. Since the ILF cannot be derived explicitly, approximation functions with different degree of errors are used to represent it. Recently, due to significant improvement of our computational power for simulating the entropic energy of the whole network, accurate approximation of the ILF has become a subject of interest. In the last decade, several high accuracy approximations with errors as low as $10^{-4}\%$ have been introduced [57, 2, 58, 59]. While accurate approximations of the ILF can reduce the error of KG energy and force approximations, there still exists a significant error in those approximations due to the intrinsic error associated with KG PDF. Such error necessitates the future efforts to be directed toward deriving a new approximation for PDF function first before deriving force and energy.

The fundamentals of non-Gaussian statistical mechanics of polymers are first reviewed in section 3.2. We propose new approximation functions for PDF in section 3.3. In section 3.4, the error of the current approximations of entropic energy and force of a polymer chain is calculated to show the relevance of new approximation functions. Finally, in section 3.5 and 3.6 new approximation functions for entropic force and energy of a single polymer chain is provided. The functions show negligible error even for short chains and are relevant for a long range of extensibility ratios.

3.2 Statistical Mechanics Treatments

In this section, the non-Gaussian PDF of existence of a chain, $P(\vec{r})$, with end-to-end vector \vec{r} and contour length nl is briefly reviewed. The probability distribution of an FJC is the same as 3-D random flight problem, which describes the probability of a chain ending at a certain point at distant r. In 1905, Pearson discussed the distribution of position of a mosquito in a forest [60]. To address this problem, several distribution functions have been developed ever-since based on the Fourier integration of the random-flight problem, first of which was developed by Rayleigh in 1919 by using the discontinuous integral of Dirichlet [49]. The probability of existence of a chain can be derived by taking the Fourier transform of characteristic function as

$$P_{exact}\left(r\right) = \frac{1}{2\pi^2 r} \int_0^\infty \rho \sin(\rho r) \left(\frac{\sin(\rho l)}{\rho l}\right)^n d\rho.$$
(3.1)

This equation would be difficult to solve analytically for chains with large number of segments, n > 10. The exact non-Gaussian distribution function for 3, 4, and 6 steps were derived by Rayleigh as sets of discontinuous polynomials [49]. The exact solution of Fourier integral of Eq.3.1, often referred to as "**Rayleigh exact distribution function**", was later derived by Treloar

[42] based on the theory of random sampling as

$$P_{exact}\left(r\right) = \frac{1}{2^{n+1}\left(n-2\right)!\pi l^{2}r} \sum_{k=0}^{k \le \frac{n-\frac{r}{l}}{2}} \left(-1\right)^{k} \binom{n}{k} \left(n-2k-\frac{r}{l}\right)^{n-2}.$$
 (3.2)

Similarly, Wang and Guth [52], Nagai [61], and Hsiung et al. [62] derived similar formulations with different mathematical approaches. To avoid the high computational cost of the exact solution (due to its piece-wise nature), several approximation methods were developed for non-Gaussian distribution. The degree of mathematical difficulty of these approximations depends on the required accuracy and the covered extensibility ratio ($t = \frac{r}{nl}$). The Gaussian distribution, for example, is simple and has a good agreement with the exact distribution at small t. It can be shown that the first order approximation of 1D random walk problem yields to the Gaussian distribution (see Appendix 3.7). However, Gaussian distribution becomes exponentially inaccurate for the chains in their fully extended length ($t \approx 1$). Thus, a more elaborate distribution function is required to capture the non-Gaussian PDF. In general, the approximation functions that are developed to approximate the Rayleigh exact PDF, Eq.3.2, can be categorized into three types (i) Taylor expansion approximations which are valid for long chains with low extensibility, (ii) Statistical approximation which are valid for long chains at all extensibility ratios and (iii) Steepest decent approximations which are valid for all chains and extensibility ratios, although it has a high computational cost [52].

(i) Taylor expansion approximation (TE) has an acceptable accuracy for long chains at small *t*. In this case Eq. 3.1 can be rewritten as

$$P_{exact}(r) = \frac{1}{2\pi^2 r} \int_0^\infty k \sin(kr) e^{\phi(k)} dk, \qquad (3.3)$$

where $\phi(k) = n \ln \frac{\sin(ka)}{ka}$. To further simplify the above equation, $\phi(k)$ can be substituted by its Taylor expansion $\phi(k) = -n \sum_{k=1}^{\infty} \frac{B_{2k-1}(2s)^{2k}}{(2k)!2k}$, where B_n is Bernoulli number. By using the first term of $\phi(k)$ Taylor series, Eq.3.3 yields the standard Gaussian distribution function, *P*_{*G*}, as [44],

$$A_n(\rho) \cong exp\left(-\frac{n(\rho l)^2}{6}\right) \longrightarrow P_G(r) = A_0 \exp\left(-\frac{r^2}{2n}\right),$$
 (3.4)

where $A_0 = \left(\frac{3}{2\pi a^2 n}\right)^{\frac{3}{2}}$. By using full expansion of $\phi(k)$ a more accurate approximation of P_{exact} can be obtained as,

$$P_T(r) = A_0 \left(1 - \frac{3}{20n} \left(5 - 10\frac{r^2}{n} + 3\frac{r^4}{n^2} \right) + \dots \right) \exp\left(\frac{-3r^2}{2n}\right).$$
(3.5)

In order to further enhance the accuracy of the approximation, the Taylor expansion can be written around its saddle point [63] as,

$$P_{T-SP}(r) \cong A_0 \exp\left(-n\left[\frac{3}{2}t^2\left(1-\frac{1}{n}+\frac{2}{5n^2}\right)+\frac{9}{20}t^4\left(1-\frac{11}{5n}\right)+\frac{99}{350}t^6\right]\right).$$
(3.6)

To simplify Eq. 3.6, one can assume $\frac{1}{n} \to 0$ for long chains $(n \gg 40)$, and thus reduce Eq. 3.6 to

$$P_{T-SP}(r) \cong A_0 \exp\left(-n\,\alpha\left(t\right)\right),\tag{3.7}$$

where $\alpha(t)$ is a function of extensibility ratio only. Since Eq. 3.7 is equal to the distribution function resulted from Taylor expansion of ILF, one can conclude that the ILF approximations are also mainly relevant for long chains.

(ii) Statistical approximation (SA) of P_{exact} , also known as Kuhn-Grün (KG) PDF, is particularly accurate for the large chains in the highly stretched state [11]. KG PDF is introduced in 1942 through the maximum term method of statistical mechanics as

$$P_{KG}(R) = c \left\{ \frac{\sinh(\beta)}{\beta \exp(t\beta)} \right\}^n, \qquad (3.8)$$

where c is normalization factor that can be A_0 or P_n^{exact} (10⁻²). The ILF parameter $\beta =$

 $\mathcal{L}^{-1}(t)$ can be implicitly calculated through Langevin function equation, $t = \mathcal{L}(\beta) \equiv \operatorname{coth}(\beta) - \frac{1}{\beta}$. Note that James and Guth (1943) [36] and Flory (1953) [64], independently derived the same formulation with different approaches. In another effort Jernigan and Flory [56] derived an amended version of KG distribution function as

$$P_{A-KG}(r) = A_0 \left[\frac{\sinh(\beta)}{\beta \exp(t\beta)} \right]^n \left[\frac{\beta}{t} \right] = \frac{\beta}{t} P_{KG}.$$
(3.9)

(iii) Steepest decent approximation (SD) is derived by Wang and Guth [52] based on the saddle point approximation of Eq.3.2, which gives

$$P_{WG}(r) = A_0 \left[\frac{\sinh\left(\beta\right)}{\beta \exp(t\beta)} \right]^n \left[\frac{\beta}{t} \right] \left[1 - t^2 - \frac{2t}{\beta} \right]^{-\frac{1}{2}} \left[1 + \frac{q(t)}{n} + \dots \right], \tag{3.10}$$

where q(t) is a specific function [52]. Using steepest decent approach, another approximation function is derived by Yamakawa [44] which can be rewritten similar to P_{WG} as ¹

$$P_{SD}(r) = A_0 \left[\frac{\sinh\left(\beta\right)}{\beta\exp(t\beta)}\right]^n \left[\frac{\beta}{t}\right] \left[1 - t^2 - \frac{2t}{\beta}\right]^{-\frac{1}{2}}$$
(3.11)

Interestingly, P_{SD} , Eq.3.11, is the first four terms of Wang and Guth approximation Eq.3.10 and P_{A-KG} , Eq.3.9, is the first three terms. As mentioned by Jerningan and Flory [56], the term $\left[\frac{\sinh(\beta)}{\beta\exp(t\beta)}\right]^n$ becomes more significant and then the other terms can be neglected for longer chains same as KG model. However, the other terms has more contribution in the accuracy of the model for shorter chains.

To date, there exists no comprehensive study to characterize the error induced by each of the aforementioned approximation methods in predicting PDF of chains with different lengths exten-

¹Original formulation presented in [44] is $P_Y(r) = 3^{\frac{3}{2}} A_0 \frac{\beta^2}{t \left[1 - \left(\frac{\beta}{\sinh(\beta)}\right)^2\right]^{\frac{1}{2}}} \left\{\frac{\sinh(\beta)}{\beta \exp(t\beta)}\right\}^n$, which can be rewritten as P_{SD} by considering $1 - t^2 - \frac{2t}{\beta} = \frac{1}{\beta^2} - \frac{1}{\sinh^2(\beta)}$.

sibility ratios. Here, a comprehensive comparison of the aforementioned approximation functions in predicting PDF and strain energy of chains with different lengths at different extensibility ratios is presented (see Fig.3.2).

 P_G and P_T have almost similar and relatively small relative with respect to the exact distribution in only very small t. Interestingly, P_{T-SP} with only three terms has extremely low relative error with respect to exact distribution in small and moderate extensibility ratios. Note that increasing the number of terms in the expansion of this approximation can improve the relative error for larger t. As expected, $P_{KG}(R)$ has a negligible error for small t which exponentially grows as t tends to 1. Despite being the most popular approximation method, $P_{KG}(R)$ can be only a good approximation for long chains that are not stretched. Therefore, it is not suitable for models of rubber elasticity to derive force and energy due to its large error in predicting the asymptotic behavior of $\ln (P_{exact})$. The W_{KG} has a considerably large error which can become even larger in shorter chains. For example, the relative error of strain energy resulted from KG PDF for a short chain with 8 segments is at least 8 times higher than that of a long chain with 64 segments. While many other approximations such as P_{A-KG} provide slightly more accurate approximations than KG, they remain unpopular due to the extreme complexity of their first derivatives. Despite the fact that P_{SD} has an acceptable accuracy even for short chains, utilizing this distribution function is almost unfeasible due to its mathematical complexity.

3.3 Approximation of Non-Gaussian Distribution

The accuracy-complexity trade-off problem in current PDF approximation functions (see section 3.2) necessitate to develop a family of precise and simple approximation that are particularly relevant for shorter chains. Comparing P_{KG} with P_{exact} for different chain lengths shows a repeating error profile which can be considered almost independent of n. In view of this profile as a multiplicative error functions, one can consider all of the previous approximation functions such as P_{WG} , P_{SD} and P_{A-KG} as special sub-classes of a master approximation function \tilde{P} which can be written with respect to P_{KG} as



Figure 3.2. Comparison between Gaussian, KG, Amended KG and Eq. 3.11 distribution function with the exact PDF (Relative error of PDF *a*, *c* and *e* and Relative error of $\ln (P_n)$ *b*, *d* and *f*) of ideal chains with different lengths *a*-*b* n = 8, *c*-*d* n = 16 and *e*-*f* n = 64.

$$\tilde{P}(r) \simeq P_{KG}(r,n) \phi(t), \qquad (3.12)$$

where $\phi(t)$ is a multiplicative correction function defined to reduce the error of P_{KG} . Here, we hypothesize that $\phi(t)$ can be chosen to control the accuracy- complexity trade off for different applications. In view of good agreement of P_{WG} , P_{SD} and P_Y with exact distribution for short chains, one can conclude $\phi(t)$ should have same properties as the ratio of these distribution and P_{KG} . As discussed in the Section 3.2, P_{WG} , P_{SD} and P_Y have almost same formulation. Thus among them, P_Y is selected to calculate an estimation of $\phi(t)$ as

$$\phi(t) \simeq \frac{P_Y}{P_{KG}} = \frac{\beta^2}{t \left[1 - \left(\frac{\beta}{\sinh(\beta)}\right)^2\right]^{\frac{1}{2}}}.$$
(3.13)

The first feature of this estimation is its limit when t approaches to 1, which tends to infinity. By considering the first order pole of ILF at t = 1 [59] and $\lim_{t\to 1} 1 - \left(\frac{\beta}{\sinh(\beta)}\right)^2 = 1$, one can conclude that $\phi(t)$ has second order pole at this point and its residue can be calculated as

$$\mathcal{R}(\phi) = \lim_{t \to 1} (t-1)^2 \phi(t) = 1.$$
(3.14)

By fitting $\phi(t)$ an approximation \tilde{P} with good accuracy with respect to P_{exact} can be obtained. In this regard, the approximation function should have same properties as $\phi(t)$, second order pole with residue of 1. The simplest function with second order pole is $(1-t)^{-2}$. In view of the second order pole of $\phi(t)$ and $(1-t)^{-2}$, it can be written as a rational function such as,

$$\phi(t) = \frac{a(t)}{(1-t)^2},$$
(3.15)

where a(t) is approximation function which is used to adjust the approximation function with the exact distribution. There are different alternative forms for estimations of a(t) such as polynomial, exponential and etc.. In this study exponential function (exp $\left[\sum_{i=1}^{m} a_i t^{2i-1}\right]$, where *m* is the number

	max. relative error [%]			
m	n = 8	n = 16	n = 32	n = 64
KG	100	100	100	100
1	11	8	9	10
2	3	4	5	5

Table 3.1. Relative error of approximated distribution function by considering 1 and 2 terms for chains with different length.

of terms used in the approximation) is selected to approximate a(t), which will result simple strain energy functions. In order to obtain best approximation with least maximum relative error in whole domain [0 - 1], predefined min-max solver (fminimax) in MATLAB is used to minimize the maximum relative error of $\tilde{P}(r)$ respect to exact distribution function. The coefficient of approximation function with one and two terms is obtained as

$$P_{approx}^{m=1}(r) = P_{KG}(r,n) \left[\frac{\exp\left(-1.75\,t\right)}{\left(1-t\right)^2} \right]$$
(3.16a)

$$P_{approx}^{m=2}(r) = P_{KG}(r,n) \left[\frac{\exp\left(-2t + 0.29t^3\right)}{\left(1-t\right)^2} \right].$$
(3.16b)

The max relative errors of these approximations for chains with different length are presented in Table 3.1 and summarized in Fig. 3.3. They illustrate good agreement with the exact PDF for chains with different lengths in the whole range of t.



Figure 3.3. The relative error of approximated distribution function respect to the exact PDF for chains with different number of segment a) m = 1 and b) m = 2.

3.4 Entropic Force of a Single Chain

In polymer physics, the elastic retraction force of a single polymer chain is associated with changes in the entropy of the chains in the course of deformation. Accordingly, the strain energy W = -TSof a single chain is calculated through Boltzmann's entropy relation, $S = k \ln (P(r))$, where S is the entropy of the chain, T the absolute temperature, and k the Boltzmann constant. Thus, the entropic force, $f_n(r)$, required to perturb the chains end-to-end distance is given by

$$f_n(r) = \frac{\partial W(r)}{\partial r} = -kT \frac{\partial \ln \left(P_n(r)\right)}{\partial r}.$$
(3.17)

In view of the complicated formulation of the exact PDF, the approximates are often used to describe the force of the chain in the course of deformation. The simplest approach is to derive the force based on the Gaussian PDF P_G (Eq. 3.4) which yields the force as a linear function of deformation ($f_G(t) = \frac{kT}{l}t$). However, P_G is valid for long chains and at small deformation regimes, only. In large deformations, P_{KG} is the most popular approximation function, which yields the following equation for polymer force

$$f_{KG}(t) = \frac{kT}{l}\beta.$$
(3.18)

Other approximations of the force can be simply derived by implementing any of the aforementioned PDF approximations into Eq. 3.17. For example using the P_{SD} (Eq. 3.11), the entropic force can be estimated as

$$f_{SD}(n,r) = \frac{kT}{l} \left\{ \beta + \frac{1}{n} \left(\frac{1}{t} - \frac{\gamma}{2t} \frac{t\beta \left(\beta - \gamma\right) + 2\left(\beta - \frac{5}{4}\gamma\right)}{\left(\beta - \gamma\right)^2} \right) \right\},\tag{3.19}$$

where $\gamma = \frac{2t}{1-t^2}$. Similar to PDFs, the complexity of accurate approximations such as Eq. 3.19 prevent them from wide acceptance (e.g. compare Eq. 3.18 with Eq. 3.19).

The entropic force derived based on P_G , P_{KG} , P_{A-KG} and P_{SD} are compared with the force of the exact PDF and shown in Fig. 3.4-*a* and*b* for short and long chains, respectively. As illustrated

in Fig. 3.4-*a*, the force resulted from the KG has large relative errors with respect to the exact entropic force for a small chain. In longer chains, the KG force has good agreement with the exact one. Furthermore, the force associated with P_{SD} has the best agreement with the exact entropic force (see Fig. 3.4-*a*-*b*). The Fig. 3.4-*c*-*d* show that the relative error of the steepest decent approximation is the minimum in both short and long chains.



Figure 3.4. Comparison of the entropic force of a single chain resulted from exact non-Gaussian distribution function and its approximations, steepest decent approximation, and inverse Langevin function (a-b), and their relative errors with respect to the exact function (c-d) for a and c) n = 8 and b and d) n = 64.

3.5 Approximation of the Entropic Force

A new approximation for the force of a chain is developed based on the following observation. The profile of the relative error, E_n , of the force derived by P_{KG} is almost identical for the chains with

different lengths, n. As shown in Fig.3.5, the relative error can be normalized by $\frac{1}{n}$, $e(t) = -nE_n$, the value of which is varying approximately between 100% and 220% (±5%). Accordingly, a new approximation function can be derived simply by multiplying a correction function, $\frac{1}{1-E_n}$, into f_{KG} . Then, by expanding the correction function using the geometric series and using the first two terms, the approximation of exact force is written as

$$E_n = \frac{f_{exact} - f_{KG}}{f_{exact}} \implies f_{exact} = f_{KG} \frac{1}{1 - E_n} \simeq f_{KG} \sum_{i=0}^n (E_n)^i \simeq f_{KG} (1 + E_n).$$
(3.20)

By replacing the error, E_n , by its normalized value $-\frac{e(t)}{n}$, the proposed function becomes

$$f_{approx}\left(n,R\right) = \frac{kT}{l}\mathcal{L}^{-1}\left(t\right)\left(1 - \frac{e\left(t\right)}{n}\right),\tag{3.21}$$

The approximation can be optimized by fitting a more general function for the normalized error shown in Fig.3.5, which can make the approximation too complex for practical applications. Here, e(t) can be estimated through a fitting procedure of a polynomial with degree of m (see Fig.3.5), which yields

• Order 0: using e(t) = 1 reduces the Eq.19 into

$$f_{approx}^{m=0}\left(n,R\right) = \frac{kT}{l}\mathcal{L}^{-1}\left(t\right)\left(\frac{n-1}{n}\right),\tag{3.22}$$

which has a relative error varying from 0% to $\frac{120}{n}$ % as shown in Fig. 3.5. The relative error of $f_{approx}^{m=0}$ is around half of the relative error of f_{KG} . In another study, Horgan and Saccomandi [65, 66] and later Beaty [67] derived almost the same formulation as Eq. 3.22 by comparing an estimation of non-Gaussian theory with the averaged stretch in the macroscopic level ($\beta = \frac{2t}{1-t^2}$) with Gent phenomenological model. Interestingly, it can be shown that Gent model has better agreement with non-Gaussian theory than KG for short chains. This simple modification can strongly improve the constitutive models [68, 21, 69], that use a probability of chains existence with different lengths. In these models, the force of the



Figure 3.5. The relative error of the ILF a) with respect to the length of chain and b) Averaged normalized for all lengths.

matrix is determined by summing up the forces of chains with different lengths.

• Order 2: a two term polynomial, $e(t) = 1 + t^i$, is used to represent e(t). By minimizing the approximation error, the second order polynomial (i = 2) is selected in this study due to its simplicity and lower relative errors. The proposed approximation can be written as

$$f_{approx}^{m=2}(n,R) = \frac{kT}{l} \mathcal{L}^{-1}(t) \left(1 - \frac{1+t^2}{n}\right).$$
(3.23)

This approximation has extremely high accuracy, comparable to that of f_{SD} (Eq. 3.19), as shown in Fig. 3.6. The maximum relative error of the proposed approximation for n = 8is equal to 1.7%, which is significantly lower than 33% error of the f_{KG} . In addition the maximum relative error of proposed entropic forces (Eq. 3.22 and 3.23) for the chains with different lengths are plotted in comparison with the maximum relative error of Langevin entropic force in Fig 3.7. It can be seen in Fig 3.7 that the maximum relative error of KG entropic force with 40 segment is about 5%. Considering this limit as an error tolerance for the approximation of Non-Gaussian entropic force, the proposed simple modification of entropic force is valid for the chains with 4 segments. Note that both proposed approximation functions can be easily implemented in most of the current elasticity models by replacing the inverse Langevin function.

In most physical-based models of rubber elasticity, breakage of the chain occurs when the chains deformation exceeds their allowed extensibility limit, which is determined by strength of C-C bonds. Therefore, it is important that models use an acceptable prediction of the force and the energy at high extensibility ratios, particularly when t is approaching 1. While for long chains there are few models to provide force and energy with enough accuracy around t = 1, for short chains no model exists that can accurately predict force around t = 1.



Figure 3.6. The relative error of the proposed entropic force for a) n = 8 and b) n = 64 along with the relative error of full steepest decent approximation.



Figure 3.7. The maximum relative error of the proposed entropic force for chains with different length along with the maximum relative error of KG approximation.

		max. relative error [%]			
m	n = 8	n = 16	n = 32	n = 64	
KG	26	13	6	3	
1 (Eq. 3.24a)	1.2	0.6	0.45	0.3	
2 (Eq. 3.24b)	0.28	0.25	0.2	0.14	
(Eq. 3.26)	1	0.68	0.65	0.67	

Table 3.2. Max. relative error of approximated distribution functions for chains with different length.

3.6 Approximation of the Entropic Energy

In view of the proposed approximations for the distribution function and the entropic forces, one can derive a set of approximations for the strain energy function. Accordingly, in view of the PDFs derived in Eq. 3.16a and 3.16b, the strain energy, W, can be obtained through $W = -kT \ln (P(r))$ as

$$W_{P-app}^{m=1}(r) = W_{KG}(r,n) + kT \left(1.75 t + 2\ln(1-t)\right), \qquad (3.24a)$$

$$W_{P-app}^{m=2}(r) = W_{KG}(r,n) + kT\left(2t - 0.29t^3 + 2\ln(1-t)\right).$$
(3.24b)

The relative errors of the proposed approximations of Eq. 3.24a and 3.24b, as shown in Fig 3.8, are significantly more accurate in comparison to KG strain energy function (see Table 3.2). We also propose a second approach to estimate the strain energy functions directly from the proposed entropic forces in Eq. 3.23 by integrating them over R. Since direct integration of force approximation is not feasible due to the complex nature of the ILF, the integration is carried out after replacing the ILF by its approximation. Recently, many accurate ILF approximations with relative error less than 0.1% have been proposed in the literature (e.g. [2, 57]) and thus using each of those, one can derive the strain energy of the chains from Eq. 3.23 as follows

$$W_{f-app}^{m=2}(n,r) = n \int_{0}^{t} \frac{kT}{l} \beta(t) \left(1 - \frac{1+t^{2}}{n}\right) dt$$
(3.25)

For example, using $\mathcal{L}^{-1}(y) = \frac{x}{1-x} + 2x - \frac{8}{9}x^2$ (max relative error 1%)[57], the internal energy can be written as,

$$W_{f-app}^{m=2}\left(n,r\right) = kT \left[\frac{8}{45}t^{5} - \frac{t^{4}}{2} - \frac{8n-17}{27}t^{3} + \left(n-\frac{1}{2}\right)t^{2} - (n-2)\left[t+\ln\left(1-t\right)\right]\right] + c$$
(3.26)

As shown in Fig 3.8, the relative errors of Eq 3.26 are significantly lower than that of W_{KG} . The relative error and the complexity of strain energy can be easily adjusted by using simpler or more accurate ILF.



Figure 3.8. The relative errors of approximations of entropic energy (Eq. 3.24a, 3.24b and 3.26) respect to the exact entropic energy for chains with different number of segments a) n = 8, b) n = 16, c) n = 32 and d) n = 64.

3.7 Conclusion

Currently, the probability distribution function, force and energy of a polymer chain is mostly derived based on the Kuhn and Grün model. However, the KG model is only valid for long chains $(n \gg 40)$ and induces a significantly high error as the length of chain decrease [56, 39, 38]. However, long isolated polymer molecules is often does not exist in reality. They are in the interaction with other molecules. In theory of rubber elasticity, the segment between two cross-link or entanglement is considered as a non-Gaussian chain. Thus, the networks mostly contain short chains in the polymers with high cross-linking, which account for their limited extensibility. While there are some other approximation models with considerably higher accuracy, their complex nature prevents their wide implementation in large-scale models. In this work, we presented a generic approach to derive a family of approximation functions for the probability distribution function, entropic force and strain energy of a polymer chain with adjustable accuracy and complexity level, which are summarized in Table 3.3. We show that with same level of complexity, our proposed functions are considerably more accurate than current functions. Particularly for short chains or chains under large deformations, our approximation functions are at least 10 times more accurate than KG approximations and thus are excellent options to replace them in constitutive models. We hope that the proposed family of approximations can help other researchers to improve the modeling accuracy in polymer physics. In addition to help engineers to optimize the accuracy-cost trade-off in large-scale simulations by allowing them to select the approximation functions based on the application.

Having a family of approximations with different accuracy-complexity would be particularly helpful in some specific applications where one certain form of the approximation function can reduce the computational loads or increase accuracy significantly. Some of application of proposed approximation of theory of rubber elasticity includes bi-modal polymeric networks, constrained swelling, stress induced orientation of the polymer chains and etc.. The proposed Non-Gaussian theory can directly affect the contribution of short and long chains in a bi-modal polymeric networks, which contains various proportions of relatively short and long chains specially in high

	Fa	Formula		Max. Rel. Error [%] for n			
	Lq.	1 onnutu	8	16	32	64	
	3.8	$P_{KG} = c \left\{ \frac{\sinh(\beta)}{\beta \exp(t\beta)} \right\}^n$		10	0		
PDF	3.16a	$P_{approx}^{m=1} = P_{KG} \left[\frac{\exp(-1.75 t)}{(1-t)^2} \right]$	11	8	9	10	
-	3.16b	$P_{approx}^{m=2} = P_{KG} \left[\frac{\exp(-2t + 0.29t^3)}{(1-t)^2} \right]$	3	4	5	5	
Entropic	3.23	$f_{KG} = \frac{kT}{l}\beta$	33.3	14.27	6.45	3.22	
Force 3.2	3.23	$f_{approx}^{m=2} = \frac{kT}{l}\beta\left(1 - \frac{1+t^2}{n}\right)$	1.73	0.74	0.35	0.17	
		$W_{KG} = nkT\left(t\beta + \ln\frac{\beta}{\sinh\beta}\right) + c$	26.6	12.2	5.9	2.9	
Strain 3.2 Energy 3.2	3.24a	$W_{P-app}^{m=1} = W_{KG} + kT (1.75 t + 2 \ln (1 - t))$	1.2	0.6	0.45	0.3	
	3.24b	$W_{P-app}^{m=2} = W_{KG} + kT \left(2t - 0.29t^3 + 2\ln(1-t) \right)$	0.28	0.25	0.20	0.14	
	3.26	$W_{f-app}^{m=2} = kT \left\{ -(n-2) \left[t + \ln \left(1 - t \right) \right] + \frac{8t^5}{45} - \frac{t^4}{2} - \frac{8n - 17}{27} t^3 \right\}$	1	0.68	0.65	0.67	
		$+\left(n-\frac{1}{2}\right)t^2\}+c$					

Table 3.3. Summary of the proposed approximates for PDF, entropic force and strain energy along with their relative errors with respect to exact ones.

elongations [70, 71, 72]. The contribution of free energy in the total change of chemical potential of a solvent resulting from swelling of a network contain short chains can be affected by considering more realistic non-Gaussian distribution instead of Wall–White end-to-end distribution function, which cannot taking to account the finite extensibility limitations and only approximate the excluded volume effect in the compact conformations region [73, 74]. The KG distribution function and entropic force of chains is used to develop a model to predict the stress induced orientation of the polymer chains [75, 76]. Another possible application of current theory is studying molecular orientation of polymers chain due to fast elongational flow.

APPENDIX

The random flights' problem was one of the interesting topics in the early 20th century. The random flight problem first introduced by Pearson in a letter to Nature 1905 [77, 60]. He tried to solve the distribution of position of a mosquito in a forest. Various distribution functions have been developed in the literature based on the Fourier integration of the random-flight problem, which is first presented by Rayleigh in 1919 [49]. In order to review the solutions of random flights' problem, different approach is presented as below.

1D Random Walk

In 1-D random walk problem, the probability of arriving to a point with distance x from the origin by n equal step can be written as binomial distribution

$$P_n(x) = \frac{1}{2^n} \frac{n!}{\left(\frac{n+x}{2}\right)! \left(\frac{n-x}{2}\right)!}$$
(3..1)

Considering $x \ll N$ and using Stirling's formula $(a! = \sqrt{2\pi a} \left(\frac{a}{e}\right)^a)$, the probability distribution function will be simplified to Gaussian distribution². The most well-known solution of end-to-end distance distribution is expressed by the Gaussian distribution, which is the probability of 1-D random links at

$$P_n(x) = \frac{1}{\sqrt{2\pi n}} \exp\left(-\frac{x^2}{2n}\right) \tag{3..2}$$

The efforts for enhancing the Gaussian theory of rubber elasticity to a more exact theory sacrifice the generality and simplicity. The non-Gaussian treatment of rubber elasticity is developed to account for the limiting extensibility of the single chain. This leads to a more accurate deformation-force relationship in the whole range of end-to-end distance up to its limiting value. The entropic force resulted from 1D random walk distribution (3..1) can be written as

$$f_{1D}(x) = \frac{kT}{2l} \left(\Psi\left(\frac{n+x+2}{2}\right) - \Psi\left(\frac{n-x+2}{2}\right) \right), \qquad (3..3)$$

²Using Gaussian PDF to calculate entropic strain energy is the basis of the Neo-Hookean constitutive model. where Ψ is the Digamma function. As it can be seen in Eq. 3..3, the entropic force has a asymptotic behavior around r = n + 2 instead of r = n.

3D Random Walk

The probability distribution of an FJC is same as 3-D random flight problem, which describes the probability of a chain ending at a certain point at distant \overrightarrow{r} can be solved by 3-D random flight problem. The probability of one step with length l in an arbitrary direction is equal to probability of existence of a point on a sphere, $\frac{\delta(r-l)}{4\pi l^2}$. Applying the Fourier integration of this probability, "*characteristic function*" of a single random step is derived as $\frac{\sin(\rho l)}{\rho l}$, where l is the length of a segment in FJC chain (Kuhn length), and ρ the Fourier integral parameter. Due to the independent nature of bonds, $P_n(r)$ can be written by the multiplication of the probabilities of each bond. Considering an equal probability for all steps, the "*characteristic function*" of FJC, $A_n(\rho)$ is given as

$$A_n(\rho) = \prod_{i=1}^n (\rho l_i)^{-1} \sin(\rho l_i) \xrightarrow{l_i=l} A_n(\rho) = \int exp(i\rho.r) P_n(r) dr = \left(\frac{\sin(\rho l)}{\rho l}\right)^n$$
(3..4)

In the next step, the probability function a chain can be derived by taking the Fourier transform of characteristic function, which first derived by Rayleigh by using the discontinuous integral of Dirichlet [49]. He used the inverse Fourier transformation of Eq.3..4 to derive the non-Gaussian PDF as

$$P_n(r) = \frac{1}{2\pi^2 r} \int_0^\infty \rho \sin(\rho r) \left(\frac{\sin(\rho l)}{\rho l}\right)^n d\rho, \qquad (3.1)$$

which would be difficult to solve analytically for large number of steps, n > 10. The exact non-Gaussian distribution function for 3, 4 and 6 steps are derived by Rayleigh as sets of discontinues polynomials [49]. The exact solution of Fourier integral of Eq.3.1, often referred to as "**Rayleigh** exact distribution function", was first derived by Treloar [42] based on the theory of random sampling. Later, Wang and Guth [52], Nagai [61], and Hsiung et al. [62] reached to the same

expression with different mathematical approach.

$$P_n^{exact}\left(r\right) = \frac{1}{2^{n+1}\left(n-2\right)!\pi l^2 r} \sum_{k=0}^{k \le \frac{n-\frac{r}{l}}{2}} \left(-1\right)^k \binom{n}{k} \left(n-2k-\frac{r}{l}\right)^{n-2}$$
(3.2)

CHAPTER 4

A GENERALIZED APPROACH TO GENERATE OPTIMIZED APPROXIMATIONS OF INVERSE LANGEVIN FUNCTION

4.1 Introduction

The inverse Langevin function $\mathcal{L}^{-1}(y)$ comes from a first-order approximation of the Rayleigh exact distribution function [45], a prevalent distribution function in polymer physics and rubber elasticity [78]. In polymer physics, the entropic force of a polymer chain with end-to-end distance r, which consists of n segments with length l is given by

$$f(n,r) = \frac{k_B T}{l} \mathcal{L}^{-1}\left(\frac{r}{nl}\right), \qquad (4.1.1)$$

where T denotes the absolute temperature and k_B the Boltzmann's constant. The Langevin functions is defined by $\mathcal{L}(y) = \operatorname{coth}(y) - 1/y$. The strain energy function of a polymer chain is then calculated by the integration of the entropic force (Eq. 4.1.1) over r [11], which yields

$$\Psi(N,r) = KTn\left(\frac{r}{nl}\beta + \ln\left(\frac{\beta}{\sinh\beta}\right)\right) \quad \beta = \mathcal{L}^{-1}\left(\frac{r}{nl}\right).$$
(4.1.2)

As the chain end-to-end distance, r, approaches its maximal value (corresponding to the contour length of a fully stretched straight chain), Nl, the force tends to infinity. This implies asymptotic behavior of $\mathcal{L}^{-1}(y)$ in the vicinity of y = 1.

The entropic forces of polymer chains as derived in Eq. 4.1.1, are well-accepted and widely used in nonlinear elasticity of soft materials (see e.g. [79]). Currently, most micro-mechanical

models of polymeric systems represent polymer chains using the approximations of an ILF, since ILF approximations cannot be expressed in an explicit form. The ILF approximation efforts can be classified into three groups: (i) power series such as Taylor series [80, 81, 82], (ii) rational (Páde) functions [83, 84, 11], and (iii) trigonometric functions [85, 86, 39].

(i) The Taylor expansion approach provides high accuracy with relatively low complexity in the majority of the domain [0 - 0.95), except in the vicinity of the asymptote, y = 1. The first 5 non-zero coefficients for the Taylor expansion of the inverse Langevin function are introduced in [11], as

$$\mathcal{L}_{Taylor}^{-1}(y) = 3y + \frac{9}{5}y^3 + \frac{297}{175}y^5 + \frac{1539}{785}y^7 + \frac{126117}{67375}y^9 + \dots + O(y^n).$$
(4.1.3)

Later, Itskov et al. [87] derived a simple recurrent formula for the Taylor series coefficients of inverse functions, which gives them in terms of Bernoulli numbers. They calculated 500 terms of the series and showed that derivation of the higher terms is only valid if higher digits are considered in the calculation of terms. Recently, Ehret [82] presented another generalized power series which has a significantly smaller error than Taylor series. Three terms of his series showed relative error smaller than the five terms of the Taylor approximation of the ILF.

(ii) Rational functions are the second class of approximations, which usually have higher complexity but better accuracy around the asymptote. The Cohen approximation is the most common ILF approximation function. It is a rational function composed of a third order polynomial as the nominator and a second order polynomial as the denominator, generally shown by [3/2], with rounded coefficients [83]. Following the Cohen formula, functions based on Páde approximations have extensively studied and several accurate functions (with accuracies close to 1%) were proposed, some of which are listed below[88, 76, 89, 90].

- Treloar [11]: $\mathcal{L}_{Treloar}^{-1}(y) \approx \frac{3y}{1-0.6y^2-0.2y^4-0.2y^6} = \frac{3y}{(1-y^2)(1+0.4y^2+0.2y^4)}$ [1/6],
- Cohen[83]: $\mathcal{L}_{Cohen}^{-1}(y) \approx y \frac{3 \frac{36}{35}y^2}{1 \frac{33}{35}y^2}$ which is further rounded to $\mathcal{L}_{Cohen}^{-1}(y) \approx y \frac{3 y^2}{1 y^2}$ [3/2],
- Puso [84]: $\mathcal{L}_{Puso}^{-1}(y) \approx \frac{3y}{1-y^3}$ [1/3],
- Jedynak [89]: $\mathcal{L}_{Jedynak}^{-1}(y) \approx \frac{3y 2.6y^2 + 0.7y^3}{(1-y^2)(1+0.1y)}$ [3/3],
- Kroger [90]: $\mathcal{L}_{Kroger}^{-1}(y) \approx \frac{3y}{(1-y^2)(1+0.5y^2)}$ [1/4] and $\mathcal{L}_{Kroger}^{-1}(y) \approx \frac{3y-0.2y(6y^2+y^4-2y^6)}{1-y^2}$ [7/2],
- Darabi and Itskov [88]: $\mathcal{L}_{Darabi}^{-1}(y) \approx \frac{3y 3y^2 + y^3}{1 y}$ [3/1].

In 2015, Kroger [90] presented an informative figure to show the trade-off challenge of different Páde approximations by showing their accuracy against their complexity. He defined complexity by the sum of the orders of the nominator and denominator of the Páde function. However, expressing the complexity of a function in this way is not a consistent indicator of complexity since the expansion of the fractional functions can yield functions with different complexity. Accordingly, this figure cannot show the relevance of these approximations, since each of them can be simplified into two or more simpler terms, which have different complexities. For example, while the Cohen formula is more complex (order 5) than the Puso formula (order 4), its expanded version, $\mathcal{L}_{Cohen}^{-1}(y) = \left(\frac{1}{1-y} - \frac{1}{1+y} + y\right)$, is less complex than the expanded version of the Puso formula $\mathcal{L}_{Puso}^{-1}(y) \left(\frac{1}{1-y} + \frac{y-1}{1+y+y^2}\right)$. Therefore, it seems that using a higher-order Páde approximates does not necessarily lead to more complex functions.

(iii) Trigonometric functions are the third class of ILF approximation functions, which were first presented by Bergstrom in 1999 [86]. He proposed a piecewise function composed of trigonometric functions which gives one of the lowest max relative errors (0.064%) among the available approximations. However the piecewise nature of the function makes its implementation challenging. To overcome this challenge, further efforts on this class were based on non-piecewise equations as follows

- Bergstrom [86]: $\mathcal{L}_{Bergstrom}^{-1}(y) \approx \begin{cases} 1.31446 \tan(1.58986y) + 0.91209y & |y| < 0.84136\\ \\ \frac{1}{sign(y) - y} & |y| > 0.84136 \end{cases}$ • Keady [85]: $\mathcal{L}_{Keady}^{-1}(y) \approx \frac{6}{\pi} \tan(\frac{\pi y}{2}) \left(\frac{1 + 0.4178 \tan^2(\frac{\pi y}{2})}{1 + 0.508 \tan^2(\frac{\pi y}{2})}\right)$
- Khiêm [39]: $\mathcal{L}_{Khiem}^{-1}(y) \approx \frac{1}{y} \pi \cot(\pi y)$

Similar to the Páde approximations, these trigonometric approximations also suffered from the tradeoff between complexity and accuracy of the method. Keady's approach was very accurate (max relative error less than 0.3%) but too complicated for implementation. Khiêm's formula was relatively simple, however, it had lower accuracy (12.3% max relative error), and has two asymptotic points (at zero and one), which also increases its complexity [39].

In recent years, there has been an increasing interest in minimizing the error of the inverse Langevin function[91, 2, 92, 93]. Several other methods were also developed to increase the accuracy of ILF approximations. Nguessong et al. [92] used a two-step modification of the Cohen formula to minimize the relative error of each step. The authors improved the accuracy of the Cohen formula by adding a non-integer power series to the original formulation, in order to reduce the relative error from 5% to 0.05%. In 2017, Petrosyan[93] presented a new formula for the inverse Langevin function with the combination of a rational function and a trigonometric function. Their approach gives 0.18% relative error.

Here, a generalized approach is proposed to develop a new class of approximations with adjustable level of accuracy. To this end, the summation of an asymptotic function (the main function) with a power series is used to estimate the inverse Langevin function. Thus, the proposed approach of this study provides a series of correcting terms to the main asymptotic functions. The correcting terms help to reduce the relative error, meaning that adding more terms will result in functions that are more accurate. The results show that new estimations calculated by the proposed method outperforms many current approximations in both accuracy and computational cost.

4.2 Proposed Approach

The inverse Langevin function $\mathcal{L}^{-1}(y)$ has two simple poles at $y = \pm 1$ with the residue $\mathcal{R}es(\mathcal{L}(y))$ defined by

$$\mathcal{R}es(\mathcal{L}(y)) = \lim_{y \to \pm 1} (y \mp 1)\mathcal{L}^{-1}(y) = \lim_{x \to \pm \infty} (\coth(x) - \frac{1}{x} \mp 1)x = -1.$$
(4.2.1)

Thus, the main function for the ILF estimation should meet two conditions; (i) be an odd function with two simple poles at $y = \pm 1$ and (ii) have a residue of -1. While some of the proposed ILF estimations met both conditions (Cohen [83], Kroger [90] and ...), many of them only meet the second condition since they consider only one pole y = +1 (Pasu[84], Darabi[88], ...). However, there are cases where the functions do not have a correct residue and/or poles. For example, the Warner approximation [94] has correct poles but the wrong residue, which leads to an error of 50% at y = 1. However, it can be modified to yield a correct residue $\left(\frac{2y}{1-y^2}\right)$. The modified version showed smaller error (max 35% near y = 0) than the original one over the whole domain.

In polymer physics, the argument of the ILF function, $y = \frac{r}{Nl}$, is always a positive value, since it represents the flexibility of a polymer chain. Thus, the ILF estimations were mostly optimized for the argument ranges between zero and one (with one pole at y = 1). In addition, power series-based approximations do not have a physical pole and thus cannot cover the ILF near the pole. Even some rational functions do not have a correct pole and/or residue. In the following, the proposed approach is introduced at 3 stages

- 1. Simplified Maclaurin Approach
- 2. Simplified Maclaurin Approach with Optimized Last-Term
- 3. Optimized Power Series

4.2.1 Simplified Maclaurin approach

The simplified Maclaurin Approach is a simple class of the proposed approach consists of two parts. The first part is the main function with correct poles and residue, which can reduce the error of the estimation to zero at x = 1. Based on the required accuracy/complexity, many of the current approximations with correct pole can be used in this step as a main function. In the second part, a power series is derived to minimize the error induced by the main function in all of the domain except the pole (y = (0 - 1)). To this aim, the Maclaurin expansion of $\mathcal{L}^{-1}(y) - f(y)$ can be used to reduce the error.

$$\mathcal{L}^{-1}(y) = f(y) + Taylor\left(\mathcal{L}^{-1}(y) - f(y)\right)$$
(4.2.2)

In Eq. 4.2.2, the main function f(y) is an odd function with simple poles at $y = \pm 1$ and a residue of -1. Given that both the ILF and the main function are odd functions, the Taylor expansion of the error function should only contain odd powers. Therefore, the proposed estimation of the ILF with degree n is written as

$$\mathcal{L}_{n}^{-1}(y) = f(y) + \sum_{i=1}^{n} a_{i} y^{2i-1}$$
(4.2.3)

To illustrate the proposed approach, let consider two possible choices for the main function, namely a Warner-like function $\frac{2y}{1-y^2}$, and a trigonometric function $\frac{\pi}{2} \tan(\frac{\pi}{2}y)$. Both functions are odd, have simple poles at $y = \pm 1$ and a residue of -1. The error of both main functions are given as the power series in the following. The resulting estimations of this approach can be written as the following for the Warner-like formula (main function $=\frac{2y}{1-y^2}$) in Eq. 4.2.4 and the trigonometric main function in Eq. 4.2.5. In these two series, the number of added terms can be defined based on the level of accuracy (O^{2i} for *i* added terms).

$$\mathcal{L}_{n,Warner}^{-1}\left(y\right) = \frac{2y}{1-y^2} + y - \frac{y^3}{5} - \frac{53}{175}y^5 - \frac{211}{875}y^7 + \dots$$
(4.2.4)

$$\mathcal{L}_{n,Trigo.}^{-1}(y) = \frac{\pi}{2} \tan\left(\frac{\pi}{2}y\right) + \left(3 - \frac{\pi^2}{4}\right)y + \left(\frac{9}{5} - \frac{\pi^4}{48}\right)y^3 + \left(\frac{297}{175} - \frac{\pi^6}{480}\right)y^5 + \dots$$
$$= \frac{\pi}{2} \tan\left(\frac{\pi}{2}y\right) + 0.53y - 0.23y^3 - 0.31y^5 + 0.24y^7, \dots$$
(4.2.5)

The above two functions have similar behavior, i.e. their relative error is reduced by adding more terms in Taylor expansion (see Fig. 4.1 and Table 4.1). The first term of the series corrects the limit of the estimation around zero, while the other terms improve the estimation over the domain. In view of the simplified Maclaurin approach, many estimation functions developed in other studies are just special subsets of this approach. For example, by considering the Warner approximation $(\frac{2y}{1-y^2})$ as the main function, the Cohen formula, $(y\frac{3-y^2}{1-y^2})$, would be the first order expansion using simplified Maclaurin approach.

Similarly, considering $\frac{y}{1-|y|}$ as the main function, some approximation functions can be derived using the proposed generalized scheme. The $\frac{y}{1-|y|}$ function is an odd function with correct poles and residue. In polymer physics since y > 0 always holds, the function can be simplified to $\frac{y}{1-y}$, which is not an odd function. Thus, the power series of the estimation contains both odd and even powers (see Eq. 4.2.6). Since this main function is not a odd function, relative errors of this estimation do not have reducing trend. For this reason, these estimations need to be considered by adding odd number of terms to reach lower relative error (see Fig. 4.2 and Table 4.1)

$$\mathcal{L}^{-1}(y) = \frac{y}{1-y} + 2y - y^2 + \frac{4}{5}y^3 - y^4 + \dots$$
(4.2.6)

Using two terms, the above equation will be the Darabi formula

$$\frac{3y - 3y^2 + y^3}{1 - y} = \frac{y}{1 - y} + 2y - y^2$$
(4.2.7)

which is relatively an accurate approximation with a relative error of 2.6%.

Similar to $\frac{y}{1-y}$ function $\frac{y^3}{1-y}$ is used by Petrosyan [93]. This main functions do not have a



Figure 4.1. Relative error of a) Eq. 4.2.4 and b) Eq. 4.2.5 with different number of terms.

Number of added terms	Eq. 4.2.4	Eq. 4.2.5	Eq. 4.2.6	Eq. 4.2.8
1	4.9	5.25	13	2.64
2	2.9	2.92	2.6	7.44
3	0.9	0.9	7.4	0.83
4	0.73	0.73	0.83	3.90

Table 4.1. Maximum relative error of Eq. 4.2.4, 4.2.5, 4.2.6 and 4.2.8 with different number of terms.

point symmetry and have pole only at y = 1. The proposed approach can be applied to this main function, which the result is presented in the Eq. 4.2.8 and Fig 4.2-b. Petrosyan used the first term of the power series in Eq. 4.2.8 and added $\frac{y^5}{5} \sin(3.5y)$ instead of the cubic term in order to reduce relative error from 0.83% to 0.18%.

$$\mathcal{L}^{-1}(y) = \frac{y^3}{1-y} + 3y + \frac{4}{5}y^3 - y^4 + \frac{122}{175}y^5 + \dots$$
(4.2.8)



(a) Eq. 4.2.6

Figure 4.2. Relative error of a) Eq. 4.2.6 and b) Eq. 4.2.8 with different number of terms.

4.2.2 Simplified Maclaurin with optimized last-term

The next step to increase the accuracy of the proposed method is to fit the coefficient of the last term of the error power series. Accordingly, after trimming the series to the desired number of terms, we minimize the induced error by fitting the last coefficient.

$$\mathcal{L}^{-1}(y) = f(y) + \sum_{i=1}^{n-1} a_i y^i + a_n y^n$$
(4.2.9)

In the proposed approach, the relative error at points 0 and 1 is almost zero (considering a simple pole at 1 and a correct limit of $\lim_{y\to 0} \mathcal{L}^{-1}(y) = 3y$ from first term of Taylor expansion of ILF. Adding one point in the second half of the domain seems to be relevant due to the importance of the error near the pole. Here, by choosing the point y = 0.75 ($\mathcal{L}^{-1}(0.75) = 4$), the formulation to adjust the coefficient of the last term with the power *n* is given as

$$a_n = \frac{\mathcal{L}^{-1}(0.75) - f(0.75) - \sum_{i=1}^{n-1} a_i 0.75^i}{0.75^n}.$$
(4.2.10)

To illustrate the significance of the optimized last-term coefficient, the approximation functions of the main function $2y/(1 - y^2)$ derived by the simplified Maclaurin approach with and without an optimized last-term are compared in Table 4.2. The relative error has been dropped by more than 50% after using optimized last-term. Using the proposed approach, the accuracy of the main functions can be improved to yield relative errors as low as 0.3% through these simple main functions. Relative errors and equations of the modified versions of the Warner-like formula and Trigonometric formula for up to 4 added terms are presented in Table 4.2. This table shows that the higher orders of the modified functions of the Warner-like and Trigonometric formulas show similar accuracy and by adding more terms, this modification can improve the original estimation. However, this improvement is not as much as that of adding 3 terms. The estimations with more than 3 terms that have a good relative error at the point y = 0.75, therefore, this modification cannot improve the accuracy any more.

Interestingly, by considering the Warner approximation $(\frac{2y}{1-y^2})$ as the main function, the very recent Kroger formula, $(\mathcal{L}_{301}^{-1} = \frac{3y - \frac{y}{5}(6y^2 + y^4 - 2y^6)}{1-y^2})$, would be the third order expansion using a simplified Maclaurin approach with an optimized last-term. By using an optimized last-term, the coefficients of the Cohen formula can further be improved to $\frac{2y}{1-y^2} + 0.9y$ which reduces the relative error from 4.9% to 3.4%.

Table 4.2. Modified version of Eq. 4.2.4 and 4.2.5 with different number of added terms by using single point error minimization.

$\mathcal{L}^{-1}\left(y ight)$	$\mathcal{L}^{-1}(y)$ relative error %		relative error %			
Warner-like Main Functions						
$\frac{2y}{1-y^2} + y - \frac{y^3}{5}$	2.9	$\frac{2y}{1-y^2} + y - 0.42y^3$	0.89			
$\frac{2y}{1-y^2} + y - \frac{y^3}{5} - \frac{53}{175}y^5$	0.9	$\frac{2y}{1-y^2} + x - \frac{y^3}{5} - 0.4y^5$	0.28			
$\frac{2y}{1-y^2} + y - \frac{y^3}{5} - \frac{53}{175}y^5 - \frac{211}{875}y^7$	0.73	$\frac{2y}{1-y^2} + y - \frac{y^3}{5} - \frac{53}{175}y^5 - 0.16y^7$	0.41			
Trigonometric Main Functions						
$\frac{\pi}{2}\tan\left(\frac{\pi}{2}y\right) + 0.53y - 0.23y^3$	2.92	$\frac{\pi}{2}\tan\left(\frac{\pi}{2}y\right) + 0.53y - 0.45y^3$	0.89			
$\frac{\pi}{2} \tan\left(\frac{\pi}{2}y\right) + 0.53y - 0.23y^3 - 0.31y^5$	0.9	$\frac{\pi}{2} \tan\left(\frac{\pi}{2}y\right) + 0.53y - 0.23y^3 - 0.4y^5$	0.3			
$\frac{\pi}{2} \tan\left(\frac{\pi}{2}y\right) + 0.53y - 0.23y^3 - 0.31y^5 - 0.24y^7$	0.73	$\frac{\pi}{2} \tan\left(\frac{\pi}{2}y\right) + 0.53y - 0.23y^3 - 0.31y^5 - 0.14y^7$	0.35			

4.2.3 Optimized power series

Since the nominal error of the Maclaurin approach cannot get smaller than 0.3%, in the next step, we propose to fit all the coefficients of the power series in Eq. 4.2.11 including a_0 . Although the

residue condition would not be satisfied, this approach can provide a simple yet accurate representation of ILF approximations. In this approach, it is highly preferable that the main function be an odd function, since we only require the odd coefficients of the power series, otherwise all terms will be needed.

$$\mathcal{L}_{n}^{-1}(y) = \begin{cases} a_{0}f(y) + \sum_{i=1}^{n} a_{i}y^{2i-1} & \text{for odd main function} \\ a_{0}f(y) + \sum_{i=1}^{n} a_{i}y^{i} & \text{for even main function} \end{cases}$$
(4.2.11)

In this equation, the coefficient a_0 is added to adjust the relative error at point y = 1, which is induced since the residue of the main function is not one anymore after setting $a_0 \neq 1$. This coefficient, along with the first term of the polynomial, will help to re-distribute the relative error in the whole domain. The presence of the main function and the condition of the correct limit when $y \rightarrow 0$ makes the relative error of the approximation equal to zero at the boundaries. By fitting a_0 and a_1 , the relative error can be minimized at these points and reduced throughout the domain. The general error minimization for ILF estimation can be calculated by using the maximum relative error of the approximation as an objective function:

$$\min_{a_{i}} \left\{ \max_{y \in [0,1)} \left\| \frac{\mathcal{L}^{-1}(y) - \mathcal{L}_{n}^{-1}(y, a_{i})}{\mathcal{L}^{-1}(y)} \right\| \right\},$$
(4.2.12)

where, $\mathcal{L}^{-1}(y)$ is the exact ILF function and $\mathcal{L}_n^{-1}(y, a_i)$ is its approximation with a order of n polynomial and a function of the coefficients of a_i . The minimization of the maximum relative error in Eq. 4.2.12 will be performed over the domain of y = [0 - 1). Here, optimization of Eq. 4.2.12 has been carried out numerically by evaluating the relative error at 100 equi-distant points in the vertical axis from [0 - 1000) to cover y = (0 - 0.999). First, the relative error is calculated at each point and then the maximum over the whole domain is identified.

Let us define \mathcal{L}_0^{-1} as the simplest ILF approximation with an asymptotic function of only one term. The function can be improved by fitting the coefficient a_0 . Thus, following the concept of error minimization, the Warner formula can be updated to $\frac{2.4y}{1-y^2}$, which has a maximum relative



Figure 4.3. One-dimensional variation of value of the objective function respect to the coefficient of main function (a_0) for different formula in Eq. 4.2.13.

error of 20%, in comparison with the 50% error of the original Warner formula and the 33.3% error of the correct asymptotic function. Applying a similar approach to the trigonometric function, $\frac{\pi}{2} \tan(\frac{\pi}{2}y)$, the revised approximation function, $\mathcal{L}_0^{-1} = 1.724 \tan(\frac{\pi}{2}y)$, will have only 9.75% relative error in comparison to the 17.75% error of the original model. Using this method, even the simplest main function, $\frac{y}{1-y}$, can be updated to $\frac{1.5y}{1-y}$ which has a relative error of 50% which is lower than 66.6% error of original function and 200% error of $\mathcal{L}_{[1/1]}^{-1}(y) = \frac{3y}{1-y}$, proposed in [2]. The value of the objective function for these three main functions can be plotted with respect to the variation of a_0 in Fig. 4.3. As shown in Fig. 4.3 the parameter a_0 can be optimized to yield the least relative error.

$$\mathcal{L}_{0}^{-1}(y) = \begin{cases} 1.724 \tan(\frac{\pi}{2}y) & e_{max} = 9.75\% \\ \frac{2.4y}{1-y^{2}} & e_{max} = 20\% \\ \frac{1.5y}{1-y} & e_{max} = 50\% \end{cases}$$
(4.2.13)

The ILF approximation functions can be further minimized by the addition of another firstorder polynomial to the main function, i.e. $\mathcal{L}_0^{-1}(y) = a_0 f(y) + a_1 y$. Accordingly, the ILF approximation is formulated with respect to two parameters a_0 and a_1 . This approximation promotes this minimization problem to a two-dimensional error minimization. The value of an objective func-



Figure 4.4. Relative error of the ILF approximation function with respect to the coefficients a_0 and a_1 for Warner-like formula in Eq. 4.2.14.

tion for these three main functions for a variation of a_0 and a_1 can be visualize as a 3-dimensional plot, which is presented in Fig. 4.4 for Warner-like approximations. In order to investigate the minimum value of the objective function with respect to the coefficients, the same procedure of one-dimensional error-minimization can be applied to this state. The maximum relative errors of first-order approximation with the trigonometric, Warner-like, and $\frac{y}{1-y}$ main functions are reduced to 2.6%, 2.4%, and 6.1%, respectively with the functions given below

$$\mathcal{L}_{1}^{-1}(y) = \begin{cases} 1.53 \tan(\frac{\pi}{2}y) + 0.52y & e_{max} = 2.6\% \\ 0.976(\frac{2.4y}{1-y^{2}} + y) = 0.976 \times \mathcal{L}_{Cohen}^{-1} & e_{max} = 2.4\% \\ \frac{0.94y}{1-y} + 1.874y = y\frac{2.814 - 1.874y}{1-y} & e_{max} = 6.1\% \end{cases}$$
(4.2.14)

Error minimization for higher-order approximates (n > 2) are more complex than first-order approximations. The maximum relative errors associated with the n = 2 approximates of the


Figure 4.5. Minimum maximum relative errors of different order polynomial for $\frac{y}{1-y}$ main function in comparison to [2].

trigonometric, Warner-like, and $\frac{y}{1-y}$ main functions are 0.58%, 0.57% and 0.70%, respectively. The coefficients of these three main functions, along with their higher orders, are presented in the Tables 4.3-4.5. The relative error in the error minimization approach can be reduced as low as 0.02% for higher orders of polynomial functions. As can be seen from the relative error for different approximate functions, it is possible to reach to very accurate approximations of the inverse Langevin function without adding complexity to the formulas. It is worth noting that all presented formulas here consist of a polynomial series and a very simple asymptotic main function. In order to compare the level of accuracy of these functions, the maximum relative error resulted from $\frac{y}{1-y}$ is plotted along with the error presented in [2]. The rational approximate functions order of [n, 1], which is presented in [2] can be simplified to summation of $\frac{y}{1-y}$ and a polynomial series. As it can be seen in Fig. 4.5, the level of relative error resulted from general minimization approach of this study can be compared with the same approach of error minimization of rational functions recently developed by Marchi and Arruda [2].

The maximum relative error of the proposed ILF approximations associated with the main function of $\frac{x}{1-x}$ and Warner-like function are presented in the Fig. 4.6. This figure shows the



Figure 4.6. Maximum relative errors of the different fractional estimations of the ILF $\mathcal{L}^{-1}(y) = \frac{\sum_{i=1}^{n} a_i y^i}{\sum_{i=1}^{m} b_j y^i}$.

significant improvements of the proposed approximations in this section with a fixed order of the fractional function. Furthermore, our proposed approximations using main function with one pole is depicted in the left hand side of the Fig. 4.6. This shows that these approximations with lower degree of complexity have lower relative error in all proposed approximations. The second set of proposed approximations with correct symmetry (Warner-like approximations) have lower maximum relative error than previously proposed approximations with same number of poles. It is worth noting that all proposed fractional approximations in this study can be written as a summation of one or two first-order fractions (considering each pole, $\frac{y}{1\pm y}$), which means that increasing the order of proposed formula can decrease the relative error without changing complexity.

It should be noted that for errors below 5%, rounding of the multiplicative coefficients have some major consequences. Most coefficients in this study are presented with three digits of significance to save space and avoid complication of the proposed formulae. However, for numerical implementation, such a reserve does not exist and users can directly implement the accurate coefficients provided in the appendix.

[<i>n</i>]	With corre and a_0	ect asymptote Taylor 0 = 1	With correct asymptote and one point error minimization $a_0 = 1$		Gene	General error minimizati approach		
	a_i	Relative error	a _i Relative		<i>a</i> ₀	a _i	Relative error	
0	N/A	66.55%	N/.	A	1.5	N/A	50%	
1	2	13%	N/2	A	0.939	1.8765	6.1%	
2	2 -1	2.6%1	2 -8/9	1.06%	0.993	2.023 -0.878	0.70%	
3	$\begin{array}{c} 2\\ -1\\ \frac{4}{5} \end{array}$	7.4%	$2 \\ -1 \\ \frac{4}{27}$	1.59%	0.9956	$1.9904 \\ -0.6864 \\ -0.2318$	0.44%	
4	2 -1 $\frac{4}{5}$ -1	0.83%	$2 \\ -1 \\ \frac{4}{5} \\ -\frac{352}{405}$	0.32%	1	2 -0.946 0.628 -0.758	0.163%	
5	2 -1 $\frac{4}{5}$ -1 $\frac{122}{175}$	3.90%	2 -1 4 5 -1 212 1215	0.4%	1	2 -1.0857 1.4463 -2.1944 0.782	0.11%	
6	$ \begin{array}{r} 2 \\ -1 \\ \frac{4}{5} \\ -1 \\ 122 \\ \overline{175} \\ -1 \end{array} $	2.02%	$ \begin{array}{r} 2 \\ -1 \\ 4 \\ \overline{5} \\ -1 \\ 122 \\ \overline{175} \\ 88904 \\ -27575 \end{array} $	0.53%	1.0003	$\begin{array}{c} 1.997 \\ -0.8732 \\ -0.4448 \\ 3.594 \\ -6.458 \\ 3.173 \end{array}$	0.046%	

Table 4.3. Approximations with the main function of $a_0 \frac{y}{1-y} + \sum_{i=1}^n a_i y^i$.

4.3 Conclusion

Here, an optimization approach is presented that can provide multiple approximates of the inverse Langevin function with different degrees of accuracy and complexity. The approximates are derived based on a main function that should meet two conditions; (i) be an odd function with two simple poles at $y = \pm 1$ and (ii) have a residue of -1. Regardless of whether the main functions

[n]	With correct and Ta $a_0 =$	asymptote ylor 1	With correct asymptote and one point error minimization $a_0 = 1$		Gene	nization	
	a _i	Relative error	a _i	Relative error	<i>a</i> ₀	a _i	Relative error
0	N/A	33.33%	N/A		1.2	N/A	20%
1	1	4.9% ²	N/#	4	0.975	0.975	2.5%
2	$1 - \frac{1}{5}$	2.9%	$-\frac{1}{80}$	0.91%	0.9943	1.0285 -0.4265	0.57%
3	$ \begin{array}{r} 1 \\ -\frac{1}{5} \\ -\frac{53}{175} \end{array} $	0.90%	$-\frac{2}{-1}\\-\frac{3376}{8505}^{3}$	0.29%	1.002	0.9978 -0.2086 -0.4213	0.20%
4	$ \begin{array}{r}1\\-\frac{1}{5}\\-\frac{53}{175}\\-\frac{8633}{67375}\end{array} $	0.73%	$ \begin{array}{r}1\\-\frac{1}{5}\\-\frac{53}{175}\\-\frac{64016}{382725}\end{array} $	0.43%	1.001	0.9958 -0.1183 -0.7583 0.323	0.13%
5	$ \begin{array}{r} 1 \\ -\frac{1}{5} \\ -\frac{53}{175} \\ -\frac{8633}{67375} \\ -\frac{60311}{21896875} \end{array} $	1.21%	$ \begin{array}{r} 1 \\ -\frac{1}{5} \\ -\frac{53}{175} \\ -\frac{8633}{67375} \\ -1.285 \\ \end{array} $	5.1%	0.9998	1.001 -0.2214 -0.047523 -1.188 0.9881	0.02%

Table 4.4. Approximations with the main function of $a_0 \frac{2y}{1-y^2} + \sum_{i=1}^n a_i y^{2i-1}$.

are rational or a trigonometric functions, the accuracy of the approximates improves as the polynomial order increases. Such approach allows us for the first time to choose the ILF approximation for specific application based on the required accuracy with an acceptable computational costs. While the derived ILF approximation does not change the order of complexity of the main functions (Warner, Cohen and ...), they are significantly faster than the newly developed higher-order Pade approximations (a complex but more accurate rational function) [58, 92, 89, 91, 93, 2]. This is an important feature in the field of elastomer physics where ILF approximations significantly influences the computational cost of the simulation, while high accuracy near singularity is needed to describe finite deformation. Having a family of approximants would be particularly helpful

[n]	With correct asymptote and Taylor $a_0 = 1$		With correct and one po minimi a ₀ =	asymptote oint error zation = 1	General error minimization approach			
	<i>a</i> :	Relative	<i>a</i> :	Relative	<i>a</i> _o	<i>a</i> :	Relative	
	сц	error	al	error	aq	al	error	
0	N/A	17.75%	N/	A	1.0975	N/A	9.75%	
1	0.53	5.21%4	N/	A	0.974	0.52	2.59%	
2	0.53	2 880%	0.53	0 80%	0 00/25	0.56395	0 5 7 %	
2	-0.23	2.00%	-0.45	0.09%	0.99425	-0.4571	0.57 70	
	0.53		0.53			0.53		
3	-0.23	0.90%	-0.23	0.3%	1.0009	-0.2783	0.17%	
	-0.31		-0.4			-0.3609		
	0.53		0.53			0.53		
4	-0.23	0 720/	-0.23	0.250/	1 0000	-0.1555	0.00%	
4	-0.31	0.75%	-0.31	0.35%	1.0008	-0.7548	0.09%	
	-0.24		-0.14			0.3203		
	0.53		0.53			0.5334		
	-0.23		-0.23			-0.2508		
5	-0.31	1.26%	-0.31	0.28%	0.9998	-0.05041	0.02%	
	-0.24		-0.24			-1.188		
	-0.13		0.17			0.9881		

Table 4.5. Approximations with the main function of $a_0 \frac{\pi}{2} \tan \frac{\pi}{2} y + \sum_{i=1}^n a_i y^{2i-1}$.

in some specific applications where one certain form of the approximation function can significantly reduce the computational loads. Examples of such systems include MacKintosh chains where a proper variation of the ILF approximation should be chosen to derive function f(x) in $\mathcal{L}^{-1}(xf(x)) = f(x)$, or the polymer networks where the response of the network is mainly obtained through $\int P(x)\mathcal{L}^{-1}(x)dx$.

CHAPTER 5

MICRO-MECHANICAL MODELING OF THE STRESS SOFTENING IN DOUBLE-NETWORK HYDROGELS

5.1 Introduction

Hydrogels contain a large amount of water (50-99%) and are a class of hydrophilic polymers that are extremely soft and mostly bio-compatible. These features make them a great candidate for many pharmaceutical and biological applications, such as drug delivery carriers matrix for cell immobilization of bone regeneration, spinal cord injuries, cartilage and fate defects, and super absorbents [95, 96]. Due to the dispersion of cross linking and the structural in-homogeneity, conventional hydrogels which are usually composed of a single network (SN) showed a poor strength level, fragile response, and limited extensibility and recoverability. Therefore, they could not be used in load-bearing applications. The lack of mechanical strength in most of natural and synthetic hydrogels in comparison with the soft bio-tissues such as cartilage, liver, tendon, skin, and arteries has indeed been one of the main challenges for material scientists in recent decades [97]. Furthermore, swelling of conventional hydrogels was primarily an appealing topic rather than their mechanical response. In recent years, swelling-deswelling and diffusion-deformation behaviors of hydrogels have been extensively studied by numerous research groups [98, 99].

Several methods of synthesis such as homogenization of structure, filler supplementation, and use of sacrificial bonds, have been developed to toughen hydrogels [100, 101]. Examples of tough hydrogels include slide-ring hydrogels, tetra-PEG hydrogels, nano-composite gels, and double network hydrogels. Among different types of tough hydrogel classes, double network hydrogels

(DN hydrogels) usually demonstrate the best mechanical properties [102].

DN hydrogels consist of highly cross-linked first network (polyelectrolyte) and loosely crosslinked second network[103]. The first network hosts the sacrificial bonds, whereas the second network is mostly responsible for the load transfer. Cross-linking density and the molar ratio of the second network to the first network are critical factors that characterize the response of tough DN hydrogels [102]. In the view of experimental data, gel properties are optimized when the molar ratio is around 20. By controlling the interactions between the first and second networks, two types of DN gels, connective (*c*-) and truly independent (*t*-) DN hydrogels, can be developed [104]. *c*-DN hydrogels have strong interactions between polymer networks, whereas such interactions are prevented in *t*-DN hydrogels. On the other hand, *t*-DN hydrogels exhibit better mechanical response than *c*-DN hydrogels if the second network is loosely cross-linked. Consequently, loosely cross-linked second network requires high molecular weight to ensure the integrity.

DN hydrogels also demonstrate J- and S- types of nonlinear behavior under large deformations with inelastic feature that is similar to the stress softening of the filled rubbers, generally referred to as the "Mullins effect" [1, 105]. Therefore, constitutive modeling of hydrogels is often practiced using the concepts that are originally developed for the study of rubber elasticity [106, 107]. The Mullins effect in the elastomeric materials has been extensively studied over the last 70 years, and there exist several constitutive models in the literature to describe this phenomenon [108, 109, 110, 38, 111, 112, 21].

The damage in DN hydrogels may result from the rupture of cross-linking, as no filler is present in a DN hydrogel matrix [1, 113]. Therefore, DN hydrogel models are associated with the inelastic response of the gel to the first network due to its highly cross-linked structure [113]. The second network is often considered to be hyper-elastic although its elasticity modulus gradually decreases due to the formation and propagation of cracks. The second network bridges cracks of the first network. Wang and Hong [114] described the response, damage and yielding of a DN hydrogel with respect to the Ogden-Roxburgh pseudo-elasticity model [115]. Later, Zhao [106] proposed a model for interpenetrating polymer networks which decomposed the polymer matrix into short and long polymer networks. The model was based on Arruda - Boyce eight chain model and the modified network alteration theory. Liu et al. [116] proposed a model for stress softening and necking instability in DN hydrogels. They considered the energy of a network in a particular direction and the energy of a mixture of polymer-solvent using Flory-Huggins theory. The model attributes stress softening to the fracture of the first network, and hardening to the hyper-elastic stiffening of the second network. Their results are verified for various DN hydrogel types, and showed a generally good agreement with the experimental data. Recently, Lu et al. [117] and Lu et al. [118] proposed a phenomenological model to describe visco-elastic and Mullins-effect behavior of the tough gels.

In this work, a micro-mechanical constitutive model is proposed to describe the non-linear response and the stress softening of DN hydrogels. The fundamentals of statistical mechanics of polymers are first reviewed in the Section 5.2. Then, the generalized network decomposition concept and the corresponding strain energy function approach is discussed in Section 5.4. Finally, section 5.7 describes the evaluation of the proposed model in comparison to experimental data.

5.2 Statistical Mechanics of Polymers

The deformation gradient, \mathbf{F} is considered as multiplication of mechanical \mathbf{F}_m and swelling parts $v_p^{-\frac{1}{3}}\mathbf{I}$ of deformation. In the swelling part, the coefficient v_p is volume fraction of gel to the fresh gel and \mathbf{I} is the identity tensor. In this study, we assumed that swelling-drying is isotopic and happened before mechanical loading. Therefore, the deformation is purely mechanical and during loading-unloading the volume of sample remains constant. Let us denote the position vector of a chain in the reference and deformed configurations by \mathbf{R} and \mathbf{r} , and their lengths by R and r, respectively. In order to consider effect of swelling/drying of the sample on constitutive model, isotropic inflation of the sample implies that the end-to-end distance of the chains \mathbf{R} is linearly alter with inflation length $a\mathbf{R}$. Accordingly, one has

$$\boldsymbol{r} = \mathbf{F}\boldsymbol{R}, \qquad r = v_p^{-\frac{1}{3}} \stackrel{d}{\lambda} R = \stackrel{d}{\lambda} R_p,$$
 (5.2.1)

where **F** denotes the micro-scale deformation gradient applied on a chain, R_p is the end-to-end distance of the chain in the swelled state, and $\overset{d}{\lambda} = \sqrt{d\mathbf{F}_m^T \cdot \mathbf{F}_m d}$ the stretch in the direction of the unit vector d. Note that only end-to-end distance of the chains and number of chains per unit of volume change due to swelling-drying process. Hereafter, the following font styles are used for scalar X, vector \mathbf{X} , and second-order \mathbf{X} . Moreover, the parameters with a bar sign over them $\bar{o} = \frac{o}{l}$ denote their normalized value with respect to the segment Kuhn length l.

5.2.1 Non-Gaussian distribution function

The polymers networks consist of polymer chains with different length, that are distributed in different directions. The probability of existence of a chain with end-to-end distance r and counter length n can be calculated through the solution of 3D random flight problem as [119],

$$P_n^{exact}\left(\boldsymbol{r}\right) = \frac{1}{2^{n+1}\left(n-2\right)!\pi l^2 r} \sum_{k=0}^{k \le m} \left(-1\right)^k \begin{pmatrix} n \\ k \end{pmatrix} \left(n-2k-\bar{r}\right)^{n-2}, \quad (5.2.2)$$

where *m* is equal to $\frac{n-\bar{r}}{2}$ and *l* is the segment length. The strain energy of a single chain based on Non-Gaussian probability can be calculated as a function of *r* through Boltzmann's entropy formula and thermodynamic balance, $\psi_c(\mathbf{r}) = -kT \ln (P_n(\mathbf{r}))$. In this relation, *T* is the absolute temperature, and *k* the Boltzmann constant.

Due to mathematical complexity and piece-wise nature, the exact Non-Gaussian PDF was not suitable for practical applications. Therefore, most current polymer elasticity models often use the KG distribution function, which is derived from the first order approximation of the Rayleigh's exact Fourier integral distribution [11]. The free energy of a single chain based on Non-Gaussian PDF can be calculated as a function of r through thermodynamic balance as,

$$\psi_c(n,\bar{\boldsymbol{r}}) = nKT\left(t\beta + \ln\frac{\beta}{\sinh\beta}\right) + c_0 = nKT\int_0^t \beta \,dt + c_0, \qquad \beta = \mathcal{L}^{-1}(t) \qquad (5.2.3)$$

where $\mathcal{L}^{-1}(t)$ is the ILF, $t = \frac{\bar{r}}{n}$ is the extensibility ratio and c_0 is correlated with the number

of chains to eliminate the energy in reference state. However, several studies suggested that KG estimation is only valid for sufficiently large chains ($n \gg 40$) [56, 120], and has significant errors with respect to the exact PDF for short chains. The first network in the DN hydrogels consists of the short and brittle chains. Therefore, the KG method cause significant errors in constitutive modeling of DN hydrogels. In order to address this shortcoming, we used enhanced KG distribution function for short chains, which is developed recently [121].

$$\hat{\psi}_c(n,\bar{r}) = nKT \int_0^t \hat{\beta}(t;n) dt, \qquad \hat{\beta} = \left[1 - \frac{1 - t^2}{n}\right] \beta.$$
(5.2.4)

The first bracket in the Eq. 5.2.4 is added to the ILF to reduce the relative error of the KG distribution for short chains. Given that Inverse Langevin function cannot be derived explicitly, rational approximation functions are used to represent it [57, 2, 58]. Therefore, this modification has same complexity as the KG model.

5.2.2 Double network hydrogels

DN gels are composed of two dissimilar interpenetrating polymer networks generally referred to as the first and second networks. The first network is a highly cross-linked brittle network with high number of sacrificial bonds. The second network is a stretchable network with hyper-elastic behavior up to very large deformation ranges, which is loosely cross-linked (Fig.5.1). Experiments show that under tensile deformation, the first network rapidly breaks due to its lack of flexibility, and the second network keeps the integrity of the gel.

Several types of polymer components are used in DN gels, among which the most popular choices are PAMPS ¹- PAAm ² gel [105] and alginate - PAAm gel [122]. In PAMPS, cross-links are formed by covalent bonds while in alginate gels, the polymers are cross-linked by ionic bonds. Accordingly, different damage mechanisms should be considered for each gel type. The model

¹poly(2-acrylamido-2-methyl-propane-sulfonic acid)

²neutral polyacrylamide



Figure 5.1. Schematic view of structural composition of the DN gels as the superposition of the first and second networks. The first network is not flexible and highly cross-linked. The second network is a loose network and is highly flexible due to its long polymer chains.

developed here is valid for those gels in which one network is hyper-elastic and the other is brittle, such as covalent DN hydrogels composed of PAMPS and PAAm networks.

The classic constitutive behavior of DN gels under uni-axial tension is plotted in Fig. 5.2 which exhibits inelastic features similar to those of elastomers, such as stress-softening, primary curve and hardening [1]. Comparing to filled rubbers, constitutive behavior of gels lacks three major features, namely (i) hysteresis after the first cycle, (ii) large permanent set, and (iii) long-term healing. In DN hydrogels, no substantial recovery in the behaviour of deformed gel can be observed even after some weeks of relaxation [1]. After the first cycle, the hysteresis in subsequent cycles is generally referred to as cyclic damage. As it can be seen in the Fig. 5.2, cyclic damage and permanent set in the hydrogels are significantly smaller than those of elastomers [1]. Therefore, the effect of stress-softening after first cycle is negligible.

Another feature of DN hydrogels is the pre-damage in the first network in their reference state, which is induced by their two-step synthesizing method [123, 124]. The two-step polymerization method is used to process the DN hydrogels, which is developed by Gong et al. [125]. The damage induced in the second step of the process is schematically shown in Fig. 5.3. A rigid and brittle network is polymerized first. It will be then immersed and swelled in a solution to synthesize the second network. This swelling causes an increase in end-to-end distance of chains, which result to breakage of the shorter chains. After polymerization of the second network, the gel shrinks to reach to the new equilibrium state, which will be hereafter referred as a reference state. In order to model this phenomena, we assumed that the chains have the end-to-end distance R in the final



Figure 5.2. Constitutive response of a DN-hydrogel specimen under quasi-static compression, which include three typical inelastic features, i.e., stress-softening, primary curve and hardening. No healing behavior has been reported. [1].

state. The damage caused in the swelling stage of the first network is considered same in the all directions.

In this work, the DN gel matrix is considered as the assembly of two independent matrices on top of each other (see Fig.5.1). During deformation, first network with short chains breaks down, while the second network remains intact and transfers the load within the matrix. Since the forces between the first network fragments are transferred by the second network, the constitutive response of the system can be schematically shown through the assembly depicted in Fig.5.1.

5.3 Constitutive Model

5.3.1 Network decomposition

By considering elastic deformation of DN hydrogel as a nearly incompressible material, its strain energy function $\Psi_N(\mathbf{C})$ can be decoupled into isochoric and volumetric parts by (see e.g. [32])

$$\Psi_N(\mathbf{C}) = \Psi_M(\bar{\mathbf{C}}) + U(J), \tag{5.3.1}$$



Distribution of chains length in the 1st Network

Figure 5.3. The schematic picture of the two-step polymerization method to prepare DN hydrogels and the damage caused by swelling.

where C denotes the right Cauchy-Green tensor, $J^2 = \det C$ and $\bar{C} = J^{-\frac{2}{3}}C$. To describe the mechanical response of DN gels, the isochoric strain energy of the matrix is considered as the total strain energies of the first (1N) and the second (2N) networks. The networks are assumed to act parallel to each other (see Fig. 5.3). Accordingly, the isochoric strain energy of the gel matrix Ψ_M can be represented as

$$\Psi_M = \sum_{i=1}^m \Psi_i \tag{5.3.2}$$

where Ψ_i denotes the strain energy of the ith network per unit reference volume of the material and m is a number of sub-networks in the material, which is equal to 2 for DN hydrogels.

5.3.2 Modular platform

The model proposed here is based on the concept of the modular platform [68], which allows a framework to be built by coupling several network models, each one of which representing a network. A network model can describe multiple damage mechanism, where each network can be



Figure 5.4. Schematic breakdown of a modular framework consisting of two network models for the first and second networks to illustrate the concept of the networks, and sub-networks. The first sub-network consists a distribution of shorts chain with different length and average end-to-end distance, R and the second sub-network considered to be a set of long chains with same length and end-to-end distance.

derived from existing models. Here, we propose a network model for the first network, and import another one for the second one. The network models can be substituted, upgraded, or removed without influencing the integrity of the framework. Network models are designed to return strain energy; scale-transition will be based on a micro-sphere concept; and entropic behavior is assumed for polymer chains. Here, we only consider permanent damage, however, the number of add-on modules can be increased later on if different inelastic features needed to be added.

In Fig. 5.4, the composition of a modular framework consisting of two network models for the first and second networks is depicted [68, 126]. From the micro-mechanical point of view, permanent damage is a consequence of decomposition of the first network during which several chains are deactivated through debonding. Since the de-bonded chains will not reattach back to the network, the damage becomes permanent. Since permanent damage is mainly associated to the first network, the second network is considered as a hyper-elastic network.

Each sub-network is subjected to a different uni-axial deformation and damage histories ac-

cording to their directions. Integrating a sub-network in all directions, the consequent network model is developed as a 3D representation of the 1D model of sub-networks. The contribution of each network in strain energy is regulated by fitting the model to the experiments. Here, by assuming the homogeneous distribution of polymer chains in all spatial directions, the macroscopic energy of each network, Ψ_i can be formulated as

$$\Psi_i = \frac{1}{A_s} \int\limits_S W_i^d du^d, \tag{5.3.3}$$

where A_s represents the surface area of the micro-sphere S, and d^{d}_{u} the infinitesimal area of A_s with the normal direction d (see Fig. 5.4). The parameter Ψ_i^{d} represents the energy of the ith subnetwork in direction d. The integration of the macroscopic energy of the 3D matrix can be carried out numerically

$$\Psi_j \cong \sum_{i=1}^k \Psi_j^{d_i} w_i, \tag{5.3.4}$$

where w_i are the weight factors associated to different spatial directions d_i for i = 1, 2, ..., k.

5.3.3 First network: Brittle network with damage

The first network is considered as an assembly of brittle sub-networks with short chains. The breakage of the short chains is considered as the main source of damage in the first network. The process initiates with the irreversible breakage of shorter chains, and eventually involves longer chains. Let \tilde{N}_1 be the total number of active chains per unit of volume in the first network in all directions. In an arbitrary direction d, the chains with the relative end-to-end distance R have different number of segments n (relative length) described by a normal distribution, $\mathcal{P}(n)$, with the average μ_n , and the standard deviation σ_n .

$$\mathcal{P}(n) = \mathcal{P}_0 \exp\left(\frac{\left(n - \mu_n\right)^2}{2\sigma_n^2}\right)$$
(5.3.5)

Therefore, the average free energy of the first network in an arbitrary direction can be calculated by considering the probability of existence of chains with different length in that direction. The summation of the energies of the whole set of chains length available in the direction d further yields the free energy of the first sub-network in this direction as

$$\overset{d}{\Psi}_{1N} = \sum_{D_n} \tilde{N}_1 \psi_c(n, \lambda) \mathcal{P}(n), \qquad (5.3.6)$$

where D_n represents the set of available chain lengths. The DN gels fully recover to their reference configuration after the load is removed. Thus, the reloading response will be identical to the unloading response until the stretch reaches the maximum stretch. The first loading response always follows a primary load curve. Such behavior suggests that the damage is permanent and is a function of the maximum stretch in that direction, $\frac{d}{\lambda_{max}}$. Accordingly, as long as $\frac{d}{\lambda_{max}}$ remains unchanged, damage will not increase in the subsequent , unloading and reloading cycles. Accordingly, the damage here is described as an interaction of two simultaneous processes of (i) breakage and debonding of polymer chains and cross-links and (ii) network rearrangement within the network. The schematic picture of the damage in the first network is illustrated in Fig. 5.5.

(i) Polymer Chain breakage: During the primary loading the end-to-end distance of some chains will reach their contour length and cannot be further extended. Here, we assume that these chains will be broken or debonded from their cross-links. This process takes place only during the primary loading. Assuming the bond to be chemical, the chains will neither debond nor heal in subsequent unloadings and reloadings. Accordingly, the number of active chains in the first network, \tilde{N}_1 , is only reduced during the primary load and thus, only with respect to the maximal stretch of the first network d_{1m}^d in the direction d, which can be written as

$$\lambda_{max}^{d_i} = \max_{\tau \in (-\infty, t]} \left[\lambda_p, \lambda(\tau) \right], \quad \boldsymbol{d}_i \in \mathbb{V}^3 \land |\boldsymbol{d}| = 1.$$
(5.3.7)

Then, in view of a finite breakage force of a polymer chain, f_b , one can determine the shortest



Figure 5.5. Stress softening in the DN gels in the course of deformation. (a) schematic view of different fragments of the first network connected by the chains of the second network, (b) internal structure of a fragment in the reference state, (c) decomposed substructure of a fragment in which shorter chains were debonded due the applied deformation. (d) schematic representation of chain length distribution, which shows existence of short chains as 1^{st} network and long chains as 2^{nd} network.

chains available in a deformed sub-network as

$$f\left(\frac{\bar{r}}{n}\right) \le f_b \quad \to \quad \overset{d}{n_{min}} = \frac{1}{\xi} \overset{d}{\lambda_{max}} v_p^{-\frac{1}{3}} \bar{R} \le n, \tag{5.3.8}$$

where $\xi = \mathcal{L}(\bar{f}_b) < 1$ represent the average limit of extensibility, which cause early breakage of the chains, and cross-links and is a material parameter. Similarly, \bar{f}_b is the normalized breakage force of a polymer chain. Furthermore, in view of the P(n), a cut-off length $n_{max} = \mu_n + 4\sigma_n$ can be introduce, above which P(n) is considered to be negligible. This assumption can be released in order to reach to higher deformation for long chains only. Accordingly, the set of available chains in the direction d can be written as

$$D_n\begin{pmatrix} d\\\lambda_{max} \end{pmatrix} = \left\{ n \middle| n_{min}\begin{pmatrix} d\\\lambda_{max} \end{pmatrix} \le n \le n_{max} \right\},$$
(5.3.9)

which confirms that the material behavior in the direction d is influenced by the loading history in that direction.

(ii) Chain Rearrangement within a Fragment: In the course of deformation, the shortest chains will be broken or disentangled from longer ones. This process will lead to some terminated chains that do not contribute to the elasticity of the network anymore, while some of them will rearrange as longer chains with higher number of segments, as illustrated in Fig. 5.5(b). The concept of chain rearrangement suggests that the detachment of chains does not necessarily lead to a full loss of their entropic energy, since some of the chains will remain in the network as part of a longer macro-molecules. Thus, we assume that the total number of active segments in the first network in each direction is decreased due to deformation. This assumption yields

$$\sum_{D_n(1)} n \,\tilde{N}_1(1) \,P(n) = \sum_{D_n\begin{pmatrix}d\\\lambda_{max}\end{pmatrix}} n \,\tilde{N}_1\begin{pmatrix}d\\\lambda_{max}\end{pmatrix} \mathcal{P}(n) + \mathcal{N}_{broken},\tag{5.3.10}$$

where \mathcal{N}_{broken} is number of inactivated segments in the network. Here, by assuming that α percent of broken chains will remain active in the network, the number of broken segment can be written as

$$\mathcal{N}_{broken} = (1 - \alpha) \sum_{D_n(1) \not \cap D_n \begin{pmatrix} d \\ \lambda_{max} \end{pmatrix}} n \, \tilde{N}_1(1) \, \mathcal{P}(n), \tag{5.3.11}$$

where α is a material parameters that governs the rate of energy dissipation. Next, considering that $\tilde{N}_1\begin{pmatrix} d\\\lambda_{max} \end{pmatrix}$ to be independent of n, and $\tilde{N}_1(1)$ to be a constant, one can write

$$\tilde{N}_1\begin{pmatrix}d\\\lambda_{max}\end{pmatrix} = N_1 \Phi\begin{pmatrix}d\\\lambda_{max}\end{pmatrix}, \qquad \Phi(x) = 1 + \alpha \frac{\sum\limits_{D_n(1) \not \in D_n(x)} n \mathcal{P}(n)}{\sum\limits_{D_n(x)} n \mathcal{P}(n)}, \qquad (5.3.12)$$

where N_1 is a number of chains in the first network before polymerization of the second network, which is considered as a material constant. Finally, substituting Eq.5.3.12 in Eq.5.3.6, the energy of a subnetwork in direction d is obtained as

$${}^{d}_{\Psi_{1N}} = v_p N_1 \sum_{D_n} \Phi\left({}^{d}_{\lambda_{max}}\right) \psi_c(n, {}^{d}_{\lambda}) P(n), \qquad (5.3.13)$$

5.3.4 Second network: Hyper-elastic response

The second network is the source of mechanical integrity of the gel and plays a key role in the elasticity of the gel. Here, using the model of Miehe et al. [55], we represent the network as an assembly of N_2 chains with the average length of n_2 segments. Thus, by generalizing the concept of full network model in rubbers [54], the energy of the second sub-network in direction d can be written as

$$\overset{d}{\Psi}_{2N} = v_p N_2 \psi_c \left(n_2, \overset{d}{\lambda} \right), \qquad (5.3.14)$$

where the parameters N_2 , and n_2 are material parameters. The second network is an elastic network with affine motion of cross-links, which consist of identical chains. In a stress free state, the chains are assumed to be in the unperturbed state in which the mean end-to-end distance of a chain is $R_0 = \sqrt{n_2}$. A comprehensive review of the available hyper-elastic models that can fit the platform is provided in Marckmann and Verron [127].

5.4 Macro-scale Response

5.4.1 3D generalization

Assuming a homogeneous spatial distribution of polymers in the gel matrix, and in view of Eqs. 5.3.4, 5.3.13, and 5.3.14, the total macroscopic energy of a three-dimensional gel matrix is given as

$$\Psi_{M} = \Psi_{1N} + \Psi_{2N} = v_{p}N_{1}\sum_{i=1}^{k} \left\{ w_{i}\Phi\left(\frac{d_{i}}{\lambda_{max}}\right)\sum_{\substack{d_{i}\\D_{n}(\lambda_{max})}} \mathcal{P}(n)\psi_{c}\left(n,\frac{d_{i}}{\lambda}\right) \right\}$$
$$+ v_{p}N_{2}\sum_{i=1}^{k} w_{i}\psi_{c}\left(n_{2},\frac{d_{i}}{\lambda}\right)$$
(5.4.1)

The constitutive equation for the first-Piola-Kirchhoff stress tensor ${\bf P}$ can be written by

$$\mathbf{P} = \frac{\partial \Psi_M}{\partial \mathbf{F}} = \frac{\partial \Psi_{1N}}{\partial \mathbf{F}} + \frac{\partial \Psi_{2N}}{\partial \mathbf{F}},\tag{5.4.2}$$

where

$$\frac{\partial \Psi_{1N}}{\partial \mathbf{F}} = v_p N_1 \sum_{i=1}^k w_i \frac{\partial \psi_{1N}}{\partial \lambda} \frac{1}{2 \lambda} \frac{\partial d_i \bar{\mathbf{C}} d_i}{\partial \bar{\mathbf{F}}} : \frac{\partial \bar{\mathbf{F}}}{\partial \mathbf{F}},$$

$$\frac{\partial \Psi_{2N}}{\partial \mathbf{F}} = v_p N_2 \sum_{i=1}^k N_2 w_i \frac{\partial \psi (n_2, x)}{\partial x} \bigg|_{x=\lambda} \frac{1}{2 \lambda} \frac{\partial d_i \bar{\mathbf{C}} d_i}{\partial \bar{\mathbf{F}}} : \frac{\partial \bar{\mathbf{F}}}{\partial \mathbf{F}}.$$
 (5.4.3)

These equations can be further simplified by means of the following identities

$$\frac{\partial \psi_c\left(n, x v_p^{-\frac{1}{3}} \bar{R}\right)}{\partial x} = v_p^{-\frac{1}{3}} \bar{R} K T \hat{\beta} \left(\frac{x v_p^{-\frac{1}{3}} \bar{R}}{n}, n\right),$$
(5.4.4)

$$\frac{\partial \Psi_{1N}}{\partial \lambda} = v_p N_1 \Phi \begin{pmatrix} d_i \\ \lambda_{max} \end{pmatrix} \sum_{\substack{d_i \\ D_n(\lambda_{max})}} \mathcal{P}(n) \left. \frac{\partial \psi_c(n,x)}{\partial x} \right|_{x=\lambda}^{d_i}$$
(5.4.5)

$$\frac{\partial d\bar{\mathbf{C}}d}{\partial\bar{\mathbf{F}}}:\frac{\partial\bar{\mathbf{F}}}{\partial\mathbf{F}}=2\bar{\mathbf{F}}(\boldsymbol{d}\otimes\boldsymbol{d}):J^{-\frac{1}{3}}\mathbf{I}=2J^{-\frac{1}{3}}\bar{\mathbf{F}}(\boldsymbol{d}\otimes\boldsymbol{d}).$$
(5.4.6)

In the Eq. 5.4.4, $\hat{\beta}$ is the modified version of Langevin elastic force for a short chain. Thus, Eq.

5.4.2 yields

$$\mathbf{P} = v_p^{\frac{2}{3}} \hat{N}_0 \left(\sum_{i=1}^k \left(P_{1N} \left(\boldsymbol{d}_i \right) + P_{2N} \left(\boldsymbol{d}_i \right) \right) \frac{w_i}{\boldsymbol{d}_i} J^{-\frac{1}{3}} \bar{\mathbf{F}} \left(\boldsymbol{d}_i \otimes \boldsymbol{d}_i \right) \right),$$
(5.4.7)

where \hat{N}_0 is equal to $N_1 kTR$ and

$$P_{1N}(\boldsymbol{x}) = \Phi\begin{pmatrix}\boldsymbol{x}\\\lambda_{max}\end{pmatrix}\sum_{D_n(\lambda_{max})}\mathcal{P}(n)\mathcal{L}^{-1}(t)\left(1-\frac{1+t^2}{n}\right), \quad t = \frac{\frac{\boldsymbol{x}}{\lambda}v_p^{-\frac{1}{3}}\bar{R}}{n}$$
$$P_{2N}(\boldsymbol{x}) = \frac{N_2}{\hat{N}_0}\sqrt{n_2}\mathcal{L}^{-1}\left(\frac{\frac{\boldsymbol{x}}{\lambda}v_p^{-\frac{1}{3}}}{\sqrt{n_2}}\right). \quad (5.4.8)$$

A proper approximation approach for the inverse Langevin function is required depending on the elongation range of polymer chains. In this study, due to the high elongation ratio of the chains (relatively large value of $\mathcal{L}(f_y)$), a fractional approximation with error of less than 0.02% is more favorable (see [57]). Accordingly

$$\mathcal{L}^{-1}(x) \cong \frac{x}{1-x} + \sum_{i=1}^{m} a_i x^i.$$
(5.4.9)

where the number of terms m = 5 and the values of a_i are given in [57]. Moreover in this study, the numerical integration over the unit sphere is evaluated by using 45 integration points over half sphere. The presence of pre-damage in the material leads to a step-wise yielding points in the stress-strain curve, which can be smoother by increasing the number of integration points (see Fig. 5.6-d). This number of integration points was found to yield the best optimization between computational costs of integrating over a sphere and the resulted error of the induced anisotropy [128, 129].

5.5 Thermodynamic Consistency

Since the strain energy of the gel matrix Ψ_M is influenced by only one internal variable, namely $^{d}_{\lambda_{max}}$, one can rewrite Ψ_M as

$$\Psi_M = \Psi_M(\bar{\mathbf{C}}, \mathbf{\Lambda}_{max}) = \tilde{\Psi}_M(\bar{\mathbf{F}}, \mathbf{\Lambda}_{max}) = \Psi_{1N}(\bar{\mathbf{C}}, \mathbf{\Lambda}_{max}) + \Psi_{2N}(\bar{\mathbf{C}}), \quad (5.5.1)$$

where

$$\boldsymbol{\Lambda_{max}} = \left\{ \begin{array}{l} \boldsymbol{d} \\ \lambda_{max} : \boldsymbol{d} \in \mathbb{V}^3 \land |\boldsymbol{d}| = 1 \right\}.$$
(5.5.2)

The second law of thermodynamics can be reduced to the Clausius-Duhem inequality to show the thermodynamic consistency of the model in an arbitrary direction d

$$\partial_{\substack{D\\\lambda_m}} \Psi_M \cdot \begin{pmatrix} \vec{D}\\\lambda_m \end{pmatrix} \le 0 \qquad \forall d.$$
 (5.5.3)

The maximum stretch remains constant during unloading and reloading. Therefore, $\overset{d}{\lambda_{max}} = 0$ in unloading-reloading while $\overset{D}{\lambda_{max}} > 0$ in the primary loading. Thus, satisfaction of the Clausius-Duhem inequality during the loading is sufficient to prove (5.5.3), as one can write

$$\frac{\partial \Psi_M}{\partial \lambda_{max}} \le 0 \qquad \forall \ \boldsymbol{d} \tag{5.5.4}$$

With respect to (5.3.2) and (5.3.4), equation (5.5.3) yields

$$\frac{\partial \Psi_M}{\partial \lambda_{max}^d} = \frac{\partial \Psi_{1N}^d}{\partial \lambda_{max}^d} \le 0 \ \forall \ \boldsymbol{d}.$$
(5.5.5)

Without losing generality, (5.5.5) can be proved for an arbitrary direction d of primary loading. For the sake of briefness, $\overset{d}{\lambda_{max}}$ and $\overset{d}{\lambda}$ are replaced by x in primary loading and in order to take the derivation of summations in the model, the summations are replaced by their equivalent integration . Using (5.3.13), one can further obtain

$$\frac{\partial \Psi_{1N}}{\partial \lambda_{max}} = \frac{\partial \Psi_{1N}}{\partial x}$$

$$= v_p N_1 \left[\frac{d\Phi(x)}{dx} \sum_{D_n(x)} \psi_c(n,x) \mathcal{P}(n) - \frac{dn_{min}(x)}{dx} \Phi(x) \psi_c(n_{min}(x),x) \mathcal{P}(n_{min}(x)) \right] \quad (5.5.6)$$

where $n_{min}(x) = \frac{1}{\xi} x v_p^{-\frac{1}{3}} \bar{R}, \ \frac{dn_{min}(x)}{dx} = \frac{1}{\xi} v_p^{-\frac{1}{3}} \bar{R}$, and

$$\frac{d\Phi(x)}{dx} = \frac{\bar{R}}{\xi} v_p^{-\frac{1}{3}} \mathcal{P}(n_{min}(x)) n_{min}(x) \frac{\alpha - 1 + \Phi(x)}{\sum_{D_n(x)} n \,\mathcal{P}(n)}.$$
(5.5.7)

By substituting (5.5.7) in (5.5.6), one can obtain

$$\frac{\partial \Psi_{1N}}{\partial x} = N_1 \frac{\bar{R}}{\xi} v_p^{\frac{2}{3}} \mathcal{P}(n_{min}(x)) \\ \left[n_{min}(x) \frac{\alpha - 1 + \Phi(x)}{\sum\limits_{D_n(x)} n \mathcal{P}(n)} \sum\limits_{D_n(x)} \psi_c(n, x) \mathcal{P}(n) - \Phi(x) \psi_c(n_{min}(x), x) \right] \le 0 \quad (5.5.8)$$

As $\alpha \leq 1$, $N_1 \frac{\bar{R}}{\xi} v_p^{\frac{2}{3}} \mathcal{P}(n_{min}(x)) > 0$, and $\Phi(x) > 0$, (5.5.8) holds if only we have the following

inequality

$$\frac{n_{\min}\left(x\right)}{\sum_{D_{n}(x)} n \mathcal{P}(n)} \sum_{D_{n}(x)} \psi_{c}(n, x) \mathcal{P}(n) - \psi_{c}(n_{\min}\left(x\right), x) \leq 0$$
(5.5.9)

(5.5.9) can be rewritten as

$$n_{\min}(x) \sum_{D_n(x)} \psi_c(n, x) \mathcal{P}(n) - \psi_c(n_{\min}(x), x) \sum_{D_n(x)} n \mathcal{P}(n) \le 0$$
(5.5.10)

As $n_{min}(x)$ and $\psi_c(n_{min}(x), x)$ are not functions of n, they can be moved inside the summation, thus

$$\sum_{D_n(x)} \mathcal{P}(n) \left[n_{\min}(x) \,\psi_c(n,x) - n\psi_c(n_{\min}(x),x) \right] \le 0 \tag{5.5.11}$$

As $n_{min}(x) \leq n$ and the strain energy of the shortest chain is always higher than the energy of the rest of the chains $(\psi_c(n,x) \ll \psi_c(n_{min}(x),x)))$, one can conclude $n_{min}(x) \psi_c(n,x) - \psi_c(n_{min}(x),x)n \leq 0$ for all $n \in D_n(x)$. While the bracket in the inequality (5.5.11) is less than zero for all chain lengths (n), the proposed model holds the condition of the thermodynamic consistency.

5.6 Analysis

The proposed model has utilized ten material parameters, seven of which belong to the 1st network $(\bar{R}, n_{max}, \mu_n, \sigma_n, \lambda_p, \alpha \text{ and } \xi)$, two to 2nd network $(N_2 \text{ and } n_2)$, and one parameter namely \hat{N}_0 is a simple multiplicative scaling factor to describe the response of the polymer matrix. Out of the seven parameters that are used in the first network, only four, μ_n, σ_n, α and ξ , should be obtained by using fitting procedure and the other three, $\bar{R}, n_{max}, \lambda_p$, can be explicitly derived from the experimental data and material conditions.

- Parameter R
 has no direct effect on the material response in the equilibrium state. The main contribution of R
 is associated to the probability parameters μ_n ∝ R
 and σ_n ∝ R
 , both of which are defined with respect to R
 . Thus, it can be completely neutralized in the calculations by setting it equal to a constant (see Fig 5.6-a). As it can be seen in Fig 5.6-a, normalized stress-strain curve does not change by variation of R as long as we consider μ_n = 2R
 and σ_n = R
 .
- *Parameter* v_p , the volume fraction of the gel to the fresh gel, can be directly measured from the samples. Note that this parameter affects the end-to-end distance, \bar{R} . Therefore, the constitutive model will consider the effect water content by adjusting the number of chains and also by amplification-attenuation of the stretch for swelled-dried sample. As shown in

Fig 5.6-b, the stress-strain curve is softened due to swelling of the sample and hardened as the material is dried.

- Parameter n_{max} is used to reduce the computational load by reducing the summation boundaries of Eq. 5.4.1. For chains with sufficiently large n, the strain energy is becoming so low that their contribution can be considered zero. Accordingly, one can introduce a cutoff length as $n_{max} = \max \left[\mu_n + 4\sigma_n, 1.5\bar{R}\lambda_{max} \right]$ above which the energy of the chains are simply considered to be zero. As shown in Fig 5.6-c, stress-strain curve does not change by variation of n_{max} from 30 to 50. Note that the smaller n_{max} , which is comparable with $\bar{R}\lambda_{max}$ act as a limiting stretch and cause asymptotic behavior in larger deformation.
- Parameter λ_P can be directly derived from the experimental data as the location of first downturn in the primary loading curve. As shown in Fig 5.6-d, λ_P can be easily identified from the stress-strain curve and is associated with the pre-stretch applied on network one during swelling procedure. Different steps of damage can be clearly seen in , which is attributed to the nature of numerical integration in 3D space. Each step of damage occurs when one point on the unit sphere reaches to the pre-defined stretch. By adding number of integration points the stress-stretch curve will be smoother and more realistic.

Next, to investigate the effects of the parameters of the 1st network, the contribution of second network is minimized by considering $N_2 = N_1$ and $n_2 = 50$. Fig. 5.7 shows a summary of the parametric analysis of μ_n, σ_n, α and ξ , where each graph represents the changes induced by changing one of the aforementioned parameters with respect to the reference set, which is presented in Table 5.1.

 Parameter μ_n and σ_n can control the trend of the damage in the material (see 5.7-a-b) by a mutual effect with the location of R
 with respect to them. As most of the internal energy in the material comes from the chains with the high extensibility, the stiffness of material relates to the percentage of the chain with n ≈ r. Thus, damage will increase when R reaches the peak of probability, μ_n.



Figure 5.6. The influence of the parameters \bar{R} , n_{max} , λ_p on the mechanical response of hydro-gels. Red solid lines represent the reference curve, and the dashed lines show the changes in material response due to the variation of the control parameters.

- *Parameter* α will affect the softening of the material as it decreases as it shown in Fig. 5.7-c. As it can be seen in this figure, the material will experience more softening due to more chain loss (smaller α) while the material deforms.
- Parameter ξ has great effect on the material stiffness during the loading. As it can be seen in Fig. 5.7-d, the stiffness and the total damage of first network increases by approaching ξ to 1. This phenomenon happens due to asymptotic behavior of chain force in the large excitability.

To represent the second network, N_2 and n_2 provide sufficient flexibility for the model of Ψ_{2N} to represent hyper-elastic response. As shown in Fig.5.8a, the parameter n_2 will change the location of asymptote in the response of the second network and thus can govern the location of up-shift in

$N_1 KT$	\bar{R}	n_{max}	μ_n	σ_n	λ_p	α	ξ	$N_2 KT$	n_2
10 [kPa]	5	30	$2\bar{R}$	\bar{R}	1	0.9	0.99	10 [kPa]	50

Table 5.1. The reference set of parameters of the proposed model.

the constitutive curves. The parameter N_2 is a multiplicative scaling factor for Ψ_{2N} and accordingly will just amplify/de-amplify the response (see Fig.5.8-b). Due to the absence of damage in repose of the second network, these two parameters have no influence on the stress softening nor any other damage mechanisms. However, a stronger second network reduces the permanent deformation due to the higher contraction force it provides.

5.7 Model Predictions vs. Experimental Results

In order to validate the presented model, we first used the data of Webber et al. [1] on uni-axial behavior of the DN hydrogel. In that study, the DN hydrogels were synthesized through a two-step sequential UV polymerization [125]. The first network was made from a 1 M aqueous solution of AMPS ³ crosslinked with 4 mol % MBAA ⁴. The second network was synthesized afterward around the first swollen network (for details see [1]). A dumbbell-shaped specimen was elongated up to certain stretch levels of 1.4, 1.46, 1.622, and 1.72 then unloaded (one complete uniaxial tension cycle). Each test were preformed on a virgin sample.

Following our previous discussion, four material parameters can be explicitly derived from experimental data and material conditions, namely

- N_0 is calculated from the stress at max stretch.
- R considered to be a constant as its variation will not change the stress-stretch behavior.
- n_{max} is assumed to be the $max \left[\mu_n + 4\sigma_n, 1.1R_0\lambda_{max}\right]$.

³2-acrylamido- 2-methylpropanesulfonic acid

⁴N,N'methylenebis(acrylamide)



Figure 5.7. Effect of the four parameters $(\mu_n, \sigma_n, \alpha \text{ and } \xi)$ of the 1st network on the material response in the course of uni-axial tension.

• λ_p is extracted from the point that the curvature of the loading curve is changed.

The remaining six material parameters were fitted using one loading-unloading cycle of the 1.72 stretch amplitude in tensile direction. The good agreement with other load-unloading curves in uni-axial tension as well as compression was obtained automatically. To this end, the least square error function was minimized with the aid of the Levenberg-Marquardt algorithm. The obtained values of the material parameters are given in Table 5.2, while the fitted curve is plotted against experimental test in Fig.5.9.

In order to show the relevance of the pre-damage, the dissipated energy in each cycle in the model is compared with the experimental values. The dissipated energy per unit of volume during



Figure 5.8. Effect of the 2^{nd} network parameters on the large deformation response of uni-axial tension. Red solid lines represent the reference curve, and the dashed lines show the changes in material response due to the variation of the control parameters.

the first cycle (Mullins effect) is calculated as follows,

$$U_{hys} = \int_{loading} P d\lambda - \int_{unloading} P d\lambda.$$
 (5.7.1)

As shown in Fig.5.9-c, the dissipated energy in the cycle of $\lambda = 1.28$ is almost negligible in comparison to cycles with higher amplitudes for which dissipated energy grows exponentially with λ . The negligible dissipated energy for small stretch suggests that the material does not show any primary damage until certain deformation level is reached. Thus, the early damage during preparation (pre-damage) of the material can be considered as the reason for the absence of the primary damage. The pre-damage is considered to be identical in all spatial directions so the chains in other directions will reach to the pre-damage stretch limit gradually. Such a homogeneous



Figure 5.9. Comparison of the nominal stress-stretch curves of the model and the experiment for the uni-axial tensile tests.

distribution of pre-damage confirms that it can be related to early swelling of the first network. The dissipated energy grows with a slower rate in mid-range stretches as the stretch applied on chains exceeds the pre-stretch values.

To test the relevance of the presented model, we compared the model predictions against three other types of DN hydrogels, namely the inorganic/organic DN [130], alginate– polyacrylamide hybrid gel and PNaAMPS-PAAm DN hydrogel [131]. For each material, one loading-unloading cycle in was selected and used for fitting of the material parameters. The parameters for each material are derived and summarized in Table 5.3. Furthermore, the prediction of the model for other loading-unloading curves are shown in Fig. 5.10.

Table 5.2. Parameters of the proposed model fitted to the one cycle of tensile test performed on a DN gel in [1].

$N_1 KT$	\bar{R}	n_{max}	μ_n	σ_n	λ_p	α	ξ	$N_2 KT$	n_2
1.992 [kPa]	4.5	10	1.29 <i>R</i>	0.075 \bar{R}	1.1	0.87	0.986	0.8 [kPa]	85

Table 5.3. Parameters of the proposed model fitted to the tensile test performed on a different set of DN gels data.

Ref.	$N_1 KT$	\bar{R}	n_{max}	μ_n	σ_n	λ_p	α	ξ	$N_2 KT$	n_2
[130]	174[kPa]	2	10	4.3	1.5	1.0	0.95	0.994	12.5 [kPa]	72
[132]	132 [kPa]	2.3	30	4.65	4.65	1.05	0.78	0.988	3.67 [kPa]	270
[131]	14[kPa]	7	60	9	2.3	1.07	0.35	0.995	52[kPa]	108



Figure 5.10. Comparison of the nominal stress-stretch curves of the model and the experiment for different DN gels.

5.8 Concluding Remarks

A micro-mechanical model for the in-elastic constitutive behavior of DN gels were proposed based on network decomposition concept. In the new model the first network hosts all the damage mechanisms and the second network is represented as a hyper-elastic network. The first network is modeled based on the network evolution model of elastomers which is modified to account for gradual decomposition of the first network in the course of deformation. Using a directional description of damage, a 3D representation of the first network is developed which can describe the evolution of damage in different directions with respect to the applied deformation. Here, the damage is defined as the result of two simultaneous procedure, (i) debonding of chains, and (ii) partial softening of the fragments of the first network. The thermodynamic consistency of the model is verified. The second network is modeled by full-network hyper-elastic model. The final model is bench-marked against several sets of experimental data specifically selected to reveal the directional softening in the material, and the model shows good agreement. This fact, besides the simplicity and the reduced fitting procedure, makes the proposed model a suitable option for commercial and industrial applications.

CHAPTER 6

A PHYSICALLY-BASED MODEL OF STRESS SOFTENING WITH NECKING PHENOMENA FOR DOUBLE NETWORK GELS

6.1 Introduction

Hydrogels are elastomeric gels with chemical (ionic, hydrogen, or covalent) and/or physical crosslinks. These materials swell in water without dissolving and can contain water up to hundred times of their dried volume. In view of their high water content and extremely soft nature, hydrogels are considered as revolutionary materials in different fields such as drug delivery carriers matrix for cell immobilization of bone regeneration, spinal cord injuries, cartilage defects, and super absorbents. Due to poor strength level and fragile response of conventional single network gels, investigation of their mechanical behavior have not been a subject of interest. However, several studies have been conducted on their swelling-deswelling and diffusion-deformation behaviors [98].

Over the last two decades, numerous strategies, such as the use of sacrificial bonds and filler supplementation, have been developed to improve the mechanical properties of hydrogels and fabricate tough hydrogels, including Nano-composite gels and double network hydrogels [102, 133]. Among different types of tough hydrogels, DN gels have attracted increasing attention due to their unique mechanical performance. The DN gels have been designed with two sets of interpenetrated cross-linked networks. The first network, e.g. PAMPS, is highly cross-linked and rigid while the second network, e.g. PAAm, is loosely cross-linked and soft.

The toughening resulted from interactions between polymer networks showed significant im-

provements in mechanical characteristics comparable to load-bearing tissues. These mechanical properties demonstrate great application potentials of DN gels in many scientific fields. The nonlinear behavior of DN hydrogels under large deformation is similar to the most of elastomeric materials especially filled rubbers, which include J-type and S-type inelastic loading and significant softening during the first unloading, known as "Mullins effect" [1, 105]. However, the behavior of the material during consecutive reloading of DN gels is almost the same, which points to negligible hysteresis in the behavior of material. Moreover, DN hydrogel with the first network with low cross-link density or γ -radiation formation demonstrate the necking instability in large deformations.

Utilizing this behavior, researchers proposed constitutive models for DN gels using the concepts close to the ones which have been developed for rubbery materials over the last 70 years [38, 111, 78]. Examples of these studies for mullins effect include Ogden-Roxburgh pseudoelasticity model [115] by Wang and Hong [114] and the modified network evolution model by Morovati and Dargazany [48]. In addition, Zhao [106], Riku and Mimura [134] and Liu et al. [116] enhanced the idea of using superposition of a damageable network and hyper-elastic network to describe necking in DN gels. Despite the fact that these model can effectively model the necking instability through finite element analysis, most of them are not compared against the experimental necking instability data.

Several studies demonstrate that the highly cross-linked first network, which contains short chains, is responsible for damage in DN hydrogels [1, 113]. Breakage of the short chains in the first network develops numerous clusters of hard network, which act like fillers in the filled rubber. In addition, the second network is accountable for preservation of the integrity of the fractured first network and hardening of the material in relatively large deformations [113]. Although, recent advances in the modelling of gels have shown significant improvements in the constitutive relation of DN gels, our understanding of load transfer mechanism within the networks has remained sparse and inconclusive. In addition, clusters of first network split into small and stiffer pieces during the necking, which act as cross-link for the second network [135].

Description of damage process and modeling of high fracture energy, stress softening and necking instability of the DN gel is a critical issue for the applicability of DN gels [135]. In this study, a continuum scale constitutive model of DN gels in quasi-static deformation is developed which can be particularly used to elucidate the inelastic features such as stress softening-hardening of material during primary loading and permanent damage during deformation. The model attributes stress softening to damage in the first network, and hardening to the hyper-elastic stiffening of the second network. In addition, irreversible disentanglement of short chains of the second network from first network cluster determines the stress softening during necking stage. The paper is organized as follows. First, the statistical mechanics of short chains are reviewed. Then, generalized network decomposition concept and the corresponding strain energy function of each network are discussed. Finally, the evaluation of the proposed model against experimental data and the concluding remark are presented.

6.2 Double Network Polymers

DN gels are consist of two polymer networks in which the second network is formed in the presence of the first network. DN gels can be considered as an interpenetrating polymer network in which multiple networks are interwoven and entangled to each other. However, these two networks are not covalently bonded to the other networks chain. A schematic view of the first network and the second network is depicted in Fig. 6.1. The first network has a high cross-link density, which results in a network with short chains. The short chains of the first network have a relatively high initial extensibility ratio, which makes them brittle and more prone to more damage. The second network is synthesized in the presence of the first network with low cross-link density. The chains in this network can be divided into two sub-networks, one with free chains and the other one entangled to chains of the first network. The free chains in the second network act as a hyper-elastic stretchable network with the ability to stretch to very large deformation ranges. Experimental evidence shows that the chains in the first network rapidly breaks in the course of deformation, and the entangled chains of the second network will be unzipped and form longer
chains. These disentanglement can be the source of the gel integrity in larger deformation.

Here, the DN gel matrix is considered as two matrices on top of each other, in which some of the second network chains entangled to the first network chains fragments (see Fig.6.1). The breakage of the shorters chains in the first network decomposes the first network into small individual fragments, while the second network chains connect the fragments to ensure the integrity of the material. Damage in the matrix is related to breakage of the first network chains and disentanglement of the interaction network, meanwhile, the second network chains exhibit a hyperelastic behavior without damage. As the second network chains in the interaction network unzip due to the breakage of first network chains, they transfer the forces between the first network fragments and are responsible for the instability in the larger deformations. The constitutive response and status of the interaction network are schematically depicted in Fig.6.2.



Figure 6.1. Schematics of a DN gel network, decomposition of its networks and their chain distributions. The highly cross-linked first network with short and brittle chains and loose second network with long and flexible polymer chains.

6.2.1 Necking instability

Polymer formation structure e.g. degree of polymerization and cross-link density significantly control the mechanical response of the material, which can cause different non-linear features

such as stress softening and material in-elasticity. For instance, the necking instability is observed in the DN hydrogel with the first network with low cross-link density or γ -radiation formation [136]. In this study, we aim to propose a constitutive model for DN hydrogel, which exhibits both stress-softening and necking inelastic behavior. Deformation process in the DN gel with necking is schematically depicted in Fig. 6.2. As it can be in this figure, the stress-stretch behavior of the material with the necking instability can be split to three individual part including

- (i) *Pre-necking* The evolution of damage in the pre-necking stage can be considered as breakage of brittle chains of the first network. The material experience the softening throughout prenecking stage due to the breakage of the first network.
- (ii) Necking instability The first network chains will be divided into the small cluster connected with long chains of the second network, which progress of this damage will cause the necking. This catastrophic breakage continues until the contribution of the first network become negligible and only acts as a filler inside the second network. Clusters split into small and stiffer pieces during the necking. Presence of the first network as a filler/cross-link play an important role in the stiffness of the material through the necking stage. The stiffness of the second network chains increases due to the increase of its cross-linking density and its behavior changes with respect to the damage in the first network. The entangled chains of the second network release from the fillers, which results in the smooth increasing deformation without further force, necking stage. The released shorter entangled chains in the second network release a considerable amount of the energy, which can be related to the energy released in the necking stage. Remarkable stress softening is observed during the necking due to the continuous releasing the chains [33].
- (iii) Hardening Hardening is the last stage where the sudden increase in stiffness of the material is observed after necking. This stage caused by limiting stretch-ability of the second network. chains. The stretch in the chains increases as high as the locking stretch of the long chains of the second network. Thus, the hardening in the material starts to grow, when the



Figure 6.2. Schematic view of the constitutive behavior and chain unzipping of a DN gel under quasi-static tension showing inelastic features such as stress softening after first loading, permanent damage and necking instability.

entanglements between the clusters and the second network disappear. The second network is considered to be the main stress contributor throughout the hardening. The hardening proceeds up to the complete failure of the material (see Fig. 6.2).

6.2.2 Network decomposition

The deformation gradient, **F** is decomposed as two series event of mechanical \mathbf{F}_m and uni-from swelling $v_p^{-\frac{1}{3}}\mathbf{I}$. The swelled part shows the volume of the sample is changed v_p times uniformly due to water absorption or release. Here, we assumed that these process happen sequential and the sample is nearly incompressible during the mechanical loading. Here, the chain end-to-end vector in the reference state by \mathbf{r}_0 and deformed configuration \mathbf{r} , and their lengths by r_0 and r, respectively. The effect of swelling/drying of the material on constitutive behavior can be considered by linear inflation of the end-to-end distance of the chains R. Thus, one can write

$$\boldsymbol{r} = \mathbf{F}_m \boldsymbol{r}_{\boldsymbol{\theta}}, \qquad r = \overset{d}{\lambda} v_p^{-\frac{1}{3}} R,$$
 (6.2.1)

where $\overset{d}{\lambda} = \sqrt{d\mathbf{F}_m^T \cdot \mathbf{F}_m d}$ is the stretch along an arbitrary direction d. Hereafter, the following font styles are used for scalar X, vector \mathbf{X} , and second-order \mathbf{X} .

The decomposition of material strain energy function, $\Psi_N(\mathbf{C})$, to isochoric and volumetric parts yields to (see e.g. [32])

$$\Psi_N(\mathbf{C}) = \Psi_M(\bar{\mathbf{C}}) + U(J), \tag{6.2.2}$$

where $\mathbf{C} = \mathbf{F}^T \mathbf{F}$ is the right Cauchy-Green tensor, $J = \sqrt{\det \mathbf{C}}$ and $\bar{\mathbf{C}} = J^{-\frac{2}{3}}\mathbf{C}$. As discussed in the section 6.2.1, the constitutive behavior of DN gels is composed of three different networks response. Therefore, the isochoric strain energy of the material can be calculated by the summation of the first (1N), the second (2N) networks and the interaction network (12) strain energy. These networks act in parallel to each other (see Fig. 6.2). Thus, the isochoric strain energy of the gel matrix Ψ_M can be written as

$$\Psi_M = \Psi_1 + \Psi_{12} + \Psi_2, \tag{6.2.3}$$

where Ψ_1 and Ψ_2 are the 1st and 2nd networks strain energies per unit reference volume of the material, respectively. Ψ_{12} denotes the isochoric energy of second network chains entangled with first network clusters per unit reference volume. Here, the first network chains breakage and debonding are considered as source of permanent damage, as the de-bonded chains will not reattach back to the network. This damage can affect both the first network and the interaction network micro-mechanically. Thus, a damageable model is considered to capture these two networks and a hyper-elastic behavior with no damage is considered for the second network to ensure integrity of the network.

Here, the model is developed through the modular platform concept [137, 68]. The framework couples different models to represent each of the networks. Here, a damage evolution model is used to capture the behavior of the first network and the interaction network. The evolution model adopted for each of these network in the term of damage rate and probability of chain distribution to model a network which is weaken in large deformation and a growing network model. A hyperelastic network inserted to the framework to capture the behavior of the second network. Note that each of these network model can be replaced, upgraded or removed without affecting the generality of the model. In this study, the network developed to model only permanent damage, however, other model can be added to consider other inelastic features such as cyclic damage, progressive damage, etc.

The entropic energy of a single chain can be calculated through polymer statistical mechanics. A micro-sphere scale-transition scheme is designed to estimate the strain energy of full-network model.

The total free energy density function for a network can be obtained through integration of the chains in each direction. The averaged free energy density function of the network with a orientation distribution function in direction d_i , $\overset{d_i}{C}$ can be written as

$$\Psi_i = \frac{1}{A_s} \int\limits_S \int C \psi_i du^d du$$
(6.2.4)

where S is the unit micro-sphere, A_s is the surface area, and d^{d}_{u} the infinitesimal area of A_s in the direction d. In addition, ψ^{d}_{j} denotes the strain energy of the ith sub-network in the direction d. The integration on the unit micro-sphere of the macroscopic energy can be estimated numerically

$$\Psi_i \cong \sum_{j=1}^k \overset{d_j}{\psi_i} w_j, \tag{6.2.5}$$

and w_i is the associated weight factor to spatial directions d_i . Here, the numerical scheme is



Figure 6.3. Schematic framework of proposed model consisting of three sub-networks. The first and interaction networks considered as a stochastic damageable models and the second network as a hyper-elastic network.

calculated through the 90 integration points presented in [129]. This scheme is selected as a result of trade off between numerical computational costs and the resulted error of the induced anisotropy [128]. Note that the resulted summation numerical scheme can be interpreted as aggregation of 90 chains in different direction and probability. In addition, different stretch in each direction leads to a non-uniform damage evolution and histories in each sub-network. 3D representation of the model can be obtained based on the summation of energy of each 1D sub-network in all direction. Thus, a damageable network evolution model of 1D sets of chains are developed here to model constitutive behavior of the material.

6.3 Micro-mechanics of a Single Chain

The free energy of a single polymer chain can be calculated through the non-Gaussian distribution of a random walk problem. The most prominent approximation of the non-Gaussian theory of rubber elasticity is the KG. The KG strain energy of a single chain can be derived using the combination of the Boltzmann's entropy relation and thermodynamic balance as,

$$\psi_c(n, \bar{\boldsymbol{r}}) = nk_B T \left(t\beta + \ln \frac{\beta}{\sinh \beta} \right) + c_0$$

= $nk_B T \int_0^t \beta \, d\tau + c_0,$ (6.3.1)

where k_B denotes the Boltzmann's constant and T is the absolute temperature. $\beta(\beta)$ is the ILF of the extensibility ratio, $t = \frac{\bar{r}}{n} = \mathcal{L}(\beta) = \coth(\beta) - \frac{1}{\beta}$ and $c_0(n)$ is added to eliminate the free energy in reference configuration. In addition, \bar{r} denotes normalized end-to-end vector with respect to the segment Kuhn length l. However, Kuhn and Grün is derived the KG model based on the assumption that the chains are sufficiently long, which the relative error decreases as the chain length increases (about 5% for n = 40) [50, 119]. This approximation has as much as 100 % relative error with respect to the exact theory for short chains (see Fig.). Thus, the KG theory is not a proper choice to describe constitutive behavior of short chains with high extensibility of the first network in the DN hydrogels. A novel and simple enhanced KG is developed recently with remarkable accuracy with respect to the exact theory for short chains, which can be written as [121]

$$\hat{\psi}_{c}(n,\bar{r}) = nk_{B}T \int_{0}^{t} \hat{\beta}(\tau;n) d\tau,$$

$$\hat{\beta} = \left[1 - \frac{1+t^{2}}{n}\right] \beta.$$
(6.3.2)

Eq. 6.3.2 a simple term with order of $\frac{1}{n}$ (the first bracket) is multiplied to the ILF to improve the accuracy of the energy function for especially the short chains. Note that the ILF cannot be derived explicitly and most of the micro-mechanical models approximate it with rational functions



Figure 6.4. The maximum relative error of the KG and enhanced KG for chains with different length.

or calculate it implicitly. Therefore, this modification has same complexity as KG theory. In addition, the ILF should be approximated by a simple approximation with good accuracy in the whole range of polymer chains extensibility [59, 2, 138]. In this study, the ILF is approximated through a first order fractional approximation with two polynomial terms (relative error of 1.0%) as (see [59])

$$\mathcal{L}^{-1}(x) \cong \frac{1}{1-x} + x - \frac{8}{9}x^2.$$
 (6.3.3)

6.4 Statistical Network Model

The polymeric response resulted from the response of individual chains and their interactions. In order to provide a full description of the constitutive model, we start with the statistical description of the material in a given representative volume element (RVE). The statistical view leads to an average response of the material, which can represent the response of the whole RVE. For the sake of simplicity, we assumed that all active chains have their average end-to-end distance, which is characterized by r_0 for the first network with the shorter chains and Gaussian most probable end-toend distance, *sqrtn* for the longer chains of the second network. This assumption can be relaxed, as the probability of the existence of the chains is a joint distribution, which can simply take into account the effect of stochastic end-to-end distance as well as chain length. The total strain energy of the network can be evaluated by aggregating the stored energy of all the active chains in the RVE. To further investigate the micro-mechanical chain distribution for the non-isolated chains, we proposed a novel and simple chain length distribution is presents of the cross-linkage or entanglement, which will be described in detail in the next section.

6.4.1 Probability of chain length between cross-links

Polymer chains are joined together due to the present of cross-links and entanglement of the chains within the polymer matrix. Both Gaussian and non-Gaussian distribution function of chain existence with n segment is developed based on the assumption of the fully isolated chain, which makes them insufficient for finding the distribution of chain length in entangled and cross-linked polymers. In order to consider the effect of the presence of other chains and cross-linkage on the distribution of chain length, we assumed the distribution can be obtained by considering the independent probability of Gaussian end-to-end and the probability of occurrence of cross-link or entanglement in the middle of the chain as

$$P_n(n, r_0) = P_G(n, r_0) P_{cl}(n)$$
(6.4.1)

where $P_G(n, r_0)$ is the probability chain existence and $P_{cl}(n)$ is the probability of the crosslinkage. The probability of the existence of a chain with n segments (with Kuhn length a) and end-to-end distance r_0 is assumed to follow 3-D Gaussian distribution as

$$P_G = \left(\frac{3}{2\pi na^2}\right)^{\frac{3}{2}} \exp\left(-\frac{3r_0^2}{2na^2}\right).$$
 (6.4.2)

In P_G , most probable chain has r_0^2 segments which confirms that the probability of existence of long chains in the matrix is much higher than the short chains. Although by best of our knowledge, the physics of entanglement and chemistry of cross-linking is too complicated and is not known completely, generally it can be considered as a random phenomena. Here, we assume that this random process is uniform and the probability of the cross-linking of all segments is the same. The



Figure 6.5. Schematic representation of a cross-linked network and probability of existence of cross-link at the end of each segment .

cross-linking probability can be calculated as a ratio of the concentrations of cross-links agents to the number backbone segments as

$$p_c = \frac{2[C]_{crosslink}}{[C]_{segments}}$$
(6.4.3)

In this equation, the concentrations of cross-links agents is multiplied by two to consider that each cross-link reacts with two segments. Thus, the probability of existence of a chain between two cross-links with n segments is the product of the probability of n - 1 joints without cross-link and two joint with cross-link (6.5), which can be written as

$$P_1(n) = p_c^2 \left(1 - p_c\right)^{n-1}.$$
(6.4.4)

Note that a polymer chain with entanglement or cross-link at a middle Kuhn segments instead of ending segments considered as two chains with shorter lengths. Combining Eqs. 6.4.2 and 6.4.4, one can obtain the probability of chain existence between two cross-links with n segment and end-to-end distance r_0 as

$$P_n(n, r_0) = P_0 \left(1 - p_c\right)^n \left(\frac{3}{2\pi n a^2}\right)^{\frac{3}{2}} \exp\left(-\frac{3r_0^2}{2n a^2}\right),\tag{6.4.5}$$

where P_0 is a normalization factor to ensure the integration of probability over all chains results one. As it can be seen in this equation the chain length distribution function, $P_n(n, r_0)$ is a function of both end-to-end distance and cross-linking probability. Increasing r_0 and decreasing p_c both



Figure 6.6. Effect of p_c and R_0 on the probability of polymer chain existence with n segments between cross-links.

leads to a wide probability with longer chains. However, their combination can produce different shape of probability function as it can be seen in Fig. 6.6.

6.4.2 Distribution alteration due to damage

The experimental evidence shows that DN gels have almost negligible hysteresis after the first cycle, the same unloading and reloading response. The material follows the primary load curve after it reaches to the maximum stretch experienced before. Based on this observation in addition to the fact that damage is permanent, one can assume damage as a function of the maximum stretch in the material, λ_{max} . This damage remains constant during unloading/reloading cycles until deformation reaches to the λ_{max} . However, recently the experiments by Mai et. al [139] showed that DN gels have deformation-induced anisotropy, which suggests that the damage is not uniform in different directions. Thus, we assume the material has a uniform distribution in the virgin state and the damage will be evolved in the direction d_i based on the maximum stretch in that direction. Here, we described the permanent damage as two coincident events of breakage of the chains bonds and creation of the longer chains. These two processes cause the alteration of the chain distribution function in two ways (i) change in the sets of available chains and (ii) amplifying the presence of longer chains

(i) *Chain breakage:*

The strain energy function of a single chain tends to infinity as the chain end-to-end distance, r, approaches the ultimate locking value nl during the primary loading. However, a chain cannot sustain indefinite force and energy. So, it will break from its cross-link or bond at an effective breakage force, f_e . Thus, the highly extended shorter chains start to break as they reach to the locking stretch sooner than longer chains. This process cause a progressive change in the chain distribution as the set of available chains will shrink in the course of deformation. By considering a finite breakage force of a chain with n segment, f_b , the domain of available chains in a damaged sub-network is determined as

$$\frac{\partial \hat{\psi}_c(n,\bar{r})}{\partial r} = \frac{k_B T}{l} \hat{\beta}(t;n) \le f_b \quad \to \quad D_n^d = \{\frac{\lambda_{max} \bar{r}_0}{\xi} \le n \le n_{max}\}, \tag{6.4.6}$$

where $\xi \approx \mathcal{L}\left(\frac{f_b}{k_B T}\right) < 1$ is the maximum extensibility rate and it control the Mullins effect in the material. Chains at the stretch equal to ξn and force equal to f_b break from its bonds or the cross-link. Similarly, the sets of available chains for the interaction network with the most probable end-to-end distance \sqrt{n} can be written as

$$D_{n}^{d} = \{ max(2, \frac{\lambda_{max}^{d^{2}}}{\xi^{2}}) \le n \le n_{max} \},$$
(6.4.7)

where the minimum value for n is restricted to avoid chains with length 1.

(ii) Evolution of longer chains:

The chains disentanglement or breakage from the cross-links lead to a partial loss of chains entropic energy upon their detachment. As a result, some the chains remain active in the network and form a longer macro-molecules. The concept of alteration of distribution function suggests that α fraction of the broken chains actively contribute in the network and the rest of will be dead-end. A detailed discussion of this concept has been provided in [48]. This assumption yields to a amplification factor, which shows that the network contain more longer chains (see Fig.) as



Figure 6.7. The probability distribution alteration in the course of deformation and the schematic view of longer chains activated due to detachment of the shorter chains.

$$N_{i}(\lambda_{max}) = N_{i}\Phi(\lambda_{max}),$$

$$\int n P_{n}(n)dn$$

$$\Phi(x) = 1 + \alpha \frac{\int n(1) \beta D_{n}(x)}{\int n P_{n}(n)dn}.$$
(6.4.8)

where α is a parameter governing the rate of energy dissipation and N_i is the initial number of chains in the *i*th network, both of which are considered as material constants. Here, we assumed that all the chains in the first network will be deactivated ($\alpha = 0$) and will not contribute in the network. In addition, due to breakage of the first network chains some of interaction network chains will be unzipped and form longer chain. Thus, all of the interaction networks chains will remain active in the network ($\alpha = 0$). These assumptions are made here to limit the number of material parameters and can be released in order to reach to more general form of the constitutive model.

6.4.3 Total energy of sub-network

The stored energy of each sub-network direction can be evaluated by calculating the average value of free energy of the all available chains in that direction. According to the statistical theory of elastomer elasticity and the alteration probability of existence of chains in an arbitrary direction, the average free energy of the damageable networks in that direction can be calculated as

$$\psi_i^d = \int\limits_{D_n^d} \tilde{N}_i \begin{pmatrix} d \\ \lambda_{max} \end{pmatrix} \psi_c(n, \bar{r}_0^i \lambda) P_n^i(n) dn,$$
(6.4.9)

where *i* stands for first (1) and interaction network (12), N_i is the total number of active chains in the unit volume of the material in the *i*th network and D_n^d the set of available chain lengths in direction *d*. r_0^i denotes the end-to-end distance in *i*th network, which is r_0 for first network and \sqrt{n} for the interaction netwok. As the breakage of the chains in the first network is responsible for disentanglement of the chain in the interaction network, the process of chain debonding is the same for both networks. However, first network chains de-bond due to the load transfer between two networks.

6.5 Hyper-elastic Model

The chains in the second network that do not entangled by the fragments of the first network can be considered as free chains with hyper-elastic behavior. As it has been mentioned, these chains are responsible for the mechanical integrity of the gel. Let us consider, this network as an assembly of N_2 chains with the uniform spatial distribution. This network contains long chains with an average length of n_2 segments with the most probable end-to-end distance same as interaction network, which has same chains with a random entanglement to first network chains. Thus, in view concept of full network model, the strain energy of the sub-networks of the second network can be obtained as

$$\psi_2^d = N_2 \psi_c \left(n_2, \lambda^d \right), \tag{6.5.1}$$

where the parameters N_2 , and n_2 are considered as material parameters. Note that this hyper-elastic model can be considered as entropic energy of chains uniformly distributed over a unit sphere.

6.6 Constitutive Model

The total macroscopic energy of gel matrix can be calculated through the concept of network decomposition (Eq. 6.2.3), micro-sphere scale-transition (Eqs. 6.2.4, 6.2.5) in and the total energy of the each sub-networks (Eqs.6.4.9, 6.5.1) as

$$\begin{split} \Psi_{M} &= \Psi_{1} + \Psi_{12} + \Psi_{2} \\ &= N_{1} \sum_{i=1}^{k} \left[w_{i} \Phi_{1} \begin{pmatrix} d_{i} \\ \lambda_{max} \end{pmatrix} \int_{D_{n} \begin{pmatrix} d_{i} \\ \lambda_{max} \end{pmatrix}} P_{n}^{1}(n) \hat{\psi}_{c}(n, r_{0} \frac{d_{i}}{\lambda}) dn \right] \\ &+ N_{12} \sum_{i=1}^{k} \left[w_{i} \Phi_{12} \begin{pmatrix} d_{i} \\ \lambda_{max} \end{pmatrix} \int_{D_{n} \begin{pmatrix} d_{i} \\ \lambda_{max} \end{pmatrix}} P_{n}^{12}(n) \hat{\psi}_{c}(n, \sqrt{n_{2}} \frac{d_{i}}{\lambda}) dn \right] \\ &+ N_{2} \sum_{i=1}^{k} w_{i} \hat{\psi}_{c}(n_{2}, \sqrt{n_{2}} \frac{d_{i}}{\lambda}) \end{split}$$
(6.6.1)

One can derive the constitutive equation of the first-Piola-Kirchhoff stress tensor \mathbf{P} based on total macroscopic energy function as

$$\mathbf{P} = \frac{\partial \Psi_M}{\partial \mathbf{F}} = \frac{\partial \Psi_1}{\partial \mathbf{F}} + \frac{\partial \Psi_{12}}{\partial \mathbf{F}} + \frac{\partial \Psi_2}{\partial \mathbf{F}},\tag{6.6.2}$$

where

$$\frac{\partial \Psi_i}{\partial \mathbf{F}} = v_p N_i \sum_{j=1}^k w_j \frac{\partial \psi_i}{\partial \lambda} \frac{1}{2 \lambda} \frac{\partial \boldsymbol{d}_j \bar{\mathbf{C}} \boldsymbol{d}_j}{\partial \bar{\mathbf{F}}} : \frac{\partial \bar{\mathbf{F}}}{\partial \mathbf{F}}, \quad i \in \{1, 12, 2\}.$$
(6.6.3)

By considering the enhanced KG entropic force, $\frac{\partial \hat{\psi}_c(n,r)}{\partial r} = \frac{KT}{l}\hat{\beta}(n,r)$, one can further simplify Eq. 6.6.3 as

$$\frac{\frac{\partial q_{i}}{\partial \lambda}}{\frac{\partial \lambda}{\lambda}} = v_{p}N_{i}k_{B}T\Phi_{i}\begin{pmatrix} d_{j}\\ \lambda_{max} \end{pmatrix} \int_{\substack{d_{j}\\ D_{n}(\lambda_{max})}} \bar{r}_{0}^{i}P_{n}^{i}(n)\hat{\beta}\left(n,\bar{r}_{0}^{i}\lambda\right)dn \quad i \in \{1,12\}$$
(6.6.4)

$$\frac{\frac{\partial d_j}{\partial \psi_2}}{\frac{\partial \lambda}{\lambda}} = v_p^{-\frac{1}{3}} \sqrt{n} k_B T \hat{\beta} \left(\frac{x v_p^{-\frac{1}{3}}}{\sqrt{n}}, n \right),$$

where $\hat{\beta} = \mathcal{L}^{-1}(t) \left(1 - \frac{1+t^2}{n}\right)$. In addition, following identities can be substituted in the Eq. 6.6.3

$$\frac{\partial d\bar{\mathbf{C}}d}{\partial\bar{\mathbf{F}}} = 2\bar{\mathbf{F}}(d\otimes d), \quad \frac{\partial\bar{\mathbf{F}}}{\partial\mathbf{F}} = J^{-\frac{1}{3}}\mathbf{I}.$$
(6.6.5)

Thus, by substituting Eqs. 6.6.3, 6.6.4 and 6.6.5 in Eq. 6.6.2 the first Piola-Kirchhoff stress can be written as

$$\mathbf{P} = v_p^{\frac{2}{3}} k_b T \sum_{i=1}^{k} \left(P_1(\boldsymbol{d}_i) + P_{12}(\boldsymbol{d}_i) + P_2(\boldsymbol{d}_i) \right) \frac{w_i}{\frac{d_i}{\lambda}} J^{-\frac{1}{3}} \bar{\mathbf{F}}(\boldsymbol{d}_i \otimes \boldsymbol{d}_i),$$
(6.6.6)

where

$$P_{i}(\boldsymbol{x}) = N_{i}\Phi_{i}\begin{pmatrix}\boldsymbol{x}\\\lambda_{max}\end{pmatrix}\int_{D_{n}^{i}(\lambda_{max})}P_{n}^{i}(n)\mathcal{L}^{-1}(t_{i})\left(1-\frac{1+t_{i}^{2}}{n}\right)dn \qquad i \in \{1, 12\},$$

$$P_{2}(\boldsymbol{x}) = N_{2}\sqrt{n_{2}}\mathcal{L}^{-1}\left(\frac{\boldsymbol{x}}{\lambda v_{p}^{-\frac{1}{3}}}\right), \qquad (6.6.7)$$

where $t_1 = \frac{\frac{x}{\lambda} v_p^{-\frac{1}{3}} \bar{r_0}}{n}$ and $t_{12} = \frac{\frac{x}{\lambda} v_p^{-\frac{1}{3}}}{\sqrt{n}}$.

6.7 Finite Element Linearization

In this section, the equations for the calculation of second Piola-Kirchhoff stress and consistent tangent modulus, required for the finite element implementation, are presented. The incompressible plane stress situation in total Lagrangian finite strain is considered, and indicial notation is used in equations for clarity.

In order to utilize the Newton-Raphson Method, the second Piola-Kirchhoff stress, S, should be linearized. Its variation could be written as

$$dS = \mathbb{C}dE \tag{6.7.1}$$

Where \mathbb{C} is the material tangent modulus, and E is the Green-Lagrange strain tensor. The second Piola-Kirchhoff stress is defined as

$$S_{ij} = \frac{\partial \Psi_M}{\partial E_{ij}} - pdetC^{1/2}C_{ij}^{-1} = 2\frac{\partial \Psi_M}{\partial \bar{C}_{mn}}\frac{d\bar{C}_{mn}}{dC_{ij}} - pdetC^{1/2}C_{ij}^{-1}$$
(6.7.2)

The fourth order deviatoric projection tensor in Lagrangian description, $\frac{d\bar{C}_{ij}}{dC_{kl}}$, is

$$\frac{d\bar{C}_{ij}}{dC_{kl}} = detC^{-1/3} \left(\mathbb{I}_{ijkl} - \frac{1}{3}C_{ij}C_{kl}^{-1} \right)$$
(6.7.3)

With I as the fourth order identity tensor. By substituting (3) into (2), and defining S^n and A

$$2\frac{\partial \Psi_M}{\partial \bar{C}_{ij}} = S^n D_i D_j \tag{6.7.4}$$

$$A = D_m D_n C_{mn} \tag{6.7.5}$$

the second Piola-Kirchhoff stress is expressed as

$$S_{ij} = det C^{-1/3} S^n \left(D_i D_j - \frac{1}{3} A C_{ij}^{-1} \right) - p det C^{1/2} C_{ij}^{-1}$$
(6.7.6)

In order to find the Lagrange multiplier p, the plane stress assumption is used, and the Cauchy stress in the out-of-plane direction is set to zero. In this manner, p is obtained

$$p = det C^{-5/6} S^n \left(F_{33}^2 D_3^2 - \frac{1}{3} A \right)$$
(6.7.7)

By replacing (7) into (6), the final expression for S_{ij} is obtained

$$S_{ij} = det C^{-1/3} S^n \left(D_i D_j - F_{33}^2 D_3^2 C_{ij}^{-1} \right)$$
(6.7.8)

The material tangent modulus is calculated by taking derivative of S with respect to E

$$\mathbb{C}_{ijkl} = \frac{\partial S_{ij}}{\partial E_{kl}} = 2\frac{\partial S_{ij}}{\partial C_{kl}} = 2\frac{\partial S_{ij}}{\partial \bar{C}_{mn}}\frac{d\bar{C}_{mn}}{dC_{kl}}$$
(6.7.9)

By defining

$$4\frac{\partial^2 \Psi_M}{\partial \bar{C}_{ij} \partial \bar{C}_{kl}} = \mathbb{C}^n D_i D_j D_k D_l \tag{6.7.10}$$

The material tangent modulus is calculated

$$\mathbb{C}_{ijkl} = -\frac{2}{3} \left(detC \right)^{-1/3} S^n \left(D_i D_j - F_{33}^2 D_3^2 C_{ij}^{-1} \right) C_{kl}^{-1} + \left(detC \right)^{-2/3} \mathbb{C}^n \left(D_i D_j - F_{33}^2 D_3^2 C_{ij}^{-1} \right) \left(D_k D_l - \frac{1}{3} A C_{kl}^{-1} \right) + \left(detC \right)^{-1/3} S^n \left(-4F_{33} D_3^2 C_{ij}^{-1} \frac{dF_{33}}{dC_{kl}} - 2F_{33}^2 D_3^2 \frac{dC_{ij}^{-1}}{dC_{kl}} \right)$$
(6.7.11)

By knowing that the shear terms in the out-of-plane direction, S_{31} , S_{13} , S_{32} and S_{23} , are zero, and using the Voigt notation, the matrix form of (1) is expressed as

$$\begin{bmatrix} dS_{11} \\ dS_{22} \\ dS_{12} \\ dS_{33} \end{bmatrix} = \begin{bmatrix} \mathbb{C}_{11} & \mathbb{C}_{12} & \mathbb{C}_{13} & \mathbb{C}_{14} \\ \mathbb{C}_{21} & \mathbb{C}_{22} & \mathbb{C}_{23} & \mathbb{C}_{24} \\ \mathbb{C}_{31} & \mathbb{C}_{32} & \mathbb{C}_{33} & \mathbb{C}_{34} \\ \mathbb{C}_{41} & \mathbb{C}_{42} & \mathbb{C}_{43} & \mathbb{C}_{44} \end{bmatrix} \begin{bmatrix} dE_{11} \\ dE_{22} \\ 2dE_{12} \\ dE_{33} \end{bmatrix}$$
(6.7.12)

In the finite element simulation in plane stress condition, the displacement in the out-of-plane direction is not an independent variable, and therefore dE_{33} should be removed from (12). As $dS_{33} = 0$ and $\mathbb{C}_{44} = 0$, the static condensation could not be utilized. Thus, to remove dE_{33} , it should be expressed in terms of dE_{11} , dE_{22} and dE_{12} . To do so, and by having

$$E_{33} = \frac{1}{2} \left(C_{33} - 1 \right) = \frac{1}{2} \left(F_{33}^2 - 1 \right)$$
(6.7.13)

 dE_{33} could be expressed as

$$dE_{33} = \frac{dE_{33}}{dE} dE = \frac{dE_{33}}{dF_{33}} \frac{dF_{33}}{dC} \frac{dC}{dE} dE = 2F_{33} \frac{dF_{33}}{dC} dE$$

= $2F_{33} \left(\frac{dF_{33}}{dC_{11}} dE_{11} + \frac{dF_{33}}{dC_{22}} dE_{22} + 2\frac{dF_{33}}{dC_{12}} dE_{12} \right)$ (6.7.14)

Finally, for the plane stress situation, (1) could be rewritten as

$$dS = (\mathbb{C} + \mathbb{C}\mathbb{C}) \, dE \tag{6.7.15}$$

where

$$\mathbb{CC} = 2F_{33} \begin{bmatrix} \frac{dF_{33}}{dC_{11}} \mathbb{C}_{14} & \frac{dF_{33}}{dC_{22}} \mathbb{C}_{14} & 2\frac{dF_{33}}{dC_{12}} \mathbb{C}_{14} \\ \frac{dF_{33}}{dC_{11}} \mathbb{C}_{24} & \frac{dF_{33}}{dC_{22}} \mathbb{C}_{24} & 2\frac{dF_{33}}{dC_{12}} \mathbb{C}_{24} \\ \frac{dF_{33}}{dC_{11}} \mathbb{C}_{34} & \frac{dF_{33}}{dC_{22}} \mathbb{C}_{34} & 2\frac{dF_{33}}{dC_{12}} \mathbb{C}_{34} \end{bmatrix}$$
(6.7.16)

and $\frac{dF_{33}}{dC_{ij}}$ is given by

$$\frac{dF_{33}}{dC_{ij}} = \frac{dF_{33}}{dF_{mn}}\frac{dF_{mn}}{dC_{ij}} = \frac{1}{2}Q_{mn}\delta_{nj}F_{im}^{-1} = \frac{1}{2}F_{im}^{-1}Q_{mj}$$
(6.7.17)

$$Q = \frac{dF_{33}}{dF} = F_{33}^2 \begin{bmatrix} -F_{22} & F_{21} & 0\\ F_{12} & -F_{11} & 0\\ 0 & 0 & 0 \end{bmatrix}$$
(6.7.18)

The term $\mathbb{C} + \mathbb{CC}$ is the tangent operator in the finite element formulation. The detailed derivation of S^n and \mathbb{C}^n are given in the appendix.

6.8 Model Validation

In the following section, model prediction on Mullins effect and necking instability is compared with the experimental results. The model's material parameters are minimized in order to simplify the model. In the first network, the parameter α is set equal to zero, which means the energy of all broken chains in this network will released and the network will have significant softening after necking initiation. Note that response the first network is dominant in the pre-necking and the material parameters of this network $(N_1, \xi, p_c^1 \text{ and } r_0)$ can be defined by using the experimental data from pre-necking stage. Moreover, the probability of entanglement of the second network chains to the first network clusters is assumed to be a small value (less than 5%) and the breakage of the cluster does not affect the number of active chains in the interaction network. The material parameters of the interaction network $(p_c^{12} \text{ and } N_{12})$ can be obtained by adjusting model in the necked stage as this network should cancel the softening due to breakage of the first network. Finally, the second network is responsible for the hardening of the material in large deformations and its material parameters (N_2 and n_2) can be obtained from the hardening stage of the experimental data. Note that the longest chain available for both first network and the interaction network is assumed that to be equal to n_2 as the free chains of the second network should be the longest chains in the matrix.

The proposed model has 8 material parameters in total in which N_1 can be obtained by scaling of the data and the model, the p_c^{12} is preset to a small value and 6 remaining parameters should be obtained through an error minimization approach. The maximum difference of the model prediction and the experimental data is considered as error and a min-max optimization scheme is used to find the material parameters.

To investigate the performance of proposed constitutive model, the experimental data for uniaxial tension tests from the work of Nakajima et al. [135] are used. The truly independent DN hydrogels used by Nakajima et. al. were synthesized through a two-step sequential photopolymerization, where the first network was made from a 1 M aqueous solution of AMPS crosslinked with 4 mol % MBAA, and the second network, PAMPS was synthesized afterward around the first swollen network (for details see [135]). In order to investigate the performance of the proposed model, it will be evaluated with a set of uni-axial tensile tests, in which virgin dumbbellshaped specimens were elongated up to certain stretch levels as high as 11.8, and then unloaded to 0 (one complete uni-axial tension cycle). Through fitting the model to the loading-unloading cycle of a tension test with the maximum stretch amplitude of 11, 8 material parameters is adjusted and the fitted curve is plotted against experimental test in Fig.6.8.

The model capability is tested against two other types of DN hydrogels. First, the model predictions are compared with the experimental data of tensile loading-unloading for SAPS(1,2,2,9)/AAm (2,0.1,0,97) DN hydrogel. The loading behavior and the unloading behavior at stretch equal to 3, 7.5 and 13 are presented in the Fig. 6.8. Furthermore, the tensile behavior of multi-network hydrogel with instability is compared with the presented constitutive law, which is presented in Fig 6.10 along with the contribution of each network. As it can be seen in this figure, the network one has significant softenning after necking initiation and the interaction network grow to cancel its effect. In each sets of experiments, one loading and one unloading is used to find the material parameters. The parameters for all experimental data are derived and summarized in Table 6.1.



Figure 6.8. Comparison of the nominal stress-stretch curves of the model and the experiment for the uniaxial tensile experiment [3].

6.9 Numerical Simulations

In order to further assess the proposed model for constitutive behavior of DN hydrogels, the necking phenomenon is modeled using the finite element method. A $1 \times 1 \text{ mm}^2$ specimen is considered in the plane stress condition, and due to the symmetry, only one quarter of the specimen is modeled and symmetrical boundary conditions are employed. The uni-axial tension test is performed by prescribing displacement on the right edge of the specimen. The geometry and boundary conditions are presented in Fig. 6.11. In order to trigger the localization, the length of the left edge has been chosen to be slightly smaller than the right edge, $l_{left} = (1 - \beta) l_{right}$, and it will be shown that by choosing small value for this parameter, the results are independent of the chosen value of this parameter. However, it should be noted that as the onset of necking in the finite element simulation is a bifurcation point, and the necking could be captured even by $\beta = 0$ and choosing specific load step size before the bifurcation point.

It should be highlighted that due to the softening of the DN gel, the boundary value problem losses ellipticity and becomes ill-posed, and a regularization method should be utilized [140, 141, 142]. However, the softening has not been regularized in this simulation. In order to demonstrate one of the consequences of loss of ellipticity, the mesh dependence, two types of meshes, namely

Experiment	$N_1 k_B T$	r_0	ξ	p_c^1	$N_{12}k_BT$	p_{c}^{12}	$N_2 k_B T$	n_2
[3]	29.5	11.5	0.999	0.195	146.6	0	6.9	236
[4]	9.66	5.5	0.999	0.27	23.35	0.01	2.21	260
[5]	190.5	15	0.997	0.33	1435	0.015	120.4	50

Table 6.1. Material parameters of the constitutive model fitted to the tensile test performed on a different set of hydrogels data.



Figure 6.9. Comparison of the nominal stress-stretch curves of the model and the experiment for the uniaxial tensile experiment [4].

aligned and unaligned, with two levels of refinements are utilized, which are shown in Fig. 6.12. 4-noded quadrilateral elements with full integration are used in this study.

According to [143], the propagating necking could be considered as a first order phase transition, and the transition stress could be calculated according to the Maxwell's rule. The experimental and simulated stress-stretch curves with $\beta = 1e - 3$, together with the calculated Maxwell's line are depicted in Fig. 6.13 for various meshes. It can be seen that the mesh dependence and oscillations in the necking propagation stage of the finite element simulation are more pronounced in the case of aligned meshes. In this case, each oscillation corresponds to localization of one



Figure 6.10. The model prediction for pre-necking and full response of the material along with contribution of each network in total response of [5].

column of meshes, and each interval is a scaled version of constitutive behavior from the peak to the point where the stress reaches the peak again in the re-hardening. Therefore, the number of oscillations is equal to the number of columns of elements. It should be highlighted that the same results and conclusions are presented in [144] for modeling of the Lüders band, which is a propagating localization in metals, very similar to the necking of the hydrogels. The influence of β on the response of the necking for one of the aligned meshes is presented in Fig. 6.14. Obviously, the results are independent of the chosen value for beta.

In the case of unaligned meshes, the simulations and experimental results are in good agreement; and the yield stress and strain, transition stress and the hardening stage are predicted with good accuracy in the simulations. The three distinct deformation stages, namely the pre-necking,



Figure 6.11. The finite element simulation of the necking of DN hydrogels; geometry and boundary conditions.



Figure 6.12. The finite element discretization of the necking of DN hydrogels; a) Aligned 2x2, b) Aligned 4x4, c) Unaligned coarse, d)Unaligned fine.



Figure 6.13. The Necking of DN hydrogels: A comparison of stress-stretch curves between the experimental results and the finite element simulation.



Figure 6.14. The finite element simulation of the necking of DN hydrogels; effect of β , i.e. imperfection size, on the response.



Figure 6.15. The finite element simulation of the necking of DN hydrogels; various stages of necking.

necking and hardening could be distinguished in this case. In the pre-necking stage ($\lambda < 2.4$), the deformation is homogeneous and no necking has occurred. After reaching the yield stress, the stress has a sudden drop following by a plateau ($2.4 \le \lambda < 4.4$), which demonstrate the necking stage. In this stage, the necking initiates from the left edge of the specimen and propagates to the right, and the stress level remains approximately constant. Finally, after the necking has propagated through the whole specimen, the deformation becomes homogeneous again ($\lambda > 4.4$) and the stress will be increasing. The aforementioned stages are shown in Fig. 6.15.

6.10 Conclusion

In this work, a micro-mechanical model based on the concept of network decomposition is developed to describe the constitutive behavior of DN gels in large deformations. In this model, the DN gel is considered as an assembly of the first and second networks, which interacts with each other at large deformations. The first network and the interaction mode are derived by advancing the previously developed network evolution model of carbon black filled rubber. Permanent damage is considered for these network, to describe the stress softening, which is a consequence of two simultaneous procedures, (i) debonding of chains, and (ii) partial disentanglement of the second network chains from first network fragments. The full network model is used for the second network, to achieve hyper-elastic behavior up to very large stretches. Upon integration of the network models in all spatial directions and summing the contribution of the two networks, a 3D representation of the polymer matrix is obtained. The performance of the model is illustrated by comparing its results with a set of experimental data, specifically selected to reveal the softening in the material. The results of the proposed model show a good agreement with the experimental data. In addition to the simplicity of the proposed model, its performance makes it a suitable option for commercial and industrial applications.

APPENDIX

Derivation of S^n and \mathbb{C}^n

In this section, necessary equations for evaluating S^n and \mathbb{C}^n are given. The free energy of the DN gel is expressed as

$$\Psi_{M} = \Psi_{1N} + \Psi_{12N} + \Psi_{2N} = \sum_{j=1,12} \Psi_{jN} + \Psi_{2N}$$
$$= \sum_{j=1,12} \left[\sum_{i=1}^{k} \omega_{i} \left[N_{j} \Phi \left(\lambda_{max}^{d_{i}} \right) \int_{n_{minj} \left(\lambda_{max}^{d_{i}} \right)}^{n_{maxj}} P\left(n \right) \psi_{c1}\left(n, \lambda^{d_{i}} \right) dn \right] \right]$$
$$+ N_{2}KT \sum_{i=1}^{k} \omega_{i} \psi_{c2}\left(n_{2}, \lambda^{d_{i}} \right)$$
(6..1)

Where the first summation is used to describe the behavior of the networks 1 and 12, as their governing equations are similar, with only minor differences in definition of some parameter. In order to calculate S^n and \mathbb{C}^n , we have

$$S^{n}D \otimes D = 2\frac{\partial \Psi_{M}}{\partial \bar{C}}$$

$$= \sum_{j=1,12} \left[2\sum_{i=1}^{k} \omega_{i} \left[N_{j}\Phi\left(\lambda_{max}^{d_{i}}\right) \int_{n_{minj}\left(\lambda_{max}^{d_{i}}\right)}^{n_{maxj}} P\left(n\right) \frac{\partial \psi_{c1}\left(n,\lambda^{d_{i}}\right)}{\partial \bar{C}} dn \right] \right] \qquad (6..2)$$

$$+ 2N_{2}KT \sum_{i=1}^{k} \omega_{i} \frac{\partial \psi_{c2}\left(n_{2},\lambda^{d_{i}}\right)}{\partial \bar{C}}$$

$$\mathbb{C}^{n}D \otimes D \otimes D \otimes D = 4 \frac{d^{2}\Psi_{M}}{d\overline{C}^{2}}
= \sum_{j=1,12} \left\{ 4N_{j} \sum_{i=1}^{k} \omega_{i} \left[\Phi\left(\lambda_{max}^{d_{i}}\right) \int_{n_{minj}\left(\lambda_{max}^{d_{i}}\right)}^{n_{maxj}} P\left(n\right) \frac{\partial^{2}\psi_{c1}\left(n,\lambda^{d_{i}}\right)}{\partial\overline{C}^{2}} dn \right. \\ \left. + \frac{\partial\Phi\left(\lambda_{max}^{d_{i}}\right)}{\partial\overline{C}} \frac{d\lambda_{max}^{d_{i}}}{d\lambda^{d_{i}}} \int_{n_{minj}\left(\lambda_{max}^{d_{i}}\right)}^{n_{maxj}} P\left(n\right) \frac{\partial\psi_{c1}\left(n,\lambda^{d_{i}}\right)}{\partial\overline{C}} dn \right. \\ \left. - \Phi\left(\lambda_{max}^{d_{i}}\right) \frac{\partial n_{minj}\left(\lambda_{max}^{d_{i}}\right)}{\partial\overline{C}} \frac{d\lambda_{max}^{d_{i}}}{d\lambda^{d_{i}}} P\left(n_{minj}\left(\lambda_{max}^{d_{i}}\right)\right) \frac{\partial\psi_{c1}\left(n_{minj}\left(\lambda_{max}^{d_{i}}\right),\lambda^{d_{i}}\right)}{\partial\overline{C}} \right] \right\} \\ \left. + 4v_{p}N_{2}KT \sum_{i=1}^{k} \omega_{i} \frac{\partial^{2}\psi_{c2}\left(n_{2},\lambda^{d_{i}}\right)}{\partial\overline{C}^{2}} \right] \tag{6..3}$$

The derivatives used in the above equations, could be calculated as follows

$$\frac{\partial \psi_{c1}\left(n,\lambda\right)}{\partial \bar{C}} = KT\left(\frac{1}{2\lambda}\bar{R}\hat{\beta}\right)D\otimes D \tag{6..4}$$

$$\frac{\partial \psi_{c2}\left(n,\lambda\right)}{\partial \bar{C}} = KT\left(\frac{\sqrt{n_2}}{2\lambda}\beta\right) D \otimes D \tag{6..5}$$

$$\frac{\partial^2 \psi_{c1}\left(n,\lambda\right)}{\partial \bar{C}^2} = KT\left(\frac{1}{2}\left(\frac{1}{\lambda}\frac{\partial \hat{\beta}}{\partial C} - \frac{1}{2\lambda^3}\hat{\beta}\right)\right) D \otimes D \otimes D \otimes D \tag{6..6}$$

$$\frac{\partial^2 \psi_{c2}\left(n,\lambda\right)}{\partial \bar{C}^2} = KT\left(\frac{1}{2}\left(\frac{1}{\lambda}\frac{\partial\beta}{\partial C} - \frac{1}{2\lambda^3}\beta\right)\right)D \otimes D \otimes D \otimes D \tag{6..7}$$

$$\frac{\partial \hat{\beta}}{\partial \bar{C}} = \frac{\bar{R}}{2n\lambda} \left(\frac{2tn}{\beta} + \left(1 - \frac{1+t^2}{n} \right) \frac{\partial \beta}{\partial t} \right) D \otimes D$$
(6..8)

$$\frac{\partial\beta}{\partial\bar{C}} = \frac{\bar{R}}{2n\lambda} \left(\frac{\partial\beta}{\partial t}\right) D \otimes D \tag{6..9}$$

$$\frac{\partial n_{\min 1}\left(\lambda\right)}{\partial \bar{C}} = \frac{\bar{R}}{2\xi\lambda} D \otimes D \tag{6..10}$$

$$\frac{\partial n_{min12}\left(\lambda\right)}{\partial \bar{C}} = \frac{1}{\xi^2} D \otimes D \tag{6..11}$$

$$\frac{\partial \Phi}{\partial \bar{C}} = (\alpha_j - 1 + \Phi) \frac{\partial n_{min}(\lambda)}{\partial \bar{C}} \frac{P\left(n_{minj}\left(\lambda_{max}^{d_i}\right)\right) n_{minj}\left(\lambda_{max}^{d_i}\right)}{\int_{n_{minj}\left(\lambda_{max}^{d_i}\right)}^{n_{maxj}} P\left(n\right) n dn} D \otimes D$$
(6..12)

Thermodynamic Consistency

Since the strain energy of the gel matrix Ψ_M is influenced by only one internal variable, namely $\overset{d}{\lambda_{max}}$, one can rewrite Ψ_M as

$$\Psi_M = \Psi_M(\bar{\mathbf{C}}, \boldsymbol{\Lambda_{max}}) = \tilde{\Psi}_M(\bar{\mathbf{F}}, \boldsymbol{\Lambda_{max}}) = \Psi_1(\bar{\mathbf{C}}, \boldsymbol{\Lambda_{max}}) + \Psi_{12}(\bar{\mathbf{C}}, \boldsymbol{\Lambda_{max}}) + \Psi_{2N}(\bar{\mathbf{C}}), \quad (6..13)$$

where

$$\boldsymbol{\Lambda_{max}} = \left\{ \begin{matrix} \boldsymbol{d} \\ \lambda_{max} &: \boldsymbol{d} \in \mathbb{V}^3 \land |\boldsymbol{d}| = 1 \end{matrix} \right\}.$$
(6..14)

The second law of thermodynamics can be reduced to the Clausius-Duhem inequality to show the thermodynamic consistency of the model in an arbitrary direction d

$$\partial_{\substack{d\\\lambda_{max}}} \Psi_M \cdot \begin{pmatrix} d\\\lambda_{max} \end{pmatrix} \le 0 \qquad \forall \ \boldsymbol{d}.$$
(6..15)

The maximum stretch remains constant during unloading and reloading. Therefore, $\overset{d}{\lambda_{max}} = 0$ in unloading-reloading while $\overset{D}{\lambda_{max}} > 0$ in the primary loading. Thus, satisfaction of the Clausius-

Duhem inequality during the loading is sufficient to prove (6..15), as one can write

$$\frac{\partial \Psi_M}{\partial \lambda_{max}} \le 0 \qquad \forall \ \boldsymbol{d} \tag{6..16}$$

With respect to (6) and (8), equation (6..15) yields

$$\frac{\partial \Psi_M}{\partial \lambda_{max}^d} = \frac{\partial \Psi_1}{\partial \lambda_{max}^d} + \frac{\partial \Psi_{12}}{\partial \lambda_{max}^d} \le 0 \ \forall \ \boldsymbol{d}.$$
(6..17)

Without losing generality, (6..17) can be proved for an arbitrary direction d of primary loading of first or interaction network. For the sake of briefness, λ_{max}^{d} and λ^{d} are replaced by x in primary loading and in order to take the derivation of summations in the model, the summations are replaced by their equivalent integration. Using (17), one can further obtain

$$\frac{\partial \Psi_{i}}{\partial \lambda_{max}} = \frac{\partial \Psi_{i}}{\partial x}$$

$$= v_{p}N_{i} \left[\frac{d\Phi_{i}\left(x\right)}{dx} \int_{D_{n}^{i}(x)} \psi_{c}(n,x)P_{n}^{i}(n)dn - \frac{dn_{min}^{i}\left(x\right)}{dx}\Phi_{i}\left(x\right)\psi_{c}(n_{min}^{i}\left(x\right),x)P_{n}^{i}(n_{min}^{i}\left(x\right)) \right]$$
(6..18)

where
$$n_{min}^{1}(x) = \frac{1}{\xi} x v_{p}^{-\frac{1}{3}} \bar{r}_{0}, \frac{dn_{min}^{1}(x)}{dx} = \frac{1}{\xi} v_{p}^{-\frac{1}{3}} \bar{r}_{0}, n_{min}^{2}(x) = \frac{1}{\xi} x^{2} v_{p}^{-\frac{1}{3}}, \frac{dn_{min}^{1}(x)}{dx} = \frac{2}{\xi} v_{p}^{-\frac{1}{3}} x$$
 and
 $\frac{d\Phi_{i}(x)}{dx} = \frac{A_{i}}{\xi} v_{p}^{-\frac{1}{3}} P_{n}^{i}(n_{min}^{i}(x)) n_{min}^{i}(x) \frac{\alpha_{i} - 1 + \Phi_{i}(x)}{\int_{D_{n}^{i}(x)}^{1} n P_{n}^{i}(n) dn}.$
(6..19)

In Eq. (6..19), $A_1 = \overline{r}_0^i$ and $A_2 = 2x$. By substituting (6..19) in (6..18), one can obtain

$$\frac{\partial \Psi_{i}}{\partial x} = N_{i} \frac{A_{i}}{\xi} v_{p}^{\frac{2}{3}} P_{n}^{i}(n_{min}^{i}(x)) \\ \left[n_{min}^{i}(x) \frac{\alpha_{i} - 1 + \Phi_{i}(x)}{\int\limits_{D_{n}^{i}(x)} n P_{n}^{i}(n) dn} \int\limits_{D_{n}^{i}(x)} \psi_{c}(n, x) P_{n}^{i}(n) dn - \Phi_{i}(x) \psi_{c}(n_{min}^{i}(x), x) \right] \leq 0 \quad (6..20)$$

As $\alpha \leq 1$, $N_1 \frac{A_i}{\xi} v_p^{\frac{2}{3}} P_n^i(n_{min}(x)) > 0$, and $\Phi(x) > 0$, (6..20) holds if only we have the following inequality

$$\frac{n_{\min}^{i}(x)}{\int\limits_{D_{n}^{i}(x)} n P_{n}^{i}(n) dn} \int\limits_{D_{n}^{i}(x)} \psi_{c}(n, x) P_{n}^{i}(n) dn - \psi_{c}(n_{\min}^{i}(x), x) \leq 0$$
(6..21)

(6..21) can be rewritten as

$$n_{\min}^{i}(x) \int_{D_{n}^{i}(x)} \psi_{c}(n,x) P_{n}^{i}(n) dn - \psi_{c}(n_{\min}^{i}(x),x) \int_{D_{n}^{i}(x)} n P_{n}^{i}(n) dn \leq 0$$
(6..22)

As $n_{min}^{i}(x)$ and $\psi_{c}(n_{min}^{i}(x), x)$ are not functions of n, they can be moved inside the summation, thus

$$\int_{D_n^i(x)} P_n^i(n) \left[n_{\min}^i(x) \,\psi_c(n,x) - n\psi_c(n_{\min}^i(x),x) \right] \le 0 \tag{6..23}$$

As $n_{min}^{i}(x) \leq n$ and the strain energy of the shortest chain is always higher than the energy of the rest of the chains $(\psi_{c}(n,x) \ll \psi_{c}(n_{min}^{i}(x),x)))$, one can conclude $n_{min}^{i}(x) \psi_{c}(n,x) - \psi_{c}(n_{min}^{i}(x),x)n \leq 0$ for all $n \in D_{n}^{i}(x)$. While the bracket in the inequality (6..23) is less than zero for all chain lengths (n), the proposed model holds the condition of the thermodynamic consistency.

CHAPTER 7

SUMMARY AND FUTURE WORKS

The main objectives of this study were to develop a constitutive model for cross-linked elastomers in large deformations. In this chapter, the dissertation is briefly summarized for each section. In the first part of this research, we focused on the derivation of a theory of polymer physics with adjustable accuracy and computational cost. In the following part, the developed theories are used to propose constitutive models in a modular platform basis to predict the complex behavior of cross-linked elastomers.

7.1 General Remarks

- In chapter 3, new accurate approximation families of the Non-Gaussian PDF, entropic force, and strain energy of a single chain are subsequently developed to describe the mechanics of a polymer chain. To date, most of the micro-mechanical non-Gaussian constitutive models are often developed using the KG distribution function, which is derived from the first order approximation of the complex Rayleigh's exact Fourier integral distribution. However, KG function is shown to be only relevant for long chains and becomes extremely inaccurate for the chains with less than 40 segments. The proposed approximations of Non-Gaussian PDF, strain energy and entropic force with similar levels of complexity are at least 10 times more accurate than KG approximations and thus are an excellent alternative option to be used in micro-mechanical constitutive models.
- In chapter 4, a novel approach is developed that can provide a family of approximation

functions for ILF with different degrees of accuracy. A simple procedure is presented, which can take current approximation functions with an asymptotic behavior and enhance them by addition of a power series of their induced error. The total error is thus correlated with number of terms in the power series. We further proposed different approaches to reduce the terms of the power series and increase the accuracy, the proposed approach is applied to four different classes of ILF approximations and shows significant improvements. The accuracy/complexity trade-off for the family of ILF approximations generated by the proposed approach is compared against those of other approaches to show the superiority of the proposed model. The level of error in this method can reach to a value as low as 0.02%.

- In chapter 5, a micro-mechanical model is developed to characterize the constitutive behavior of DN elastomers in quasi-static large deformations. This module of the platform is focused on describing the non-linear behavior and permanent damage in elastomers. The main source of the damage in the material is assumed to be an irreversible chain detachment and breakage of the chains in the first network. The proposed model enables us to describe the damage and the way it influences the micro-structure of the material. The model is validated with uni-axial loading and unloading experiments of the DN elastomers. The proposed model contains a few material constants and shows a good agreement with cyclic uni-axial test data.
- In **chapter 6**, a micro-mechanical model based on the concept of modular platform is developed to describe the constitutive behavior of DN elastomers with necking instability. In this platform, the model is considered as an assembly of the three different networks. The first network and the interaction mode are derived by advancing the previously developed network evolution model of carbon black filled rubber. The hyper-elastic full network model is utilized for the second network. The matrix behavior is divided into three parts including
 - *Pre-necking* The first network is dominant in the response of the gel at the this stage.
 - Necking The breakage of the first network to smaller network fractions (clusters)
induces the stress softening observed at this stage. The disentanglement of the second network chains from broken first network chains is considered as the main contributor to the response of gel at the necking stage.

 Hardening - Limiting stretch of the long chains in second network is the main reason of the hardening in large deformations. The contribution of clusters decreases during the necking as the second network starts hardening.

The numerical results of the proposed model are validated and compared by uni-axial cyclic tensile experimental data of DN gels. Finally, a finite-element implementation of the proposed model is presented to simulate the initiation and propagation of the necking instability.

7.2 Potential Future Research

In line with this study, several new questions outside the scope of this dissertation may arise. Some of these questions that require further investigations and can be a starting point for future studies are listed below:

- Fatigue lifetime predication of the elastomeric materials is well studied in recent years, in which the reported mechanical behavior during cyclic loading shows a significant damage accumulation in the material. However, there is still the gap in the literature regarding the modelling of material stress softening during the cyclic test.
- Some of newly developed cross-linked elastomeric materials have the ability to heal without any external intervention. There are a few studies that tried to predict damaging and healing process of these materials. However, our understanding of the physical nature of the healing over time has still remained inconclusive.
- The experimental results show that the material behavior may differ from sample to sample. Current practice in the constitutive modeling of the material is to consider the average response as a target to predict. However, the uncertainty in the response of the material can

cause significant loss in the sensitive applications. So, the addition of the uncertainty feature to the proposed framework can predict the behavior of the material with different levels of desired uncertainty.

- Micro-mechanical modeling of the time-dependent behavior of elastomers is still challenging due to the extreme nonlinear nature of their response. In order to understand the nature of this time-dependent behavior, the behavior of a single isolated polymer chain can be investigated. Several advancements on numerical molecular modelling are made in recent years which can help us understand and validate the micro-structural behavior of the material. This understanding can be integrated by developed frameworks to predict nonlinear time dependent behavior of the material.
- Several new elastomeric materials are developed in recent years, in which the behavior of the material is improved by adding Nano-filler or interpenetrating multiple networks in the matrix. The developed framework can be enhanced to be used in the design of a new material. By understanding the effects of each component in the final response of the material, one can optimize the behavior of the material based on the required specifications.

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