Modeling crack growth and phase separation in soft materials: A finite strain phase field approach to microscopic surfaces and interfaces

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 Modeling crack growth and phase separation in soft materials: A finite strain phase field approach to microscopic surfaces and interfaces

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ABSTRACT

Elastomers and polymeric gels are soft materials consisting of crosslinked polymer networks. They are highly nonlinear materials capable of undergoing large deformation. In this work, we formulate a finite strain phase field model to study surfaces and interfaces in soft materials considering the coupling between deformation and interface structure for ideal solid and liquid interfaces. The phase field model is combined with visco-poroelastic theory, and implemented into finite element code using a rate based variational principle. The model is first applied to viscous fracture of elastomers using a non-conserved phase field variable to track the stress-activated damage of polymer networks. Crack surface is modeled as a coherent diffusive interface between intact material and vacuum. The model provides a thermodynamically consistent way of calculating arbitrary crack growth. By examining the numerical results of steady state viscous crack, we explain viscous toughening mechanism and the rate dependency of fracture energy via the extrinsic viscoelastic dissipation. In the second example, we study phase separation of gels using conserved phase field model which serves as a general model for the effect mismatch strain of coherent phase boundary on morphology of coexisting phases. Our numerical results reveal formation of sponge structures, which consist of compartment of majority phase imbedded in thin network of connected minor phase. A theory is proposed for mechanism of sponge structure formation as the consequence of competition between minimizing interface energy and strain energy from nonlinear deformation of curved phase boundary.
CHAPTER I
INTRODUCTION

1.1 Soft Materials and Rubber-like Elasticity

Perception of softness infiltrates our lives when we touch materials and test their stiffness with our own skins and muscles. The “founding father of soft matter science” Pierre-Gilles de Gennes concludes in his Nobel Lecture that the two major features of soft materials are complexity and flexibility (de Gennes 1991). Indeed, there are varieties of classes of materials considered to be soft, including polymers, surfactants, liquid crystals, colloidal grains, as well as complex multicellular organisms. We limit the scope of this work to soft solids which can maintain certain shape, and are capable of recovering at least part of deformation, including elastomers, polymeric gels, and biological materials such as muscles, tendons, cartilage and blood vessels. They share the general deformation mechanism of rubber-like elasticity with the basic molecular structure of that of the natural rubber: a crosslinked long chain polymer network.

Attention of this work is focused on two idealized model of soft solids: elastomers and polymeric gels. An elastomer is a crosslinked long chain polymer network, and a polymeric gel is an elastomer swelled by small molecule solvent. Both elastomer and gels are highly flexible, meaning they both have low stiffness and the ability to undergo large elastic deformation comparing to hard materials such as plastic, metal and ceramics. Deformation mechanism of elastomers and gels is entropic elasticity (Treloar 1975). A long polymer chain assumes some randomly coiled
configuration in the stress-free state, and stretches by the entropy reducing reorientation of chain segments. For a polymer chain consists of $N$ segments per chain (a chain defined as between two crosslinking points), its length in the coiled state is $l\sqrt{N}$ (Flory 1941) and is $lN$ in the fully straightened state, where $l$ is length of a single segment. The theoretical stretch limit of the polymer chain is $\sqrt{N}$, and $\sqrt{N} \gg 1$ considering that there is usually a large number of segments in one polymer chain. On contrary, a hard solid deforms by stretching intermolecular bonds, and the theoretical stretch limit is usually limited to 1.2 (Macmillan & Kally, 1972) beyond which bond dissociation will occur.

Stretching the entropic string of the crosslinked polymer network requires much less energy than the intermolecular bonds because of the low activation energy of segment rotation in polymer chains. Rubber-like elastic behavior of elastomers and gels can be activated by thermo-energy in the room temperature. In an ideal rubber-like network (chain length distribution obeying Gaussian distribution), the shear modulus is given by (Mark & Erman 1999):

$$\mu = \sigma kT$$

(1.1)

where $k$ is the Boltzmann constant, $T$ is temperature and $\sigma / N\Omega$ is chain density. $\Omega = l^3 \approx 10^{-29} m^3$ is typical size of a chain segment. Depending on the chain density, a modulus of an elastomer ranges from $10^5 Pa$ to $10^6 Pa$. Nevertheless, Eq. (1.1) is a universal scaling relation for modulus both elastomers and gels. $\mu$ is sensitive to the architecture of the polymer network (crosslinking density and network topology), by not
to chemical constitution of the polymer chains (Flory 1953). For example, an elastomer becomes stiffer when the crosslinking density increases, because $\sigma$ increase as chain becomes shorter. $\mu$ increase with temperature because the larger entropy change with deformation (Mark & Erman 1999).

With flexible and open structure, an elastomer could absorb liquid to form a polymeric gel, through the process known as swelling. Swelling decreases chain density by filling the volume with small molecule solvents. Modulus of dry network $\mu$ decrease to $\mu' = \mu / \lambda$ (Hong et al 2008) after swelling, where $\lambda$ is defined as ratio of swollen length to dry length of the sample. Typical modulus of a gel ranges from $1kPa \sim 100kPa$. Similar to elastomers, $\lambda$ is insensitive to type of polymer and swelling medium and their bonding interaction (mixing enthalpy), but on the architecture of polymer network and the swelling ratio.

The combined property of low stiffness and the ability to sustain large deformation attracts unique applications. Although elastomers have become common engineering materials, their roles as seals, gaskets, adhesives and tires which provide conformation between two complex structures, are still irreplaceable. On the other hand, gels are relatively novel materials with current and emerging applications mainly in three areas:

1) Liquid absorbent. Liquid absorbent is the tradition and widest applications of gels, such as personal hygiene products and underground liquid retention agents for both water and oil. Gels used for this purpose are also known as the superabsorbent
polymers, termed from the ability of a gel to swell by absorbing liquid of hundreds of its original weight.

2) Soft active sensors and actuators. Gels are known as stimuli-responsive materials, due to the coupling between solvent concentration and deformation. Because of their softness, solvent concentration can be controlled by the chemistry of the swelling process through swelling or shrinking the polymer network, and a gel can deform by non-mechanical driving forces. Examples include thermo-sensitivity (Otake et al. 1990), pH sensitiveness (Marcombe et al. 2010), eletro-sensitiveness (Shiga, 1997), and so on. Stimuli response gels have vast amount of potential applications such as drug delivery system (Hoare & Kohane 2008), antifouling active coating, micro-fluidic valves (Richter et al. 2004), micro actuators (Carpi & Smela 2009; Hu et al. 1995), micromechanical engines (Steinberg et al. 1966) and etc.

3) Artificial tissues. Gels (hydrogels in particular) are soft and wet materials that mimic living tissues. The distinct low modulus of gels comparing to all other engineering materials allows a gel made devices to conform and deform with surrounding tissues without causing damage. Secondly, cells are capable of perceiving and responding to the stiffness of the substrate it attached to (Discher et al 2005). Gels acts as tissue scaffolds that integrate the implant with the living environment by providing the tunable mechanical environment (by changing crosslinking density and swelling ratio) for cell growth (Drury & Mooney 2003).
1.2 Modelling Surfaces and Interfaces in Soft Materials

In soft materials, there exist many types of microscopic surfaces and interfaces, such as phase boundaries, bi-material interfaces, external surfaces and lipid bi-layers. There are two theoretical approaches using different description for them: sharp interface and diffusive interface (Boettinger et al. 2002; Chen 2002; Emmerich 2008). Sharp interface theory follows the intuitive perception of surface and interfaces as discontinuities, and treats them as 2D planar geometrical objects with no thickness. A surface or interface is described with a set of generalized coordinates with a desired number of degree of freedom depending on modeling purpose (Herring 1951; Suo 1997). Sharp interface theory is convenient when studying global aspect of surface and interface with known motion for its numerical efficiency and the use of directly measurable parameters, such as interface energy and interfacial concentration. Using predefined degree of freedom is also the greatest limitation of sharp interface theory. For example, one can improve the detail of shape of a sharp interface by discretizing it into more and more elements, however, additional equation is needed (Suo 1997) such as nucleation, triple-junction, branching and interaction with other discontinuities.

Diffusive interface theory simply considers surfaces or interfaces to be finite thickness transition zone between two phases. Unlike sharp interface theory, they are modeled as component of the bulk material using a unified description. A convenient and thermodynamically consistent method of introducing diffusive interface is to use the phase field model. Because of the popularity of phase field model, it is often referred to interchangeably with the diffusive interface theory.
Phase field model are connected to two principle characteristics: a continuous field of phase field variable is introduced to differentiate domains of dissimilar microstructures (Laudau & Khalatikow 1963); the phase field variable changes smoothly from one phase to another, creating a finite width diffuse interface (van der Waals 1894). Depending on the nature of the problem, the internal variable in a phase field model could be an axillary independent variable (Laudau & Khalatikow 1963; Cahn and Allen 1977), or a physical parameter (Cahn & Hillard 1958). To extend the continuum description to a heterogeneous system, Cahn and Hillard (1958) first introduce the expansion of free energy with respect to the local derivative of a state variable $\phi$:

\[
\Pi = \int_{\Omega} W(\phi, \nabla \phi, \nabla^2 \phi...) dV
\approx \int_{\Omega} \left[ W(\phi) + \frac{1}{2} \tau (\nabla \phi)^2 \right] dV = \int_{\Omega} W(\phi) dV + \gamma l,
\]

as the sum of the local (uniform bulk contribution) and gradient energy (local variation). The gradient energy is non-zero in the transition zone between two phases, which captures the excess energy of the interface or surface. $\tau$ represents magnitude of the lowest order approximation to energy cost for forming the transition zone. The diffusive interface theory asymptotically recovers the sharp interface theory that the total gradient energy equals to the product of interface tension $\gamma$ and the total area of phase boundary.

A consistent description of the interface energy with the sharp interface limit is crucial for the phase field model. One extreme type of interface is an ideal-liquid interface, on which the molecules are capable of rearranging themselves. The corresponding interface energy per unit current area is independent of the state of
deformation. The other extreme is an ideal-solid interface that preserves its atomic structure after deformation and the molecular area density and associated interface energy is independent of strain. In general, the interface energy may vary with deformation, and its partial derivative with respect to strain is often referred to as the surface stress (Gurtin et al. 1998). Mathematically speaking, in the finite strain context, it is unclear whether the gradient should be taken with respect to the deformed configuration or the reference configuration. It has recently been shown that by using the gradient in the deformed configuration, the interface energy function could recover the behavior of surface tension (Levitas and Samani 2011) which recovers the case of an ideal-liquid interface.

In this work we aim to incorporate description of discontinuities with that of bulk material and formulate a unified model for the evolution of surfaces and interfaces. An external surface will be treated as an interface between two solids with one side having zero modulus and effectively behaving as a fluid or vacuum. Based on this consideration, we will refer to both surface and interface as interfaces throughout this dissertation. Attention is focused on two examples: crack surface and phase boundary.

In the context of phase field model, the crack surface is a transition zone between the virgin material and the fully damaged one. Phase field variable is introduced to mark the vanishing of strain energy. Modelling failure as a phase transformation process can be traced back to the classical Ericksen bar problem (Ericksen 1975; 1991): if a one-dimensional elastic bar is loaded to a critical state that the free energy bifurcates into the form with multiple minima, and the homogeneously deformed bar phase separates into
co-existing phases with different stretches. Truskinovsky (1996) suggests that the problem can be extended to 1D fracture by considering the limit that one state degenerates to zero stiffness and can be stretched infinitely. In this case, the residual energy of the fully broken bar in the continuum limit recovers the fracture energy of the material. The concept is later combined with the diffusive interface approach, and a self-consistent field theory for 2D and 3D crack propagation problems (Aranson et al. 2000; Karma et al. 2001) is developed. The model successfully reproduces the Griffith threshold for crack initiation (Karma et al. 2001; Hakim 2009), as well as branching (Karma and Lobkovsky, 2004) and oscillating instabilities (Henry and Levine 2004) in linear elastic solids. The model is recently extended to for finite strain fracture of rubbers (Miehe et al. 2013).

Compared to currently popular sharp interface based computational method such as cohesive element (Moes et al. 1994) and nodal enrichment strategy (Dolbow & Belytschko 1999), the phase field model introduces smoothed continuum crack surface and avoids the formidable task of describing complex shape of branched and kinked crack. Nevertheless, the phase field fracture model is still in its infancy and the topic is vastly open. The method itself is not yet fully developed. On the hand, phase field method opens the possibility of studying arbitrary crack growth and the coupling with physical processes of the process zone and the bulk, which could potentially answer many classical fracture problems remaining from the last century.

Another type of interface completely different from a crack surface is a phase boundary. On a phase boundary, there is a difference in the equilibrium volumetric
strain (misfit strain) of the two phases, as the equilibrium swelling ratio bifurcates in an thermodynamically unstable gel. Internal elastic strain is induced spontaneously within the system as a consequence, which drastically influences the phase behavior of the system. In this work, we limit the discussion to coherent interfaces where materials remain continuous, a case common to polymeric gels capable of undergoing large elastic deformation. On an incoherent interface, on the other hand, the elastic strain can be released through damage of polymer network or sometimes the reformation of crosslinkings, which is relevant to phase separation in physical gels and polymerization induced phase separation. Due to its complexity, this problem has not been well investigated.

Phase separation has been a well-known phenomenon in stimuli-responsive gels (Tanaka 1979, Li & Tanaka 1992), which occurs when a gel is quenched beyond the critical temperature. It is a kinetic process that competes with the volume phase transition (Matsuo and Tanaka 1987, Onuki 1988). A direction evidence for phase separation is after a gel is being quenched, the initially transparent gel would turn opaque due to light diffraction of the suddenly formed of coexisting phases. Phase separation is the consequence of instability the polymer solvent mixture undergoing the coil-globule transition. Gel phase separation has been extensively investigated experimentally as a critical phenomenon (Tanaka et al. 1985; Shibayama & Tanaka 1993; Takeshita et al. 2001). On the other hand, evolution of coexisting phases in a phase-separated gel is governed by competition between interface and elastic strain
effects, which is universal for phase separation in many elastic systems. However, the mechanics of this process is not well understood.

Historically, the elastic effect is first incorporated into the phase field formulation by the classical work of Cahn (1961) himself, which shows that the linear elastic strain energy alters the miscibility gap of the phase separated system. Onuki (1989) shows that the slowing down of phase separation in an elastic system because of the locking effect. Apart from equilibrium behavior and kinetics, the focus on theoretical understanding of phase-separated elastic system is the morphology. Three basic morphology types of heterogeneity include droplet, network and cellular structures. Consider an asymmetric mixture having a majority and a minority phase, in the droplet structure, the minority phase forms isolated islands (often referred to as precipitation) imbedded in the continuous matrix of the majority phase. Inversely, in the cellular structure, the minority phase interconnects and forms compartments that isolate the majority phase. Network structure is the intermediate structure between the above two ones, where both phases are continuous. Naturally, the connectivity controls the mechanical property and kinetic behavior of the heterogeneous material. For example, a phase-separated gel forms a stiff skin made of the polymer poor phase, which slows down the transportation of solvents and prevents a gel from losing solvent to the environment. In this work, we study the 2D plane strain model of heterogeneous structures: droplet and sponge structures.

Without elastic strain effects, the morphology of coexisting phases is determined by the minimization of interface energy. Since interface energy scales with area of
interfaces, the droplet structure would be the most energetically favorable one with the minimum area of interfaces, as often observed in phase-separated fluids. A unique effect on morphology arises when the coexisting phases has different elastic moduli. The growing precipitate would lose the spheroid shape when it is softer than the matrix, which leads to the formation of spongy structure where the elongated precipitation interconnects to form a continuous network (Onuki 1997). On the other hand, current theoretical study has pointed out that predominance of nonlinear elastic deformation over the interface energy would lead to the formation of sponge structure, as is commonly observed in gels but not uniquely limited to this system. Sponge structure has been reported by a few phase field simulations for large strain during phase separation for polymer gels (Sekimoto 1989, Zhou 2001). Another interesting study is from the theoretical investigation of phase separation in viscous polymer blends. If the coexisting phases have very different viscosity, the more viscous phase would be kinetically frozen to form a transient gel. During this stage, the system behaves as a phase separated physical gel and it assumes the morphology of a sponge structure (Tanaka 2000). The exact mechanics origin of sponge structure is not clear, which we will seek to illustrate in this work with the help of the phase field model.

1.3 Dissertation Outline

The heart of this work is the use of weak formulation, which is associated with the variation of free energy functions and dissipative functions to capture arbitrary dissipative processes in a material. Describing a system using the weak form is
equivalent to the usual approach of differential equations such as stress balance, transportation and Ginzburg-Landau equations. A weak form can be conveniently discretized with Galerkin method, and readily applied to the finite element method for numerical calculation. In chapter II, we formulate weak forms for the finite strain inelastic deformation of elastomers and gels based on a continuum model considering concurrent mass-transportation and viscoelastic deformation (Wang & Hong 2012). Following Biot’s theory (Biot 1962), we extend the study of visco-poroelastic behavior to the nonlinear regime by combining the swelling theory (Tanaka & Fillmore 1979, Hong et al 2008) and nonlinear viscoelastic deformation theory. We apply the model to investigate typical cases of inhomogeneous deformation of gels, and use numerical examples to explain the separation of poroelastic and viscoelastic relaxation processes through length scale change. Furthermore, we present a self-consistent interface theory in section 3.1 by extending the Ginzburg-Landau type phase field model to the finite deformation regime (Hong & Wang 2012). The model adds the description of interfaces to the continuum framework for inelastic deformation of soft solids, and allows the evolution of the bulk and the interface to be modelled as a whole.

The rest of chapter III and chapter IV of this dissertation may be read independently. The majority of chapter III is devoted to study fracture of viscous elastomers using the material model developed in chapter II and interface model developed in section 3.1. The numerical examples serve to elucidate the dependency of fracture energy on crack velocity in soft elastomers via investigating a traveling crack tip for the coupling between damage and viscous dissipation. In chapter IV, we modify the
phase field model to consider conserved phase field variable, and apply it to investigate the phase separation of gels. Using the model, we propose the theory for the mechanism of formation of the common but unconventional spongy and cellular structures in soft materials. In section 4.1, an introduction is given on the physics of stability and phase separation of polymer solution and gels. In section 4.2, we study the finite strain elastic effect on phase-separated morphology from a semi-analytical analysis for nonlinear deformation associated with a coherent phase boundary with both sides has a large volumetric mismatch strain. We then use phase field model to simulate the phase separation process considering large strain deformation and mass transportation in section 4.3, and the numerical results confirm the finite strain effect on morphology.
CHAPTER II
CONTINUUM MODELS FOR FINITE STRAIN VISCO-POROELASTIC DEFORMATION

2.1 Inelastic Deformation of Gels

We start from the simple conceptual picture of a chemical gel: a covalently crosslinked polymer network swelled by small molecule solvent. A chemical gel is a poroelastic solid capable of two basic modes of deformation (Hong et al. 2008). The short time mode is the volume conserved stretching of polymer chains accompanied by the local rearrangement of solvents, and the gel behaves just like an incompressible dry elastomer. The long time mode involves the diffusion controlled process of long-range transportation of solvents, and the gel swells or shrinks in volume (Hirokawa et al. 1984; Hirotsu et al. 1987). In a physical gel (Hennink and Nostrum 2002), the crosslinks in the stretched polymer network is under constant dissociation and recombination and consideration for viscoelasticity becomes important.

While both poroelasticity and viscoelasticity are phenomenological approach for rate-dependent transient processes. They are governed by distinct mechanisms. Let the characteristic relaxation time of poroelastic and viscoelastic relaxation time of the materials be $t_d$ and $t_v$, respectively. $t_d$ is determined by the diffusion controlled process and is size dependent as $t_d = L^2 / D$, where $D$ is the diffusion constant and $L$ is some diffusion length depending on the geometry of the problem. By contrast, $t_v$ is a property
of the polymer network and is size independent. The comparison between the two time scale yields the visco-porous coupling length: \( L_c = \sqrt{D t_v} \). If the system size is smaller than \( L_c \), we have \( t_v > t_d \), and solvent diffusion would equilibrates much faster than viscous deformation. On the other hand, if the system size is greater than \( L_c \), the time-dependent deformation of a gel is visco-dominated. The system is visco-poroelastic if its size is around length scale \( L_c \), such a case includes problems such as swelling of gel consisting of physical bonds (including physical gels) (Fleury et al 2007; Schexnailder and Schmidt 2009), deformation of a microgel (Chen et al 2010), case II diffusion (Weitsman 1987, 1990) and fracture of gels (Baumberger 2009).

2.2 Nonequilibrium Thermodynamics of an Open System with Inelastic Deformation

We consider a gel to be a simple mixture of solvent molecules and a polymer network. Define the undeformed dry polymer network as the reference state. A unit volume of the dry polymer network consists of \( C \) solvent molecules. Let the size of each solvent molecular be \( \Omega \). The polymer network is swelled to \( 1 + \Omega C \) times of its original size after absorbing solvents. When \( C = 0 \), a gel simply reduces to a dry elastomer. Work is done to a gel in two ways: applying a field of mechanical forces and exchanging solvent molecules with external buffers (Fig. 2.1). The total free energy of the system is given by:

\[
\int \tilde{W} dV - \int t_v \nu dA - \int \tilde{\mu} dA,
\]

(2.1)
where $dV$ is an element of volume, $N\,dA$ is an element of surface, with $N$ being unit outward-pointing vector and $dA$ an element of area. Denote $W$ as the Helmholtz free energy density of the system, $tda$ as element of traction applied, $IdA$ as element solvent flux through a surface and $\bar{\mu}$ the buffer’s chemical potential.

Figure 2.1. Sketch of a gel under combined mechano-chemical load

State of a non-viscous polymer chain is determined by strain and solvent concentration, whereas a viscous polymer chain contains additional internal degrees of freedom. Following the usual approach of finite-strain viscoelastic theory, we simplify the structure the polymer network as a combination of a *permanent network* and a *transient network*. The mechanical behavior of the decomposed network is captured by the generalized Maxwell model (Fig. 2.2). Deformation of both networks can be time dependent. The permanent network is undergoes fully recoverable deformation as represented by the $0^{th}$ spring and dashpot. The transient network is capable of reconfiguration, and undergoes partially recoverable deformation as represented by the $n$ branches of spring-dashpot series as a whole. Without losing generality, we limit our consideration for transient network to the $1^{st}$ spring-dashpot and drop the superscripts. An arbitrary viscoelastic behavior could be fitted by adding spring-dashpots, and the
governing equation is simply a repetition of that for the 1st spring-dashpot series. To measure deformation, we let coordinates \( \mathbf{X} \) to be attached to the permanent network in the undeformed state, which relocate to \( \mathbf{x}(\mathbf{X},t) \) at time \( t \). The deformation is described by the deformation gradient

\[
F_{ik}(\mathbf{X},t) = \frac{\partial x_i(\mathbf{X},t)}{\partial X_k}.
\] (2.2)

For transient network, we decompose \( \mathbf{F} \) into elastic and inelastic part

\[
F_{ik} = F_{im}^e F_{mK}^i,
\] (2.3)

by introducing a virtual intermediate state that corresponds to the elastically unloaded state. \( \mathbf{F}^e \) is the deformation gradient of the intermediate state with respect to the reference state, and \( \mathbf{F}^i \) is that of the current state with respect to the intermediate state. Since a material in the virtual state does not have to be a continuum body, \( \mathbf{F}^e \) does not satisfy compatibility equation, and have no corresponding displacements. With additional state variable \( \mathbf{F}^i \), the changing rate of free energy is

\[
\dot{W} = \frac{\partial W}{\partial F_{ik}} \frac{\partial v_i}{\partial X_k} + \frac{\partial W}{\partial F_{ik}^i} \dot{F}_{ik}^i + \frac{\partial W}{\partial C} \dot{C}.
\] (2.4)

**Figure 2.2.** Spring dashpot representation of the generalized Maxwell model
Free energy is dissipated through irreversible processes of solvent migration and viscous deformation. The rate of dissipation due to solvent migration should be a function of the solvent flux $J$:

$$\dot{W}^s = R_{KL}^s J_K J_L,$$  \hspace{1cm} (2.5)

where $J$ is the number of solvent molecules going through unit reference area of polymer network per unit time. Viscous dissipation rate is a function of strain rate $D$:

$$\dot{W}^\nu = R_{KL}^{i} D_{ik} D_{jl} + R_{KL}^{ii} D_{ik}^{i} D_{jl}^{i}.$$ \hspace{1cm} (2.6)

where $D$ is the symmetric part of deformation rate $D = (\mathbf{F} \cdot \mathbf{H} + \mathbf{H}^T \cdot \mathbf{F}^T)/2$, similarly $D^i = (\mathbf{F}^i \cdot \mathbf{H}^i + \mathbf{H}^{iT} \cdot \mathbf{F}^{iT})/2$. Here $\mathbf{H}$ and $\mathbf{H}^i$ are the inverse of deformation gradient $\mathbf{F}$ and $\mathbf{F}^i$, respectively. We consider quadratic forms Eqs (2.5, 2.6) to be general forms of dissipation rate functions, since their positive-definiteness ensures the total free energy of a closed system keeps constant or decreases, as required by the second law of thermodynamics. $R^s$, $R^\nu$ and $R^{ii}$ are generalized viscosity tensors, all being symmetric and positive-definite.

The conservation of total energy leads to

$$\int \dot{W} dV - \int t_i v_i dA - \int \Pi l dA + \int \dot{W}^s dV + \int \dot{W}^\nu dV = 0$$ \hspace{1cm} (2.7)

for an arbitrary physical process, which is equivalent to minimizing the energy functional under maximum energy dissipation principal (Onsager 1931):

$$\Pi[v, \mathbf{F}^i, J, C] = \int \dot{W} dV - \int t_i v_i dA - \int \Pi l dA$$

$$+ \frac{1}{2} \int R_{KL}^s J_K J_L dV + \frac{1}{2} \int \left(R_{KL}^{i} D_{ik} D_{jl} + R_{KL}^{ii} D_{ik}^{i} D_{jl}^{i}\right) dV.$$ \hspace{1cm} (2.8)
A gel is subject to the additional constraint of conservation of solvent molecules, which requires that the time derivative of solvent concentration to be related to the diffusion flux as

$$\dot{C} + \frac{\partial J_K}{\partial X_K} = 0. \quad (2.9)$$

The constraint can be enforced by adding a Lagrange multiplier $\mu(X,t)$:

$$\int \left[ v \cdot \dot{F}^i, J, C, \mu \right] = \int \dot{W} dV - \int \dot{t}_i v_i dA - \int \bar{t} IdA$$

$$+ \frac{1}{2} \int \left( R_{i,j \ell}^s D_{j \ell} D_{i \ell} + R_{i,j \ell}^v D_{j \ell} D_{i \ell} \right) dV$$

$$+ \frac{1}{2} \int R_{k,\ell}^s J_K J_L dV - \int \mu \left( \dot{C} + \frac{\partial J_L}{\partial X_L} \right) dV \quad . \quad (2.10)$$

Variation of Eq. (2.10) can be readily used as weak form to solve for arbitrary deformation of a visco-poroelastic material. In the following sections of this chapter, we will present two material models as examples to the general framework.

2.3 Kelvin-type Visco-poroelastic Gel

2.3.1 Explicit Material Model

In this section, we study deformation of a gel with viscous relaxation represented by the Kelvin model (Wang & Hong 2012) ($0^{th}$ dashpot and spring in Fig. 2.1). The simple viscous model servers to elucidate kinetic behavior of a gel by studying the decoupling between porous and viscous relaxation through change of length scale. Without additional dashpot-spring series, the kinematic split [Eq. (2.2)] is unnecessary, and the simplified energy functional [Eq. (2.10)] becomes:
\[ \Pi [\mathbf{v}, \mathbf{J}, C, \mu] = \int \dot{\mathbf{W}} \, dV - \int t_i v_i \, dA + \frac{1}{2} \int R_{ijkl} D_{jk} D_{kl} \, dV \]
\[ + \frac{1}{2} \int R_{ijkl} J_{ik} J_{jl} dV - \int \mu I dA - \int \mu \left( \hat{C} + \frac{\partial J_L}{\partial X_L} \right) dV . \]

(2.11)

To give the explicit form of \( W \), we adopt the Flory-Rehner (1943) model, and divide
\( W \) into two packages: the elastic energy of stretching the polymer network \( W^e \), and the
energy of mixing the solvent with polymer chains \( W^m \). Consider the simple model of
neo-Hookean network for strain energy, we have:

\[ W^e (\mathbf{F}, p) = \frac{\varrho k T}{2} \left( I_1 - 3 \right) - \frac{p^2}{2 \kappa} - p (\det \mathbf{F} - 1 - C \Omega) . \]

(2.12)

where \( p \) is an unknown hydrostatic pressure and \( I_1 = F_{ik} F_{ik} \) is the first invariant of
strain. The last two terms are energy penalty terms that invokes the usual molecular
incompressibility of the polymer-solvent mixture, where \( \kappa \gg \varrho k T \) is the bulk modulus
of the solvent polymer mixture.

\[ \Omega C + 1 = \det \mathbf{F} . \]

(2.13)

Flory-Huggins model is used for the energy of mixing (Flory, 1942; Huggins, 1941):

\[ W^m = - \frac{k T}{\Omega} \ln \left[ \Omega C \left( 1 + \frac{1}{\Omega C} \right) + \frac{\chi}{1 + \Omega C} \right] . \]

(2.14)

where \( \chi \) is the Flory-Huggins parameter for the enthalpy of mixing.

For simplicity, we assume the dissipative properties of the material to be
isotropic in the current state for both solvent migration and viscous deformation. Let
dissipation rate \( \dot{W}^* \) to be dependent on the true solvent flux \( \mathbf{j} \), i.e. the number of solvent
molecules going through unit current area of polymer network per unit time, we have
\[ \dot{W}^v = \det \mathbf{F} \frac{j_i j_i}{m}. \]  

(2.15)

The mobility of solvent migration is related to the diffusion constant \( D \) through the well-known Einstein relation (e.g. Feynman et al. 1963) \( m = cD/kT \), in which \( c \) is the true solvent concentration, \( c = C/\det \mathbf{F} \). The viscous dissipation rate \( \dot{W}_v \) depends on the deviatory part of strain rate \( d_{ij} = D_{ij} - \delta_{ij} D_{kk} \)

\[ \dot{W}_v = \det \mathbf{F} \eta d_{ij} d_{ij}, \]  

(2.16)

as the gel is incompressible, which can be connected to the general dissipation form Eq. (2.6) by letting \( R_{iiij} = \eta \left( \mathbf{I}^4 - \mathbf{I} \otimes \mathbf{I} / 3 \right) \det \mathbf{F} \), where \( \mathbf{I} \) is the fourth rank identity tensor, and \( \eta \) is viscosity.

Substitute Eqs (2.12-2.16) into Eq. (2.11), variation of the functional \( \Pi \) yields

\[
\partial \Pi = -\int \frac{\partial S_k}{\partial X_k} \partial \mathbf{v}_i dV + \int (s_{ik} N_k - t_i) \partial \mathbf{v}_i dA \\
+ \int \left( \frac{J_k F_{ik} F_{ik}}{m \det \mathbf{F}} \right) \partial J_L dV - \int \left( \dot{\mathbf{C}} + \frac{\partial J_L}{\partial X_L} \right) \partial \mathbf{v} dV + \int \left( \mu - \bar{\mu} \right) \partial \mathbf{v} dA \\
- \int \left( \left( \det \mathbf{F} - \Omega C - 1 \right) + \frac{p}{\kappa} \right) \partial \rho dV \\
+ \int \left( p \Omega + \frac{\partial W}{\partial C} - \mu \right) \partial \mathbf{v} dV = 0
\]  

(2.17)

where

\[ s_{ik} = \frac{\partial W}{\partial F_{ik}} + \eta d_{ij} H_{kj} \det \mathbf{F} - p H_{ki} \det \mathbf{F}. \]  

(2.18)

To minimize the functional \( \Pi \), Eq. (2.17) must hold true for arbitrary test fields \( \partial \mathbf{v}(\mathbf{X}) \), \( \partial \mathbf{J}(\mathbf{X}) \), \( \partial \mathbf{C}(\mathbf{X}) \), \( \partial \rho(\mathbf{X}) \) and \( \partial \mu(\mathbf{X}) \). Equivalently, we have differential equations
\[ \frac{\partial s_{ik}}{\partial X_k} = 0, \quad (2.19) \]

\[ J_k = -\frac{D}{kT} \frac{\det F - 1}{\Omega} H_{ki} H_{li} \frac{\partial \mu}{\partial X_l}, \quad (2.20) \]

\[ p = \kappa (\det F - \Omega C - 1), \quad (2.21) \]

\[ \mu = p\Omega + \frac{\partial W}{\partial C}, \quad (2.22) \]

as well as solvent conservation Eq. (2.9) in the bulk, and

\[ s_{ik} N_k = t_i, \quad (2.23) \]

\[ \mu = \mu, \quad (2.24) \]

on a surface. It could thus be recognized that the tensor \( s(X, t) \) given by Eq.(2.18) is the nominal stress, the Lagrange multiplier \( \mu(X, t) \) introduced to enforce the solvent conservation is just the chemical potential, and \( p(X, t) \) is the osmotic pressure (Hong 2008).

To reduce number of unknowns in finite element calculation, we eliminate the variable \( J \) by substituting the kinetic law [Eq.(2.20)] to the weak form Eq.(2.17). We also insist local equilibrium of solvent, \( \mu = \bar{\mu} \), on the surface next to a buffer. Then we rescale the weak form by element time increment as:
\[
\Delta t \delta \Pi = - \int \frac{\partial S_{ik}}{\partial X_k} \delta x_i dV + \int (s_{ik} N_K - t_i) \delta x_i dA \\
- \int \dot{\epsilon} \delta u dV + \frac{D}{kT} \left( \frac{\det F - 1}{\Omega} H_{K_i} H_{L_i} \frac{\partial \mu}{\partial X_k} \delta u - \frac{\partial \mu}{\partial X_k} dV \right) \\
+ \frac{D}{kT} \left( \frac{\det F - 1}{\Omega} H_{K_i} H_{L_i} \frac{\partial \mu}{\partial X_k} N_K \delta u dA \right) \\
- \int \left( \left( \det F - \Omega C - 1 \right) + \frac{P}{K} \right) \delta p dV + \int \left( \Omega p + \frac{\partial W}{\partial C} - \mu \right) \delta C dV = 0
\]

(2.25)

The weak form Eq.(2.25), together with the expression for nominal stress, Eq.(2.18), are implemented into a finite element code for the commercial software COMSOL Multiphysics 4.3b. In all calculations, implicit time discretization and a direct solver are used. The spatial interpolation of the displacement field is one order higher than that of the chemical potential, in order to match the element order between stress and chemical potential. Pressure is interpolated on Gaussian points with interpolation function an order lower than the displacement using a mixed form.

### 2.3.2 Visco-porous relaxation coupling length

Consider the 1D problem of an infinitely large layer of gel under uniaxial deformation while immersed in a solvent bath (Fig. 2.3). Initially, the gel swells freely and reaches equilibrium with external solvent. The thickness of the gel in the dry state is \(L\) and is \(l_0 = \lambda_0 L\) in the free swelling state. Following Hong et al. 2008, the initial swelling stretch \(\lambda_0\) can be obtained by equating stress in Eq. (2.18) to be zero:

\[
N\sigma (\lambda_0^2 - 1) + \ln \left( 1 - \frac{1}{\lambda_0} \right) \lambda_0^2 + 1 + \frac{N}{\lambda_0^3} = 0.
\]

(2.26)
\( \lambda_0 \) is determined by dimensionless parameters \( \Omega \) and \( \chi \), where \( \Omega = \Omega \ell / (kT / \Omega) \) characterizes the ratio between elastic energy and the mixing energy, and \( \chi \) characterizes the portion of mixing enthalpy in total mixing energy. A constant load \( s \) is applied on top surface of the gel and the through thickness stretch \( \lambda(X,t) \) evolves with time as the solvent migrates through the top surface of the gel. The out of plane swelling ratio is fixed as a constant \( \lambda_0 \). Meanwhile, the gel is free to slide on the impermeable substrate. Since the gel is infinitely large, the stretch ratio in the plane of the layer is a constant \( \lambda' \). To determine \( \lambda' \), we notice that in the direction in the plane of the layer, the total in-plane stress should vanish as there is no external force applied, which leads to a global constrain (Hong et al. 2010):

\[
\int_0^t \left[ \frac{\Omega \ell}{kT} \left( \lambda' - \frac{1}{\lambda'} \right) + \frac{\eta}{\lambda_0 \lambda_{\lambda'}} \frac{\partial \lambda'}{\partial t} + \frac{kT}{\Omega} \left( \lambda_0 \lambda \ln \left( 1 - \frac{1}{\lambda_0 \lambda} \right) + \frac{1}{\lambda} + \frac{\chi}{\lambda_0 \lambda \lambda'}^2 \right) \right] dX. \tag{2.27}
\]

The time dependent evolution of \( \lambda' \) is given by the transportation equation Eqs. (2.9, 2.20) (Hong et al. 2008):

\[
\lambda_0 \frac{\partial \lambda'}{\partial t} = -\frac{\partial}{\partial X} \left[ \frac{D(\lambda \lambda_0 \lambda' - 1)}{\Omega kT \lambda^2} \frac{\partial}{\partial X} \mu \right] \tag{2.28}
\]

where the chemical potential is given by Eq. (2.22) as

\[
\mu = kT \left[ \ln \left( 1 - \frac{1}{\lambda_0 \lambda' \lambda} \right) + \frac{1}{\lambda_0 \lambda_0 \lambda'} + \frac{\chi}{\lambda_0 \lambda' \lambda^2} \right] + \Omega \frac{kT}{\lambda_0 \lambda'} \left( \lambda - \frac{1}{\lambda} \right) + \frac{\Omega \eta}{\lambda} \frac{\partial \lambda'}{\partial t} - \frac{\Omega \xi}{\lambda_0 \lambda'}, \tag{2.29}
\]
The system subjects to boundary condition:

\[
\frac{s\Omega}{kT} = \lambda_0 \lambda' 
\left[ N \sigma \left( \lambda - \frac{1}{\lambda} \right) + \lambda_0 \lambda' \ln \left( 1 - \frac{1}{\lambda_0 \lambda' \lambda} \right) + \frac{1}{\lambda} + \frac{\chi}{\lambda_0 \lambda' \lambda^2} \right],
\]

(2.30)

at \( X = 0 \), and

\[
\frac{\partial \lambda}{\partial X} = 0,
\]

(2.31)

at \( X = L \). The coupled ODEs can be solved by finite element method for unknown field \( \lambda(X,t) \) and the constant \( \lambda' \) for given applied stress \( s \).

We consider representative values of material parameters (Flory 1953):

\( \alpha \Omega = 10^{-3} \) and \( \chi = 0.1 \), and Eq.(2.27) gives an initial stretch \( \lambda_0 = 3.4 \). A dimensionless stress \( s/\alpha kT = 10 \) is applied. Fig. 2.4 shows typical relaxation behavior by plotting the total thickness of the gel \( l \) as a function of time. As \( s \) is much larger than the modulus of the material and it lead to significant decreases in total thickness and finite strain deformation in the material. The Gel undergoes simultaneous processes of viscoelastic creep and poroelastic creep, corresponding to the two time derivative terms in the governing ODE [Eqs. (2.28, 2.29)]. We can examine the asymptotic behaviors
considering a small applied stress that causes a small deformation $\lambda \approx \lambda_0 (1 + \varepsilon)$. In addition, we notice the initial swell ratio $\lambda_0 > 1$, and linearize the governing equation. If the diffusion coefficient is very large compare to viscosity, the viscous stress vanishes, and we have

$$\frac{\partial \varepsilon}{\partial t} = \frac{\sigma \Phi}{kT} D \left[ \frac{\partial^2 \varepsilon}{\partial x^2} - \varepsilon \left( \frac{\partial \varepsilon}{\partial x} \right)^2 \right] \approx \frac{\sigma \Phi}{kT} D \frac{\partial^2 \varepsilon}{\partial x^2}.$$  \hspace{1cm} (2.32)

The form of the ODE introduces a kinetic coefficient $D_c = D \sigma \Phi / kT$ for mechanically driving diffusion process in gels and we have characteristic diffusion relaxation time:

$$t_d = \frac{L^2}{D_c}.$$  \hspace{1cm} (2.33)

In the other limit if the diffusion coefficient is very small compare to viscosity, the transportation equation vanishes. The deformation is the same everywhere, and the homogeneous relaxation carries an intrinsic time scale

$$t_v = \frac{\eta}{\sigma kT},$$  \hspace{1cm} (2.34)

which is characteristic time for viscoelastic relaxation in absence of solvent molecules migration. Equating the two time scales gives rise to the visco-porous coupling length:

$$L_c = \sqrt{D_c t_v} = \sqrt{\frac{D_0 \eta}{kT}}.$$  \hspace{1cm} (2.35)

at which the two processes take comparable periods of time. Consider a typical hydrogel with diffusion constant $10^{-11} m^2/s$, and typical viscous relaxation time $0.1 s$, the critical
coupling length is $L_c = 1\mu m$, which is at the mesoscopic level, as shown by experiments (Kalcioglu et al 2012).

Figure 2.4 Total thickness as a function of time for creeping of an infinitely large layer of gel under compression calculated for samples of size $L/L_c = 10$ (blue), 1 (green), 0.1 (red). Time normalized by (a) the viscoelastic relaxation time, and (b) the characteristic diffusion time.

From above consideration, we can normalized all length by $L_c$ and denote the dimensionless size $\hat{L}$. As shown by Fig. 2.5(a), for sample made of same material but of different sizes, the distinction between the two relaxation processes is clearer for sample with larger dimensionless size $\hat{L}$, i.e. a gel of lower viscosity or larger physical size. In other words, the viscoelastic and poroelastic timescales are separated (Mohan et al 2012). In such a case, one may neglect the viscous effect of a macroscopic gel with relatively low viscosity. While the viscoelastic deformation is almost independent of the specimen size, as shown by Fig. 2.5(a), the poroelastic deformation in the second stage is highly size dependent. To show the size dependency, we replot the same creep curves in Fig. 2.5(b) by normalizing time with diffusion time $t_d$. In the renormalized plot, the
creep strains in the poroelastic stage all collapse into the same curve. As deformation is limited by the diffusion of solvent into the gel, the characteristic time of the second stage is given by $L^2/D_c$. On the other hand, for a sample smaller than the intrinsic length scale, the poroelastic and viscoelastic stages overlap with each other, and it appears as if the material has only one relaxation mode.

2.4 Zener-type Visco-poroelastic Gel

In this section, we extend the model to more general viscoelastic behavior exemplified by the Zener model (1st spring-dashpot series in Fig. 2.1). Comparing to the Kelvin model, the Zener model is capable of capturing both creeping and stress relaxation behaviors. As discussed in section 2.1, a general viscous polymer network can be represented by combination of permanent and transient networks. We assume that deformation and dissipation in both types of networks are uncoupled, and can be calculated via summing their individual contribution. Let both networks to be neo-Hookean, and the strain energy density is:

$$W^e(F, F^e) = \frac{\omega k T}{2} \left( I_1^e - 3 - 2 \log(\det F^e) \right) - \frac{p^2}{2\kappa^e} - p \left( \det F - 1 - C\Omega \right)$$

$$+ \frac{\sigma^e k T}{2} \left( I_1^e - 3 - 2 \log(\det F^e) \right) - \frac{p^\epsilon}{2\kappa^\epsilon} - p^\epsilon \left( \det F^\epsilon - 1 - C\Omega \right)$$

where the second line is contribution from the transient network. Here $I_1^e = F^e : F^e$ is the first invariant of elastic strain of transient network. $\kappa^\epsilon$ is a large bulk modulus that enforces the molecular incompressibility in the transient state.
Assume the viscous deformation are Newtonian-like, the dissipation function reduces to

$$\dot{W}^\nu = \det \mathbf{F} \left( \eta^{is} d_{ij}^i d_{ij}^i + \eta^{ib} d_{ik}^i d_{kn}^i \right)$$  \hspace{1cm} (2.32)

where $\eta^{is}$ and $\eta^{ib}$ are shear and bulk viscosity of the transient network respectively.

Because the strain in the intermediates is not compatible, one can add an arbitrary rotation to the intermediate state without affecting the total energy of the system. To eliminate the redundant rotation, we assume the intermediate state to be rotation free by constraining inelastic spin $\mathbf{w}' = \left( \mathbf{e}^i \cdot \mathbf{H}' - \mathbf{H}' \cdot \mathbf{e}^T \right)/2 = 0$ using a large viscosity:

$$\dot{W}^{\nu'} = \det \mathbf{F} \eta^a w_{ij}^j w_{ij}^j ,$$  \hspace{1cm} (2.33)

where $\eta^a >> \eta, \eta^a >> \eta^{is}, \eta^a >> \eta^{ib}$.

Substitute Eqs. (2.13-2.15, 2.31-2.33) into Eq. (2.10), the variation of the total power functional yields the weak form:

$$\delta \Pi = -\int \frac{\partial s_{ik}}{\partial X_L} \delta v_i dV + \int (s_{ik} N_K - t_i) \delta v_i dA + \int (-\sigma_{ij}^e + \eta^{is} d_{ij}^i + \eta^{ib} d_{ik}^i \delta_{ij}) \delta v_i dV$$

$$+ \int \left( \frac{J_k F_{ik} F_{il}}{m \det \mathbf{F}} + \frac{\partial \mu}{\partial X_L} \right) \delta j_i dV - \int \left( \dot{\mathbf{C}} + \frac{\partial J_L}{\partial X_L} \right) \delta \dot{j} dV + \int (\mu - \bar{\mu}) \delta l dA$$

$$- \int \left( \left( \det \mathbf{F} - \Omega C - 1 \right) + \frac{p}{\kappa} \right) \delta \rho dV +$$

$$+ \int \left( p \Omega + \frac{\partial W}{\partial \mathbf{F}} - \mu \right) \delta C dV = 0$$  \hspace{1cm} (2.34)

where the nominal stress is

$$s_{ik} = \frac{\partial W^e}{\partial F_{ik}} - p H_{ki} \det \mathbf{F}.$$  \hspace{1cm} (2.35)
The weak form Eq. (2.17) holds true for arbitrary test functions $\mathbf{v}(X), \mathbf{F}^i(X), \mathbf{J}(X), \mathbf{C}(X), \mathbf{p}(X)$ and $\mathbf{u}(X)$. The minimization problem produces differential equations Eqs. (2.19-2.22) as well as the internal stress equilibrium in the 1st spring dashpot series in the intermediate state:

$$
\sigma^e_{ij} = \eta^{ij} d^i_j + \eta^{ib} d^i_{kk} \delta^b_j, \quad (2.36)
$$

where $\sigma^e_{ij}$ is the elastic stress on the 1st spring in the intermediate state, given by

$$
\sigma^e_{ij} = F^e_{jk} \det^{-1} F^e \partial W^e / \partial F^e_{ik}.
$$

Following the previous section, we can simplify the weak form by eliminate variable $J$ and insist local equilibrium of solvent $\mu = \bar{\mu}$. The rescaled and simplified weak form is:

$$
\begin{align*}
\Delta t \delta \Pi & = -\int \frac{\partial s_{ik}}{\partial X_k} \delta x_i dV + \int (s_{ik} N_k - t_i) \delta x_i dA \\
& + \int_{\Omega} \left( -\sigma^e_{ij} + \eta^{ib} d^i_j + \eta^{ib} d^i_{kk} \delta^b_j \right) \left( H_{ki} \delta F^e_{ik} - \frac{H_{ki} \delta F^e_{ik}}{3} \right) dV \\
& - \int C \delta \mu dV + \frac{D}{kT} \int \frac{\det F - 1}{\Omega} H_{ki} H_{Li} \frac{\partial \mu}{\partial X_L} \delta \frac{\partial \mu}{\partial X_K} dV \\
& + \frac{D}{kT} \int \frac{\det F - 1}{\Omega} H_{ki} H_{Li} \frac{\partial \mu}{\partial X_L} N_k \delta \mu dA \\
& - \int \left( (\det F - \Omega C - 1) + \frac{p}{\kappa} \right) \partial p dV + \int \left( \Omega \partial p + \frac{\partial W}{\partial C} - \mu \right) \partial C dV = 0.
\end{align*}
$$

The weak form Eq. (2.35), together with the expression for nominal stress, Eq. (2.35), are implemented into finite element codes and solved using COMSOL 4.3b with similar setting to previous section.

A Zener model carries intrinsic time scales
\[ t_v^\infty = \frac{\eta^i}{\alpha kT}, \quad t_v^0 = \frac{\eta^i}{\alpha kT + \sigma^\infty kT}, \]  

(2.38)

where \( t_v^0 \) characterize time for viscoelastic relaxation to occur, and \( t_v^\infty \) characterize the full relaxation of viscous deformation. If \( t << t_v^0 \), the materials behaves elastically with instantaneous modulus \( \mu^0 = \alpha kT + \sigma^\infty kT \), if \( t >> t_v^\infty \), the materials behaves elastically with long time modulus \( \mu^\infty = \alpha kT \). At intermediate time, the material behavior is time dependent. Similarly to Eq. (2.29), Eq. (2.38) is an over-estimation if the gel is swollen as the modulus decreases with swelling.

Similar to Eq. (2.30), the combination of \( t_v^0, t_v^\infty \) and the effective diffusion constant \( D_c \) gives rise to two visco-porous coupling lengths:

\[ L_c^\infty = \sqrt{\frac{\eta^i \Omega}{kT}}, \quad L_c^0 = \sqrt{\frac{D \eta^i \Omega \mu^\infty}{kT \mu^0}}, \]  

(2.39)

and obviously, \( L_c^\infty > L_c^0 \). At a characteristic length much smaller than \( L_c^0 \), solvent diffusion equilibrates much faster than viscous deformation, and the evolution process of a gel is limited by the viscosity. At a characteristic length much larger than \( L_c^\infty \), the overall evolution process is limited by diffusion. We rescale all stresses by \( \alpha kT \), all lengths by \( L_c^0 \), all fluxes by \( L_c^0 / \Omega_c \), and time by \( t_v^0 \), and denote normalized variable with a hatted symbol.
To illustrate the difference between Kelvin and Zener model, let us consider the unconstrained uniaxial deformation of a gel block. The block has dimensionless size $L \times \hat{L}$ when dry. It swells freely and has reached equilibrium with the surrounding solvent in the initial state. Using representative values of material parameters (Flory 1953): $\omega \Omega = 10^{-3}$ and $\chi = 0.1$, Eq.(2.27) gives an initial stretch $\lambda_0 = 3.4$. For the Zener model, we consider a highly viscous case with $\omega^v / \omega = 9$. The instantaneous modulus is $(\omega + \omega^v)\Omega = 10^{-2}$. During deformation, the surface of the block is permeable to solvent molecules. At $\hat{t} = 0$, a constant nominal stress is applied on the top surface. The bottom
surface is constrained from vertical displacement, and the lateral sides are taken to be traction free.

Snapshots of the deformation of the Kelvin type gel with $\hat{L} = 3$ are shown in Fig. 2.4. In the first stage, $0 < \hat{t} < 1$, the deformation is homogeneous and the uniform field of chemical potential decreases with the applied mechanical load. The volume of the gel is conserved in this stage, and the gel behaves like an incompressible material. The solvent migration takes place mostly in the second stage, starting from the thin surface layer of the gel. Due to solvent migration, the deformation of the gel is no longer uniform, and the volume of the gel increases in the second stage. After a long enough time, when the global equilibrium has been reached, the deformation becomes uniform again. Snapshots of the deformation patterns of a Zener gel with $\hat{L}_e = 3$ are shown in Fig. 2.9 (a,b). Similar to a Kelvin gel, the deformation is decoupled into the viscoelastic stage and the poroelastic stage. However, it is able to deform instantaneously to the applied load, during which it behaves as an incompressible materials with instantaneous modulus $\mu^0$. Since the gel size is large, poroelastic deformation occurs when the viscous deformation is fully relaxed. In the decoupled case, the second stage relaxation of the Zener gel is identical to the Kelvin gel.
CHAPTER III

PHASE FIELD MODEL

FOR FINITE STRAIN INELASTIC FRACTURE

3.1 Finite Strain Phase Field Models

3.1.1 Continuum Approximation of Heterogeneous Systems

We study an inhomogeneous system containing dissimilar phases by marking each material point with an internal variable \( \phi \). On the interface, \( \phi \) changes abruptly but continuously, and we assume the free energy density is a function of the gradient of \( \phi \). Although whether such gradient is taken with respect to the current coordinates \( \nabla_x \phi \) or to the reference coordinates \( \nabla \phi \) is a question yet to be discussed, the general form of free energy \( W(F, \phi, \nabla \phi) \) is always valid, given the relation:

\[
\nabla \phi = F \cdot \nabla_x \phi.
\]

Work is done to the system by boundary traction \( t \). The total potential energy of the system is:

\[
\Pi(x, \phi) = \int W(F, \phi, \nabla \phi) dV - \int t \cdot \chi dA.
\]

In the equilibrium state, \( \Pi \) is minimized for arbitrary small changes \( \delta x \) and \( \delta \phi \) as:

\[
\begin{align*}
- & \int \frac{\partial}{\partial X_k} s_{ik} \delta x_i dV - \int \left( t_i - \frac{\partial W}{\partial F_{ik}} N_K \right) \delta x_i dA \\
+ & \int \left( \frac{\partial W}{\partial \phi} - \frac{\partial}{\partial X_k} \left( \frac{\partial W}{\partial \phi_k} \right) \right) \delta \phi dV + \int N_K \frac{\partial W}{\partial \phi_k} \delta \phi dA = 0
\end{align*}
\]
Considering the arbitrariness of test functions, each term in the parentheses of the integrant mush vanish in order for the above equation to hold. We obtain the governing equation of the system for stress balance condition:

\[ \frac{\partial s_{ik}}{\partial X_k} = 0, \]  

(3.4)

and evolution of phase field variable

\[ \frac{\partial W}{\partial \phi} - \frac{\partial}{\partial X_k} \left( \frac{\partial W}{\partial \phi_k} \right) = 0 \]

(3.5)

in the bulk, as well as

\[ s_{ik} N_k = t_i \]  

(3.6)

\[ N_k \frac{\partial W}{\partial \phi_k} = 0 \]  

(3.7)

on the boundary, where \( s_{ik} = \frac{\partial W}{\partial F_{ik}} \) is the nominal stress. The equilibrium state of the material depends on the energy landscape \( W(\phi) \). Without additional constraint, the system will evolve toward the minimum of \( W \). If \( W \) has multiple minima, formation of metastable state corresponding to a local minimum of \( W \) is possible.

We assume \( W \) can be divided into addable parts as strain energy \( W^e \) for coupled phase change and deformation, local phase field energy \( W^m \) for bonding energy of the bulk phase, and interface energy \( W^i \):

\[ W(F, \phi, \nabla \phi) = W^e(F, \phi) + W^m(\phi) + W^i(F, \phi, \nabla \phi). \]  

(3.8)

Both \( W^e \) and \( W^m \) describe the properties of the bulk material, and they will be discussed in the following sections with specific problems. Property of interface is
contained in $W^i$. Despite the lack of knowledge for relating specific interface microstructure to $W^i$, in this work we present two simply interface model that captures the essential thermodynamic characteristics of typical solid and liquid interfaces.

### 3.1.2 Ideal Solid and Ideal Liquid Interface Models

Interface energy of an ideal solid interface is deformation independent. Following Cahn and Hilliard’s approach (1961), a possible interface energy density is:

$$W^i = \frac{\tau}{2} \frac{\partial \phi}{\partial X_k} \frac{\partial \phi}{\partial X_k}.$$  \hspace{1cm}(3.9)

Since $W^i$ is only a function of material coordinates, the stress field [Eq. (3.7)] is not influenced by the presence of the interface and vice versa. The equilibrium thickness of the interface remains constant in the reference configuration, while the “actual” thickness of a boundary will change with deformation in the current state. In the small strain limit, this treatment will recover interface model classically used for hard materials (Cahn 1961; Onuki, 1988, 1989; Onuki and Furukawa 2001).

Gradient energy is written with respect to the current spatial coordinates $\nabla \phi$ for an ideal liquid interface (Levitas and Samani 2002):

$$W^i = \frac{\tau}{2} \det F \frac{\partial \phi}{\partial x_i} \frac{\partial \phi}{\partial x_i} = \frac{\tau}{2} \det FH_{ki} \frac{\partial \phi}{\partial x_i} \frac{\partial \phi}{\partial x_i} H_{Li}.$$  \hspace{1cm}(3.10)

To reveal the liquid like nature of such interface, we examine the nominal stress by substituting Eq. (3.8, 3.10) into Eq. (3.7):
\begin{align}
    s_{ik} &= \frac{\partial W^e}{\partial F_{ik}} - \tau \det F H_{m_j} \frac{\partial \phi}{\partial X_m} \frac{\partial \phi}{\partial X_L} H_{l_i} H_{k_i} + \frac{\tau}{2} \det F H_{m_j} \frac{\partial \phi}{\partial X_m} \frac{\partial \phi}{\partial X_L} H_{l_i} H_{k_i}, \quad (3.11)
\end{align}

which contains additional terms related to the gradient of the phase field variable. The physical significance of these terms can be made clear when written in the current configuration. Utilizing the simple geometric relation, \( \sigma \det F = s \cdot F \), we have the true stress

\begin{align}
    \sigma_{ij} &= \frac{F_{jk}}{\det F} \frac{\partial W^e}{\partial F_{ik}} - \tau \frac{\partial \phi}{\partial x_i} \frac{\partial \phi}{\partial x_j} + \frac{\tau}{2} \frac{\partial \phi}{\partial x_n} \frac{\partial \phi}{\partial x_n} \delta_{ij}. \quad (3.12)
\end{align}

Compared to the through-thickness stress (in the direction of \( \nabla \phi \)), the hoop stress along the interface is higher by \( \tau |\nabla x \phi|^2 \). To find the interface energy, we integrate the total free energy along the normal direction of the interface as \( \partial (W^e + W^m) / \partial \xi \), which yields (Hong & Wang 2013):

\begin{align}
    W_e + W_m - s \lambda - (W_e^0 + W_m^0 - s \lambda^0) = \frac{\eta}{2} \frac{\det F}{\lambda^2} \left( \frac{\partial C}{\partial \xi} \right)^2. \quad (3.13)
\end{align}

where \( W_e^0, W_m^0, s \lambda^0 \) are corresponding quantities in the homogeneous phase. Adding the contribution of gradient energy, the total excess energy per unit current volume of a diffuse interface equals \( \tau |\nabla x \phi|^2 \). Therefore, the added hoop stress equals the excessive energy per unit volume in the current state. By integrating through the thickness of an interface, the resultant line force equals the interface energy per unit area in the current configuration, namely, the surface tension.
In summary, Eq. (3.9) produces the ideal solid interface with constant thickness and interface energy in reference state; Eq. (3.10) produces the ideal liquid interface, on which neither the actual thickness in the current state nor the surface tension depends on deformation. Both models provide thermodynamically consistent means of introducing the coupling between interface structure change and the deformation of the material.

3.2 Phase Field Model for Fracture of Hyperelastic Materials

3.2.1 Introduction to Physics of Fracture of Elastomers and Gels

We briefly review the crack growth in elastomer and gels from a fracture mechanics perspective. The energetic barrier for crack growth is characterized by the fracture energy $\Gamma$, the energy required to create unit area of crack surface, or equivalently the stress intensity factor/fracture toughness $K_c$, which characterizes the limiting stress in the singular filed in front of the crack tip. The two quantities are related by $\Gamma = K_c^2/E$ for a mode I crack, wher $E$ is the young’s modulus of the material. The necessary condition for defects growth is when sufficient strain energy could be released to overcome the energy barrier $\Gamma$, known the Griffith criterion (Griffith 1921). Consider a material containing a defect of size $A$, and the total potential energy of system to be $\Pi$, the critical condition is written as

$$G = -\frac{\partial \Pi}{\partial A} = \Gamma$$

(3.14)

where $G$ is known as the energy release rate. Both $G$ and $\Gamma$ has the same unit of surface energy $J/m^2$. 
The relation between microstructure and fracture toughness is of both great theoretical and practical interest. One important reason is strength and fracture energy of soft solid varies greatly, from the ductile and stretchable bungee-cord to the brittle and crushable Jell-O, and many common synthetic gels are fragile materials which fail to meet the strength requirement for both its current and potential applications. One example is the breast implant. State-or-art breast implant consists of silicon gels usually encased in an elastomer shell to further increase the structural integrity (Brown et al 2005). The devices could be damaged easily during implantation, trauma, or simply from mechanical pressure of traditional mammographic examination even it is used in a non-loading caring part of human body. It is reported that the silicone gel based implant suffers from at least 1% rupture after 6-year post implant (Cummingham & McCue 2009).

Fracture energy of a brittle hard solid is the energy of breaking one layer of atomic bonds to create new surface, which equals twice of the surface energy of the materials. Typically, $\Gamma$ is on the order of $1J/m^2$ [e.g. $1J/m^2$ for window glass (Griffith 1921) and $5J/m^2$ for the 111 face of diamond (Harkins 2004)]. On the other hand, $\Gamma$ of elastomers range from $10^2 J/m^2$ to $10^5 J/m^2$ (Lake &Thomas 1967; Gent 1996), the higher limit of which is comparable to that of ductile metals. $\Gamma$ can be separated as extrinsic and intrinsic parts as:

$$\Gamma = \Gamma_v + \Gamma_i. \tag{3.15}$$

$\Gamma_v$ attributes from viscous dissipation around the crack tip, and its magnitude depends on viscosity and crack velocity: the more viscous the elastomer is and the faster a crack
propagates, the more energy will be dissipated. In the quasi-static limit when no viscoelastic effect is present, the residual barrier for crack growth is the intrinsic fracture energy $\Gamma_f$. The magnitude of $\Gamma_f$ is on the order of $10^2 J/m^2$ for all ideal elastomers without strain crystallization, which is much greater than surface energy of common brittle material. Lake and Thomas (Lake & Thomas 1967) proposes a model that suggests the origin of the large value of $\Gamma_f$ is due to the loss of strain energy in the polymer chains as they rupture. Immediately prior to fracture, the polymer chain is likely to be fully extended with each link being comparably stretched (Fig. 3.1). The strain energy per link approximately equals the bond energy, and the total energy needed to rupture the fully extended chain is the energy required to stretch one link to the breaking limit multiplied by the number of links in the entire chain. Given the large amount of links per chain in rubber, such a mechanism explains the discrepancy between the fracture energy threshold of rubber and that of brittle crystals. After chain rupture, all the strain energy is lost due to local dissipation on the chain. In essence, the intrinsic fracture energy consists of mostly the intrinsic viscous dissipation and a small value of bonding energy of a single link $\Gamma_f = \Gamma_v + \Gamma_0$.

![Figure 3.1 Schematic drawing of stretched polymer network in front of the crack tip](image-url)
In a dry elastomer, $\Gamma_v$ contributes to the major part of (Ahagon & Gent 1975). $\Gamma_v$ is absent in gels, and they are actually weak and brittle solids. For example, the nominal fracture energy of styrene-butadiene rubber reduces from $10^4 \text{J/m}^2$ to $60 \text{J/m}^2$, when swollen with 75% volume fraction of bromobenzene, a solvent with relatively low viscosity (Grosch 1968). Note that the effect of size change by swelling is already accounted for in the measurement of nominal fracture energy. It is suggested that swelling does not change $\Gamma_I$ as nominal chain density remains constant, while viscoelastic dissipation is greatly reduced, which is shown by the rate dependency of $\Gamma$. $\Gamma$ diminishes with increasing swelling ratio, which reduces to $\Gamma_I$ at the high swelling limit (low elastomer fraction), accompanying this process is the decrease of dynamic loss modulus which vanishes as the dry elastomer becomes fully swollen (Tsunoda et al, 2000).

Let us recall the stress distribution near the crack tip for a mode I crack: the perpendicular stress $s$ approaches infinity as $s \sim K_c / \sqrt{L}$ when distance to crack tip $L$ decreases. The singular field is cut off from the process zone surrounding the crack tip in which damage start to occur and work is done against friction and other irreversible processes. Invoke the relation $\Gamma = K_{IC}^2 / E$, size of the process zone relates to the fracture toughness by:

$$L_p \sim \frac{K_{IC}^2}{s_c^2} = \frac{\Gamma_I E}{s_c^2}$$

(3.16)
$L_p$ defines an intrinsic length scale for the crack, which is the smallest possible flaw of the material. For brittle metal and ceramics, $L_p$ is the size of an atom. Damage and fracture is influenced by defects on the atomic level, such as dislocations and solute atoms. $L_p$ of an elastomer is comparable to the chain length, hence the toughness of the elastomer is not affected by molecular level detail of the chain, but by the network structure.

Cohesive strength $s_c$ is the failure stress of the perfect material. In the polymer network, $s_c$ is determined by the breaking point of chemical bonds, and its magnitude is much greater than the entropic modulus of the polymer network. Hence a single polymer chain is typically highly stretchable with several hundred times the failure strain. On the other hand, because of the network level inhomogeneity, shorter chains in the polymer network ruptures before the network is fully stretched, and the accumulated damage leads to the fail of the network before all chains can be fully stretched. For example, it has been shown that polymer network of gels contains long range spatial heterogeneities (Matsuo et al 1994) the order of $10^{-6} \sim 10^{-4} \mu m$ (Matsuo et al 1994; Shibayam 2011), which is much greater than the chain length. Quantitative process of how the inhomogeneity evolves into the flaws and leads to the initiation of crack in the gels still remains a challenging question, it is obvious that the actual cohesive strength $\sigma_c$ is greatly reduced and is much smaller than the theoretical strength of a single chain. For this reason, most synthetic gels are not only brittle, but weak material, which fails at extremely low stress comparing to their counterpart of dry elastomers in the absent of
viscous toughening. On the other hand, if the polymer network is highly uniform, a gel can become highly stretchable, such as the recently discovered Tetra-PEG gel (Matsunaga et al 2009).

3.2.2 Finite Strain Phase Field Fracture Model

To apply the general phase field framework for crack growth problem, we introduce phase field variable \( \phi \in (0,1) \) that serves to differentiate the fully damage (\( \phi = 0 \)) and virgin (\( \phi = 1 \)) state of the material. We supply an explicit form of the free energy density function [Eq. (3.8)] suggested by Karma et al (2001):

\[
W = W^e [g(\phi), \mathbf{F}] + h[1 - g(\phi)] + \frac{\tau}{2} (\nabla \phi)^2,
\]

(3.17)

with the ideal solid interface model [Eq. (3.9)], and the local phase field energy \( h[1 - g(\phi)] \). As an example, we consider a linear elastic material and write the strain energy as \( W^e = g(\phi) \varepsilon : \mathbf{C} : \varepsilon \), which depends on both strain \( \varepsilon \) and a damage function \( g(\phi) \). Here \( \mathbf{C} \) is the stiffness matrix of the material. \( g(\phi) \) interpolates \( W^e \) between the damage and virgin state. A commonly used form is:

\[
g(\phi) = 4\phi^3 - 3\phi^4,
\]

(3.18)

which describes the smooth and monotonous decay of \( W^e \) with increased level of damage. \( g(1) = 1 \) in the virgin material, and regular continuum model is recovered. In the fully damage limit, \( g(0) = 0 \), and \( W^e \) vanishes. The arbitrary level of damage imposes isotropic softening in the material, and stiffness changes as \( g(\phi) \mathbf{C} \). It is noted
that in numerical simulation, a small residual value is kept \( g(\phi) = 4\phi^3 - 3\phi^4 + \phi_d \) (\( \phi_d \ll 1 \)) to enable numerical calculation.

With homogeneous strain, we rewrite Eq. (3.15) as \( W = g(\phi)\mathbf{\varepsilon} : \mathbf{C} : \mathbf{\varepsilon} \) at the absence of interface energy. Parameter \( h \) defines a critical energy for damage initiation. Since \( g(\phi) \) increases monotonously with \( \phi \), when \( \mathbf{\varepsilon} : \mathbf{C} : \mathbf{\varepsilon} < h \), the virgin state is energetically more favorable and damage is impossible; when deformation is increased to the level such that \( \mathbf{\varepsilon} : \mathbf{C} : \mathbf{\varepsilon} > h \), the fully damage state is more energetically favorable and damage occurs spontaneously.

We modify the strain energy density for a neo-Hookean material as:

\[
W^e[\mathbf{F}, g(\phi)] = g(\phi) \frac{\mu_0}{2} \left( I_1 - 3 - 2\log(\det \mathbf{F})\right) + \frac{\kappa_0}{2} g_\kappa(\phi) (\det \mathbf{F} - 1)^2. \tag{3.19}
\]

In an ideal rubber, the initial shear modulus is given by \( \mu_0 = \sigma_0 kT \) [Eq. (1.1)]. \( g(\phi) \) is interpreted physically as the portion of remaining stress effective polymer chains survived damage (Miche et al 2013). We interpolate between virgin and fully damaged state by consider the damage network as ideal rubber with reduced shear modulus \( \mu(\phi) = \sigma_0 g(\phi) kT \), where \( \sigma_0 g(\phi) \) is the effective chain density. For an incompressible rubber, we use \( \kappa_0 \gg \mu_0 \) as the initial bulk modulus. Obviously, the fully damage material is no longer incompressible, and the damage function \( g_\kappa(\phi) \) must differ from \( g(\phi) \) to allowed the bulk modulus to become comparable to the shear modulus. An explicit form \( g_\kappa(\phi) \) is given by Eq. (3.43), which will be discussed in section 3.4.1. Eq. (3.19) presents a stiff numerical problem since \( \mu_0 \) and \( \kappa_0 \) differs by orders of
magnitudes. Alternatively, we can use the modified strain energy by applying Legendre transform similar to Eq. (2.12):

\[ W^e[F, g(\phi), p] = \frac{g(\phi)}{2} \mu_0 \left[ I_1 - 3 - 2 \log(\det F) \right] - \frac{p^2}{2\kappa_0 g_x(\phi)} - p(\det F - 1). \]  

(3.20)

where \( p \) is the hydrostatic pressure.

Damage is a dissipative process. We assume it obeys linear kinetics and evolves isotropically. The rate of dissipation per unit volume is:

\[ \dot{W} = \frac{\dot{\phi}^2}{m}, \]  

(3.21)

where \( m \) is the mobility of \( \phi \). Eq. (3.21) includes all forms of dissipations during the short event of snapping of atomic bonds in the process zone. For quasi-static and viscoelastic cracks of our interest, we will limit the discussion to the Griffith limit (Karma and Hakim 2009), i.e. damaging of the material is a conservative process, and the strain energy is converted into interface energy and being stored in the crack surface. We ensure such conservation by using a very large \( m \), such that dissipation in Eq. (3.21) is negligible, with only a small residual number as a mean of numerical regularization.

With the additional dissipation term, we write the power of the system by modifying Eq. (3.2):

\[ \Pi[v, \dot{\phi}, \nabla \phi] = \int \dot{W}(F, \phi, \nabla \phi) dV - \int f_i v_i dA + \int \frac{\dot{\phi}^2}{2m} dV. \]  

(3.22)

Similar to Eq. (3.3), minimization of functional Eq. (3.21) yields the coupled governing equation sets:
\[
\frac{\partial s_{iK}}{\partial X_i} = 0
\]  \hspace{1cm} (3.23)

\[
\frac{\dot{\phi}}{m} + \frac{\partial W}{\partial \phi} - \tau \frac{\partial}{\partial X_L} \left( \frac{\partial \phi}{\partial X_K} \right) = 0
\]  \hspace{1cm} (3.24)

in the bulk and boundary conditions

\[
s_{iK} N_K = t_i, \quad N_K \frac{\partial W}{\partial \phi_K} = 0.
\]  \hspace{1cm} (3.25)

In particular, Eq. (3.5) is replaced by the time dependent Ginsburg-Landau (GL) equation. The term \( \partial W / \partial \phi \) consists of \( \partial W^e / \partial \phi \) as the mechanical driving force for crack growth and \( \partial W^m / \partial \phi \) from local phase field energy as the resistance to crack growth.

The nominal stress is given by:

\[
s_{iK} = \frac{\partial W}{\partial F_{iK}} - p H_{K}, \quad \det \mathbf{F}.
\]  \hspace{1cm} (3.26)

where the hydrostatic pressured is:

\[
p = \frac{\partial W}{\partial \det \mathbf{F}} = \kappa(\phi)(\det \mathbf{F} - 1).
\]  \hspace{1cm} (3.27)

The weak form Eq. (3.22), or Equivalently, the strong form Eq. (3.23–3.27) is implemented into a finite element code with the commercial software COMSOL Multiphysics 4.3b to solve for the inhomogeneous fields \( \mathbf{x}(t), \phi(t) \). Convergent solution is obtained with implicit time discretization and a direct solver. Both fields \( \mathbf{x}(t), \phi(t) \) are interpolated with 2\textsuperscript{nd} order Lagrange element.
Consider the 2D plane strain problem of a wide strip consisting of a long crack in the center, and is subject to mode I loading (Fig 3.2). Materials are fully broken with $\phi = 0$ on the initial crack surface, and are intact with $\phi = 1$ in the bulk. Since crack surface far away from the crack tip is stress-free and does not change during simulation, we neglect diffusive interface in such region for computational efficiency. Initially, we allow sufficient time for the GL equation to equilibrate and form a diffusive interface. The sample is then loaded under displacement control. Due to the symmetry of the problem, an active crack is observed to propagate only mode I along 1 direction, whereas the simulation does not prevent it to kink into arbitrary direction or to develop branches.
A crack initiates when the energy release rate $G$ equals fracture energy $\Gamma$, known as the Griffith condition. The critical value of $G$ is referred to as critical energy release rate $G_c$. In an elastic material, $\Gamma$ simply equals to twice the interface energy $\gamma$, and we refer to the value $\Gamma_i = 2\gamma$ as intrinsic fracture energy. $\Gamma_i$ is the energy required to propagate crack surface for unit length without additional dissipation.

$G$ can be calculated from the $J$-integral:

$$G = J = \int_C \left( WN_1 - N_j s_{jk} \frac{\partial u}{\partial X_1} \right) dL.$$  

(3.28)

where $C$ is a large contour containing the crack tip and connects the two opposite crack surfaces and $N$ is the outward normal vector of $C$. While Eq. (3.25) is only applicable to homogeneous elastic materials, it has been shown that if crack surface is modelled as diffusive interface (Karma and Hakim 2009), we have:

**Figure 3.3.** Diffusive crack tip and schematic drawing showing the contour integral in Eq. (3.28). Color scale corresponds to value of phase field variable $\phi$. 
\[
\int_{C'} \left( WN_1 - N_j s_{jk} \frac{\partial u_k}{\partial X_1} \right) dL = \frac{v}{m} \int_{\Sigma} \frac{\partial \phi}{\partial t} \frac{\partial \phi}{\partial X_1} dS. \tag{3.29}
\]

where \( v \) is crack velocity, \( C' \) is a large loop surrounding the crack tip and traverses the diffusive interface (Fig. 3.2), \( \Sigma \) is the area inside loop \( C' \), and \( W \) is total free energy density including both local phase field and gradient energy. The right hand side of Eq. (3.29) is dissipation from phase field damage, which vanishes for slow propagating crack. We separate \( C' \) into segments \( A \rightarrow B \) and \( B \rightarrow A \), where \( B \rightarrow A \) is inside the virgin material and \( A \rightarrow B \) traverses the diffusive interface. Eq. (3.29) becomes:

\[
\int_{C'} \left( WN_1 - N_j s_{jk} \frac{\partial u_k}{\partial X_1} \right) dL = G - \Gamma_i = 0, \tag{3.30}
\]

where

\[
G = \int_{B \rightarrow A} \left( WN_1 - N_j s_{jk} \frac{\partial u_k}{\partial X_1} \right) dL \tag{3.31}
\]

recovers the energy release rate, and

\[
\Gamma_i = -\int_{A \rightarrow B} \left( WN_1 - N_j s_{jk} \frac{\partial u_k}{\partial X_1} \right) dL, \tag{3.32}
\]

recovers the intrinsic fracture energy, and Eq. (3.30) is simply the Griffith condition. In our simulation, the remote part of the diffusive interface is neglected, and the J integral is can be also evaluated on an alternative loop \( C'' \) which excludes the diffusive interface as shown by Fig. 3.3. Since diffusive interface does not affect the remote field, we will simply obtain the energy release rate and Eq. (3.30) is no longer hold.

When we calculate J-integral on loop \( C' \), segment \( A \rightarrow B \) is far away from the crack tip and is free of normal stress. Eq. (3.31) reduce to the integration for local and
gradient energy along the diffusive interface, which is nothing but the interface energy (Onuki 1999, Karma and Hakim 2009):

$$\Gamma_i = 2\gamma = 2\sqrt{2\hbar \tau} \int_0^1 \sqrt{1 - g(\phi)} d\phi.$$  \hspace{1cm} (3.33)

Substitute the explicit form of \(g(\phi)\) Eq. (3.15), we have

$$\Gamma_i \approx 2\sqrt{h \tau}.$$  \hspace{1cm} (3.34)

Here we have evoked the ideal solid interface model for the crack surface in the free energy function Eq. (3.14). As discussed in section 3.2.2, \(\Gamma_i\) and the characteristic interface width

$$L_u \sim \sqrt{\tau / h}$$  \hspace{1cm} (3.35)

are both constants independent of deformation, which reflects the fact that the microstructure of the crack surface of a solid material does not change with deformation at given level of damage.

We normalize all energy with \(h\) and all length with \(L_u\), and mark all normalized quantities with the hat symbol \(\hat{}\). Energy release rate is then normalized by the interface fracture energy, e.g. \(\hat{G} = G / \gamma = 2G / \Gamma_i\). Dimensionless height of the sample is \(\hat{H} = 20\), which is much larger than the diffusive interface thickness. Sample width is taken to be \(10\hat{H}\), and the initial crack length is \(5\hat{H}\), both of which are much larger than the height. The dimensionless shear modulus \(\hat{\mu}_0\) is the sole parameter of the model, and we will discuss physical meaning of it later in this section. In addition, a large initial bulk modulus \(\hat{\kappa}_0 = 10^5 \hat{\mu}_0\) is used to impose incompressibility of the material.
Denote $\lambda$ as the far field stretch ratio of the material in the perpendicular direction behind the crack tip. The energy release rate of the sample is:

$$\hat{G} = \frac{\hat{\mu}_0}{2} \left( \lambda^2 + \frac{1}{\lambda^2} - 2 \right) \hat{H}.$$  \hfill (3.36)

Crack initiates when the Griffith condition is satisfied: $\hat{G}_c = 2$. From Eq. (3.36), we obtain the failure strain of the material:

$$\lambda_c = \sqrt{\frac{2}{H\hat{\mu}_0}} + 1 + \sqrt{\left( \frac{2}{H\hat{\mu}_0} + 1 \right)^2 - 1}.$$  \hfill (3.37)

In Fig. 3.5, we compare the numerical results for $\hat{\mu}_0$ ranging from $10^{-1}$ to $10^4$ against Eq. (3.37). It is shown that phase field model successfully capture the Griffith criterion for crack initiation. Furthermore, as the crack grows, the strain energy is continuously being converted for growing interface, on which the interface energy remains a constant.

**Figure 3.4** Snapshot (deformed state) of a propagating crack calculated for (a) soft solid with $\hat{\mu}_0 = 1$ (b) hard solid with $\hat{\mu}_0 = 10^3$, both are incompressible neo-Hookean material. Color scale represents value of phase field variable $\phi$. 

(a) 

(b)
independent of deformation. To show that the crack growth behavior is size independent, we compare numerical results for samples of various sizes, which demonstrate that the effect of diffusive interface is truly localized in the process zone, whereas in the far field, the phase field model asymptotically approaches the sharp interface prediction.

![Figure 3.5](image)

**Figure 3.5** Failure strain as a function of dimensionless modulus $\hat{\mu}_0$. Analytical results [Eq. (3.37)] are compared with FEM results of $\lambda_c$ taken from the steady state propagating crack. To demonstrate localization of diffusive interface, we vary the sample size by 10 times by considering a) sample with dimensionless height $\hat{H} = 20$, width $10\hat{H}$, initial crack length $5\hat{H}$; b) sample with dimensionless height $\hat{H} = 200$, width $100\hat{H}$, initial crack length $50\hat{H}$.
Fig. 3.5 also shows that failure strain increases with $\hat{\mu}_0$. Typical deformed shape of propagating crack with $\hat{\mu}_0 = 10^3$ and $\hat{\mu}_0 = 1$ are plotted in Fig. 3.4. The material in front of the crack tip is highly stretched before failure when $\hat{\mu}_0$ is comparable to 1, whereas the deformation is small when $\hat{\mu}_0$ is much greater than 1. To understand the change in failure behavior, we recall the scaling estimation $L_p \sim \Gamma \mu_0 / s_c^2$ [Eq. (3.16)], where $s_c$ is the critical stress for damage initiation. Notice $L_p$ and $L_a$ both characterizes the damage zone size, we let $L_p = L_a$, which yields:

$$\hat{s}_c \sim \sqrt{\mu_0}.$$  

(3.38)
When $\hat{\mu}_0 >> 1$, damage initiates at small strain as material breaks at a stress much lower than the modulus of the material as $s_c << \mu_0$ [Fig. 3.6(b)]. Crack propagates with small crack tip opening displacement, as typically observed in a hard material. Otherwise, damage initiates at finite strain as failure initiation stress $s_c$ is on a comparable order of magnitude to $\mu_0$ [Fig. 3.6(a)]. One can observe a large crack opening, typical for a soft material. It is noted that in both cases the material is brittle and their strengths are sensitive to flaws since there is no additional energy dissipation mechanism.

As introduced in section 3.2.1, for a typical non-crystalline rubber such as natural rubber, the intrinsic fracture energy of crosslinked polymer network is $\Gamma_I \sim 100J/m^2$. Consider the intact modulus to be $\mu_0 \sim 1MPa$, and the size process zone to be typical length of a chain $L_a \sim 100nm$, the dimensionless modulus is $\hat{\mu}_0 = \mu_0 L_a / \Gamma_I = 0.1$. Another example is a typical single network gel in the free swelling state with $\Gamma_I \sim 1J/m^2$. We estimate its intact modulus to be $\mu_0 \sim 100kPa$, and the process zone size to be length of intrinsic static inhomogeneity $L_a \sim 10\mu m$. The dimensionless modulus is $\hat{\mu}_0 = \mu_0 L_a / \Gamma_I = 1$, which is used in the numerical examples shown by [Fig. 3.4(a)]. For the dry elastomer case, the failure strain would be significantly larger with smaller $\hat{\mu}_0$, and calculating their failure is still a numerically challenging task due to the highly distorted mesh.
3.4 Phase Field Model for Finite Strain Viscoelastic Fracture

3.4.1 Damage Incorporated Finite Strain Viscoelastic Materials

In this section, we aim to incorporate viscoelastic deformation into phase field fracture model. Viscoelastic behavior is conceptually captured by combination of the spring and dashpot dampers. In this work, we consider two typical cases: Kelvin model [Fig. 3.7(a)] and Zener (standard viscoelastic) model [Fig. 3.7(b)]. Kelvin material is represented by a dashpot and spring in parallel, which is capable of time dependent and fully reversible deformation. Recall derivation for the swollen Kelvin gel [Eqs (2.11), (2.16), (2.17)], we can set the swelling ratio to be 1, eliminate diffusion term and add the phase field the dissipation term [Eq. (3.21)], or equivalently, simply add the viscous dissipation term to the elastic phase field fracture formulation [Eq. (3.22)]. Modified the power functional reads:

\[
\Pi[v, \dot{v}, \phi, p] = \int \dot{W}(F, p, \phi, \nabla \phi) dV - \int t_v dA + \frac{\dot{\phi}^2}{2m} dV + \int \frac{\det F \eta(\phi)}{2} dV, \quad (3.39)
\]

where \( W \) is given by Eq. (3.20). Similar to the elastic case, the variation of Eq. (3.39) yields the coupled governing equations [Eqs. (3.24), (3.24)] for \( x \) and \( \phi \). Following previous section, the new nominal stress can be calculated from the explicit form of \( W \) Eq. (3.20), together with the contribution from the viscous stress \( \tau \):

\[
s_{ik} = \frac{\partial W}{\partial F_{ik}} + \tau_{ij} H_{kj} \det F - p H_{ki} \det F. \quad (3.40)
\]

We consider the polymer network behaves as a Newtonian fluid, and the current viscous stress is
\[ \tau = \eta(\phi)d \]  

which is proportional to strain rate \(d\).

**Figure 3.7** Spring dashpot representation of the damage incorporated (a) Kelvin model and (b) Zener model. Dashpot elements undergo relative rapid decay with damage described by power law damage function \(g'(\phi)\) [Eq. (3.43)] (denoted by thick arrows) and spring element undergo relative gradual decay with damage described by polynomial damage function \(g(\phi)\) [Eq. (3.18)] (denoted by thin arrows). Together, they impose the decrease of relaxation time with damage in the viscoelastic material.

**Figure 3.8** A comparison between polynomial damage function \(g(\phi) = 4\phi^3 - 3\phi^4\) (dash line) and power-law damage function \(g'(\phi) = a^{4\phi^4 - 3\phi^5 - 1}\) (solid lines) with different \(a\).

Compared to elastic fracture, the viscous fracture problem requires additional consideration for the change of relaxation behavior of the material besides softening.
We characterize the time took for the stretched transient network to find equilibrium configuration with viscoelastic relaxation time \( t_v \). \( t_v(\phi) \) is a decreasing function of damage because of the additional free volume and micro-voids created in damaged the polymer network. In the extreme case of near completely damaged, the material would reduce to the fully elastic behavior. From Eq. (2.29), Kelvin model has a single relaxation time \( t_v(\phi) = \eta(\phi)/NkTg(\phi) \). If \( t_v(\phi) \) is going to be a decreasing function of \( \phi \), \( \eta(\phi) \) must decrease faster that \( g(\phi) \). We assume the viscous decay to be:

\[
\eta(\phi) = \eta_0 g'(\phi)
\]

(3.42)

with a power-law damage function:

\[
g'(\phi) = a^{4\phi - 3\phi - 1},
\]

(3.43)

which introduces more rapid decay over the polynomial damage \( g(\phi) \) when \( a >> 1 \) (Fig. 3.4). It is noted that \( a \) simply needs to be a very large number, and the shape of \( g'(\phi) \) is not sensitive to \( a \), even \( a \) changes by orders of magnitude. In addition, we also apply the power-law damage function to the decay of bulk modulus as:

\[
\kappa(\phi) = \kappa_0 g'(\phi).
\]

(3.44)

to include the effect of increasing compressibility in the damaged polymer network, by introducing a faster change of bulk modulus on \( \phi \) over shear modulus.

Details of the Zener model have been discussed in section 2.4. It can be represented as the combination of a spring-dashpot series (Maxwell model) in parallel (permanent network) with an additional spring (transient network) as shown by Fig. 3.7(b). Unlike the Kelvin material, a Zener material is capable of instantaneous
deformation. As discussed in section 2.1, the total deformation $F$ in the Zener model is the superposition of the elastic part $F^e$ for instantaneous recovery and inelastic part $F^i$ for time dependent recovery through multiplicative decomposition [Eq. (2.3)]. We incorporate phase field model into Zener model by modifying power functional Eq. (3.22) as:

$$
\Pi[v, \dot{v}, \dot{\phi}, p] = \int \dot{W}(F^e, \dot{F}^i, p, \phi, \nabla \phi) dV - \int t_v dA \\
+ \int \frac{\dot{\phi}^2}{2m} dV + \int \frac{\partial \det F \eta'(\phi)}{2} d_i d_j dV
$$

(3.45)

where the last term is the dissipation on the dashpot as a Newtonian damper. Minimization of above power functional yields the governing equation set Eqs (3.23-3.27), with modified nominal stress:

$$
s_{ik} = \frac{\partial W}{\partial F_{ik}} - p H_{ki} \det F,
$$

(4.6)

and an auxiliary equation:

$$
\frac{\partial W}{\partial F^i} \cdot \frac{F^{i^T}}{\det F^i} = \tau^i,
$$

(4.7)

for balance of the internal stress on the dashpot and the spring of the transient network. Here $\tau^i$ is the viscous stress on the dashpot in the current state, which is linearly proportional to strain rate of the dashpot as:

$$
\tau^i = \eta'(\phi) d^i.
$$

(4.8)

The viscous decay $\eta'(\phi) = g'(\phi)\eta_0^i$ is controlled by the power-law damage function similar to the Kelvin material.
We consider both transient and permanent network to be neo-Hookean, and apply the damage formulation Eq. (3.20):

\[
W^\iota(x, F', p, \phi) = \frac{\mu_0}{2} g(\phi) (I_1 - 3 - 2 \log(\det F)) + \frac{\mu_1}{2} g(\phi) (I_1' - 3 - 2 \log(\det F'))
- \frac{p^2}{2\kappa(\phi)} - p(\det F - 1)
\]

(3.49)

We have assigned the same damage function \( g(\phi) \) for both networks which enforces proportional degradation of elastic energy. However, the exact form of damage function on the transient network is not important, but serves merely for smooth transition to fully damaged behavior. Because viscosity of the dashpot decreases with the power-law damage function and the stress on which is transmitted through the transient network, the stress on the damaged transient network is immediately relaxed compared to the permanent network.

Similar to the Kelvin material, damage of the bulk modulus \( \kappa(\phi) \) follows Eq. (3.44). It is noted that the volumetric strain are related as \( \det F = \det F^\iota \det F^i \). Theoretically, we need to constraint two of the three volumetric strains. For the incompressible virgin material in the plane strain case, we can simply apply energy penalty on \( \det F \), and directly dictate \( \det F^i = 1 \) by eliminate one degree of freedom of \( F^i \). As the damaged material becomes compressible, we consider two extreme cases to simplify analysis. If we let the inelastic part to be incompressible with \( \det F^i = 1 \) during damage, we allow the elastic part of volumetric deformation to change with total deformation, which implies the bulk relaxation is infinitely slow compared to deviatoric relaxation. On the other hand, if we let the inelastic part to be incompressible with
\[ \det F^e = 1 \] during damage, we imply the volumetric deformation always equilibrates instantaneously. Obviously the actually process should be the intermediate case between the two limits. Nevertheless, our numerical results show that the damage process is not sensitive to either setting, and we use the first case in the following examples.

For a Kelvin model, we solve for the weak form Eq. (3.39), together with material model Eq. (3.20) and damage law Eqs (3.42, 3.43). For a Zener material, the weak form is Eq. (3.45), together with material model Eq.(3.49) and damage law Eqs (3.42, 3.43). The equations are implemented into finite element codes using COMSOL Multiphysics 4.3b to solve for the inhomogeneous fields \( x(t), \phi(t), p(t) \) for a Kelvin model and \( x(t), F'(t), \phi(t), p(t) \) for the Zener model. Implicit time discretization and a direct solver are used. Both fields \( x(t), \phi(t) \) are interpolated using Lagrange element of the same order, and \( p(t), F'(t) \) is interpolated in mixed form on Gaussian points with elements of an order lower.

### 3.4.2 Numerical Examples for Viscous Fracture

We normalize all energy with \( h \), all length with \( L_v \), and time with \( t_v \). All normalized quantities is marked with the hat symbol \( \hat{\cdot} \). The Kelvin model contains a single material parameters \( \hat{\mu}_0 = \mu_0 / h \) and the Zener model contains two parameters \( \hat{\mu}_0 = \mu_0 / h \) and \( \chi = \mu'' / \mu' \), where \( \chi \) characterizes the relative change of modulus during relaxation from the glassy state to the fully relaxed state. Since the system is dissipative, the viscous crack growth behavior is in general history dependent, and
additional parameter is needed to describe the loading history, which will be introduced with specific examples.

In the first numerical example, we consider a special loading method that produces a viscous crack propagating with localized viscous deformation. The geometry and initial condition of the sample follows that in previous section (Fig 3.2). We first let the displacement of the long edge increase quasi-statically such that viscous deformation is fully relaxed. The sample is brought to the overcritical state with remote stretch $\lambda'_c > \lambda_c$ [Eq. (3.37)], and we denote the corresponding energy release rate as $G'_c$, and $G'_c > \Gamma_I$. During loading, we manually prevent crack growth by neglecting the mechanical driving force terms in the GL equation [Eq. (3.25)]. Then we fix displacement of the long edge, and slowly relax the GL equation to allow the overcritical crack to propagate. The accelerating crack would be stabilized by the viscous dissipation and reach a steady state. With displacement control in the far field, viscous deformation is absent outside an effective process zone, which includes the diffusive interface and the neighborhood of the crack tip undergoing viscous relaxation. We can evaluate the energy release rate of the crack by taking the J integral [Eq. (3.28)] on an arbitrary large loop surrounding the effect process zone:

\[
\hat{G}'_c = \frac{\hat{b}_0}{2} \left( \lambda_c^2 + \frac{1}{\lambda_c^2} - 2 \right) \hat{H} = \hat{\Gamma}.
\]

(3.50)

Since there is no work done to the system, total fracture energy $\hat{\Gamma}$ equals to the strain energy consumed for crack to propagate unit distance. $\hat{\Gamma}$ contains contributions from
both the interface energy and dissipation inside the effective process zone, and we have 
\[ \hat{\Gamma} > \hat{\Gamma}^*. \]

**Figure 3.9** Snapshots of characteristic viscous dissipation zone [shown by green contour \( \hat{W}_{dV}/L_o = 1 \), Eq. (3.52)] in steady state viscous crack (deformed configuration). Color scale corresponds to value of phase field variable \( \phi \). (a) Kelvin model and large sample \( \hat{H} = 500 \); (b) Kelvin model and small sample \( \hat{H} = 20 \); (c) Zener model and large sample \( \hat{H} = 500 \); (d) Zener model and small sample \( \hat{H} = 20 \);

We take typical parameters \( \hat{\mu}_0 = 1, \chi = 10, \hat{H} = 500 \) for a highly viscous and soft rubber. The deformed shape of the steady state viscous crack is shown by Fig. 3.9(a) for a Kelvin material and Fig. 3.9(c) for a Zener material. The crack is stretched quasi-statically to \( \lambda' = 1.09(\hat{G}' = 14) \), then allowed to propagate to steady state under displacement control \( \lambda = \lambda' \). The total fracture energy is \( \hat{\Gamma} = \hat{G}' = 7\hat{\Gamma}^* \). In the
propagating crack tip, the material is unrelaxed and much stiffer than the fully relaxed state. As a result, the critical failure strain is reduced. Hence, as we compare the deformed shape of the viscous crack with the elastic crack of the same material [Fig. 3.4(a)], the blunt crack tip is replaced by the sharp crack tip assuming a cone shape for both viscoelastic models.

![Figure 3.10](image)

**Figure 3.10** Normalized dissipation rate as a function distance to crack tip along the symmetry plane for viscous crack at various steady state velocity.

The dissipation zone can be visualized by plotting viscous dissipation rate $\hat{W}^d$ $r \rho d_{ij} : d_{ij}$ for Kelvin model and $r \rho d'_{ij} : d'_{ij}$ for Zener model. As shown by Fig. (3.9), the dissipation zone surrounds and travels together with the crack tip as material relax behind it and new material is being stretched in front of it. Fig. 3.10 shows $\hat{W}^d$ as a function of distance to crack tip (determined by level set $\phi = 0.9$) on the symmetry plane of the sample. The negative coordinates denotes materials behind the crack tip, and the positive value denotes that in front of the crack tip. It is shown that the effective
process zone is divided into spatially the intrinsic process zone where damage occurs but \( \dot{W}^d \) vanishes, and the viscous dissipation (extrinsic) zone surrounding the intrinsic zone where there is no damage but \( \dot{W}^d \) is finite. The spatial uncoupling is the direct result of our viscous damage model, which enforces \( t_v \) to be much shorter for the damaged material than the virgin material. In the limit that the viscosity decreases infinitely rapid with damage, the process zone becomes completely elastic, we recover the assumption used for simulating the viscous crack with rate-independent cohesive elements (Rahulkumar et al 2000). For non-viscous damage zone, we can rewrite the decoupled total fracture energy in the form (Persson et al. 2005):

\[
G = \Gamma_I + \Gamma_d = \Gamma_I [1 + f(v)].
\] (3.51)

The second term in Eq. (3.49) is Gent’s assumption for the fracture energy of a viscous rubber and \( f(v) \) is a universal and material insensitive dissipation function determined by crack velocity.

For a steady state crack, we can collect total extrinsic dissipation by summing total dissipation rate in the material as:

\[
\Gamma_d v = \int_{43} \dot{W}^d dV.
\] (3.52)

Fig. 3.10 shows \( \dot{W}^d \) as a function of distance in the material. A characteristic dissipation rate can be defined as:

\[
\dot{W}^d_c = v \Gamma_I,.
\] (3.53)
which means that power density of viscous dissipation provides comparable barrier to crack grow as interface energy. The contour of $\dot{W}_c$ is shown by Fig. 3.9, inside which is the characteristic dissipation zone for major dissipation.

![Figure. 3.11](image)

**Figure. 3.11** FEM results of normalized total fracture energy at steady state propagation as a function of normalize crack velocity for various sample sizes for Zener model with $\dot{\mu}_0 = 1$, $\chi = 10$.

As shown by Fig. 3.11, the fracture energy increases monotonously with crack velocity and appears to approach a limiting value. Unlike the elastic case, $\Gamma$ seems to be dependent on sample size, which can be understood by examining the characteristic dissipation zone. As shown by Fig. 3.10, its size increases with crack velocity. In the case of high crack velocity or small sample size, the dissipation zone size has become larger than the sample size, and the total fracture energy is determined by the boundary effect that the size of dissipation zone limits to the sample size. On the other hand, in the case of low velocity or large sample size, the dissipation zone is much smaller than the sample size, and fracture energy is size independent as shown by the low velocity portion of curves on Fig 3.11. In this case, the total fracture energy recovers the scaling
equation Eq. (3.51) and scales with intrinsic fracture energy of the material, while the function $f$ depends only on crack velocity.

Although the decoupled intrinsic and extrinsic zone is widely used in numerical simulations, this assumption is still untested due to the limitation spatial measurement for polymer chain damage on the microscopic level. As an illustration, we investigate the effect of the coupled damage process by considering $t_v$ as a constant independent of damage and the corresponding viscosity decay in the form as $\eta(\phi) = \eta_0 g(\phi)$. As a result, the damaged material is still highly viscous. As shown by Fig 3.12, in both Kelvin and Zener models, instead of forming crack-like localized damage zone, the diffusive interface expands in size by growing toward all directions. The non-localized growth can be shown by examining the reference configuration, where a blunted tip forms and the diffusive interface increases in thickness. We can understand the process

![Figure 3.12 Snapshots of blunted cracks in Kelvin and Zener models. Blunting appears when the intrinsic process zone becomes rate dependent. Here we assume viscous relaxation is assumed to be a constant unchanged with damage. Color scale represents value of phase field variable.](image-url)
qualitatively as the bridging effect of the damaged but still highly viscous material, which decrease the stress concentration at the crack tip. Blunting is a unique result that could only be detected with diffusive interface approach. The exact reason for blunting to be a numerical artifact or reflecting some unknown damage process is still not clear.
CHAPTER IV

PHASE FIELD MODEL FOR GEL PHASE SEPARATION
AND MECHANISM OF SPONGE STRUCTURE FORMATION

4.1 Thermodynamic Stability of Gels

4.1.1 Polymer in a Poor Solvent

Stability of a polymer solvent mixture is determined by the competition between mixing entropy and polymer-solvent interaction. We consider a polymer solution with $n_1$ solvent molecules and $n_2$ polymer molecules. Following the lattice model, these molecules occupy a total of $M = n_1 + N n_2$ sites of equal volume, where $N$ is the number of segments per polymer chain. Imaging we insert a semi-permeable separator that divide the system into two domains. The separator is impermeable to polymers, but open to solvent molecules. An arbitrary fluctuation causes the solvent concentration to become different in the two domains. We refer to the domain with higher solvent concentration as the *swollen phase* and the other as the *dry phase*. Superscript $s$ and $d$ is used to differentiate whether a quantity belongs to the swollen or the dry phase. We mark the polymer molecules according to domain and track the number of solvent molecules associated with each polymer molecule using variable:

$$J = \frac{n_1 + N n_2}{N n_2}.$$  \hfill (4.1)

We define free energy density:
\[ W^m(J) = \frac{\Pi(J)}{\Omega N n_s}, \quad (4.2) \]

as total free energy \( \Pi \) divided by total volume of polymer molecules. After fluctuation, total free energy density of the inhomogeneous system is:

\[ W^m = f W^m(J^s) + (1-f) W^m(J^d), \quad (4.3) \]

where \( f \) is the fraction of polymer molecules in the swollen phase. \( f \) can be calculated by conservation of total number of solvents \( J^s f + J^d (1-f) = J^i \), where \( J^i \) is initial composition. Equivalently, we have:

\[ \frac{J^i - J^d}{J^s - J^i} = \frac{f}{1-f}, \quad (4.4) \]

which is the well-known lever-rule.

\[ \]
inhomogeneous lays on the straight line AB determined by points 
\((J^s, W^m W(J^s)), (J^d, W^m(J^d))\), as shown by Fig. (4.1). We have the stability criterion:

\[
\frac{\partial^2 W^m}{\partial J^2} = 0. 
\] (4.5)

When \(\frac{\partial^2 W^m}{\partial J^2} > 0\), the homogeneous system is more energetically favorable. Because \(W^m\) is a convex function, and any point on the line AB belongs to the epigraph set of \(W^m\) [Fig. 4.1(a)]. When \(\frac{\partial^2 W^m}{\partial J^2} < 0\), spontaneous phase separation occurs to form the heterogeneous system, as \(W^m\) is a concave function of \(J\), and any point on line AB belongs to the concave set of function \(W^m\) [Fig. 4.1(b)].

\[\text{Figure 4.2} \quad \text{Double-well mixing energy [Eq. (4.7)] as a function of normalized composition } \varphi = (J - \varphi^d)/(\varphi^s - \varphi^d).\]

Eq. (4.5) is a local stability criterion considering infinitely small composition fluctuation. To study the globally stability, we examine a commonly considered unstable system that \(W(J)\) is a double-well shaped function:

\[W^m = h'\left(J - \varphi^d(T)\right)^2\left(J - \varphi^l(T)\right)^2,\] (4.6)
where \( h \) is a parameter charactering the magnitude of thermo energy, \( \mathcal{G}^d \) and \( \mathcal{G}^s \) are the two minima in the energy landscapes [Fig. 4.2(a)]. Defining normalized concentration as \( \varphi = \frac{(J - \mathcal{G}^d)}{(\mathcal{G}^s - \mathcal{G}^d)} \), we rewrite above equation in the compact form:

\[
W^m = h \varphi^2 (1 - \varphi)^2. \tag{4.7}
\]

We can construct a common tangent line AB over the double well which intersect \( W^m \) at \( \varphi = 0, \varphi = 1 \). Mathematically, it is equivalent to solve:

\[
\frac{\partial W^m}{\partial \varphi} \Big|_{\varphi=0} = \frac{\partial W^m}{\partial \varphi} \Big|_{\varphi=1}. \tag{4.8}
\]

together with the conservation equation Eq. (4.3). As shown by Fig. 4.2, any point \( \varphi \in (0,1) \) on \( W(\varphi) \) and line A’B’ are the convex set of the common tangent line AB. Hence homogeneous phase with composition \( J \in (\mathcal{G}^s, \mathcal{G}^d) \) is unstable and would phase separate, and the coexisting phase of composition \( \mathcal{G}^s(\varphi = 1), \mathcal{G}^d(\varphi = 0) \) is the lowest energy configuration.

We introduce temperature dependency of the free energy density by writing miscibility gap as:

\[
\mathcal{G}^d = 1 - \sqrt{T}, \mathcal{G}^s = 1 + \sqrt{T}, T \in (0,1). \tag{4.9}
\]

Solution to Eqs. (4.3, 4.5, 4.8) is collected to construct the phase diagram on the \( T - J \) plane. \( T = 0 \) is the critical temperature of the system. Solution to Eq. (4.3) and Eq. (4.5) is the binodal line, and solution to Eq. (8) marks the spinodal line. The composition within the spinodal is linearly unstable, and phase separation occurs.
barrierlessly with arbitrary small fluctuation. The composition between binodal and spinodal is metastable, and phase separation requires a finite magnitude fluctuation.

The composition between binodal and spinodal is metastable, and phase separation requires a finite magnitude fluctuation.

A more realistic free energy density function for polymer solution is given by the Flory-Huggins model (Flory 1953; Huggins 1941):

$$ W_m = h[\phi_s \ln \phi_s + \chi(\phi_s, T) \phi_s (1 - \phi_s)], $$

(4.10)

where $h = kT/\Omega$ is thermo energy density, $\phi_s = 1 - 1/J$ is the molar fraction of solvent molecules, and $\chi$ is the Flory-Huggins interaction parameter. $\chi$ characterizes the average bonding energy between solvent and functional groups on the polymer chains.

In the regular solution model, $\chi$ is a only a function of temperature as $\chi = \chi(T)$. Critical condition of the system [Eq. (4.8)] is fulfilled at $\chi = 0.5$. When $\chi < 0.5$, the polymer is in a good solvent, where the mixing energy overwhelms the polymer-solvent interaction and the homogenous state is stable. Otherwise, the polymer is in a poor solvent that tends to demix, which is also known as the coil-globule transition. In a
higher order theory, we consider $\chi$ to depend on both composition and temperature. For example, in the pNIPA solution, we have:

$$\chi = \chi_0 + \chi_1 (1 - \phi), \quad \chi_0 = -12.95 + 0.04496T, \quad \chi_1 = 17.92 - 0.05690T, \quad (4.11)$$

The free energy of pNIPA solution is shown by Fig. 4.3. The system has a lower critical solution temperature at $T = 302K$, above which phase separation would occur, as shown by the phase diagram Fig. 4.4(b).

### 4.1.2 Phase Diagram of Gels

The stability of a gel is directly related to the coil-globule transition of the polymer solvent mixture. The total free energy density of a gel consists of contributions from both strain energy of the crosslinked polymer network and the mixing energy as

$$W(F, C) = W^e(F) + W^m(C) \quad \text{[e.g. Eq. (4.6) or Eq. (4.10), as discussed in the section 2.2].}$$

In particular, the stability analysis in the previous section can be applied directly to the free energy density function of a gel. The concentration $J$ has additional physical meaning as swelling ratio, as $J = \Omega C + 1$ as given by Eq. (4.1).

To investigate the effect of elastic strain energy, we assume swelling to be isotropic by letting $F = \lambda I$ where $\lambda$ is linear swelling ratio $\lambda = J^{1/3}$, as the simplest case of deformation. We consider neo-Hookean model for strain energy, and the double-well model [Eq. (4.6)] for mixing energy:

$$W(J, T) = \frac{\mu}{2} \left( 3J^{2/3} - 3 - 2 \ln J \right) + \hbar \left( \frac{J - \theta^u}{\theta^u - \theta^s} \right)^2 \left( \frac{\theta^s - J}{\theta^s - \theta^u} \right)^2. \quad (4.12)$$

Alternatively, if we consider Flory-Huggins model [Eqs. (4.10, 4.11)] as mixing energy:
\[ W(J,T) = \frac{\mu}{2} \left( 3J^{2/3} - 3 - 2\ln J \right) \]
\[ + h \left[ (J-1)\ln\left(1 - \frac{1}{J}\right) + \left( \chi_0(T) + \frac{\chi_1(T)}{J} \right) \left(1 - \frac{1}{J} \right) \right]. \]

(4.13)

In this work, we limit the scope to 2D system under plane strain deformation with fixed through thickness stretch. Under this consideration, the strain energy part of Eqs. (4.12, 4.13) is substituted by:

\[ \frac{\mu}{2} (2J - 2 - 2\ln J). \]

(4.14)

The 2D model may give results that are quantitatively different from the more realistic but computationally intensive 3D models. Nevertheless, our focus is the effect of the elastic deformation on morphology, and predicting the exact phase behavior is less important. 2D model is sufficient for this goal, and the conclusion can be extended to the actual 3D system.

Similar to the case of polymer solutions, phase diagram of gels can be constructed based on free energy density Eq. (4.12) and Eq. (4.13) (Fig. 4.4). The phase behavior of a gel is similar to that of the corresponding polymer solution, because the stability of the system is governed by the chemical interaction between polymer and solvent. In both double-well and Flory-Huggins models, the miscibility gap on the phase diagram of the gel is smaller than the polymer solution due to the excess elastic energy of stretching the heterogeneous system over the homogeneous system. Comparing the two models, the miscibility gap of double well model is finite while that of the Flory-Huggins model diverges at certain temperature. For a polymer solution, this scenario is the \( \theta \) condition where the swollen phase is infinitely diluted. However, in a gel, the
polymer network cannot be infinitely stretched in the swollen phase, which would introduce special phase separated behavior to be discussed in section 4.3.2.

**Figure 4.4** Theoretical phase diagram of gels in the $T$-$J$ plane. (a) double well model using temperature dependency of Eq. (4.9) (b) Flory-Huggins model using thermodynamic data of pNIPA. Solid black line and blue lines are binodal and spinodal of pure polymer solution. Dotted black line and blue lines are corrected binodal and spinodal of gels with additional contribution from isotropic plane strain swelling of neo-Hookean network with dimensionless modulus $\mu / h = 0.01$.

**Figure 4.5** Equilibrium swelling curve (red line) and spinodal (blue line) of pNIPA gel with $\hat{\mu} = 0.01$. The two lines intersect at point $a,c$, and $abcd$ is the Maxwell hysteresis in volumetric phase transition.
On the other hand, if we consider a gel to be an open system in contact with an infinite reservoir of solvents, equilibrium $J$ is given by the solution of isobar curve (Fig. 4.5):

$$s = \mu \left( J^{1/2} - \frac{1}{J} \right) + \frac{kT}{\Omega} \left[ \ln \left( 1 - \frac{1}{J} \right) + \left( \chi_0 - \chi_1 \right) \frac{1}{J^2} - 2 \chi_1 \frac{1}{J^3} \right] = 0,$$

where $s$ is the isotropic swelling stress given by Eq. (2.18). As shown by Fig. 4.5, a gel tends to decrease solvent concentration and collapses at higher temperature. When the dimensionless modulus $\mu/h > 0.057$, the isobar contains a Maxwell loop, and we can observe the discontinuous volume phase transition. Coinciding with the stability curve, segment of isobar inside the spinodal denotes phase region where a gel is linearly unstable with negative bulk modulus. When a gel is heated to the point $a$ during a quasi-state process, it collapses abruptly to the state with low swelling ratio given by point $b$ on the isobar. Similarly, sudden discontinuous swelling could be observed for a cooling process with a jump of point $c$ to $d$.

The analysis for phase stability assumes the gel to be a closed system, which corresponds to an infinitely large gel, where the overall concentration remains constant through time. The analysis for volume phase transformation assumes the gel to be able to instantaneously exchanging solvent and maintaining thermodynamic equilibrium with a reservoir, which corresponds to an infinitely small gel. Both volume phase transformation and phase separation could occur in a finite size gel. More specifically, in the short time limit, the long-range solvent transportation is prohibited, and the gel phase separates into swollen and dry phases. In the long time limit, the gel is able to
exchange solvent with environment, and the deformation becomes homogenous again, and the swelling ratio is given by the global minimum of the free energy density function.

4.2 Finite Strain Effect on Curved Coherent Phase Boundary

4.2.1 Core-shell Phase Separation Model

The gel phase diagram is obtained by assuming both swollen and shrunk phase to be isotropically swollen, and neglects the effect of deviatoric deformation caused by the mismatch strain between the two phases. The core-shell structure is a minimum model representing characteristics of deformation and constraints between coexisting phases with a curved coherent interface. We consider phase separation to occur in a closed and bonded sphere, which produces a spherical core and a coaxial shell separated by a sharp but coherent interface (Fig 4.6). The inhomogeneous deformation and concentration can be calculated as a 1D axisymmetric problem.

Since the overall swelling ratio is fixed, the radius of the sphere remains unchanged during phase separation. We normalized all length by radius of the sphere. Taking the initial homogenous swelling state as the reference state, we denote the distance of a material particle to the center as $R$ in the reference state, and $r(R)$ in the deformed state. From the symmetry of the problem, the inhomogeneous deformation is measured by radial stretch $\lambda_r = \partial r / \partial R$ and circumferential stretch $\lambda_\theta = r / R$.

We focus on the long time limit where system has reached both chemical and mechanical equilibrium, a state in which the chemical potential is already a constant
everywhere and the transportation equation vanishes. Utilizing symmetry, we can simplify the equation for mechanical equilibrium as:

\[
\frac{ds_r}{dR} + \frac{s_r - s_\theta}{R} = 0 ,
\]

where the nominal stress is given by \( s_r = \partial W / \partial \lambda_r, s_\theta = \partial W / \partial \lambda_\theta \), and \( W = W / J^i \) is free energy density take reference with respect to the as casted swollen state. Inside the core, stress is homogeneous, and above equation reduces to \( s_r = s_\theta = s_c \), where \( s_c = \partial W / \partial \lambda_c / 2 \) is an constant hydrostatic pressure. We denote the corresponding homogeneous stretch as \( \lambda_c = \lambda_\theta = \lambda_c \). As total volume is conserved, the outer boundary is fixed:

\[
r(\hat{1})=1 .
\]

To maintain continuity on the coherent interface, we have:

\[
\lambda_\theta(A) = \lambda_c ,
\]

where \( A \) is radius of the core in the reference state. In the current state, the core radius is \( a = \lambda_c A \). If the size of the system is large enough, we can neglect surface tension, and balance of normal stress on the phase boundary requires:

\[
\lambda_r(A) = s_c .
\]

In addition, the total free energy of the system minimized with respect to the core size \( A \) such that the driving force for nucleus growth vanishes:

\[
\frac{d}{dA} \Pi = 0 .
\]
where the total free energy of the system is:

$$\Pi(r, a, A) = 2\pi \int_{A}^{r} W'RdR + \pi A^2 W', \quad (4.21)$$

The unknown displacement $r$ together with $a$ and $A$ are solved from Eqs. (4.16-4.21) numerically. We limit the analytical discussion of this section to gel described by double-well system described by Eq. (4.6). The conclusion will be examined in the next section with numerical calculation for more general geometry of co-existing phases using both double-well and Flory-Huggins models.

**Figure 4.6** Schematic drawing of core-shell structure formed by phase separation of an isolated gel sphere. Bifurcation produces the competing D/S (dry in swollen) and S/D (swollen in dry) structure. Darkness of the blue shade indicate swelling ratio of each domain.

### 4.2.2 Morphology Competition

The double-well model contains three parameters, $\mu, \vartheta^s, \vartheta^d$, and one model input, the initial swelling ratio $J^i$. Taken as case swollen state as reference, we have
three parameters for a specific initial state $\hat{\mu}$, $\mathcal{G}^* = \mathcal{G} / J^i, \mathcal{G}^{rd} = \mathcal{G}^{r} / J^i$. We first analyze the limit $\hat{\mu} \to 0$, where contribution of deviatoric deformation $\hat{W}_c$ vanishes.

There are two solutions to Eqs. (4.16-4.21):

$$
\begin{cases}
 r = \sqrt{1 - \mathcal{G}^* (1 - R^2)}, (R < A) \\
 r = \sqrt{\mathcal{G}^{rd} R}, (R \geq A)
\end{cases}
A = \frac{\mathcal{G}^* - 1}{\mathcal{G}^* - \mathcal{G}^{rd}},
$$

(4.22)

and

$$
\begin{cases}
 r = \sqrt{1 - \mathcal{G}^{rd} (1 - R^2)}, (R < A) \\
 r = \sqrt{\mathcal{G}^* R}, (R \geq A)
\end{cases}
A = \frac{1 - \mathcal{G}^{rd}}{\mathcal{G}^* - \mathcal{G}^{rd}},
$$

(4.23)

Although the deviatoric deformation is present in the shell in both solutions, it has no effect on the energy of the system. The result recovers behavior of a liquid solution, as the volumetric strain $J^r = \lambda_r \lambda_v$ is a constant in both shell and cores, with a jump across the phase boundary. In the first solution, we have $J^r = \mathcal{G}^{rd}, J^i = \mathcal{G}^* (R \geq A)$, on the other hand, swollen and dry phase are arranged in the opposite way with $J^r = \mathcal{G}^* (R < A), J^i = \mathcal{G}^{rd} (R \geq A)$ in the second solution. The two solutions correspond to two possible microstructures: (1) dry core imbedded in swollen shell [D/S structure, Fig. 4.6(b)]; (2) swollen core imbedded in dry shell [S/D structure, Fig. 4.6(c)].

The two morphologies compete through minimization of the total free energy [(Eq. 4.21)]. Without strain energy, both structures merely defer in shape, and they are identical in mixing energy. The high order effect of interface energy would dominate,
which favors the structure with shorter interface length, $l = 2\pi a$. For D/S structure, 

$$a = \sqrt{v^d},$$

where

$$v^d = \frac{\varrho^d}{\varrho^s - \varrho^d}$$ \hspace{1cm} (4.24)

is the volume fraction of the dry phase in the current state. For S/D structure, $a = \sqrt{v^s}$, where

$$v^s = \frac{1 - \varrho^d}{\varrho^s - \varrho^d}$$ \hspace{1cm} (4.25)

is the volume fraction of the swollen phase in the current state. Equating Eq. (4.24) and Eq. (4.25), we have critical criterion:

$$\varrho^d \varrho^s = \varrho^s + \varrho^d.$$ \hspace{1cm} (4.26)

In the small strain limit, above equation reduces to $1 - \varrho^d = \varrho^s - 1$, which is the case of symmetric initial composition. For asymmetric initial composition, S/D structure is more energetically favorable when the shell occupied by the majority phase and vice versa. In the extremely large strain limit $\varrho^d \gg 1, \varrho^s << 1$, $\varrho^d \varrho^s < \varrho^s + \varrho^d$ and D/S structure is always energetically favorable because the core size has approached zero for D/S structure and 1 for S/D structure.

For a weakly elastic system with $\hat{\mu} << 1$, the effect of elastic strain causes a small perturbation to the solution of the incompressible system as $r = r_0 + \psi r_1$, $A = A_0 + \psi A_1$, where $\psi << 1$, and $r_0$, $A_0$ is the $0^{th}$ solution given by Eqs. (4.23, 4.24). The first order correction to total free energy is:
\[ \Pi' = 2\pi \int_{A} W'RdR + \pi W'A^2 \approx 2\pi \int_{A_0} W(r_0) RdR + \pi \lambda_0^2 W(r_0), \] (4.27)

which attributes to deviatoric stretch \( \lambda_{r_0} = \partial r_0 / \partial R, \lambda_{\rho_0} = r_0 / R \) from the zeroth order solution Eqs. (4.23, 4.24). We substitute neo-Hookean model for elastic energy associated with \( \lambda_{r_0}, \lambda_{\rho_0} \), and access the free energy difference between S/D and D/S structures:

\[ \Pi'_s = \Pi'^{S/D} - \Pi'^{D/S} = \frac{\mu}{2} \left[ (1 - \gamma^d) \ln \gamma^s - (1 - \gamma^s) \ln \gamma^d \right], \] (4.28)

which is the driving force for formation of S/D structure over D/S structure.

**Figure 4.7** Normalized excess strain energy of S/D structure over D/S structure \( \Pi'' / \mu \) of a weak elastic system. (a) \( \Pi'' / \mu \) in the composition space. (b) \( \Pi'' / \mu \) as a function of volume fraction of the swollen phase for given swelling ratio of the swollen phase.

As shown by Fig 4.7, the strain energy always favors the S/D structure with \( \Pi_s > 0 \). For a given \( \nu' \), magnitude of \( \Pi'_s \) increases with the miscibility gap, i.e. the mismatch strain between dry and swollen phases. In the small miscibility gap limit,
where \((g^r - 1) < 1, (1 - g^d) < 1\), the volumetric mismatch strain is infinitesimal. We linearize strain and applying Taylor expansion to Eq. (4.28) to obtain:

\[
\Pi_s' \approx \frac{\mu}{2} \left[ (1 - g^d)(g^r - 1) - (1 - g^d)(1 - g^d) \right] = 0.
\] (4.29)

Contribution of strain energy to free energy becomes equal for both D/S and S/D structure, and the elastic effect to morphology competition vanishes.

**Figure 4.8** Schematic drawing of forming (a) D/S structure (b) S/D structure via phase separation as superposition of two-step process: (1) cut along the phase boundary and allow core and shell to free swell (2) shell is deformed and weld back to the core to recover coherent interface. The darkness of the blue shade corresponds to swelling ratio of each phase.

To unveil the nonlinear kinematic effect causing the energetic preference of S/D structure, where phase boundary curves toward the swollen phase rather than the dry phase, we decompose the phase separation process with additional intermediate geometrically incompatible states (Fig. 4.8), and analyze the incremental deformation of the shell (Fig. 4.9). In the initially homogeneous material, we make a cut at \( R = A \) and
apply isotropic swelling $\lambda_c$ and $\lambda_s$ to the core and the shell respectively, where $\lambda_c$ and $\lambda_s$ corresponds to the equilibrium swelling ratio after phase separation for either D/S or S/D structure. The process produces an isolated core of radius $\lambda_c A$ and a hollow shell of inner radius $\lambda_s A$, outer radius $\lambda_s$. In the second step, the shell is deformed to recover continuity and the coherent phase boundary. Obviously, creating free swelling state for either structures requires the same energy despite the difference of the shape being cut into, and the strain energy preference for S/D structure attributes to the inhomogeneous deformation in the second step.

![Figure 4.9](image)

**Figure 4.9** Schematic drawing of the kinematic nonlinearity of coherent phase boundary. Inhomogeneous strain increases for incremental deformation when the shell is compressed to form D/S structure. Inhomogeneous strain decreases for incremental deformation when the shell is stretched to form S/D structure.

We deform the free swollen shell to fit the core by applying a radial displacement $u = \lambda_s - 1$ to its outer surface. In the finite deformation regime, $u$ is comparable to 1.
We decompose $u$ into many consecutive small increments $\Delta u$, such that $\Delta u << 1$ and we can linearize the kinematics for each step. We analyses each increment using the previous one as reference state, and a quantity measured w.r.t. the end of $j^{th}$ increment is denoted with superscript $j$, e.g. $\Delta \Pi^j$ is the change of $\Pi$ for the $j^{th}$ increment.

We consider incremental strain of the $j^{th}$ step as a superposition:

$$\varepsilon^j_r = \varepsilon^j_{nr} + \varepsilon^j_{\theta}, \varepsilon^j = \varepsilon^j_{nr} + \varepsilon^j_{\theta},$$

where $\varepsilon^j_{nr}, \varepsilon^j_{\theta}$ are the incremental strain at the outer edge, and $\varepsilon^j_{ir}, \varepsilon^j_{i\theta}$ are the excess inhomogeneous strain. Enforcing $\varepsilon^j_{nr}, \varepsilon^j_{\theta}$ alone on every element annulus section $d\theta$ applies homogeneous deviatoric deformation, while leaves overlap between elements. The process increase strain energy by $\Delta \Pi^j$. We can recover compatible state by enforcing $\varepsilon^j_{ir}, \varepsilon^j_{i\theta}$, and strain energy increases by $\Delta \Pi_2^j$ during the process.

If D/S structure were to form, we firstly obtain a dry core and a swollen shell with $\lambda_c = \sqrt[\gamma]{\bar{d}}, \lambda_s = \sqrt[\gamma]{\bar{s}}$ by cutting and free swelling, then compress shell to fit the core by applying displacement $u = \sqrt[\gamma]{\bar{d}} - 1 < 0$. During the second step, we compare between two consecutive incremental deforming steps $j$ and $j + 1$. In the $j + 1$ step we deform the shell with larger radial thickness than the $j$ step because deformation of the $j$ step already compresses the shell itself. Obviously, the overlapping between element annulus section with homogenous strain $\varepsilon^{j+1}_{nr}, \varepsilon^{j+1}_{n\theta}$ becomes greater for the $j + 1$ step, and a larger inhomogeneous deformation $\varepsilon^{j+1}_{ir}, \varepsilon^{j+1}_{i\theta}$ is required to recover compatible strain. Hence the strain energy associated with inhomogeneous deformation $\Delta \Pi_2^j$ increases
with increments. On the other hand, if S/D structure were to form, we firstly obtain the reverse structure with $\lambda_s = \sqrt{q^s}$, $\lambda_d = \sqrt{q^d}$ by cutting and free swelling, then stretch the dry phase shell to fit the core by applying $u = \sqrt{q^d} - 1 > 0$. If we compare between two consecutive incremental deforming steps $j$ and $j+1$, the $j+1$ step deforms a thinner shell because of deformation of the $j$ step. The overlapping between element annulus section with homogenous strain $\epsilon_{nr}^{j+1}, \epsilon_{n\theta}^{j+1}$ becomes smaller, and smaller inhomogeneous deformation $\epsilon_{nr}^{j+1}, \epsilon_{n\theta}^{j+1}$ is required to recover compatible strain. Hence the strain energy associated with inhomogeneous deformation $\Delta \Pi_2^j$ decreases with increments (Fig. 4.9).

Finally, we can compare between the S/D and D/S structure for the strain energy of inhomogeneous deformation of the shell to form the coherent curved phase boundary. In the linear regime, i.e. $\Delta \Pi_2^1$, we neglect nonlinear effect, and $\Delta \Pi_2^1$ is equal for both stretching and compressing the shell of the same amount. The strain energy penalty for forming S/D structure by stretching the shell and that of D/S structure is the same, as $\Pi_s' = 0$ [Eq. (4.29)]. In the nonlinear strain regime, the increase of radial thickness requiring larger the inhomogeneous strain to compress the shell while the decrease of radial thickness requires less inhomogeneous strain to stretch the shell. Hence, more strain energy is required to compress the shell to form D/S structure, and the S/D structure more energetically favorable.

Finally, another case is when elastic energy becomes comparable to thermo energy with $\tilde{\mu} \sim 1$, the composition of shell and core is coupled with deformation and
the volumetric strain becomes a function of $r$. Numerical results of a typical case with parameters $\hat{\mu} = 0.1, \theta^s = 2, \nu^s = 0.3$ are shown by Fig. 4.11. The concentration difference is smaller than that the miscibility gap given by the phase diagram as the strong elastic constraint reduces the mismatch strain between swollen and shrunk phases in order to lower strain energy. The constraint from the phase boundary also reduces the deviatoric strain in the shell compared to the asymptotic solution [Eqs. (4.23, 4.24)] for both S/D and D/S structures. S/D structure is nevertheless energetically favored because of the highly inhomogeneous stretch required to form the D/S structure. As shown by Fig 4.10, the trend of the driving force $\Pi_s$ follows asymptotic solution Eqs. (4.23, 4.24), and the magnitude of $\Pi_s$ is reduced for strong elastic case. For very stiff gel, the strain energy overwhelms the mixing energy, and homogeneous phase becomes stable again, whereas the bifurcated solution vanishes.

![Figure 4.10](image)

**Figure 4.10** Comparison between asymptotic numerical solution for normalized excess strain energy of S/D structure over D/S structure $\Pi''/\mu$. 
Figure 4.11 Comparison between asymptotic solutions (dash lines) and numerical solutions (solid lines) for strong elastic system. (a) Swelling ratio as a function of $R$ in S/D structure; (b) Swelling ratio as a function in $R$ of D/S structure; (c) Components of stretch ratio as a function of $R$ of S/D structure; (d) Components of stretch ratio as a function of $R$ of D/S structure.
4.3 Phase Separation of Gels and Formation of Sponge Structures

4.3.1 Strongly Coupled Conserved Phase Field Model

We use the diffusive interface model to study the morphology formed by phase separation under the influence of finite mismatch strain between swollen and dry phases. The finite strain phase field model (section 3.1) is extended to incorporate strong coupling between phase field variable and deformation, and diffusion as kinetic law for phase evolution. As discussed in section 4.1, swelling ratio $J$, or equivalently, the number concentration of solvent $C$ is the natural order parameter of the system. In the following work, we will refer to $J$ as the phase field variable. Phase field method allows us to study the inhomogeneous deformation cause by the large volumetric strain mismatch.

We write the total free energy of an open and deformable system to be:

$$\Pi[v, C, J] = \int \dot{W}(F, C, \nabla J) dV - \int [v, J] dA - \int \mu dA$$

$$+ \frac{1}{2} \int \frac{DC}{kT} \det F \left( J_k F_{ik} F_{il} J_l dV + \mu_s \left( \dot{C} + \frac{\partial J_k}{\partial x_k} \right) \right)$$

(4.30)

where we have followed the notation and definition in section 2.3. Comparing to the homogeneous system, we consider additional dependency of the free energy on the gradient of the phase field variable $W = W(F, C, \nabla J)$. Specifically for a gel, we write:

$$W = W^e + W^m + \frac{1}{2} \tau (\nabla_s J)^2$$

(4.31)

where the last term is the ideal liquid interface model given that the majority of the phase boundary are consists of small molecule solvent, which could constantly rearrange to maintain a constant surface tension in the current configuration. We assume the
polymer network to be elastic and the strain energy can be given by the neo-Hookean.

The mixing energy is given by either Eq. (4.6) for the double-well model or Eq. (4.10) for the pNIPA gel.

Utilizing the variational principle and the divergence theorem, minimization of energy function yields:

\[
\partial \Pi = -\int \frac{\partial s_{ik}}{\partial X_i} \delta V_i dV + \int (s_{ik} N_k - t_i) \delta V_i dA \\
+ \left( \int \frac{DJ_k F_{ik} F_{ij}}{kT \Omega \text{det} \mathbf{F}} \right) \delta I_j dV - \int \left( \dot{C} + \frac{\partial I_L}{\partial X_L} \right) \delta \mu_s dV + \int (\mu_s - \bar{\mu_s}) \delta dA. 
\]

In order for above equation to hold for arbitrary test function, we have coupled differential equation systems:

\[
\frac{\partial s_{ik}}{\partial X_i} = 0, \quad (4.33)
\]

\[
\dot{C} + \frac{\partial}{\partial X_L} \left( -\frac{D}{kT} \text{det} \mathbf{F} - 1 \right) H_{kl} H_{li} \frac{\partial \mu_s}{\partial X_L} = 0, \quad (4.34)
\]

where:

\[
s_{ik} = \frac{\partial W}{\partial F_{ik}} - \tau \text{det} \mathbf{F} H_{mj} \frac{\partial J}{\partial X_M} \frac{\partial J}{\partial X_L} H_{kl} H_{ki} + \frac{\tau}{2} \text{det} \mathbf{F} H_{mj} \frac{\partial J}{\partial X_M} \frac{\partial J}{\partial X_L} H_{li} H_{kl}, 
\]

\[
\mu_s = \frac{dW}{dC} + \frac{1}{2} \frac{\partial}{\partial C} \text{det} \mathbf{F} H_{kl} \frac{\partial J}{\partial X_K} \frac{\partial J}{\partial X_L} H_{li} - \tau \frac{\partial}{\partial X_L} \left( \text{det} \mathbf{F} H_{kl} H_{ki} \frac{\partial J}{\partial X_K} \right), 
\]

the nominal stress \(s(X,t)\) and chemical potential \(\mu(X,t)\) can be solved from explicit free energy function Eq. (4.31). In addition, there are boundary conditions:
\[ s_{ik} N_k = t_i, \quad (4.37) \]

\[ \mu_s = \bar{\mu}_s. \quad (4.38) \]

The weak form Eq.(4.32) is implemented into a finite element code with the commercial software COMSOL Multiphysics 4.3b for the unknown displacement, composition and chemical potential field for a gel undergoing phase separation.

### 4.3.2 Morphology of Phase Separated Gels

We calculate the phase separation in gels on a square 100*100 mesh. To simulate a closed system without boundary effect, we apply periodic boundary condition on all four sides. The system size is set to be much larger than the interface thickness, and we let \( H = 30L_a \). To overcome the interface energy barrier for critical nucleus formation, we introduce a small concentration fluctuation into the system to drive the initial phase separation. We first consider the double well model for the ease of theoretical analysis.

#### 4.3.2.1 Small Strain Limit

Fig. 4.12 shows morphologies of phase separated gel with small miscibility gap. The parameter used are \( \bar{\mu} = 0.01, \varrho^d = 19.99, \varrho^v = 20.01 \), with mismatch strain \( \Delta J = 0.02 \) between the swollen and dry phase. The morphology depends on the initial swelling ratio \( J^i \). When \( J^i = 19.94 \), initial fluctuation lead to the formation of islands of dry phase embedded in the swollen matrix [Fig. 4.12(a)]. With symmetric composition \( J^i = 20.00 \), a bi-continuous pattern consisting of labyrinth of swollen and
dry phase forms [Fig. 4.12(b)]. Finally when $J' = 20.06$, we obtain islands of swollen phase imbedded in the continuous dry phase [Fig. 4.12(c)] which inverses the dry island structure.

**Figure 4.12** Snapshots of morphology of phase separated gel with small miscibility gap ($\theta' = 20.1, \theta^d = 19.9$). Pattern is determined by minimization of interface energy which lead to (a) islands of dry phase with $J' = 19.94, \nu' = 0.2$ (b) bi-continuous strip with $J' = 20.04, \nu' = 0.5$ (c) islands of swollen phase $J' = 20.06, \nu' = 0.8$. Color scale shows relative swelling ratio $(J - \theta^d)/(\theta^s - \theta^d)$, where the blue color is swollen phase and red color is dry phase.

The morphology evolves in two possible ways. For a given morphology, it can grow in a self-similar manner without changing the topology. For example, after the composition fluctuation stabilizes, the dry island structure grows by merging islands. During this process, the characteristic size, i.e. the average radius of islands, increases and number of islands decreases while the volume fraction and connectivity of both phases remain unchanged. Secondly, for a given characteristic size, different topology can competes with each other; either volume fraction or connectivity can change individually or together during this process, and morphology evolves in a non-self-similar manner. In the early stage of phase separation, when time is shorter than the
time for diffusion within critical nucleus $t < D/L_w^2$, different morphology compete with each other to form the lowest energy configuration. In the late stage of phase separation when $t > D/L_w^2$, the characteristic size is limited by diffusion. With fixed topology, the morphology evolves by coarsening.

**Figure 4.13** Typical morphology in 2D two phase coexisting system. (a) droplet (b) labyrinth (c) sponge

Since we consider ideal-liquid interface, the interface energy is proportional to interface length in the current state. As shown by Fig 4.13, to estimate the interface length density, we count the interface length in representative unit cell size of size $L$. We consider some certain volume fraction of the swollen phase $v'$. Without losing generality, we let $v' > 0.5$. In the droplet structure, the dry phase is the isolated phase, and total interface length per unit cell is $L\sqrt{\left(1 - v'\right)/\pi}$. In the labyrinth structure, both phase are continuous, and total interface length per unit cell is $2L$. In the sponge structure, the minor phase, i.e. the dry phase is continuous and swollen phase is isolated. Total interface length per unit cell is $L\sqrt{v'/\pi}$. If we compare the three cases, the droplet structure is energetically favorable when $v' > 0.7$, and labyrinth structure is
energetically favorable when $0.3 < v' < 0.7$. The sponge structure is energetically favorable when $0.3 < v'$. However, in this case, the swollen phase has become the minor phase, and the ‘sponge structure of continuous dry phase’ simply recovers the classical droplet structure with dry phase being the continuous matrix. In conclusion, the droplet structure is always energetically favorable compare to the sponge structure in the small strain limit as long as the interface energy dominates.

\[ J / J' \]

\[ \Delta J = 6 \] between

**Figure 4.14** Snapshots of sponge structure in phase separated gel using double well model with finite miscibility gap ($\varphi_s = 30, \varphi_d = 5$). The initial composition is $J_i = 13$. Color scale shows relative swelling ratio $J / J'$, with blue being the swollen phase and red being the dry phase.

Fig. 4.14 shows the typical morphology with finite strain miscibility gap. The parameters used are $\hat{\mu} = 0.01, \varphi_d = 5, \varphi_s = 30$, with mismatch strain $\Delta J = 6$ between
the swollen and dry phase. When the initial composition is \( J^i = 18 \), the theoretical current volume fraction of the dry phase is \( \nu^s = 0.25 \). However, despite being the minor phase, the dry phase forms a continuous network instead of isolated islands (sponge structure). The sponge structure forms by nucleation of the swollen phase from initial fluctuation. Once the fluctuation stabilizes, the topology of the morphology remains unchanged, and the sponge structure grow by coarsening, as compartment of swollen phases merging which each other to form larger compartments. The morphology is determined by initial composition. With the same miscibility gap, we let \( J^i = 20 \), and the theoretical current volume fraction of the dry phase is \( \nu^s = 0.20 \). Phase separation lead to the formation of strip structure. When we let \( J^i = 22 \), and the theoretical current volume fraction of the dry phase is \( \nu^s = 0.15 \). We recover the droplet structure of the dry phase. Comparing the small strain case, the phase inversion limit has shift from \( \nu^i = 0.5 \) to about \( \nu^i = 0.2 \) and the morphology with continuous dry phase is favored.

The competition between morphology can be understood by examining the deformation of the heterogeneously stretched phases as shown by the distortion of the mesh in Fig. 4.15 and Fig. 4.16. In the sponge structure, islands of swollen phase deform isotropically, which are surrounded by the highly deviatorically stretched but continuous dry phase. The characteristic deformation resembles that given by the core-shell model arranged as S/D structure. In this case, the sponge structure forms as the elastic energy overwhelms the interface energy. On the other hand, in the droplet structure, islands of dry phase deform isotropically, while the swollen phase is continuous and highly deviatorically stretched, which corresponds to deformation of
core-shell model arranged as the inversed D/S structure. As the excess strain energy decrease with $\nu^s$, it is not sufficient to dominate over interface energy, and droplet structure forms.

**Figure 4.15** Snapshots of morphology in phase separated gel using double well model with finite miscibility gap ($\mathcal{G}^s = 30, \mathcal{G}^d = 35$). (a) Bi-continuous strips with when using initial composition $J^i = 20$. (b) Droplet structure with when using initial composition $J^i = 22$. Color scale shows relative swelling ratio $J/J'$, with blue being the swollen phase and red being the dry phase.

### 4.3.3 Phase Separation of pNIPA Gel

We consider the more realistic system of pNIPA gel using Eqs (4.10, 4.11) as mixing energy. Firstly, we calculate phase separation process under small strain mismatch by quenching to $T = 305K$, and binodal of the phase diagram Fig. 4.4(b) predicts the corresponding swelling ratio of the coexisting phases to be $\mathcal{G}^s = 4.2, \mathcal{G}^d = 1.6$. Fig. 4.14 shows typical evolving morphology with initial composition $J^i = 3$. In this case, we observe droplets of swollen phase ($J = 3.2$) imbedded in a continuous matrix of shrunk phase ($J = 1.8$) as predicted by the
minimization of interfacial tension. Because of the strain mismatch between the coexisting phases, the compositions differ from the equilibrium values given by the homogeneous phase diagram as the self-constraint tends to decrease the concentration difference (and mismatch) between the two phases. After the composition fluctuation stabilizes, the separated phases coarsen by classical coarsening process as the island size increase in both spatial coordinates and material coordinates.

Figure 4.16 Snapshots of droplet structure in pNIPA gel with small miscibility gap ($\mathcal{G}^s = 4.2, \mathcal{G}^d = 1.6$). Color scale shows relative swelling ratio $J/J'$, with blue being the swollen phase and red being the dry phase.
Fig. 4.17  Snapshots of sponge structure in a PNIPA gel with finite miscibility gap ($\delta^i = 540, \delta^d = 1.4$). Color scale shows relative swelling ratio $J / J^i$, with blue being the swollen phase and red being the dry phase.

Fig. (4.17) shows morphology formed by phase separation under deep quenching to 306K. In this case, there is a large miscibility gap $\delta^i = 540, \delta^d = 1.4$ given by the phase diagram. As predicted by our previous analysis, the sponge structure forms with dry phase being the continuous phase although it is also the minority phase. Because of the elastic constrain, swelling ratio difference between the two phases is smaller than prediction of the phase diagram: the actual swelling ratio of swollen phase is $J = 16$, that of the dry phase is $J = 1.8$. A more interesting case is when even deeper quenching
to 308K is applied. In this case $\theta^d = 1.3$, although $\theta^s$ still exist, it is a very large number that can be consider as infinity, hence there is no co-existing phases possible.

After the temperature jump, the fluctuation amplifies and the gel separates into highly swollen domains ($J >> 1$) and dry domains ($J \approx 1$). Because of the infinite strain mismatch, morphology also exhibits a sponge pattern. Different from shallow quenching with finite miscibility gap, the amplification of composition difference between dry and swollen phase seems to never stop or stabilize Fig. 4.18, as no equilibrium could be reached. Unlike coarsening, a growing swollen island occupies increasingly larger space, but takes less amount of polymer. The composition in a swollen domain keeps changing. The process is mainly driven by the osmotic pressure gradient due to the energy of mixing, rather than the interface energy.

![Figure 4.18](image.png)

**Figure 4.18** Snapshots of sponge structure in a PNIPA gel with infinite miscibility gap ($\theta^s = \infty, \theta^d = 1.3$). Color scale shows relative swelling ratio $J / J^i$, with blue being the swollen phase and red being the dry phase.

In the long limit, overall deswelling becomes significant at time $L^2 / D$, with $L$ being a characteristic length for the overall geometry of the gel, e.g. the thickness of a
thin film. The long-term morphology of a small gel is always a homogeneous shrunk state, with the excessive solvent expelled to the surrounding environment. When time is limited or the gel is large, long-range solvent transportation is prohibited, allowing heterogeneous structure to be kinetically locked. During shallow quenching, coarsening is relatively slow due to the elastic pinning effect. Instead of having the domains of coexisting phases coarsen to a macroscopic size, a gel would simply lose solvent to the surrounding environment and recover a homogeneous collapsed state. During deep quenching, domain dilation causes the rapid local swelling. Although the current model assumes the polymer network to be fully elastic and never breaks, it is easy to imagine that in an actual deep quenching process, the polymer chains in a highly swollen domain may reach its extension limit and fracture prior to the overall collapsing. The damaged swollen domain will then become a solvent-filled pore and result in a spongy gel with permanent porous structure.
CHAPTER V
CONCLUSIONS

In summary, we have advanced the field of mechanics of soft materials in the following aspects:

A finite strain continuum mechanics framework for coupled viscoelastic poroelastic model is formulated, which can be used to study both kinetic and equilibrium of inhomogeneous deformation of physical gels, chemical gels and dry polymers. Material models and kinetic laws for specific elastomers and polymeric gels can be incorporated conveniently via constructing free energy density and dissipation functions, as well as other constraints depending on the modeling purpose. We presented an example model for swollen neo-Hookean network coupled with concurrent linear diffusion and standard viscoelasticity behavior. The model is implemented into finite element code to investigate inhomogeneous deformation and concentration fields for arbitrary deformation. Using the numerical model, we proposed the theory for decoupling between viscoelastic and poroelastic relaxation process through change of length scales.

To study interface and surface in soft solids, we advanced the phase field model to the finite strain regime. We have considered the coupling between deformation and interface microstructure change. Using the ideal solid and ideal liquid model, we enable the consideration for rearrangement of interface structure with finite deformation in a
unified framework. The phase field model also enables the study of motion of interface and surface in soft material coupled with arbitrary physical process. The model is applied to inelastic fracture using the uncoupled non-conserved phased field model. In the second application of the theory, we formulated a strongly coupled conserved phase field model to study large strain diffusive phase separation in solid materials, which is applied to phase separation in thermo-sensitive gels.

Using phase field model, we formulated finite strain damage theory for viscoelastic solids. Finite element code is developed for the model, which allows the simulation of arbitrary crack growth. We proposed description of viscous decay behavior in viscoelastic solid and investigate the relation between relaxation of process zone and blunting of materials. The model explains the velocity dependency of fracture energy in viscous material and viscous trumpet shape of viscous crack from the localized viscous dissipation zone in front of the crack tip.

We have explained the mechanism for formation of sponge structures in coexisting phases due to finite mismatch strain across the coherent phase boundary. Sponge structure is defined as the morphology of coexisting phase where the minority phase is the continuous one. We found that above some critical mismatch strain, sponge structure forms regardless of the volume fraction and the energetic penalty form interface energy. The sponge structure attributes to the non-linear kinematic effect of a deformed curved phase boundary. Our theory adds the morphology correction to the classical phase diagram, and we predicted sponge and cellular to be a universal structure in soft materials.
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