Mechanics and Physics of Soft Materials

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Accessibility
Mechanics and Physics of Soft Materials

A dissertation presented

by

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Mechanics and Physics of Soft Materials

Abstract

Materials where thermal energy is comparable to the interaction energy between molecules are called soft materials. Soft materials are everywhere in our life: food, rubber, polymer diaper, our own body, etc. The thermal fluctuation endows soft materials with fundamentally different behavior comparing to hard materials like metals and ceramics. This dissertation studies three aspects of the mechanics and physics of soft materials, as is reviewed below.

First, soft materials are generally swellable and viscous. The combination of diffusion and viscous flow gives rise to a length scale, \( \Lambda = \sqrt{\eta D \Omega / kT} \), which is called poroviscous length. Here \( \eta \) is the viscosity, \( D \) is diffusivity, \( \Omega \) is the volume of the molecule, \( kT \) is the thermal energy. The emergence of a length scale results in size dependent relaxation. We show that the coupling between diffusion and viscous flow explains the Brownian motion in supercooled liquids, where the classical result of Stokes-Einstein relation generally fails. The concurrent diffusion and viscous flow cannot be described by the classical hydrodynamics, where all the material transport is lumped into velocity field. We formulated a continuum theory to modify the classical hydrodynamics. In particular, the new theory predicts a new bulk viscosity that could exist in incompressible material. We generalize this idea of bulk viscosity to binary
systems and study the mixing of materials that is limited by local structural rearrangement instead of diffusion. This model develops formulation of non-equilibrium thermodynamics by removing the common assumption of local equilibrium.

Second, capillarity has strong influence on the morphology of soft materials. The competition between capillarity and elasticity gives rise to the elastocapillary length $\gamma/\mu$. Here $\gamma$ is the surface energy, $\mu$ is the shear modulus. We show that elastocapillary effect explains the complex nucleation of crease, a widely observed surface instability in soft elastic materials. We also explore the possible competition between capillarity and osmosis in gels, which defines the osmocapillary length $\gamma/\Pi$. Here $\Pi$ is the osmotic pressure inside the gel. If additional hydrostatic pressure $\Pi$ is applied onto the gel, the solvent inside the gel equilibrates with the pure solvent in the stress free liquid phase. We show that at small enough length scale or for a gel that is nearly fully swollen, surface tension can pull liquid solvent out from the gel phase, a phenomenon we termed osmocapillary phase separation.

Third, soft materials are nearly incompressible. The incompressibility and softness makes elastomers ideal for the design of seals. Although the failure of seals has been studies for decades, existing studies mainly focus on the damage and degradation of materials. Here we study the leak of a seal due to elastic deformation without any damage. We call such a failure mode the elastic leak. We point out that elastic leak is involved in any leak event no matter whether material is damaged or not. We also show that the reversible nature of the elastic leak enable seal series to achieve higher sealing capability.
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Chapter 1.

Introduction

1.1 Soft materials and hard materials

Simply by comparing the stiffness of a material to our body, we can broadly put materials into two categories. The materials that are much stiffer than our body are called hard materials. The materials that are similar or softer than our body are called soft materials. Superficial as it may sound, the distinction between hard materials and soft materials is fundamental. The different behavior of soft materials and hard materials arises from the relative significance of thermal activation. Hard materials are characterized by interaction energies between molecules that are much higher than the thermal energy at room temperature, while soft materials are characterized by interaction energies between molecules that are comparable to thermal energy at room temperature [1]. This means that in the absence of any external driving force, over daily time scale, the structure of a hard material is essentially static, while the structure of a soft material actively fluctuates. When a small driving force is applied to a hard material, the microscopic structure does not rearrange and the material recovers the original configuration when the driving force is removed. On the contrary, when a small driving force is applied to a soft material, the fluctuation of the microscopic structure is biased and the material relaxes with dissipation (Figure 1.1).
Figure 1.1. A schematic showing the difference between hard materials and soft materials. Here the change of the material structure is represented by the movement of a bead. The interaction energy is represented by periodic energy wells.

The significance of thermal activation is reflected in many aspects of the mechanics and physics of soft materials. If we take the driving force as stress, a hard material responds elastically with small deformation while a soft material responds viscoelastically with large deformation. Accordingly, hard materials are used to construct machine and buildings, where stability and accurate control of displacement is wanted. Soft materials are used in tires, soundproofing materials and adhesives, where flexibility and damping are wanted. If we take the driving force as chemical potential difference, a hard material is impermeable to surrounding materials while a soft material mixes with surrounding materials. For example, we can use steel to contain liquefied gas, we can use glass bottle to hold wine and we can wash off contamination and reuse these containers. On the other hand, meat get the flavor from marinate within hours, polymer diapers absorb liquid almost instantly and once mixing happens it is nontrivial to demix. If we look at biological systems including ourselves, driving forces and response may
take many more complex forms, but thermal activation is nevertheless crucial behind these processes [2].

The effect of thermal activation scales up at higher temperature and longer time. Hard materials at room temperature and daily time scale behave like soft materials at high temperature and long time scale. For example, metal is a typical hard material at room temperature. It responds to stress elastically and does not mix with surrounding materials. However, near the melting temperature metal undergoes viscous flow, which is known as creep [3]. Near the melting temperature metal also mixes with neighboring metal, which is demonstrated in Kirkendall effect [4]. As another example, concrete is a hard material on daily time scale. However, creep of concrete can cause the failure of bridges over the time scale of 10 years [5].

A material has many different microscopic interactions. A soft material may be ‘soft’ in some of these interactions yet ‘hard’ in others. The mixture in the strengths of microscopic interactions is crucial for the study of soft materials. For example, compressing causes electron orbital overlapping for both soft materials and hard materials. The consequent energy penalty due to Pauli repulsion cannot be overcome by thermal fluctuation. As a result, soft materials often have bulk modulus similar to the hard materials [6]. Since it is so much easier to shear a soft material than to compress it, soft materials are commonly modeled as perfectly incompressible [7]. As another example, polymeric gel is often crosslinked with covalent bonds. While the sliding between polymer chains are easily facilitated by thermal fluctuation, covalent bonds are permanent at room temperature. Consequently, while polymeric gel undergoes large deformation like a soft material, it can elastically recover the deformation like a hard material [8].

The above discussions give an overview of the mechanics and physics of soft materials. The following part of the dissertation will focus on three specific aspects.
Chapter 2-4 studies coupled diffusion and viscous flow. Chapter 5-6 studies the capillary effects. Chapter 7-8 studies the incompressibility and its relevance in the leak of elastomeric seals. Following paragraphs outline the three parts in more details.

### 1.2 Coupled diffusion and viscous flow

Diffusion and viscous flow are both thermally activated kinetic processes in soft materials. Viscous flow gives a time scale $\tau_v \sim kT/\eta\Omega$. Here $kT$ is the product of Boltzmann constant and the temperature. $\eta$ is the shear viscosity. $\Omega$ is the volume of the molecule. Diffusion gives a time scale $\tau_D \sim L^2/D$. Here $L$ is the characteristic length scale of the problem and $D$ is the diffusivity of the material. Note that $\tau_v$ is independent of the size of the problem but $\tau_D$ depends on the size of the problem. With sufficient small $L$, we can make $\tau_D < \tau_v$. With sufficient large $L$, we can make $\tau_D > \tau_v$. The crossover of these two time scales gives a material specific length scale $\Lambda = \sqrt{D\eta\Omega/kT}$, which we call the poroviscous length. When diffusion and viscous flow are independent kinetic processes, certain perturbations of the material could be relaxed by either viscous flow or diffusion. The emergence of a length scale means that the relaxation of soft materials is intrinsically size-dependent. For small samples where $L < \Lambda$, relaxation of diffusion is relatively fast. For large samples where $L > \Lambda$, viscous flow is relatively fast. Correspondingly, different samples may relax with different rate limiting processes depending on their sizes.

Chapter 2 studies how coupled diffusion and viscous flow influences the Brownian motion in soft materials. If viscous flow is the only kinetic process, the diffusivity of a probe is predicted by the Stokes-Einstein relation: $D_p \sim kT/\eta a$, where $D_p$ is the long time diffusivity of the probe, $a$ is the size of the probe. If diffusion is the
only kinetic process, the diffusivity of a probe is predicted by: 
\[ D_p \sim \Omega D / a^3 \], where \( D \) is the self-diffusivity of the material. By analyzing the existing experimental data of Brownian motion in supercooled liquids, it is shown that both viscous flow facilitated Brownian motion and diffusion facilitated Brownian motion are observed in the same material. The transition between the two mechanisms happens when the size of the probe is comparable to \( \Lambda \).

Chapter 3 develops a continuum theory for pure substance where diffusion and viscous flow are treated as independent concurrent processes. The idea of inert marker as used in the original experiment of Kirkendall effect [4] is adopted to define the marker velocity field. The marker velocity is different from the average molecular velocity used in classical fluid mechanics [9]. Specifically, divergent marker velocity field is possible for incompressible material if divergence of diffusion flux is non-zero. A bulk viscosity naturally emerges. It measures the effect that after the composition of a piece of material homogenized, local structural rearrangement may still take a finite amount of time. The local chemical equilibrium is not established until the structural relaxation is completed. When diffusion relaxation is fast enough, the volume expansion of the material is limited by this bulk viscosity. Since the material is treated as incompressible, this bulk viscosity is distinct from the bulk viscosity defined for compressible fluids. A general category of boundary value problems where chemical equilibrium is satisfied is identified. The result used in chapter 2 is then rigorously derived using this new theory.

Chapter 4 extends the idea of bulk viscosity to binary systems and studies the general consequence of local chemical non-equilibrium. Diffusion is assumed to be either very fast or very slow and does not affect the chemical equilibrium at the relevant time scale. The single bulk viscosity for a pure substance becomes a matrix of bulk viscosities in a binary system. The bulk viscosities are related to two distinct relaxation modes: dilation and swap. In the dilation mode, the volume of the material changes while the
composition remains constant. In the swap mode, the composition of the material changes while the volume remains constant. Although local chemical equilibrium is widely assumed in non-equilibrium thermodynamics [10], such an assumption has no fundamental basis. This chapter develops a basic model for local chemical non-equilibrium. Such local chemical non-equilibrium is important to problems like the lithiation of Silicon electrodes [11], the swelling of glassy polymers [12], the creep of physically crosslinked gels [13] and the mechanical behavior of cells [14].

1.3 Elastocapillary effect and osmocapillary effect

The free energy of a material is the sum of the bulk energy and the surface energy. While the bulk energy like elastic energy and chemical energy scales with the volume of the material, surface energy scales with the surface area of the material. As the size of the material decreases, surface energy plays an increasingly important role in the free energy minimization. For hard materials, since the interactions between molecules are strong, the bulk energy density is high. Consequently, the effect of surface energy is negligible at physically relevant length scales. For soft materials, since the interactions between molecules are much weaker, the bulk energy density is much lower. Consequently the effect of surface energy is important at physically relevant length scales. Surface energy leads to different phenomena when it competes with different bulk energies.

The competition between surface energy and elasticity is called elastocapillary effect. The elasticity of the material is characterized by the shear modulus $\mu$. The surface energy of the material is characterized by the surface tension $\gamma$. The combination of these two quantities gives the elastocapillary length $\gamma/\mu$. For soft materials with shear moduli ranging from $\sim10\text{Pa}$ to $\sim10\text{MPa}$ and surface tension $\sim10\text{mN/m}$, elastocapillary length varies from nanometer scale to millimeter scale. Elastocapillary effect is especially important in the nucleation of creases. Neglecting
The elastocapillary effect would result in singular surface profile at the crease tip and non-smooth bifurcation [15]. Chapter 5 shows that these non-physical behaviors are removed once the elastocapillary effect is accounted, Figure 1.2. Specifically, it is shown that the defect sensitivity of the nucleation of crease could be characterized by comparing the defect size with the elastocapillary length. When the elastocapillary length is much larger than the defect size, the system approaches a defect free behavior, where a crease bifurcates subcritically from a flat surface at the critical strain of wrinkle. When the elastocapillary length is much smaller than the defect size, the system seemingly bifurcates supercritically from a flat surface at a much lower critical strain. For intermediate defect size, crease can nucleate at any strain between these two limits.

![Figure 1.2. The schematic bifurcation diagram of crease and wrinkle. The inlets are the schematic of the surface morphology of crease and wrinkle. (a) Neglecting elastocapillary effect, the crease has a singular tip and the critical point of wrinkle can never be reached (dotted line). (b) Considering elastocapillary effect, the crease tip is not rounded by surface tension and the critical point of wrinkle can be reached if the system is defect free.](image)

Chapter 6 studies the competition between surface energy and osmosis, which we call the osmocapillary effect. A covalent network of polymer can imbibe a solvent to form
a gel. The driving force to imbibe the solvent could be characterized by the osmotic pressure $\Pi$. If additional hydrostatic pressure $\Pi$ is applied onto the gel, the solvent inside the gel equilibrates with the pure solvent in the stress free liquid phase. The competition between capillarity and osmosis defines the osmocapillary length $\gamma / \Pi$. In a cavity on the surface of the gel, capillary force may suck the solvent out of the gel to form a pure liquid phase, Figure 1.3. It is shown that such osmocapillary phase separation occurs when capillarity balances osmosis, and when the diffusion of solvent in the gel prevails over the condensation of solvent from the vapor. Osmocapillary phase separation can occur even when the gel is isolated from the vapor, or when the solvent is nonvolatile. We relate osmocapillary phase separation to phenomena of practical significance, including the wettability of gels, the transparency of gels, the liquid bridge at the tip of an atomic force microscope, the adhesion between a gel and another substance, the surface morphology of gels, and the production of tight oil.

![Figure 1.3](image)

**Figure 1.3.** The osmocapillary phase separation in a cavity. $\kappa$ denotes the curvature of the liquid surface. (a) If the capillary force is stronger than osmosis, liquid is pulled out from the gel. (b) If the capillary force is weaker than osmosis, liquid is absorbed into gel.

### 1.4 Incompressibility and the leak of a seal

The incompressibility of elastomers makes it ideal for the design of seals. When a piece of elastomer is squeezed into a rigid gap, the elastomer adapts to the shape of the
gap due to its softness. When a pressure is applied on one end of the elastomer, the elastomer passes the pressure to the rigid confinement with little deformation due to its incompressibility. Ideally, a well-confined seal can seal arbitrary large pressure, because all the pressure is carried by the incompressible mode of deformation [16]. However, in practice, the deformation of the elastomeric seal cannot be perfectly confined. Leak eventually happens as deformation develops.

![Diagram](image)

**Figure 1.4.** Schematic of the working principle of an elastomeric seal. Initially, the seal is slightly larger than the gap. When the seal is squeezed in, the softness of the elastomer enables the seal to automatically fit any surface roughness with low assembly force. When the seal is pressurized, the incompressibility of the elastomer enables the seal to withstand high pressure with little deformation.

Chapter 7 introduces the concept of elastic leak, which is the leak of elastomeric seals due to elastic deformation without any material damage. A theoretical model of elastic leak is described, and the process of a seal deforming and leaking is visualized through a transparent experimental setup. The elastomer seals the fluid by forming contact with surrounding hard materials. As the fluid pressure increases, the contact stress also increases but not as much. When the fluid pressure surpasses the contact stress, the elastomer and the hard materials lose contact in some region, forming a leaking path. The critical fluid pressure for elastic leak depends on the geometry and
constraint of the seal, but is insensitive to the rate at which the fluid is injected. This study points to the significance of elastic deformation in modes of failure that also involve material damage.

Chapter 8 studies the elastic leak of multiple seals in series. When multiple seals are installed in series and the spaces between the seals contain compressible fluids (e.g., gas or gas–liquid mixture), the seals often damage sequentially, one after another. This chapter demonstrates that the serial seals achieve high sealing capacity if individual seals undergo elastic leak, without material damage. When individual seals leak elastically, fluid fills the spaces between the seals. Instead of damage one after another, all the seals share the load. The elastic leak of individual seals greatly amplifies collective sealing capacity of serial seals.
Chapter 2.

Brownian motion in the supercooled liquids

2.1 Failure of Stokes-Einstein relation

Einstein assumed that the Brownian motion of a probe in a host liquid is facilitated by viscous flow \[17\]. The host liquid consists of molecules of one species. The probe can be a colloidal particle, a molecule of another species, or a molecule of the same species as that of the host liquid. A decrease in temperature slows down both the Brownian motion of the probe and the viscous flow of the host liquid. That is, as the temperature decreases, the diffusivity of the probe \( D_p \) decreases and the viscosity of the host liquid \( \eta \) increases. The probe-liquid pair is said to obey the Stokes-Einstein relation if \( D_p \eta / kT \) is independent of temperature, where \( kT \) the temperature in the unit of energy. The Stokes-Einstein relation holds for many probe-liquid pairs over wide ranges of temperature \[18, 19\].

The Stokes-Einstein relation, however, fails for some probes in some supercooled liquids, where a modest decrease in temperature slows down the viscous flow in a liquid greatly, but does not slow down the Brownian motion of a probe as much. That is, the decrease in \( D_p \) does not cancel out the increase in \( \eta \), causing \( D_p \eta / kT \) to increase by orders of magnitude \[20-27\]. Figure 2.1 plots the experimental data of \( D_p \eta / kT \) as functions of temperature for seven probe-liquid pairs. The Stokes-Einstein relation approximately holds for the pairs BPEA-OTP and rubrene-OTP, but fails for the other five pairs. The failure of Stokes-Einstein relation has been studied as an important aspect of glass transition \[28-30\].
Figure 2.1. Experimental data for molecular probes in supercooled liquids. (a) Data for several probes in TNB [21]. (b) Data for several probes in OTP [24].

A plausible cause of this failure is as follows. Due to thermal agitation, molecules of the host liquid constantly bombard the probe. At a short time scale, the bombardments do not cancel out, but give rise to a net force, motivating the probe to drift. For the probe to drift, the surrounding molecules of the host liquid must move apart by changing neighbors. At high temperature when a substance is a liquid, molecules change neighbors through viscous flow, and the Stokes-Einstein relation holds. At low temperature when the substance is a glass, molecules change neighbors by collective and localized molecular rearrangement, such as free volume activation and ring displacement [31]. The Stokes-Einstein relation does not apply. Such collective and localized molecular rearrangement will be called “molecular hopping”. As the substance cools from a liquid to a glass, molecular hopping gradually dominates over viscous flow. The flux of molecular hopping offers additional mobility to the probe, and makes its Brownian motion faster than the prediction of Stokes-Einstein relation. This picture is
supported by molecular dynamic simulations which show that the self-diffusion flux of the host liquid split into a fast group and a slow group [32-37], where it is further verified that the slow group of the molecules satisfy the Stokes-Einstein relation [37] and thus corresponds to the self-diffusion by viscous flow.

In this chapter, a theory that quantitatively relates the Brownian motion of a probe to the molecular hopping in a liquid is developed. Although supercooled liquids are dynamically heterogeneous and show anomalous diffusion at a short time scale, transport becomes homogeneous and assumes Fickian behavior at time scale longer than the time for structural relaxation [29, 38, 39]. Consequently we model a supercooled liquid as a homogeneous and isotropic continuum, and model molecular hopping as Fickian diffusion. We show that, when molecular hopping is the prevailing mechanism of transport, the mobility of the probe is proportional to the hopping diffusivity of the host liquid, and is inversely proportional to the volume of the probe. Furthermore, we hypothesize that in a supercooled liquid the two processes—molecular hopping and viscous flow—facilitate the Brownian motion of the probe concurrently. Molecular hopping prevails over viscous flow when the probe is small and temperature is low. Our theory generalizes the Stokes-Einstein relation with one additional term, and fits the experimental data of the seven probe-liquid pairs to a single curve.

2.2 Brownian motion facilitated by molecular hopping

Einstein assumed that the probe drifts when molecules of the host liquid change neighbors by viscous flow (Figure 2.2a). We first recall the steps that lead to the Stokes-Einstein relation. Stokes [40] solved the boundary-value problem of a spherical particle, radius $a_p$, moving in a host liquid of viscosity $\eta$. His solution showed that the velocity $V_p$ of the particle is linear in the force $F$ acting on the particle, $V_p = M_p F$, with the
mobility $M_p = 1/(6\pi a_p \eta)$. Einstein related the mobility and the diffusivity of the particle, $D_p = kT M_p$ [17]. The combination of the two results gives the Stokes-Einstein relation:

$$D_p = \frac{kT}{6\pi a_p \eta}. \quad (2.1)$$

In solving the boundary-value problem, Stokes assumed that the particle is a rigid sphere, the host liquid is a continuum, and the velocity of the host liquid at the liquid/particle interface is the same as that of the particle. These assumptions may not hold for probes of various shapes and sizes. In practice, one calculates $a_p$ from (2.1) using the experimentally measured diffusivity of a probe and the viscosity of the host liquid. The result so obtained is called the Stokes radius of the probe. If the Stokes radius is independent of temperature (namely, if $D_p \eta / kT$ is independent of temperature), the probe-liquid pair is said to obey the Stokes-Einstein relation.

**Figure 2.2.** Brownian motion of a probe facilitated by two mechanisms of molecular movements in the host liquid. (a) Molecules of the host liquid move by viscous flow. The probe drags the surrounding molecules of the liquid. (b) Molecules of the host liquid move by molecular hopping. The probe causes compression in the front and tension in
the back, causing a hopping flux of molecules of the host liquid from front to the back of the probe.

Here we assume that a probe can also drift when molecules of the host liquid change neighbors by hopping (Figure 2.2b). The molecules of the host liquid hop randomly due to thermal fluctuation, even in the absence of any probe. When a net force motivates the probe to drift forward, the liquid ahead of the probe is in compression, and the liquid behind the probe is in tension. This bias in stress drives molecules of the host liquid to hop from the front to the back of the probe more frequently than the other way around. As the molecules in the host liquid moves to the back of the probe, the probe drifts forward.

We adapt Herring’s theory [41] of self-diffusion in solids to model hopping in supercooled liquids. The theory adopts a Fickian-type model of diffusion, $J = -\left(\frac{D_{\text{hop}}}{\Omega kT}\right) \nabla \mu$, where $J$ is the hopping flux of molecules of the host liquid, $\mu$ the chemical potential of molecules in the host liquid, $D_{\text{hop}}$ the hopping diffusivity of the host liquid, and $\Omega$ the volume per molecule in the host liquid. Hopping keeps the density of the host liquid unchanged, so that the flux is divergence-free, $\nabla \cdot J = 0$.

Consider a spherical probe, radius $b_p$, subject to force $F$, drifting at velocity $V_p$. We require that the flux of molecules neither penetrate into the probe nor leave a gap on the boundary of the probe. Thus, on the boundary of the probe, the velocity of the probe sets up a flux of molecules of the host liquid in the radial direction, $J_r(\theta) = \left(\frac{V_p}{\Omega}\right) \cos \theta$, where $\theta$ is the angle of the radial direction measured from the direction of the velocity of the probe. The chemical potential exerts traction normal to the boundary, $\sigma_n = -\mu/\Omega$. 

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This traction is compressive ahead the probe and tensile behind the probe. Balancing the forces acting on the probe, we obtain that

\[ F = -\int_0^\pi \sigma \sin \theta \cos \theta d\theta. \]

The above theory leads to a linear relation between the velocity of the probe and the force acting on the probe, \( V_p = M_p F \), where \( M_p \) is the mobility of the probe due to the hopping of the molecules of the host liquid. The hopping flux scales with the velocity of the probe, \( J \sim V_p / \Omega \), the gradient of the chemical potential scales with the force acting on the probe, \( \nabla \mu \sim \Omega F / b_p^3 \), and the flux is proportional to the gradient of chemical potential \( J \sim \left( D_{\text{hop}} / \Omega kT \right) \nabla \mu \). These scaling relations link the mobility of the probe to the hopping diffusivity of the host liquid, \( M_p \sim D_{\text{hop}} / kT b_p^3 \). We determine the numerical coefficient in this relation by solving the boundary-value problem. Herring’s theory shows that the chemical potential satisfies the Laplace equation, \( \nabla^2 \mu = 0 \).

Solving this partial differential equation in spherical coordinates, we obtain the distribution of the chemical potential, \( \mu(r, \theta) = V_p kT b_p^3 \cos \Theta / 2D_{\text{hop}} r^2 \). We have set the chemical potential remote from the probe to be zero. The chemical potential is positive ahead the probe, and negative behind the probe. This difference in chemical potential drives molecules of the host liquid to hop from the front to the back of the probe, facilitating the probe to drift forward. On the basis of this solution, we obtain the mobility of the probe due to the hopping of molecules in the host liquid, \( M_p = 3D_{\text{hop}} \Omega / 2\pi kT b_p^3 \). Using the Einstein relation, \( D_p = kT M_p \), we link the diffusivity of probe to the hopping diffusivity of the host liquid:

\[ D_p = \frac{3\Omega}{2\pi b_p^3} D_{\text{hop}}. \] (2.2)
The diffusivity of the probe is linear in the hopping diffusivity of the host liquid, and is inversely proportional to the volume of the probe. Our theory assumes that the probe is a rigid sphere, and the host liquid is a continuum. These assumptions may not hold in experiments. In the spirit of the Stokes-Einstein relation, we will calculate $b_p$ from (2.2) using measured diffusivities and will call the radius so obtained the Herring radius. If the Herring radius is independent of temperature (namely, if $D_p / D_{hop}$ is independent of temperature), the probe-liquid pair is said to obey the Herring-Einstein relation.

### 2.3 Concurrent molecular hopping and viscous flow

As discussed earlier, in a supercooled liquid viscous flow and molecular hopping are concurrent mechanisms of transport. We hypothesize that the diffusivity of the probe is the sum of the contributions from viscous flow (2.1) and molecular hopping (2.2):

$$D_p = \frac{kT}{6\pi a_p \eta} + \frac{3\Omega}{2\pi b_p^3} D_{hop}. \quad (2.3)$$

The viscosity $\eta$ and the hopping diffusivity $D_{hop}$ characterize molecular transport in the host liquid. Since viscous flow and molecular hopping are distinct processes, the Stokes radius $a_p$ and the Herring radius $b_p$ are distinct parameters. We say that a probe-liquid pair satisfies the hypothesis if (2.3) holds for temperature-independent values of $a_p$ and $b_p$.

We determine the hopping diffusivities of the two host liquids, TNB and OTP, using the experimental data of self-diffusion contained in Figure 2.1. In the figure, the Stokes-Einstein relation is a horizontal line, on which the experimental data at high temperature fall. For each host liquid, we use the data of self-diffusivity $D_{self}$ at high temperature ($T / T_g > 1.37$ for TNB and $T / T_g > 1.36$ for OTP) in Figure 2.1 to fit the
Stokes radius $a_{s}$. That is, at high temperature we assume that the Stokes-Einstein relation is valid, $D_{s} \eta / kT = 1 / 6 \pi a_{s} \eta$, neglecting the effect of hopping. We obtain $a_{s} = 3.2\text{Å}$ for TNB, and $a_{s} = 3.4\text{Å}$ for OTP. At low temperature, the self-diffusivities of the two host liquids violate the Stokes-Einstein relation by orders of magnitude. We assume that the difference between the experimentally determined $D_{s} \eta / kT$ from the prediction of the Stokes-Einstein relation is entirely due to hopping. Specializing (2.3) for self-diffusion, we write

$$D_{s} = \frac{kT}{6 \pi a_{s} \eta} + D_{h}.$$  

(2.4)

In writing (2.4), we require that the Herring radius to satisfy $2 \pi b_{s}^{3} / 3 = \Omega$. For the data of $D_{s} \eta / kT$ for the two host liquids TNB and OTP in Figure 2.1, subtracting the contribution of the Stokes-Einstein relation, we obtain $D_{h} \eta / kT$. In doing so, we cannot obtain any information on $D_{h}$ at the high temperature ranges where the Stokes radii are calculated. Subsequent discussion and plots only use the data in the remaining ranges of temperature, which are more than 90% of the original ranges of temperature.

**Figure 2.3.** Diffusivity of probes normalized by the hopping diffusivity in the host liquids. (a) Data for several probes in TNB. (b) Data for several probes in OTP.
As noted before, some probe-liquid pairs (BPEA-OTP and rubrene-OTP) approximately obey the Stokes-Einstein relation, but others do not (Figure 2.1). In the latter cases, we find that the ratio $D_p / D_{hop}$ approaches constant at low temperature (Figure 2.3). For instance, for the probe tetracene in the liquid TNB, $D_p / D_{hop}$ is constant at low temperature, when $T / T_g < 1.18$ (Figure 2.3). That is, when a probe-liquid pair violates the Stokes-Einstein relation, the pair obeys the Herring-Einstein relation.

To ascertain our hypothesis that viscous flow and molecular hopping in a supercooled liquid facilitate Brownian motion concurrently, we compare equation (2.3) and the experimental data for the seven probe-liquid pairs (Figure 2.4). The vertical axis is a dimensionless measure of the deviation from the Stokes-Einstein relation. The horizontal axis is a dimensionless measure of the relative magnitude of the two mechanisms of molecular transport—viscous flow and molecular hopping. For each probe-liquid pair, the experimental data fit (2.3) remarkably well by temperature-independent $a_p$ and $b_p$ (Table 2.1). The values $a_p$ and $b_p$ are on the order of the size of the molecules. Since the viscous flow and molecular hopping are independent processes, and the shape of each probe is very different from a sphere, $a_p$ and $b_p$ can be very different for the same probe-liquid pair. The transition from viscous flow to molecular hopping as prevailing mechanism of transport is evident (Figure 2.4). Viscous flow prevails when temperature is high and probes are large, as represented by horizontal lines in Figure 2.1. Molecular hopping prevails when temperature is low and probes are small, as represented by horizontal lines in Figure 2.3.
Figure 2.4. The fitting of the experimental data for seven probe-liquid pairs to the theoretical prediction. The horizontal line corresponds to the Brownian motion facilitated by viscous flow (i.e., the Stokes-Einstein relation). The linear relation corresponds to the Brownian motion facilitated by molecular hopping (i.e., the Herring-Einstein relation).

Table 2.1. The Stokes radius and the Herring radius of various probes in different host liquids

<table>
<thead>
<tr>
<th>Probe Liquid</th>
<th>Tetracene</th>
<th>OTP</th>
<th>TNB</th>
<th>BPEA</th>
<th>Rubrene</th>
</tr>
</thead>
<tbody>
<tr>
<td>TNB</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>a_p = 0.5 Å</td>
<td></td>
<td></td>
<td>a_self = 3.2 Å</td>
<td>a_p = 1.9 Å</td>
<td></td>
</tr>
<tr>
<td>b_p = 2.7 Å</td>
<td>N/A</td>
<td></td>
<td>b_self = 6.8 Å</td>
<td>b_p = 12.4 Å</td>
<td></td>
</tr>
<tr>
<td>OTP</td>
<td>a_p = 3.2 Å</td>
<td>a_self = 3.4 Å</td>
<td>N/A</td>
<td>a_p = 3.3 Å</td>
<td>a_p = 6.4 Å</td>
</tr>
<tr>
<td></td>
<td>b_p = 4.1 Å</td>
<td>b_self = 5.6 Å</td>
<td></td>
<td>b_p = 12.0 Å</td>
<td>b_p = 2.02 Å</td>
</tr>
</tbody>
</table>

2.4 Discussions

For each liquid, the two mechanisms of transport define a characteristic length, 
\[ \Lambda = \sqrt{\frac{\eta D_{hop} \Omega}{kT}} \] [42-44]. The characteristic length increases as temperature drops
(Figure 2.5). The horizontal axis of Figure 2.4 can be written as $9a_p \Lambda^2 / b_p^3$, which is a dimensionless measure of the size of a probe relative to the characteristic length $\Lambda$. When a probe is small compared to this characteristic length, the Brownian motion of the probe is mainly facilitated by molecular hopping in the host liquid. When a probe is large compared to this characteristic length, the Browning motion of the probe is mainly facilitated by the viscous flow of the host liquid.

![Graph](image)

**Figure 2.5.** The characteristic length $\Lambda = \sqrt{\eta D_{\text{hop}} \Omega / kT}$ plotted as a function of temperature. The volume per molecule in the host liquid is $\Omega = 0.64$nm$^3$ for TNB and $\Omega = 0.37$nm$^3$ for OTP [45].

We have considered molecular probes undergoing Brownian motion in supercooled liquids facilitated by two concurrent mechanisms by which the molecules in the host liquid change neighbors. In principle, any probe undergoes Brownian motion in any host in which molecules change neighbors by any mechanism. For example, near the melting point of a crystal, diffusion of vacancies is a dominant mechanism of transport but other concurrent mechanisms like power law creep exist [46]. We expect that a probe (e.g., a ceramic particle) undergoes Brownian motion in a crystal (e.g., a metal).
In summary, we have assumed that molecules of a supercooled liquid move by two concurrent processes: viscous flow and molecular hopping. We have developed a theory that allows both processes to facilitate the Brownian motion of a probe. Molecular hopping prevails over viscous flow when the probe is small and temperature is low. Our approach quantitatively explains the experimental data, and generalizes the Stokes-Einstein relation. The Brownian motion of a probe in a medium depends on the mechanisms of transport in the medium, the size of the probe, and temperature. The Brownian motion of probes sheds light on mechanisms of molecular transport in complex matter.
Chapter 3.
Mechanics of supercooled liquids

3.1 Coupled diffusion and viscous flow

In the classical formulation of the hydrodynamics of a pure substance, the velocity is defined as the average molecular velocity over a spatial element that is microscopically large yet macroscopically small [47]. The linear kinetic model for incompressible fluid has shear viscosity as the only kinetic parameter [9]. The theory has no intrinsic length scale and the diffusivity of a particle inside the fluid follows the Stokes-Einstein relation [17].

In recent decades, however, evidence has accumulated that the Stokes-Einstein relation fails in many supercooled liquids [48-53]. Moreover, in many cases dynamic heterogeneity forms in supercooled liquid, giving rise to a length scale [54-59]. In the last chapter, it is shown that both the failure of Stokes-Einstein relation and the lack of length scale can be solved by introducing a diffusion mechanism that is independent of viscous flow. There, the effect of diffusion and viscous flow are intuitively superposed together. However, such a superposition cannot be justified under classical hydrodynamics, where the effect of any material flux is captured in the velocity field. A diffusion flux separate from viscous flow cannot be defined unless the definition of velocity is modified.

This chapter develops a continuum theory that incorporates diffusion and viscous flow as distinct, concurrent processes. We separate the material transport into two parts, diffusion and convection, where the convection field is defined by the marker velocity field instead of the average velocity field. The general linear kinetic model is derived, which consists of one shear viscosity, one bulk viscosity and one diffusivity. The bulk
viscosity describes the local chemical non-equilibrium. A general category of problem where chemical equilibrium is satisfied everywhere is identified. As an example, we apply the theory to the problem of Brownian motion of a spherical probe in a supercooled liquid.

3.2 Homogeneous state

This section generalizes Newton’s law of viscosity to describe a supercooled liquid of a single species of molecules, subject to external forces, and connected to a reservoir of the same species of molecules (Figure 3.1). The piece of liquid contains a large number of molecules, but is still small enough to serve as a representative elementary volume. In this continuum picture, the piece evolves through a sequence of homogeneous states, represented by a parallelepiped that changes its shape and volume. Let \( d_{ij} \) be the rate of deformation, and \( R \) be the rate of injection (namely, the number of molecules transferred from the reservoir to the piece per unit volume per unit time). The external forces apply to the piece a state of stress \( \sigma_{ij} \), and the molecules in the reservoir have the chemical potential \( \mu \).

Molecules in a liquid are often nearly incompressible. As an idealization, we assume that the volume per molecule in the liquid, \( \Omega \), remains constant, independent of the stress and the chemical potential of the molecules in the reservoir. At a given time, the volume of the piece is \( V \), the trace of the rate of deformation is \( d_{kk} \), and the piece changes its volume at the rate \( Vd_{kk} \). The reservoir transfers volume of molecules to the piece at rate \( \Omega RV \). The idealization of molecular incompressibility, along with the conservation of the number of molecules, requires that

\[
d_{kk} = \Omega R. \tag{3.1}
\]
That is, the increase of the volume of the piece equals the volume transferred from the reservoir.

**Figure 3.1.** A composite thermodynamic system consists of a body of liquid, a set of external forces, and a reservoir of molecules. The body evolves through a sequence of homogeneous states, represented by a parallelepiped that changes its shape and volume at a rate of deformation $d_{ij}$, and absorbs molecules from the reservoir at rate $R$ per unit volume. The external forces apply to the body of liquid a state of stress $\sigma_{ij}$. The reservoir and the body of liquid exchange the species of molecules that constitute the liquid, and the chemical potential of the species of molecules in the reservoir is $\mu$.

The piece, the external forces, and the reservoir together constitute a composite thermodynamic system. The composite system exchanges energy, but not molecules, with a heat bath of a fixed temperature. We restrict our analysis to isothermal processes, and do not list temperature as a variable. Consistent with the idealization of molecular incompressibility, we further assume that the Helmholtz free energy per molecule in the piece remains constant, independent of the applied stress and the chemical potential of
the molecules in the reservoir. The Helmholtz free energy per molecule in the piece of fluid is set to zero. The potential energy of the external forces changes at the rate \(-V\sigma_y d_y\), and the potential energy of the reservoir changes at the rate \(-V\mu R\). The Helmholtz free energy of the composite system is the sum over the parts (i.e., the piece of liquid, the external forces, and the reservoir of molecules): \(0 - V\sigma_y d_y - V\mu R\). Thermodynamics requires that the Helmholtz free energy of the composite system should never increase, giving
\[
- V\sigma_y d_y - V\mu R \leq 0. \tag{3.2}
\]
This thermodynamic condition, subject to idealization of molecular incompressibility, \(d_{kk} = \Omega R\), becomes that
\[
\left(\sigma_y + \frac{\mu}{\Omega} \delta_{ij}\right) d_y \geq 0. \tag{3.3}
\]
Condition (3.3) holds for arbitrary rate of deformation \(d_y\), a total of six independent variables.

When the equality in (3.3) holds for arbitrary rate of deformation \(d_y\), the composite system is in thermodynamic equilibrium. This condition of equilibrium leads to
\[
\sigma_y + \frac{\mu}{\Omega} \delta_{ij} = 0. \tag{3.4}
\]
This condition corresponds to a total of six independent equilibrium equations, \(\sigma_{12} = \sigma_{23} = \sigma_{31} = 0\) and \(\sigma_{11} = \sigma_{22} = \sigma_{33} = -\mu / \Omega\). For the liquid, the external forces, and the reservoir to equilibrate, the liquid must be in a hydrostatic state, and the hydrostatic stress in the liquid must compensate the chemical potential of molecules in the reservoir.
When the inequality in (3.3) holds for arbitrary rate of deformation $d_{ij}$, the composite system is not in thermodynamic equilibrium. We satisfy this inequality by prescribing a kinetic model that linearly relates two symmetric tensors, $\sigma_{ij} + \left(\frac{\mu}{\Omega}\right)\delta_{ij}$ and $d_{ij}$. For an isotropic liquid, the linear relation between two symmetric tensors takes the general form [9]:

$$\sigma_{ij} + \frac{\mu}{\Omega}\delta_{ij} = 2\eta \left(d_{ij} - \frac{1}{3}d_{kk}\delta_{ij}\right) + \beta d_{kk}\delta_{ij}.$$  (3.5)

where $\eta$ and $\beta$ are constants. The thermodynamic inequality (3.3) holds when both $\eta$ and $\beta$ are nonnegative. Given the material constants $\Omega$, $\eta$ and $\beta$, this kinetic model and the constraint (3.1) together provide a total of seven independent equations among the fourteen variables $d_{ij}$, $R$, $\sigma_{ij}$, and $\mu$.

The kinetic model (3.5) can also be motivated in a different way. The deviatoric part of the rate of deformation, $e_{ij} = d_{ij} - \frac{1}{3}d_{kk}\delta_{ij}$, describes the rate at which the piece changes its shape. The mean stress is $\sigma_m = \sigma_{kk}/3$, and the deviatoric stress is $s_{ij} = \sigma_{ij} - \sigma_m\delta_{ij}$. Note the identity $\sigma_{ij}d_{ij} = s_{ij}e_{ij} + \sigma_m d_{kk}$, and write (3.3) as $s_{ij}e_{ij} + \left(\sigma_m + \mu/\Omega\right)d_{kk} \geq 0$. This inequality suggests a kinetic model: $s_{ij} = 2\eta e_{ij}$ and $\sigma_m + \mu/\Omega = \beta d_{kk}$. The thermodynamic inequality holds when both $\eta$ and $\beta$ are nonnegative. This kinetic model is equivalent to (3.5).

The constant $\eta$ represents the shear viscosity that resists the change in shape, and the constant $\beta$ represents the bulk viscosity that resists the change in volume. In the limit $\beta/\eta \to 0$, the change in volume is much faster than change in shape, so that we may assume that $\sigma_m + \mu/\Omega \to 0$, and the composite system is in partial thermodynamic equilibrium with respect to exchange molecules between the piece and
the reservoir. In the limit $\eta / \beta \to 0$, the change in shape is much faster than change in volume, so that we may assume that $d_{kk} = 0$, and the piece changes shape without changing volume.

The kinetic model (3.5) generalizes Newton’s law of linear, isotropic, viscous flow. Note that our model differs from the model of compressible viscosity. We have assumed that molecules in the liquid are incompressible, so that an increase in volume of the liquid is entirely due the injection of molecules from the reservoir to the piece. By contrast, for compressible viscosity, the number of molecules in an element of liquid is fixed, and an increase in the volume of the element is entirely due to the reduction in density.

### 3.3 Inhomogeneous state

We now consider a body of liquid evolving through a sequence of inhomogeneous states. A continuum theory regards the body as a collection of small pieces. As the body evolves, each piece evolves through a sequence of homogeneous states, as described in the previous section. Different pieces communicate through the balance of forces, compatibility of geometry, and transfer of molecules. In classical hydrodynamics, each small piece (commonly called a material particle, a material point, or a material element) is identified by a set of molecules, which do not change identity as the body of liquid evolves. This practice, however, is inapplicable here. As a small piece of liquid transfers molecules to surrounding small pieces by the diffusion of molecules, the small piece does not consist of the same molecules and may even disappear after some time.

Here we break away from this practice in classical hydrodynamics, and describe the kinematics of the body not by tracking pieces of the liquid, but by tracking markers dispersed in the liquid. Indeed, markers are commonly used in experiments. Examples include precipitates that visualize the creep of a solid solution, and particles that
visualize the flow of a fluid. The markers should be small compared to the length characteristic of the inhomogeneous field, so that the markers are carried by the flow without affecting it. The markers should be large compared to the size of the individual molecules, so that the markers themselves diffuse negligibly. As common with many basic concepts, the relation between markers in experiments and markers in the continuum theory deserves careful examination. This paper proceeds by describing the idealized behavior of the markers within the continuum theory.

**Figure 3.2.** The definition of diffusion flux using the net flux of molecules and the velocity of markers. Imagine a plane fixed in space, with \( \mathbf{n} \) being the unit vector normal to the plane. The net flux of molecules \( \mathbf{N} \) is a vector, such that \( \mathbf{N} \cdot \mathbf{n} \) is the number of molecules crossing the plane per unit area and per unit time. Dispersed in the liquid are markers moving at the velocity \( \mathbf{v} \). The net flux of molecules and the velocity of markers can be independently measured. Define the diffusion flux by \( \mathbf{J} = \mathbf{N} - \mathbf{v} / \Omega \), where \( \Omega \) is the volume per molecule.
Denote the velocity of the markers by a field \( \mathbf{v} \). When two nearby markers drift apart, the piece of the liquid between the markers elongates. In general, compatibility of geometry relates the rate of deformation to the gradient of the marker velocity, 
\[
d_{ij} = \left( v_{i,j} + v_{j,i} \right) / 2.
\]
Following a practice in materials science [60-62], we identify fluxes of three types (Figure 3.2). Markers in a liquid are analogous to leaves on a river. The flow of water carries the leaves, but is unaffected by their presence. The motion of the markers defines convection. The molecular flux in excess of convection defines diffusion. The velocity of markers defines the convective flux, \( \mathbf{v}/\Omega \). Consider a plane fixed in space, with \( \mathbf{n} \) being the unit vector normal to the plane. Let \( N \) be the net flux of molecules—that is, \( N_i n_i \) is the number of molecules crossing the plane per unit area per unit time. The velocity of markers, \( \mathbf{v} \), and the net flux of molecules, \( N \), can be independently measured in macroscopic experiments. Classical hydrodynamics assumes that the net flux equals the convective flux, \( N = \mathbf{v}/\Omega \). The two quantities, however, are unequal when pieces of the liquid exchange molecules. The difference between the net flux and the convective flux defines the diffusion flux of molecules:
\[
\mathbf{J} = N - \mathbf{v}/\Omega. \tag{3.6}
\]
That is, the net flux of molecules is the sum of the diffusion flux and the convective flux.

Due to molecular incompressibility, the number of molecules in any fixed volume is constant. The conservation of the number of molecules requires that
\[
d_{kk} + \Omega J_{k,k} = \Omega R. \tag{3.7}
\]
Even in the absence of injection, \( R = 0 \), the divergence of the velocity field does not necessarily vanish. This behavior differs from that of hydrodynamics of incompressible fluids. Equation (3.7) is applicable to an inhomogeneous field, whereas (3.1) is applicable to a homogeneous field.
Figure 3.3. A composite thermodynamic system consists of a body of liquid, the surface of the body, a set of external forces, and a set of reservoirs of molecules.

The body is subject to loads of several kinds (Figure 3.3). Let $\gamma$ be the surface energy of the liquid per unit area. Associated with the change in the area $A$ of the body, the surface energy of the body changes at the rate $\gamma dA/dt$. The body is subject to external forces. Let $b$ be the external force per unit volume in the body, and $t$ be the external force per unit area on the surface of the body. Associated with the velocity of the markers, the potential energy of the external forces changes at the rate $-\int b v_i dV - \int t v_i dA$. Upon diffusing from the bulk to the surface, molecules are assumed to plate out on the surface, but do not leave the body. Associated with the molecules plated out, the surface of the body advances at velocity $\Omega / n_i$, the traction normal to the
surface $t_j n_j$ does work, and the potential energy of the external forces changes at the rate $-\int t_j n_j \Omega J_j n_j dA$. Each small piece of the body may be in contact with a reservoir of the same species of molecules. Let $\mu$ be the chemical potential of molecules in the reservoir, and $R$ be the rate at which the reservoir injects molecules into the piece. The whole body can be connected with a field of reservoirs, so that both $\mu$ and $R$ are fields. Associated with the transfer of molecules from the reservoirs to the body, the Helmholtz free energy of the reservoirs changes at a rate $-\int \mu R dV$. The surface, the body, the external forces, and the reservoirs together constitute a composite thermodynamic system. Thermodynamics requires that the Helmholtz free energy of the composite system should never increase:

$$\gamma \frac{dA}{dt} - \int b_i v_i dV - \int t_i v_i dA - \int t_j n_j \Omega J_j n_j dA - \int \mu R dV \leq 0.$$  \hfill (3.8)

Recall that we have assumed that the Helmholtz free energy of the liquid itself is unaffected by the loads and is taken to be zero. The thermodynamic condition (3.8) holds for an inhomogeneous field, which should be compared to the thermodynamic condition for a homogeneous field (3.2).

Let $\kappa$ be the mean curvature of an element of the surface of the body. For example, the mean curvature of a spherical particle of radius $a$ is $\kappa = 1/2a$, and the mean curvature of spherical cavity of radius $a$ is $\kappa = -1/2a$. Recall an identity in differential geometry: as the surface moves at velocity $(v_i + \Omega J_i)n_i$, the area of the surface changes at the rate $dA/dt = \int \kappa (v_i + \Omega J_i)n_i dA$. Pieces in the body communicate through the balance forces, $\sigma_{g,j} + b_i = 0$, giving $\int b_i v_i dV = \int \sigma_{g,i} v_i dV - \int \sigma_{g,j} n_j v_i dA$. Also note an identity $\int \mu J_i dV = \int \mu J_i n_i dA - \int \mu J_i dV$. 

The above relations allow us to rewrite the thermodynamic condition (3.8) as

\[
\int \left( t_i - \sigma_j n_j - \gamma \kappa n_i \right) v_i dA \\
+ \int \left( \mu + \Omega t_{j,n} - \Omega \gamma \kappa \right) J_i n_i dA \\
+ \int \left( \sigma_j + \frac{\mu}{\Omega} \delta_j \right) v_{i,j} dV \\
+ \int -\mu \sigma J_i dV \geq 0
\]

(3.9)

The inequality holds when the composite system is not in thermodynamic equilibrium, whereas the equality holds when the composite system is in thermodynamic equilibrium. The thermodynamic condition (3.9) holds for two independent and arbitrary fields: the velocity of markers, \( \mathbf{v} \), and the diffusion flux of molecules, \( \mathbf{J} \). Consequently, the integrand of each of the four integrals must be nonnegative.

We satisfy the four distinct conditions as follows. We assume local thermodynamic equilibrium at the surface of the body, so that the first two integrands vanish, namely,

\[
\sigma_j n_j = t_i - \gamma \kappa n_i , \quad \text{(3.10)}
\]

\[
\mu = -\Omega t_{j,n} + \Omega \gamma \kappa . \quad \text{(3.11)}
\]

These equations represent four distinct boundary conditions. In the absence of the surface energy, (3.10) recovers the familiar balance of forces on the surface, and (3.11) relates the chemical potential on the surface to the normal traction. In the absence of the traction due to external forces, (3.10) and (3.11) reduce to the expressions for the Laplace pressure and the Thompson effect [63]. The third integrand in (3.9) is nonnegative once we adopt the kinetic model of viscous flow (Section 3.2). The fourth integrand in (3.9) is nonnegative once we adopt a model of diffusion, \( J_i = -\left( D / \Omega k T \right) \mu_j \), where \( D \) is the diffusivity.
3.4 Governing equations

We now summarize the governing equations. Using the relation
\[ d_y = \left( v_{i,j} + v_{j,i} \right) / 2 \, , \] we write the generalized model of viscosity as
\[ \sigma_{ij} + \frac{\mu}{\Omega} \delta_y = \eta \left( v_{i,j} + v_{j,i} \right) + \left( \beta - \frac{2\eta}{3} \right) v_{k,k} \delta_y \, . \] (3.12)

The balance of forces gives
\[ \sigma_{ij} + b_i = 0 \, . \] (3.13)

The model of diffusion connects the diffusion flux to the gradient of the chemical potential:
\[ J_i = - \frac{D}{\Omega kT} \mu_j \, . \] (3.14)

The molecular incompressibility, the conservation of the number of molecules, and the relation \( d_{kk} = v_{k,k} \) together give that
\[ v_{k,k} + \Omega J_{k,k} = \Omega R \, . \] (3.15)

Equations (3.12-15) represent thirteen independent partial differential equations for the thirteen fields \( v_i, \sigma_{ij}, J_i, \mu \).

Inserting (3.12) into (3.13), we obtain that
\[ \eta v_{i,kk} + \left( \frac{\eta}{3} + \beta \right) v_{k,k} - \frac{\mu_i}{\Omega} + b_i = 0 \, . \] (3.16)

Inserting (3.14) into (3.15), we obtain that
\[ v_{k,k} - \frac{D}{kT} \mu_{k,k} = \Omega R \, . \] (3.17)

Equations (3.16) and (3.17) represent four distinct partial differential equations for the four fields, \( v_i, \mu \). These four differential equations are solved along with the four independent boundary conditions (3.10) and (3.11).
We will be usually interested in problems with vanishing body force $b$ and vanishing rate of injection $R$. In the latter case, the body is disconnected from reservoirs of molecules. The value of $\mu$ at a particular piece in the body can be interpreted by the following operation. When we connect the piece in the body to a reservoir, $\mu$ is the chemical potential of the molecules in the reservoir needed to equilibrate with the piece without exchanging molecules. Thus the reservoir serves as an instrument that measures chemical potential, analogous to a thermometer that measures temperature.

A comparison of (3.16) and (3.17) gives a length:

$$\Lambda = \sqrt{\frac{\eta D_\Omega}{kT}}. \quad (3.18)$$

The length characterizes the relative rate of viscous flow and diffusion. For any given boundary-value problem, the geometry of the body specifies additional lengths. Let $a$ be a length representative of the geometry of the body. In the limit $a \gg \Lambda$, diffusion is negligible, (3.17) reduces to $v_{k,k} = 0$, and (3.16) recovers the Stokes equations for viscous flow [9]. In the limit $a \ll \Lambda$, viscous flow is negligible, (3.17) reduces to the equation for diffusion [41]. The length $\Lambda$ is a material specific property. We also identify a characteristic time:

$$\Gamma = \frac{\eta \Lambda}{\gamma}. \quad (3.19)$$

This time is also a material specific property.

### 3.5 Chemical equilibrium

In the special case where chemical equilibrium is satisfied on the boundaries while there is no body force and no injection inside the body, we can prove that the chemical equilibrium is satisfied in the whole field as well. To show this, take one more partial derivative in (3.16) to cancel out the $\mu_{k,k}$ term in (3.17):
This is an equation of \( v_{k,k} \). At boundaries, chemical equilibrium gives \( \sigma_m = -\mu / \Omega \). Then (3.12) shows that \( v_{k,k} = 0 \) on the boundaries. Since equation (3.20) describes a physical system, it must have a unique solution. In this case it is \( v_{k,k} = 0 \) throughout the body, which means chemical equilibrium is satisfied everywhere. The governing equations (3.16-17) become:

\[
\eta V_{i,kk} = \frac{\mu_i}{\Omega}, \quad (3.21)
\]

\[
\mu_{kk} = 0. \quad (3.22)
\]

In this chapter, we will limit our discussion to the equilibrium case and leave the study of non-equilibrium case to the next chapter.

### 3.6 Brownian motion

Consider a spherical particle of radius \( a \) moving in a supercooled liquid. Take the velocity of particle to be \( V_r \). Taking advantage of the azimuthal symmetry of the problem, rearrange (3.21-22) in spherical coordinate:

\[
\nabla^2 V_r = \frac{1}{\eta \Omega} \frac{\partial \mu}{\partial r}, \quad (3.23)
\]

\[
\eta \nabla^2 V_\theta = \frac{1}{\Omega r} \frac{\partial \mu}{\partial \theta}, \quad (3.24)
\]

\[
\nabla^2 \mu = 0, \quad (3.25)
\]

where Laplace operator in the spherical coordinate has the following expression:
\[ \nabla^2 = \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) \] (3.26)

Equation (3.23-25) are the governing equation of the problem.

On the surface there should be no fluid penetrate into the particle, which gives the normal boundary condition that at \( r = a \): \( v_r + \Omega J_r = V_p \cos \theta \). Here \( \theta \) is the angle from the direction of \( V_p \). Tangent to the particle surface we assume the common no-slip boundary condition for the velocity field. We assume that the marker velocity is continuous at the surface of the particle: \( v_\theta = -V_p \sin \theta \). At infinity, neither the velocity field nor the chemical potential is perturbed, i.e. at \( r \to \infty \): \( v_r = 0 \), \( v_\theta = 0 \), \( \mu = 0 \).

The analytical solution of the above boundary value problem could be found through separation of variable. The chemical potential is

\[ \mu = \frac{3\eta \Omega V_p a^3}{2(a^2 + \Lambda^2)r^2} \cos \theta. \] (3.27)

The velocity is:

\[ v_r = \frac{V_p a^3}{2(a^2 + \Lambda^2)r} \left( 3 - \frac{a^2 + 4\Lambda^2}{r^2} \right) \cos \theta, \] (3.28)

\[ v_\theta = -\frac{V_p a^3}{4(a^2 + \Lambda^2)r} \left( 3 + \frac{a^2 + 4\Lambda^2}{r^2} \right) \sin \theta. \] (3.29)

Note that this velocity field is divergent free, as a result, the bulk viscosity \( \beta \) does not contribute to the solution. The solution is visualized in Figure 3.4. For large probe \( (a >> \Lambda) \), the flux due to diffusion is negligible. The velocity field recovers the classical solution of Stokes flow. For small probe \( (a << \Lambda) \), the flux due to diffusion dominates. However the velocity does not vanish near the probe because we have enforce nonslip boundary condition \( v_\theta = -V_p \sin \theta \).
Figure 3.4. The fields of velocity (small arrows) and chemical potential (color maps) around a probe moving in a liquid. (a) When $a = 10\Lambda$, the movement of the probe is mainly accommodated by viscous flow. (b) When $a = 0.1\Lambda$, the movement of the probe is mainly accommodated by diffusion.

As the probe moves at velocity $V_p$, the liquid exerts a resistant force $F$ on the probe. The linearity of the boundary-value problem requires that the force be linear in the velocity $F = MV_p$, where $M$ is the mobility of the probe in the liquid. We obtain the resistant force by integrating the traction on the surface of the probe,

$$F = \int_0^\frac{s}{0} (\sigma_r \cos \theta - \sigma_{\theta\phi} \sin \theta) \cdot 2\pi a \sin \theta \cdot a d\theta,$$

where the stress could be evaluated:

$$\sigma_r = -\frac{\mu}{\Omega} + 2\eta \frac{\partial v_r}{\partial r} = \frac{3\eta V_p a^3}{2(a^2 + \Lambda^2)r^2} \left( 2 \frac{a^2 + 4\Lambda^2}{r^2} - 3 \right) \cos \theta,$$  \hspace{1cm} (3.30)

$$\sigma_{\theta\phi} = \eta \left( \frac{\partial v_\theta}{\partial r} + \frac{\partial v_r}{r \partial \theta} - \frac{v_\theta}{r} \right) = \frac{3\eta V_p a^3 (a^2 + 4\Lambda^2)}{2(a^2 + \Lambda^2)r^4} \sin \theta.$$  \hspace{1cm} (3.31)
\[
\sigma_\theta = -\frac{\mu}{\Omega} + 2\eta \left( \frac{\hat{v}_\theta}{r \; \hat{\theta}} + \frac{v_r}{r} \right) = -\frac{3\eta V_p a^3 \left( a^2 + 4\Lambda^2 \right)}{2 \left( a^2 + \Lambda^2 \right) r^4} \cos \theta.
\]  
(3.32)

The diffusivity of the probe relates to the mobility of the probe by the Einstein relation
\[ D_p = kT M \] [17]. The above calculation gives the diffusivity of probe:
\[ D_p = \frac{kT}{6\pi \eta a} + \frac{D\Omega}{6\pi a^2}. \]  
(3.33)

This is the same as (2.3) derived in the last chapter if we take the effective radius
\[ b_p = \frac{\sqrt{9}}{a} . \] The effective radius and the geometric radius of the particle do not agree because the nonslip boundary condition \( v_\theta = -V_p \sin \theta \) does not allow velocity field to vanish, which was assumed in the derivation of (2.3). Since there is no reason to require the nonslip boundary condition for the marker velocity field, this difference in effective radius bears no physical consequence.

### 3.7 Concluding remarks

As the temperature drops, a supercooled liquid may be partially jammed: viscous flow slows down greatly, but diffusion does not slow down as much. We regard viscous flow and diffusion as distinct processes, and formulate a continuum theory to evolve a body of such a liquid under the influence of external forces, surface tension, and reservoirs of molecules. Because small pieces of the liquid exchange molecules and do not retain identities, we describe kinematics not by tracking the small pieces of the liquid, but by tracking the velocity of markers and the net flux of molecules. We describe viscous flow and diffusion using two independent kinetic models. The relative rate of the two kinetic processes defines a characteristic length that demarcates two types of behavior. Large objects evolve by viscous flow, and small objects evolve by diffusion.
Chapter 4.

Viscous mixing

4.1 Introduction

The previous chapter introduced the idea of bulk viscous relaxation that prevents the system from chemical equilibrium. In this chapter, we look at such chemical non-equilibrium in a more general setting, a binary solution. We assume that diffusion is so fast that chemical potentials of the two species of molecules in the solution are uniform. When such a binary solution homogenizes, the time needed for homogenization is independent of the length scale of inhomogeneity, which we call the viscous mixing.

![Diagram of binary solution modes](image)

**Figure 4.1.** A piece of a binary solution evolves in three modes. Shear: the piece preserves the numbers of the two species of molecules, but changes the shape. Dilation: the piece preserves the ratio of the two species of molecules and the shape, but changes the volume. Swap: the piece preserves the shape and the volume, but changes the ratio of the two species of molecules.
A piece of the solution evolves by viscous mixing when subject to mechanical forces, in contact with reservoirs of the two species of molecules. We classify three modes of macroscopic changes: shear, dilation, and swap (Figure 4.1). The piece shears when it conserves the numbers of the two species of molecules, but changes shape. The piece dilates when it preserves the ratio of the two species of molecules and the shape, but changes the volume. The piece swaps when it preserves the shape and the volume, but changes the ratio of the two species of molecules.

During shear, the solution does not exchange molecules with the reservoirs, and creeps in the same way as commonly studied in fluid mechanics. During dilation, the solution imbibes two species of molecules at a constant ratio. During swap, the solution imbibes one species of molecules, but exudes the other. We have assumed that the two species of molecules diffuse so fast that their chemical potentials in the solution are uniform, set by those in the reservoirs. Consequently, during dilation and swap, the two species of molecules mix in the interior of the solution.

During viscous mixing in general, the solution shears, dilates, and swaps concurrently. All three modes break and form intermolecular bonds. We place the three modes on equal footing, as concurrent nonequilibrium processes. Our theory thus removes the bias that assumes local chemical equilibrium but allows the nonequilibrium process of creep. This biased assumption is unrealistic in viscous mixing, even though it is commonly made in theories of diffusion-limited mixing [10].

Concurrent deformation and diffusion have been studied intensely in many systems. Examples include glasses [61], gels [13, 64], glassy polymers [12] and electrodes of lithium-ion batteries [65]. Many of these theories assume local chemical equilibrium. Furthermore, many theories assume that the hosts can deform but do not diffuse. Here we assume that all molecules in the solution diffuse rapidly, and shear, dilation, and swap limit the rate of mixing.
We specify the kinematics of viscous mixing using rates of deformation and insertion. We then derive a thermodynamic inequality that identifies thermodynamic forces. The difference in the partial Gibbs functions of the molecules in the reservoirs and those in the solution drive the insertion of molecules, and the deviatoric stress drives the deviatoric deformation of the solution. The thermodynamic inequality, along with linearity and isotropy, dictates a kinetic model of four independent viscosity-like coefficients. We discuss ways to determine the four coefficients experimentally. A thermodynamic model of ideal mixing of molecules of unequal sizes helps to illustrate the general theory. We then use the theory to analyze steady, transient, and inhomogeneous viscous mixing. We also discuss materials in which viscous mixing is likely to prevail.

4.2 Rates of deformation and injection

Consider a binary solution of two species of molecules, A and B. Subject a piece of the solution to mechanical forces, and to chemical contact with reservoirs of the two species of molecules (Figure 4.2). The reservoirs may contain molecules other than species A and B, but the chemical contact is permeable only to species A and B, so that the piece of the solution always consists of the two species only. The solution evolves by shear, dilation, and swap. For the time being, we assume that the piece of the solution is large enough to behave like a representative volume element, but is small enough to evolve through a sequence of homogeneous states.
Figure 4.2. A piece of binary solution is in chemical contact with reservoirs of species A and B, and is subject to external forces. The piece evolves by the rates of injection and the rate of deformation.

The rates of deformation and injection specify the kinematics of a solution evolving by a sequence of homogeneous states. If the solution is a parallelepiped at one time, it may change shape and volume, but will remain to be a parallelepiped. Denote the rate of deformation of the solution by a symmetric tensor as a function of time, \( d_{ij}(t) \).

For example, denote an edge of the parallelepiped by \( l(t) \), and the rate of extension of the edge is \( \dot{l}/l \). A superimposed dot indicates a derivative with respect to time. Similarly, for a parallelepiped of volume \( V(t) \), the rate of dilation is \( \dot{V}/V \), which equals the trace of the rate of deformation, \( \dot{V}/V = d_{kk} \). The deviatoric part of the rate of deformation, \( e_{ij} = d_{ij} - d_{kk} \delta_{ij}/3 \), describes the rate of shear, namely, the rate at which the solution changes its shape. The symmetric and traceless tensor \( e_{ij} \) constitutes five independent rates.
The piece of the solution contains \( n_A(t) \) molecules of species A and \( n_B(t) \) molecules of species B. We can specify the composition of the solution by the number fraction of one of the species, \( \xi = n_B / (n_A + n_B) \). The composition, in general, also changes with time, \( \xi(t) \). For a solution of fixed numbers of the two species of molecules, the volume of the solution is taken to be independent of the applied stress. This assumption of molecular incompressibility is accurate so long as the applied stress is small compared to the intermolecular interaction. Under this assumption, the volume of the solution is a function of the numbers of molecules of the two species, \( V(n_A, n_B) \). The partial derivatives, \( V_A = \partial V(n_A, n_B) / \partial n_A \) and \( V_B = \partial V(n_A, n_B) / \partial n_B \), are known as the partial volumes of the two species of molecules in the solution. Because the volume of the solution is an extensive variable, \( V(n_A, n_B) \) is a homogeneous function of degree one, and the partial volumes are functions of composition, \( V_A(\xi) \) and \( V_B(\xi) \). The reservoirs inject the two species of molecules into the solution at the rates of \( \dot{n}_A \) and \( \dot{n}_B \). Analogous to the definition of the rate of deformation, which is independent of the size of the piece of the solution, we define the rates of (volumetric) injection by \( i_A = V_A \dot{n}_A / V \) and \( i_B = V_B \dot{n}_B / V \). At a given time, the volume of the solution is \( V = V_A(\xi)n_A(t) + V_B(\xi)n_B(t) \), and changes at the rate \( \dot{V} = V(i_A + i_B) \).

Define the volume fraction \( \phi = n_BV_B / (n_AV_A + n_BV_B) \), which establish a map between \( \phi \) and \( \xi : \phi = \xi V_B(\xi) / \left[ (1-\xi)V_A(\xi) + \xi V_B(\xi) \right] \). For non-zero \( V_A(\xi) \) and \( V_B(\xi) \), this map is invertible, which means \( \phi \) and \( \xi \) can equivalently represent the composition of the material. In the later discussion we will use \( \phi \) to describe the composition for the convenience.
Recall that the rate of dilation is $\dot{V}/V = d_{kk}$, so that

$$d_{kk} = i_A + i_B.$$  \hfill (4.1)

The assumption of molecular incompressibility thus relates the rate of dilation to the rates of volumetric injection of the two species. The deviatoric part of the rate of deformation, along with the rates of injection, constitutes a total of seven independent rates, $(i_A, i_B, e_{ij})$.

### 4.3 Thermodynamic inequality and driving forces

We now associate the seven independent rates with their conjugate thermodynamic forces. The solution, the reservoirs and the external forces together constitute a composite thermodynamic system. We focus our analysis on isothermal processes, and do not list temperature as variable. The mechanical forces acting on the solution result in a state of stress $\sigma_{ij}$. As the solution deforms, the potential energy of the mechanical forces changes at the rate of $-\sigma_{ij} d_{ij} V$. The reservoirs have fixed chemical potentials of the two species of molecules, $\mu_A$ and $\mu_B$. As the reservoirs inject molecules into the solution, the free energy of the reservoirs changes at the rate $-\mu_A \dot{n}_A - \mu_B \dot{n}_B$.

We assume that the Helmholtz free energy of the solution is also independent of the applied stress—that is, we neglect the elasticity of the solution. The Helmholtz free energy of the solution is a function of the numbers of molecules of the two species, $F(n_A, n_B)$. Define the partial Helmholtz free energies by $F_A = \partial F(n_A, n_B)/\partial n_A$ and $F_B = \partial F(n_A, n_B)/\partial n_B$. Because the Helmholtz free energy of the solution is an extensive variable, $F(n_A, n_B)$ is a homogeneous function of degree one, and the partial free energies of the solution are functions of its composition, $F_A(\phi)$ and $F_B(\phi)$. At a given
time, the free energy is $F = F_A(\phi)n_A + F_B(\phi)n_B$, and changes at the rate
$$\dot{F} = F_A(\phi)\dot{n}_A + F_B(\phi)\dot{n}_B.$$ 

In general, the composite system is not in thermodynamic equilibrium. The Helmholtz free energy of the composite system is the sum over the parts. Thermodynamics requires that the Helmholtz free energy of the composite system should never increase:
$$\left( F_A\dot{n}_A + F_B\dot{n}_B \right) \leq - \left( \mu_A\dot{n}_A + \mu_B\dot{n}_B \right) - V\sigma_y\delta_{ij} \leq 0. \tag{4.2}$$

In this expression, the equality holds when the composite system is in a state of thermodynamic equilibrium, and the inequality holds when the composite system evolves.

Define the mean stress by $\sigma_m = \sigma_{kk}/3$, and the deviatoric stress by $s_{ij} = \sigma_{ij} - \sigma_m\delta_{ij}$. Note the identity $\sigma_{ij}\delta_{ij} = s_{ij}e_{ij} + \sigma_m\delta_{kk}$. Using $i_A = V_A\dot{n}_A/V$, $i_B = V_B\dot{n}_B/V$, and $d_{kk} = i_A + i_B$, we write (4.2) as
$$\left( \frac{\mu_A - F_A}{V_A} + \sigma_m \right) i_A + \left( \frac{\mu_B - F_B}{V_B} + \sigma_m \right) i_B + s_{ij}e_{ij} \geq 0. \tag{4.3}$$

We have expressed the thermodynamic inequality (4.3) in terms of the seven independent rates $(i_A, i_B, e_{ij})$.

Inequality (4.3) identifies $\zeta_A = (\mu_A - F_A)/V_A + \sigma_m$ and $\zeta_B = (\mu_B - F_B)/V_B + \sigma_m$ as the thermodynamic forces conjugate to the rates of volumetric injection $i_A$ and $i_B$. These chemical driving forces represent the imbalance between the chemical potentials in the reservoir and the partial free energies in the solution. Due to the assumption of molecular incompressibility, the solution changes volume on receiving molecules, so that the mean stress contributes to the two chemical driving forces. Inequality (5) also identifies the deviatoric stress $s_{ij}$ as the mechanical driving force conjugate to the
The deviatoric rate of deformation $e_{ij}$. The deviatoric stress $s_{ij}$ is a symmetric and traceless tensor, and represents a total of five independent mechanical driving forces. In total, inequality (4.3) identifies seven thermodynamic forces $(\zeta_A, \zeta_B, s_{ij})$ conjugate to the seven independent rates $(i_A, i_B, e_{ij})$.

The composite system is in a state of thermodynamic equilibrium when the equality in (4.3) holds. That is, thermodynamic equilibrium requires that all seven thermodynamic forces vanish, so that

$$s_{ij} = 0,$$  \hfill (4.4)

$$F_A(\phi) - \sigma_m V_A(\phi) = \mu_A,$$  \hfill (4.5)

$$F_B(\phi) - \sigma_m V_B(\phi) = \mu_B.$$  \hfill (4.6)

These conditions of thermodynamic equilibrium correspond to a total of seven independent equations: $\sigma_{11} = \sigma_{22} = \sigma_{33} = (F_A - \mu_A)/V_A = (F_B - \mu_B)/V_B$, and $\sigma_{12} = \sigma_{23} = \sigma_{31} = 0$. For the binary solution, mechanical forces, and chemical reservoir to equilibrate, the solution must be in a hydrostatic state of stress, and the hydrostatic stress must balance the difference between the chemical potentials of the two species in the reservoir and the partial free energies of the two species in the solution.

Equations (4.5) and (4.6) recover the well-known conditions of thermodynamic equilibrium: the partial Gibbs function for every species is the same in all parts in chemical contact. The two equations of equilibrium relate four variables: the composition of the solution $x_B$, the hydrostatic stress acting on the solution $\sigma_m$, and the chemical potentials of the two species of molecules in the reservoirs, $\mu_A$ and $\mu_B$. For example, when the chemical potentials of the two species of molecules in the reservoirs are fixed at known values, $\mu_A$ and $\mu_B$, both the hydrostatic stress $\sigma_m$ acting on the
solution and the composition $x_b$ of the solution must adjust for the composite system to reach a state of thermodynamic equilibrium. The hydrostatic stress that equilibrates the solution and the reservoir is known as the osmotic stress (Figure 4.3).

**Figure 4.3.** A binary solution is in chemical contact with a reservoir of the two species of molecules, and is subject to a hydrostatic stress. The hydrostatic stress needed for the composite system to reach thermodynamic equilibrium is called the osmotic stress.

### 4.4 The kinetic model

The composite system is out of thermodynamic equilibrium when the inequality in (4.3) holds. We satisfy the thermodynamic inequality by prescribing a kinetic model. The simplest kinetic model assumes that the solution is isotropic, and that the rates are linear in the thermodynamic forces. The combination of linearity and isotropy requires that the kinetic model should take the form:

\[
\sigma_m = \frac{\mu_A - F_A}{V} + \sigma_m = \beta_A i_A + \beta_B i_B ,
\]

\[
s_{ij} = 2\eta e_{ij} ,
\]

(4.8)
\( \frac{\mu_B - F_B}{V_B} + \sigma_m = \beta_{BA} i_A + \beta_{BB} i_B. \)  

(4.9)

Equations (4.7-4.9) constitute seven independent kinetic equations. The viscosity \( \eta \) resists the change in the shape of the solution, whereas the coefficients \( \beta_{\alpha \beta} \) resist the insertion of molecules into the solution. We assume the Onsager reciprocity, \( \beta_{BA} = \beta_{AB} \).

The four viscosity-like coefficients \( \eta \) and \( \beta_{\alpha \beta} \) have the same molecular origin: molecules in the solution change neighbors by breaking and forming intermolecular bonds. In general, the coefficients are functions of the composition of the solution, \( \eta(\xi) \) and \( \beta_{\alpha \beta}(\phi) \). The kinetic model (4.7-4.9) reduces (4.3) to

\[ \beta_{AA} i_A^2 + 2\beta_{AB} i_A i_B + \beta_{BB} i_B^2 + \eta e_{ij} e_{ij} \geq 0. \]

The quadratic form is positive-definite for any combination of the seven independent rates \( (i_A, i_B, e_{ij}) \) if and only if \( \eta > 0 \), \( \beta_{AA} > 0 \), \( \beta_{BB} > 0 \) and \( \beta_{AA} \beta_{BB} - \beta_{AB}^2 > 0 \).

The kinetic model (4.7-4.9) generalizes Newton’s model of creep. Note that our model differs from the model of compressible viscosity. We have assumed that molecules in the solution are incompressible, so that an increase in volume of the solution is entirely due to the insertion of molecules from the reservoir to the solution. In contrast, for compressible viscosity, the number of molecules in an element of solution is fixed, and an increase in the volume of the element is entirely due to the reduction in density.

As noted in the Introduction, many existing theories of concurrent diffusion and deformation assume local chemical equilibrium, but allow nonequilibrium process of creep. The assumption of local chemical equilibrium corresponds to \( F_A - \sigma_m V_A = \mu_A \) and \( F_B - \sigma_m V_B = \mu_B \). The injection of two species of molecules is equivalent to a combination
of dilation and swap. The nonequilibrium process of creep corresponds to shear, 
\[ s_y = 2\eta e_y. \]

Under the assumption of local chemical equilibrium, any change in the chemical potential in the reservoirs would instantaneously change the composition and hydrostatic stress in the solution. Whereas the assumption is adequate when the local chemical processes are fast compared to diffusion, this assumption is unrealistic when creep limits mixing. During viscous mixing, the solution shears, dilates, and swaps concurrently. All three modes break and form intermolecular bonds. There is no reason to hold the biased assumption that dilation and swap are much faster than shear. Our kinetic model (4.7-4.9) places the three modes on equal footing, as concurrent nonequilibrium processes.

Recall that we specify the composition of the solution by the volume fraction, 
\[ \phi = n_B V_B / (n_A V_A + n_B V_B). \] In general, the composition of the solution changes with time, \( \phi(t) \). Given two species of molecules A and B, the theory regards that the following eight functions are known: \( F_A(\phi), F_B(\phi), V_A(\phi), V_B(\phi), \eta(\phi), \beta_{AA}(\phi), \beta_{BB}(\phi), \) and \( \beta_{AB}(\phi) \).

Write the kinetic equations (4.8) and (4.9) as

\[
\frac{\mu_A - F_A(\phi)}{V_A(\phi)} + \sigma_m = \frac{\beta_{AA}(\phi)V_A(\phi)\dot{n}_A + \beta_{AB}(\phi)V_B(\phi)\dot{n}_B}{V_A(\phi)n_A + V_B(\phi)n_B}, \tag{4.10}
\]

\[
\frac{\mu_B - F_B(\phi)}{V_B(\phi)} + \sigma_m = \frac{\beta_{AB}(\phi)V_A(\phi)\dot{n}_A + \beta_{BB}(\phi)V_B(\phi)\dot{n}_B}{V_A(\phi)n_A + V_B(\phi)n_B}. \tag{4.11}
\]

Given the applied loads, \( \mu_A, \mu_B, \) and \( \sigma_m \), the kinetic model thus gives the nonlinear ordinary differential equations to evolve the two functions \( n_A(t) \) and \( n_B(t) \).

The kinetic model of viscous mixing contains a time scale. The left-hand side of (4.10) and (4.11) contains thermodynamic forces to restore equilibrium, and the right-hand side contains rates of injection. The kinetic model of viscous mixing is thus
analogous to that of viscoelasticity. The coefficients \( \eta \) and \( \beta \) have the dimension of viscosity, (stress)(time). The partial free energy \( F_A \) has the dimension of energy per molecule, which is on the order of \( kT \). Let \( \Omega \) be the mean volume per molecule. We obtain a time scale for viscous mixing,

\[
\tau_c = \frac{\eta \Omega}{kT}.
\]

(4.12)

Here we have used the viscosity to define the time scale; we can of course use any viscosity-like coefficient \( \beta \), as well as their combinations. As noted in Introduction, the time needed to homogenize a solution by viscous mixing is independent of the length scale of inhomogeneity.

### 4.5 Inhomogeneous viscous mixing

We now consider a body of an inhomogeneous solution. Imagine that we divide the body into many small pieces. Each piece evolves through a sequence of homogeneous states, as described above. Different pieces communicate with one another by conserving the two species of molecules, preserving geometric compatibility, and balancing mechanical forces.

As mentioned in the Introduction, we assume that diffusion is fast, so that the chemical potentials of the two species in the solution are homogeneous, set by values in the reservoir, \( \mu_A \) and \( \mu_B \). The evolution is limited by the rates of deformation and insertion. These rates, as well as the stress, can be inhomogeneous.

Because of mixing, each piece of solution in the body does not preserve the number and identity of molecules. The notion of a “material particle” in continuum mechanics becomes questionable. Imagine that we disperse a field of makers in the solution. When molecules are inserted into the solution between two markers, the two markers drift apart. Thus, the relative movements of the markers describe the
deformation of the solution. Let \( \mathbf{x} \) be the coordinate of a place in space. Denote the velocity of the makers by the field \( v_i(\mathbf{x},t) \). The rate of deformation relates to the field of velocity as

\[
d_{ij} = \frac{1}{2} \left( \frac{\partial v_i}{\partial x_j} + \frac{\partial v_j}{\partial x_i} \right).
\]  (4.13)

Denote the field of stress in the solution by \( \sigma_{ij}(\mathbf{x},t) \). Inside the solution, the balance of mechanical forces requires that:

\[
\frac{\partial \sigma_{ij}}{\partial x_j} + b_i = 0,
\]  (4.14)

where \( b_i \) is the density of body force. On the surface of the solution, the stress balances the traction, \( \sigma_{ij} n_j = T_i \), where \( n_j \) is the unit vector normal to the surface, and \( T_i \) is the traction. Equations (4.1), (4.7-4.9) constitute 17 independent equations that govern the 17 independent fields: \( v_i, d_{ij}, \sigma_{ij}, i_A, i_B \).

A combination of the incompressibility condition (4.1) with the kinetic model (4.7-4.9) allows us to rewrite the generalized Newton’s model of creep as:

\[
\sigma_{ij} + \gamma \mathbf{d}_{ij} = 2\eta e_{ij} + \kappa d_{kk}.
\]  (4.15)

This expression expresses the stress tensor as a function of the rate of deformation. The quantity \( \gamma \) gives the contribution of chemical forces to stress:

\[
\gamma \equiv \frac{(\beta_{BB} - \beta_{AB})}{\beta_{AA} - 2\beta_{AB} + \beta_{BB}} \mu_A - F_A + \frac{(\beta_{AA} - \beta_{AB})}{\beta_{AA} - 2\beta_{AB} + \beta_{BB}} \mu_B - F_B.
\]  (4.16)

Given constant and uniform values of chemical potentials, the quantity \( \gamma \) is a function of the composition, \( \gamma(\phi) \) and is generally not uniform. The effective viscosity \( \kappa \) is defined as
\[ \kappa = \frac{\beta_{AA}\beta_{BB} - \beta_{AB}^2}{\beta_{AA} - 2\beta_{AB} + \beta_{BB}}, \quad (4.17) \]

Using the generalized viscosity model (4.15) in equation (4.14) together with relation (4.13) we obtain that

\[ \left( \eta (v_{i,j} + v_{j,i}) \right)_{i,j} + \left( (\kappa - \frac{2}{3}\eta) v_{k,k} \delta_{i,j} \right) - \gamma' \xi_j + b_i = 0. \quad (4.18) \]

For a given field of composition in the body, equations (4.18) are three partial differential equations for the three components of the velocity. In the case where the viscosity coefficients do not depend on composition, these equations simplify as

\[ \eta v_{i,j} + \left( \kappa + \frac{1}{3}\eta \right) v_{j,i} - \gamma' \xi_j + b_i = 0. \quad (4.19) \]

These equations can be solved together with boundary conditions written in terms of imposed velocity, \( v_i = V_i \), or imposed surface traction, \( \sigma y n_j = T_i \). Equation (4.19) generalizes the Stokes flow equations to a binary mixture. In these generalized flow equations the composition plays the role of a local internal variable whose rate of evolution is given by

\[ \left( 1 - \phi \frac{V_B'}{V_B} \right) \dot{\phi} = (1 - \phi) i_B - \phi i_A. \quad (4.20) \]

The chemical component of the driving force for viscous relaxation acts as a body force through the term \( -\gamma' \xi_i \).

In the case where the solution has initially uniform composition and is subjected to no surface traction nor stresses, the solution will remain at rest. However, the composition will evolve homogeneously if the partial free energies in the solution do not match the value of chemical potential in the environment. For general loading conditions in terms of boundary conditions and heterogeneous body force, the evolution of composition is heterogeneous.
Consider homogeneous and time-dependent viscous mixing. Up to a difference in rigid-body motion, the homogenous rate of deformation $d_\theta(t)$ corresponds to an affine field of marker velocity, $v_i(x,t) = d_\theta(t)x_j$. Any state of homogeneous stress $\sigma_\theta(t)$ balances forces in the solution, assuming a zero body force. The theory of viscous mixing relates eight rates $(i_A, i_B, d_\theta)$ to eight driving forces $(\mu_A, \mu_B, \sigma_\theta)$ through eight equations: the condition of molecular incompressibility (4.1), and the seven kinetic relations (4.7-9). We next consider several types of behavior.

4.6 Steady states

When the solution is isolated from the reservoirs but is subject to stresses, the solution undergoes purely deviatoric creep, which preserves the numbers of molecules in the solution, and keeps the composition $\phi$ fixed. Purely deviatoric deformation can be used to determine the shear viscosity as a function of composition, $\eta(\phi)$.

Next consider a solution in chemical contact with reservoirs of fixed chemical potentials $\mu_A$ and $\mu_B$, and subject to a fixed state of stress $\sigma_\theta$. Starting with an initial composition, $\phi(0)$, the solution evolves its composition in time, $\phi(t)$. The solution in general cannot reach a state of equilibrium. That is, given $\mu_A$, $\mu_B$, and $\sigma_m$, in general we cannot find a composition $\phi$ to satisfy both conditions of equilibrium, $\mu_A = F_A(\phi) - \sigma_mV_A(\phi)$ and $\mu_B = F_B(\phi) - \sigma_mV_B(\phi)$.

The solution, however, will approach a steady state. In the steady state, the solution maintains a constant composition, $\phi$, while the reservoirs inject molecules into the solution at a fixed ratio, $i_A / i_B = (1 - \phi) / \phi$. The two kinetic equations (4.8) and (4.9) become that...
\[
\frac{\mu_A - F_A(\phi)}{V_A(\phi)} + \sigma_m = \kappa_A(\phi) d_{kk}, \tag{4.21}
\]

\[
\frac{\mu_B - F_B(\phi)}{V_B(\phi)} + \sigma_m = \kappa_B(\phi) d_{kk}, \tag{4.22}
\]

where \( \kappa_A = (1 - \phi)\beta_{AA} + \phi\beta_{AB} \) and \( \kappa_B = (1 - \phi)\beta_{AB} + \phi\beta_{BB} \) are two types of dilation viscosities.

When \( \mu_A, \mu_B, \) and \( \sigma_m \) are specified, (4.21) and (4.22) do predict a steady state. Eliminate \( d_{kk} \) from (4.21) and (4.22), giving

\[
\kappa_A \frac{F_B}{V_B} - \kappa_B \frac{F_A}{V_A} = \kappa_A \frac{\mu_B}{V_B} - \kappa_B \frac{\mu_A}{V_A} + (\kappa_A - \kappa_B) \sigma_m. \tag{4.23}
\]

Here we assume that \( V_A > 0, V_B > 0, \) and all the kinetic coefficients are finite. From the thermodynamic theory of solution, \( F_A(0) = F_B(1) = 0 \) and \( F_A(1) = F_B(0) = -\infty. \) The thermodynamic inequality requires that \( \beta_{AA} > 0 \) and \( \beta_{BB} > 0. \) The left-hand side (4.23) approaches \(-\infty\) when \( \phi \to 0, \) and approaches \(+\infty\) when \( \phi \to 1. \) By the continuity of the free energy function, the left hand-side of (4.23) spans all real numbers, so that at least one solution of (4.23) exists for any given values of \( \mu_A, \mu_B, \) and \( \sigma_m. \)

A steady state may be a convenient experimental setup to measure the viscosity-like coefficients. For example, in contact with reservoirs of fixed chemical potentials \( \mu_A \) and \( \mu_B, \) and in the absence of any stress, the solution will reach a steady state of a certain compositions \( \phi \) and a certain rate of dilation \( d_{kk}. \) Equations (4.21) and (4.22) enable us to determine \( \kappa_A \) and \( \kappa_B \) for the specific composition. We then repeat the experiment with reservoirs of different values of the chemical potentials, so that the solution reaches a steady state of a different composition. Such experiment will allow us to measure the two viscosities of dilation as functions of composition, \( \kappa_A(\phi) \) and \( \kappa_B(\phi). \)
They correspond to the two combined coefficients, \( \kappa_A = (1-\phi) \beta_{AA} + \phi \beta_{AB} \) and \( \kappa_B = (1-\phi) \beta_{AB} + \phi \beta_{BB} \). However, to determine all three viscosity-like coefficients, \( \beta_{AA}(\phi) \), \( \beta_{AA}(\phi) \), and \( \beta_{AB}(\phi) \), we will need a third independent measurement.

In a steady state, the kinetic model gives seven independent algebraic equations, (4.7), (4.21) and (4.22), among 15 variables, \( \phi \), \( d_{ij} \), \( \sigma_{ij} \), \( \mu_A \), \( \mu_B \). The algebraic equations are nonlinear in the composition \( \xi \), but are linear in the other 14 variables. After specifying eight variables, we can use the kinetic model to calculate the other seven variables. In the above, we have fixed the chemical potentials of the two species of molecules in the reservoirs and the six components of stress, and then use the kinetic model to calculate the composition and the six components of the rate of deformation. Of course, we can also achieve a steady state by specifying other combinations of eight variables.

4.7 Evolution toward equilibrium

As noted above, the steady states only determine two viscosity-like coefficients \( \kappa_A = (1-\phi) \beta_{AA} + \phi \beta_{AB} \) and \( \kappa_B = (1-\phi) \beta_{AB} + \phi \beta_{BB} \). To determine all three viscosity-like coefficients, \( \beta_{AA} \), \( \beta_{AA} \), and \( \beta_{AB} \), we need to conduct transient experiments. As an example, consider pur swap. A container with rigid and permeable walls is filled with a solution, and is in contact with reservoirs of fixed chemical potentials \( \mu_A \) and \( \mu_B \). The rigid walls suppress deformation, \( d_{ij} = 0 \). As the solution and the reservoirs exchange molecules, the solution evolves the composition \( \phi(t) \) and the hydrostatic stress \( \sigma_m(t) \). After some time, the solution reaches a state of thermodynamic equilibrium, with the composition and hydrostatic stress determined by (4.5) and (4.6).
In pure swap, the two rates of volumetric injection counteract, \( i_A = -i_B \). Inserting this expression into (4.8) and (4.9), and eliminating the hydrostatic stress, we obtain that

\[
\frac{\mu_B - F_B(\phi)}{V_B(\phi)} - \frac{\mu_A - F_A(\phi)}{V_A(\phi)} = 2\alpha \dot{\phi},
\]

(4.24)

where \( \alpha = \beta_{AA} + \beta_{BB} - 2\beta_{AB} \). Equation (4.24) is an ordinary differential equation that evolves the composition in time, \( \phi(t) \).

Given the values of chemical potentials \( \mu_A \) and \( \mu_B \), (4.5) and (4.6) determine the state of equilibrium. Let \( \phi_{eq} \) be the composition of the solution in equilibrium with the reservoirs of the fixed chemical potentials \( \mu_A \) and \( \mu_B \). Linearizing (4.24) around the state of equilibrium, we obtain an ordinary equation of form \( \dot{\phi} = (\phi_{eq} - \phi) / \tau \). The relaxation time \( \tau \) depends on \( \xi_{eq} \), and is proportional to the viscosity-like coefficient \( \alpha \).

The linear ordinary differential equation gives that \( \phi_{eq} - \phi(t) = (\phi_{eq} - \phi(0)) \exp(-t/\tau) \).

Experimentally, we can start with a binary solution near a state of thermodynamic equilibrium, \( \phi_{eq} \), and measure the relaxation time, which gives a value of the viscosity-like coefficient \( \alpha \) at \( \phi_{eq} \). By adjusting the chemical potentials of the reservoir and repeat the experiment around variations states of equilibrium, we can determine the function \( \alpha(\phi) \).

### 4.8 Gel like systems

In the special case where A is not allowed to exchange between the material and the reservoir, we have \( i_A = 0 \), then (4.9) gives:
(4.28) is an ODE of $\phi$ alone and $\beta_{BB}$ is the only relevant kinetic coefficient. The character time scale of relaxation is $\tau_{\text{swell}} \sim kT / \beta_{BB} V_B$. Recall that the relaxation time for migration of A is $\tau_A \sim L^2 / D_A$. In practice, $i_A = 0$ corresponds cases where $\tau_A \gg \tau_{\text{swell}}$.

For example, when A is a polymer and B is a small molecule solvent, the diffusion of A is negligible. Effectively $\tau_A \to \infty$. The relaxation time for diffusion of B is $\tau_B \sim L^2 / D_B$. If $\tau_B \ll \tau_{\text{swell}}$, we have homogeneous $\mu_B$ at the time scale of $\tau_{\text{swell}}$ and we expect homogeneous swelling as predicted by ODE (4.25).

In gel like systems, the polymer chains are bulky and entangled. The diffusion of polymer chains are negligible comparing to the diffusion of small molecules. In these systems the polymer chains could be taken as the immobile A in the above discussion. Then our model readily explains recent experiments on hydrogels—mixtures of macromolecules and water. As an example, alginate is a widely studied physical gel due to its importance in biomedical applications, such as tissue engineering. In this context, it is important to understand the relaxation mechanisms in alginate, as stress relaxation of the substrate is known to affect the cell behavior [66]. The two processes of poroviscous and viscous relaxation have been highlighted in recent stress relaxation experiments [13, 67]. In these experiments, the diameter of the sample is of the cm size, and the diffusion coefficient of water through in alginate was estimated as $D_{\text{water}} = 10^{-8}$ m²/s [13]. The diffusion coefficient and the sample size establish a timescale for poroviscous relaxation: $\tau_D = 10^5$ s. When the time of observation is much shorter than the time for poroviscous relaxation, viscous relaxation is observed, and is independent of the sample size. Viscous relaxation is attributed to the continuous breaking of the ionic
crosslinks. The timescale depends on the calcium concentration and the distance between crosslinks. The viscous relaxation time is of the order of 10s [13, 67, 68]. When the time of observation is much larger than the time for viscous relaxation, Gentile et al. [67] reported a transition to a diffusion-dominated regime.

Another example where concurrent viscous relaxation and poroviscosity could play an important role is in cells. Cells broadly consist of the cytoplasm—a gel-like solution of water and macromolecules—enclosed in a water permeable membrane. Water permeation permeates quickly through the membrane, but much slower through the cytoplasm [14]. Recently, the poroelastic theory was successfully applied to describe various aspects of the cell response [14, 69]. A typical cell as a size of the order of 10 µm. The diffusivity of water in the cell is \( D = 10^{-11} \text{m}^2/\text{s} \) [69], which gives a timescale for poroelastic relaxation is \( \tau_D = 10 \text{s} \). This timescale is relevant for biological processes, which take places over the timescales of the order 10-100s, such as cell migration of blebbing. However, experiments using AFM showed that the timescale for viscous relaxation is also of the order of 10s, while in this case poroelasticity has relaxed [70]. Therefore, it is conceivable that both poroelasticity and viscosity act concurrently. The viscous effect is all the more important that the size is small.

For covalently crosslinked gels, one usually distinguishes two modes of deformation: poroelasticity and viscoelasticity [64]. Similar distinction can be established for physically crosslinked gels. In physical gels, the crosslinks between the polymer chains can break and reform, leading to a viscous behavior. We call the two modes of deformation resulting from long-range migration and local deformation poroviscosity and viscous creep.
4.9 Summary

Although local equilibrium is a common assumption made in most non-equilibrium thermodynamics, such assumption has no fundamental physical basis. In this chapter, we have formulated the basic kinetic theory of local chemical non-equilibrium. The local chemical non-equilibrium is expected to be important when diffusion is either too fast or too slow comparing to the viscous relaxation. Under this condition, a material may relax in three viscous modes: shear, dilation and swap. In particular, the dilation mode may lead to steady state which does not relax toward equilibrium. In the special case of gel-like material, our model extends the existing poroelastic and viscoelastic model of gels and cells.
5.1 Crease and its nucleation

Crease is a surface instability observed in soft material under large compressive strain. It is widely observed in nature [71-73] and has many potential engineering applications [74-78]. Crease has been known as a distinct instability mode from the linear instability mode, wrinkle [15, 79]. While wrinkle forms at a well defined critical strain and results in a wavy pattern all over the surface, a crease nucleates at scattered strains and results in localized cusps on the surface. Theoretically, a crease in a homogeneous material is treated as a region of self contact with a singular crease tip. Such a model results in a unique critical strain to initiate a crease [15, 71, 80]. However, experimentally it is known that a crease initiates by nucleation and growth. The nucleation strain may be strongly influenced by local defects and the elastocapillary effect [81]. Yet, the study of the crease nucleation could not progress any further without a tool to characterize the defect sensitivity.

Here we show that the defect sensitivity of crease nucleation is governed by the dimensionless ratio between the defect size and the elastocapillary length. When the elastocapillary length is much larger than the defect size, the system approaches its defect free behavior, where the crease always initiates at the critical strain for wrinkle and bifurcates from flat surface subcritically. The unstable wrinkle then collapses into creases as the wrinkle deepens. When the elastocapillary length is much smaller than the defect size, the unstable part of the bifurcation path is inaccessible. Formation of stable creases is observed well below the critical strain for wrinkle.
Our theory modifies the existing understanding of crease by showing that the crease tip in a homogeneous material cannot be singular. The Laplace pressure due to surface tension limits the maximum curvature that can be obtained. As the surface tension removes the singularity at a crease tip, crease and wrinkle are connected on one single bifurcation path. The theory predicts that a crease could be initiated at any strain between the critical strain for wrinkle, and the critical strain for crease that is predicted by existing theories [15]. This prediction is experimentally tested on an extremely soft hydrogel film where the elastocapillary length is on the order of 0.1 millimeter.

5.2 Elastocapillary nucleation on a thick elastomer

We use a bilayer system [82] to study the crease nucleation on an elastocapillary surface. As is sketched in Figure 5.1a, a uniform layer of soft elastic material with thickness $H$ is bonded to a prestretched stiff elastic substrate. The substrate is then released under control, compressing the material with strain $\varepsilon$. The amplitude of surface instability $A$ is defined as the difference between the peak and the trough of the surface profile. The surface energy $\gamma$ and the shear modulus of the soft material $\mu$ gives the intrinsic length scale for the problem, the elastocapillary length $\gamma / \mu$.

Consider the simplest case where $\gamma / \mu << H$. For a just nucleated crease, $A << H$, the only relevant length scale is $\gamma / \mu$. We propose the bifurcation diagram for this case as Figure 5.1b. The surface becomes unstable to infinitesimal perturbation at the critical strain of wrinkle [83], $\varepsilon_{\text{wrinkle}}$. The system then bifurcates subcritically and the surface wrinkles. As the wrinkle deepens, self-contact happens and creases form. The depth where the self-contact forms must scale with the only length scale $\gamma / \mu$. 
Figure 5.1. (a) Schematic of the bilayer system with the definition of the geometric quantities. (b) Schematic of the bifurcation diagram of the upper layer in (a). Cyan line represents the flat state. Red line represents the wrinkle/crease state. Each inlet is the
deformation near the surface corresponding to a point on the loading path marked by a black circle. (c) The free energy diagram corresponding to the bifurcation diagram. $W$ is the free energy per period of wrinkle or per crease.

As a crease deepens, the elastic energy is released and the surface energy is increased. By simple scaling argument the decrease in elastic energy comparing to the flat state scales with $\mu A^2$ and the increase in surface energy comparing to the flat state scales with $\gamma A$, as is sketched in Figure 5.1c. At small amplitude, $\gamma A$ dominates over $\mu A^2$ and the creased surface is unstable relative to the flat surface. At large amplitude, $\mu A^2$ dominates over $\gamma A$ and the flat surface is unstable relative to the creased surface. When the decrease in elastic energy and the increase in surface energy exactly cancel each other, the flat surface and the creased surface have the same free energy and can coexist in thermodynamic equilibrium. This strain is called the Maxwell strain, $\varepsilon_{\text{Maxwell}}$. Above this strain, creased surface becomes thermodynamically more favorable than the flat surface, which means a crease nucleation will grow into the flat surface. In other words, any state with $\varepsilon > \varepsilon_{\text{Maxwell}}$ is a super-strained state, similar to the idea of supercooling and supersaturation in classical nucleation theory.

As the crease deepens even more, $A \gg \gamma / \mu$, the energy budget is dominated by the decrease in elastic energy and capillarity is negligible. The system approaches a scale free behavior, which corresponds to the commonly defined critical strain for crease [15, 71, 84], $\varepsilon_{\text{crease}}$. Near the crease tip, however, the surface energy always dominates over the elastic energy. The Laplace pressure due to surface tension favors flat surface. As a result, the crease tip will always be rounded instead of singular. When the depth of the
crease is comparable to the thickness $H$, the crease is stabilized by its interaction with the substrate [82]. Further deepening of the crease requires increase in compression.

Figure 5.2. The bifurcation diagram for system with different defect size $d$. When $d \ll \gamma / \mu$, a crease nucleates near $\varepsilon_{\text{wrinkle}}$. When $d \sim \gamma / \mu$, a crease may nucleate at any strain between $\varepsilon_{\text{wrinkle}}$ and $\varepsilon_{\text{crease}}$, depending on the local detail of the defect. When $d \gg \gamma / \mu$ yet $d \ll H$, a crease nucleates at $\varepsilon_{\text{crease}}$.

The above model implies a defect sensitive behavior as shown in Figure 5.2. Any defect has a character size $d$. When $d \ll \gamma / \mu$, the capillary effect dominates over the defect effect. A defect of such size would be smoothened out by capillary force. Consequently the system approaches the defect free behavior and a crease nucleates near $\varepsilon_{\text{wrinkle}}$. When $d \sim \gamma / \mu$, the capillary effect and the defect effect are comparable. Because the bifurcation point of wrinkle is subcritical, the system show strong defect sensitivity. A crease may nucleate at any strain between $\varepsilon_{\text{wrinkle}}$ and $\varepsilon_{\text{crease}}$, depending on the local detail of the defect. For a uniaxially compressed sample, if the surface tension is negligible, existing theory predicts that $\varepsilon_{\text{wrinkle}} = 0.46$ and $\varepsilon_{\text{crease}} = 0.35$ [15]. This
corresponds to a ~10% strain range where creases could nucleate. When $d >> \gamma / \mu$ yet $d << H$, the defect effect dominates over the capillarity, the system approaches the behavior of classical crease without elastocapillary effect. A crease nucleates at $\varepsilon_{\text{crease}}$. As the crease grows deeper, $A >> d$, the defect effect becomes negligible and the bifurcation paths of different defect sizes coincide with the perfect system.

5.2 The effect of finite thickness

![Figure 5.3](image_url)

**Figure 5.3.** The critical strain for wrinkle changes with $\gamma / \mu H$ as a result of the competition between surface tension effect and substrate effect. Long wavelength is limited by the substrate while short wave length is limited by the surface tension.

The discussion above can be generalized to different $\gamma / \mu H$. The critical strain for any $\gamma / \mu H$ is obtained from linear perturbation analysis (Appendix A.1-2). For each fixed $\gamma / \mu H$, the critical condition also depends on the wavelength $\lambda$, and the loading condition (plane strain, plane stress, etc.). A few results for plane strain condition are presented in Figure 5.3. It shows that longer wavelength is more penalized by the
substrate effect and shorter wavelength is more penalized by the surface tension effect. When the wavelength is either short comparing to $\gamma/\mu$ or long comparing to $H$, the critical strain is greatly increased. In practice, the instability mode with the lowest critical strain initiates the first. Consequently, for each $\gamma/\mu H$ the minimal critical strain for any wavelength is identified as the critical strain for wrinkle, $\varepsilon_{\text{wrinkle}}$.

**Figure 5.4.** The postbuckling behavior based on finite element simulation. The amplitude of surface undulation is normalized by the elastocapillary length. The dashed line marks the critical strain for crease predicted by scale free argument.

The postbuckling behavior for any $\gamma/\mu H$ can be simulated using finite element method (Appendix A.3). In general, upon self-contact, the surface tension may change. Here we assume that the surface tension remains constant for simplicity. A few results for plane strain condition are presented in Figure 5.4. In all the simulations the strain of bifurcation agrees with the critical strain of wrinkle predicted by linear perturbation. A kink on the bifurcation path corresponds to the formation of self-contact. The bifurcation paths for different $\gamma/\mu H$ all qualitatively agree with Figure 5.1b. We define the critical strain for crease $\varepsilon_{\text{crease}}$ as the lowest strain of the bifurcation path. As $\gamma/\mu H$
decreases, the critical strain of crease approaches the prediction of the scale free argument, \( \varepsilon_{\text{crease}} = 0.35 \) [15, 71], which corroborates our theory.

5.3 Experimental verification

The nucleation of creases can be visually observed in experiments. We test our theory by observing the defect sensitive nucleation of creases on an elastocapillary surface. According to Figure 5.2, the nucleation of a crease happens between \( \varepsilon_{\text{crease}} \) and \( \varepsilon_{\text{wrinkle}} \). Practically, only growing nucleation could be observed, which requires super-straining above \( \varepsilon_{\text{Maxwell}} \). As a result, we expect any experimentally identified nucleation to fall between \( \varepsilon_{\text{Maxwell}} \) and \( \varepsilon_{\text{wrinkle}} \).

An experimental setup realizing Figure 5.1a is constructed (Figure A.2). Soft hydrogel is used as the testing material for the large \( \gamma / \mu \) they can achieve. Here shear modulus is measured by dynamic shear rheometer (Figure A.3). The surface tension of the gel is taken to be the surface tension of the pre-crosslinked solution. With \( \gamma / \mu \sim 0.1 \text{mm} \) we can visually identify the pre-existing defects where \( d \sim \gamma / \mu \). Humidity chamber and fast loading rate is employed to minimize the deswelling of the hydrogel during the experiments (Figure A.4, Figure A.5). Fast speed camera monitors the surface morphology as the hydrogel is compressed. The nucleation strain is then visually identified by examining the captured video.

In Figure 5.5a and Figure 5.5b, we demonstrate the defect sensitivity of the system by comparing the nucleation on two samples with \( \gamma / \mu H \sim 0.1 \). For the sample with visible defects \( d \sim \gamma / \mu \), the first crease nucleates from the visible defects at 51% compressive strain (Figure 5.5a). For the sample with invisible defects \( d \ll \gamma / \mu \), the
first crease nucleates with 11% higher strain, qualitatively agree with our discussion about Figure 5.2.

**Figure 5.5.** Defect sensitivity of the system is demonstrated by comparing (a) a sample with visible defects $d \sim \gamma/\mu$ and (b) a sample without visible defects $d \ll \gamma/\mu$. For both samples $\gamma/\mu = 0.113 \text{mm}$, $H = 1.0 \text{mm}$. The scale bar is 0.3mm. (c) Experimentally measured nucleation strains are compared with $\varepsilon_{\text{Maxwell}}$ and $\varepsilon_{\text{wrinkle}}$.

In Figure 5.5c we quantitatively compare experimentally measured nucleation strain for crease with the $\varepsilon_{\text{wrinkle}}$ and $\varepsilon_{\text{Maxwell}}$. Here $\varepsilon_{\text{wrinkle}}$ is obtained through linear
perturbation as described above. $\varepsilon_{\text{Maxwell}}$ is obtained from existing measurement by Chen et al [81] on PDMS, which was fitted to the power law $\varepsilon_{\text{Maxwell}} = 0.44 = 0.17(\gamma / \mu H)^{0.49}$. Assuming the surface energy vanishes upon self-contact, $\varepsilon_{\text{Maxwell}}$ should be a material independent property for all gels. To exclude any effect of the interaction between neighboring creases, only the nucleation strain for the first crease on each sample is plotted. Results from a similar experiment by Mora et al [85] are included as well. It is shown that the nucleation strain is indeed a distribution rather than a single function of $\gamma / \mu H$. Moreover, the distribution is confined between $\varepsilon_{\text{wrinkle}}$ and $\varepsilon_{\text{Maxwell}}$, in agreement with our theory. One data point is observed to fall slightly below the Maxwell condition ($\gamma / \mu H \approx 0.01$). This may due to the approximate model for Maxwell condition we used.

![Image of nucleation history](image)

**Figure 5.6.** The nucleation history of two representative samples. (a) A sample with $\gamma / \mu = 0.0081$ mm. It shows one nucleation near $\varepsilon_{\text{Maxwell}}$ followed by the majority of the nucleation near $\varepsilon_{\text{wrinkle}}$. (b) A sample with $\gamma / \mu = 0.113$ mm. All the nucleation happens near $\varepsilon_{\text{wrinkle}}$. We do observe nucleation above $\varepsilon_{\text{wrinkle}}$. This is because that we only control
the overall loading strain. As more creases forms, the actual local surface strain is released below the overall loading strain.

After the nucleation of the first crease, more creases nucleate as the sample is further compressed. We observe that although the first few creases may nucleate at a strain much below $\varepsilon_{\text{wrinkle}}$, most creases nucleate almost simultaneously near $\varepsilon_{\text{wrinkle}}$. In our experiments, the sample thickness is fixed at $H=1\text{mm}$, while $\gamma/\mu$ varies from about 10$\mu$m to about 500 $\mu$m. In fact, defects of 10$\mu$m to 500 $\mu$m scale occur rather scarcely on an as-fabricated surface. Consequently, few creases are possibly nucleated from defects of $d \sim \gamma/\mu$. The majority of the creases nucleate from defect of $d \ll \gamma/\mu$, which have nucleation strain very close to $\varepsilon_{\text{wrinkle}}$. As examples, we plot the crease density against the loading strain for two representative samples in Figure 5.6. A few snapshots of the deformed surface are excerpted from the captured videos. We see that the first nucleation may happen close to $\varepsilon_{\text{Maxwell}}$ (as in Figure 5.6a,b) or way above it (as in Figure 5.6c,d). But the majority of the creases nucleates in a narrow strain range around $\varepsilon_{\text{wrinkle}}$ and distributes homogeneously over the surface. Since the formation of crease may release the surface strain elsewhere, the local surface strain should be progressively lower than the loading strain we controlled. Taking into account this strain releasing effect, the majority of the creases nucleate in an even narrower strain range.

5.4 Concluding remarks

In summary, we have successfully characterized the defect sensitive nucleation of a crease using the dimensionless group $\gamma/\mu H$. Here the elastocapillary length $\gamma/\mu$ bears similar meaning to the critical radius $\gamma/\Delta G$ in the classical theory of nucleation,
where $\Delta G$ is the free energy change per volume upon phase transformation. If the defect size is much larger than $\gamma / \mu$, as the surface is slightly super-strained above $\varepsilon_{\text{Maxwell}}$, a crease can readily nucleate and grow. If the defect size is much smaller than $\gamma / \mu$ the surface can be super-strained all the way toward $\varepsilon_{\text{wrinkle}}$. However, no surface could be super-strained above $\varepsilon_{\text{wrinkle}}$. A crease will nucleate simultaneously and homogeneously near $\varepsilon_{\text{wrinkle}}$, similar to spinodal condition in the classical theory of phase transition.
Chapter 6.

Osmocapillary phase separation

6.1 Osmosis and capillarity

Osmotic phenomena have appeared in writings since antiquity [86, 87]. For example, to detach a block of desired size from a large rock, Egyptians would drive wedges of dry wood into slots in the rock, and then soak the wood with water till the swelling wood split the rock. As a second example, an animal bladder, filled with wine and plunged in water, swells greatly and sometimes even bursts. As a third example, the Bible reported that Moses turned brackish water into drinking water, possibly using an ion-exchanging process.

We now know the basic ingredients to set up osmosis. In a system of several substances, one substance—designated as solvent—can migrate from place A to place B, but the other substances cannot. The chemical potential of the solvent in place A is higher than that in place B; the difference in the chemical potential provides the driving force for the migration of the solvent. The animal bladder is a semipermeable membrane: water can pass through it, but alcohol cannot. Outside the bladder, the pure liquid water has a high chemical potential of water. Inside the bladder, the wine is a mixture of alcohol and water, and has a low chemical potential of water. This difference in chemical potential of water motivates pure water outside the bladder to pass through the membrane and dilute the wine.

Osmosis plays essential roles in nature and engineering. Living cells undergo osmotic swelling and collapse when the aqueous solution outside the cell changes concentration. Tall trees demonstrate the spectacular power of osmosis [88]. When air is less humid than soil, the difference in humidity drives the ascent of sap in trees. In the
xylem of tall trees, liquid water is often under hydrostatic tensile stress in excess of 1 MPa [89]. Osmosis-induced high tensile stress in liquid water has been demonstrated in artificial trees on chips [90]. Biological and bioinspired actuators rely on swelling polymers in response to diverse stimuli [91, 92]. Superabsorbent diapers keep babies dry even when babies sit on swollen diapers [93]. Seals made of swelling elastomers are deployed in oilfields to enable hydraulic fracture [94]. Desalination of water has developed into an industry since the time of Moses [95].

In an osmotic phenomenon, osmosis—the tendency to mix the solvent to other substances—usually competes against some other forces. For the bladder filled with wine and plunged in water, osmosis competes against the elasticity of the membrane. During desalination, external forces must be applied to saltwater to push pure water through membranes, against osmosis. Desalination separates water from solutes, and is a process of reverse osmosis. During the ascent of sap, the trees harness the difference in the chemical potentials of water in the soil and in the air, separate water from the soil, and raise water to the treetops.

Here we explore a phenomenon in which osmosis competes against capillarity. We begin with a hydrogel—a covalent network of hydrophilic polymer swollen with water. The chemical potential of water in the hydrogel is readily set by equilibrating the hydrogel with a water vapor of known relative humidity, or with an aqueous solution of known concentration [96]. Assume that the hydrogel is initially in equilibrium with unsaturated water vapor. What will happen if we isolate the hydrogel from the vapor by immersing the hydrogel in a hydrophobic liquid (i.e., oil)? Upon introducing a cavity on the surface of the hydrogel, the interface energy may suck water out of the hydrogel to form a pure liquid phase (Figure 1a). On the other hand, osmosis promotes the low-humidity hydrogel to imbibe water. When capillarity balances osmosis, the two phases—
hydrogel and pure liquid water—coexist in equilibrium. We call this phenomenon osmocapillary phase separation.

**Figure 6.1.** Formation of a liquid phase in a cavity on an interface. (a) Osmocapillary phase separation. In a cavity on a hydrogel-oil interface, the interface energy competes against osmosis and sucks water out of the hydrogel. (b) Capillary condensation. In a cavity on the interface between a non-porous solid and a vapor, the interface energy causes vapor to condense into liquid water. (c) In a cavity on the surface of a non-volatile gel, osmocapillary phase separation still happens, but capillary condensation is impossible. (d) In a cavity on a gel-vapor interface, osmocapillary phase separation and capillary condensation are concurrent processes.

In the configuration of Figure 1a, the cavity is filled with liquid water diffusing from the hydrogel, which serves as a reservoir of water. Even without the hydrogel, a cavity on a solid surface may be filled with liquid water condensing from humid air, which is also a reservoir of water (Figure 1b). Such capillary condensation has been widely studied [97]. Although both osmocapillary phase separation and capillary condensation can fill a cavity on an interface, water comes from different reservoirs. In capillary condensation, water comes from the humid air. In osmocapillary phase separation, water comes from the hydrogel.

A polymer network may also imbibe solvent other than water. When a gel of a nonvolatile solvent is exposed to air, capillary condensation is impossible, but
osmocapillary phase separation can still happen (Figure 1c). If the solvent of the gel is volatile, capillary condensation and osmocapillary phase separation are concurrent processes (Figure 1d). We show that osmocapillary phase separation dominates over capillary condensation for small cavities.

Because the chemical potential of solvent in a gel can be readily tuned, osmocapillary phase separation can occur in cavities of a large range of sizes. The competition between osmosis and capillarity defines a length, which we call the osmocapillary length. When the osmocapillary length is large compared to the size of the cavity, the capillary force sucks pure liquid solvent out of the gel. We will describe various ways to increase the osmocapillary length. Although osmocapillary phase separation has not been well-studied, related phenomena are important in many applications. Examples include the wettability of gels, the transparency of gels, the liquid bridge at the tip of an atomic force microscope (AFM), the adhesion between a gel and another substance, the surface morphology of gels, and the production of tight oil. We will describe these phenomena at the end of the paper.

6.2 Chemical potential of solvent in various states

We review the chemical potentials of solvent in various states of aggregation. The chemical potential of a pure substance is a function of pressure and temperature, and coincides with the Gibbs function per molecule of the substance. Under the isothermal conditions, the chemical potential $\mu$ of a pure solvent obeys the thermodynamic relation $d\mu = v dP$, where $v$ is the volume of solvent (either vapor or liquid) divided by the number of solvent molecules, and $P$ is the pressure. In thermodynamic equilibrium, the chemical potential of solvent is the same everywhere. We set the chemical potential of solvent to zero when pure liquid solvent and pure
gaseous solvent coexist in equilibrium. In this reference state, the pressure is the same in the pure liquid and in the pure vapor; we denote the pressure of saturation by $P_{\text{sat}}$.

When gaseous solvent is isolated from liquid solvent, the pressure in the vapor, $P$, can differ from the pressure of saturation. The vapor is taken to obey the law of ideal gases, $P_v = kT$, where $kT$ is the temperature in the unit of energy. An integration of $d\mu = vdP$ gives the chemical potential of solvent in its pure vapor phase:

$$\mu_v = kT \log \left( \frac{P}{P_{\text{sat}}} \right). \quad (6.1)$$

The chemical potential of solvent in the vapor relates to $P/P_{\text{sat}}$. For a vapor of water, the ratio $P/P_{\text{sat}}$ defines the relative humidity. Equation (6.1) recovers the reference state when the vapor is saturated—that is, $\mu_v = 0$ when $P = P_{\text{sat}}$.

When the pure liquid solvent is isolated from its vapor, the hydrostatic stress in the liquid, $\sigma$, can differ from the pressure of saturation. We take $\sigma$ to be positive when the stress in the liquid is tensile. Liquid solvent is assumed to be incompressible—that is, the volume per solvent molecule in the liquid phase, $\Omega$, is independent of the stress. An integration of $d\mu = vdP$ gives the chemical potential of solvent in its pure liquid phase:

$$\mu_l = -\Omega \left( \sigma + P_{\text{sat}} \right). \quad (6.2)$$

The chemical potential of solvent in its pure liquid phase is linear in the applied hydrostatic stress. Equation (6.2) recovers the reference state when the liquid solvent equilibrates with the gaseous solvent—that is, $\mu_l = 0$ when $\sigma = P_{\text{sat}}$.

Experiments are often conducted under the atmospheric pressure, $P_{\text{atm}}$. The air contains the vapor of the solvent, and is modeled as an ideal-gas mixture. The chemical potential of solvent in the air is still given by (6.1), with $P$ being the partial pressure of solvent in the air, and $P_{\text{sat}}$ still being the pressure of saturation when pure liquid solvent and pure gaseous solvent equilibrate. When the pure liquid is under atmospheric pressure, $\sigma = -P_{\text{atm}}$, the chemical potential of solvent in the liquid is $\mu_l = \Omega \left( P_{\text{atm}} - P_{\text{sat}} \right)$. 

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For example, $P_{\text{sat}} \sim 3\text{kPa}$ for water at room temperature and $P_{\text{atm}} \sim 100\text{kPa}$. Consequently, the atmospheric pressure greatly increases the chemical potential of water in its pure liquid phase. Equating the chemical potential of solvent in the liquid and that in the air, we obtain the partial pressure of the solvent in the air in equilibrium with the liquid water:

$$P_0 = P_{\text{sat}} \exp \frac{P_{\text{atm}} - P_{\text{sat}}}{kT/\Omega} \quad (6.3)$$

For water, taking $\Omega = 3.0 \times 10^{-29}\text{m}^3$, $T = 300 \text{ K}$ and $k = 1.38 \times 10^{-23}\text{J/K}$, we obtain that $kT/\Omega = 138\text{MPa}$, which is much larger than the atmospheric pressure. Consequently, the atmospheric pressure increases the equilibrium partial pressure of water negligibly, $P_0 \sim P_{\text{sat}}$.

Denote the chemical potential of pure liquid solvent under atmospheric pressure by $\mu_0 = \Omega (P_{\text{atm}} - P_{\text{sat}})$. Rewriting (6.1), we express the chemical potential of solvent in an ideal-gas mixture as

$$\mu_r = \mu_0 + kT \log \left( \frac{P}{P_0} \right). \quad (6.4)$$

For pure liquid solvent subject to hydrostatic stress $\sigma$, define an excess stress by $\sigma' = \sigma + P_{\text{atm}}$. Rewriting (6.2), we express the chemical potential of solvent in the pure liquid as

$$\mu_l = \mu_0 - \Omega \sigma'. \quad (6.5)$$

Now consider a pure liquid solvent with a curved surface. The ambient is subject to the atmospheric pressure. The chemical potential of solvent beneath the curved liquid-vapor interface is

$$\mu_\gamma = \mu_0 - \Omega \kappa \gamma, \quad (6.6)$$

Here $\gamma$ is the energy per unit area of the interface, and $\kappa$ is the sum of the two principal curvatures of the interface. A positive $\kappa$ corresponds to a cavity, and a negative $\kappa$
corresponds to a droplet. Equation (6.6) also applies to an oil-water interface, where \( \gamma \) is the energy per unit area of the oil-water interface, the oil is subject to the atmospheric pressure, and \( \mu_\gamma \) is the chemical potential of water near the curved water-oil interface.

As mentioned before, the chemical potential of solvent in a gel, \( \mu_{\text{gel}} \), can be readily changed by equilibrating the gel with a solvent vapor of known partial pressure [96]. The chemical potential of solvent is negative in a gel in equilibrium with an unsaturated solvent vapor. We define the osmotic pressure \( \Pi \) of the gel by the relation

\[
\mu_{\text{gel}} = \mu_0 - \Omega \Pi. \tag{6.7}
\]

This definition of the osmotic pressure in a gel is analogous to that of the osmotic pressure in a liquid solution. For a liquid solution in equilibrium with a pure solvent, the osmotic pressure in the solution is measurable as a pressure, e.g., by the rise of the solution against gravity. For a gel in equilibrium with a pure liquid solvent, \( \mu_{\text{gel}} = \mu_i \), the osmotic pressure in the gel balances the excess stress in the pure liquid solvent, \( \Pi = \sigma' \).

### 6.3 Osmocapillary length

We now return to the cavity on the hydrogel-oil interface (Figure 6.1a). For a hydrogel containing a large quantity of water, the energy per unit area of the hydrogel-oil interface is nearly identical to that of the water-oil interface. When the hydrogel extrudes water, the resulting water-oil interface is less curved than the hydrogel-oil interface, so that the net interface energy reduces. Thus, the capillarity promotes the separation of the hydrogel into two phases: hydrogel and pure liquid water. The water-oil interface is still slightly curved, and sets up a difference in stress on the two sides of the interface, known as the Laplace stress. The oil is under the atmospheric pressure. Inside the cavity, the energy of the oil-water interface causes a state of tensile excess stress in the liquid water (\( \sigma' > 0 \)). Equating the chemical potentials of water, \( \mu_\gamma = \mu_i \), one obtains \( \sigma' = \gamma \kappa \).
The Laplace stress in the liquid water relative to the oil is tensile, and tends to suck water out of the hydrogel. On the other hand, osmosis promotes the low-humidity hydrogel to imbibe water. When capillarity balances osmosis, the two phases—hydrogel and pure liquid water—coexist in equilibrium. Equating the chemical potentials, \( \mu_{\text{gel}} = \mu_{\gamma} \), we obtain the condition of osmocapillary equilibrium:

\[
\Pi = \gamma \kappa .
\] (6.8)

When the hydrogel is a reservoir of water with a fixed chemical potential (and therefore a fixed osmotic pressure), the condition of equilibrium determines the curvature of the water-oil interface.

The ratio \( \gamma / \Pi \) defines a length, which we call the osmocapillary length. If the size of the cavity, \( L \), is small comparing to the osmocapillary length, there exists a continuous surface of curvature \( \kappa \) covering the cavity that satisfies \( \gamma \kappa = \Pi \), and phase separation happens. However, for a large cavity, \( L > \gamma / \Pi \), phase separation does not happen. In the limit that the hydrogel is in equilibrium with the saturated vapor, \( \Pi = 0 \), osmocapillary phase separation can occur in a cavity of any size. In the other limit that the hydrogel is completely dry, \( \Pi = \infty \), osmocapillary phase separation cannot happen in a cavity of any size.

For a hydrogel prepared in equilibrium with a vapor of relative humidity \( P / P_0 \), the osmocapillary length is

\[
\frac{\gamma}{\Pi} \approx \frac{\gamma \Omega}{kT \log (P / P_0)} .
\] (6.9)

For a representative values \( \gamma = 70 \text{mJ/m}^2 \) and \( kT / \Omega = 138 \text{MPa} \), we plot the osmocapillary length as a function of relative humidity (Figure 6.2). The osmocapillary length decreases steeply at the dry end and increases steeply at the wet end. The osmocapillary length is
roughly 5nm at 90% relative humidity, and increases to roughly 50nm at 99% relative humidity.

Figure 6.2. Osmocapillary length for hydrogel prepared at various values of relative humidity.

In a sealed environment, the relative humidity in the vapor can be controlled by an aqueous solution. Let \( c \) be the concentration of the solute (i.e., the number of particles of the solute divided by the volume of the solution). The osmotic pressure of the solution is given by the Van’t Hoff equation \( \Pi = ckT \). This osmotic pressure sets the osmotic pressure in the hydrogel if the vapor over the aqueous solution equilibrates with the hydrogel. In this case, the osmocapillary length is given by

\[
\frac{\gamma}{\Pi} = \frac{\gamma}{ckT}.
\]  

(6.10)

For example, take the surface tension of an aqueous solution to be still \( \gamma = 70 \text{mJ/m}^2 \). For a sucrose solution of 0.1M, the osmotic pressure is \( \Pi = 0.25 \text{MPa} \), and the osmocapillary length is 0.28\( \mu \)m. For a colloidal solution of 0.1mM, the osmotic pressure will be lowered to \( \Pi = 0.25 \text{kPa} \), and the osmocapillary length will be increased to 280\( \mu \)m.
We now consider a gel of nonvolatile solvent (Figure 6.1c). Still, a pure liquid solvent in a cavity equilibrates with solvent in the gel when capillarity balances osmosis, \( \gamma \kappa = \Pi \), where \( \gamma \) is the energy per unit area of the solvent-air interface, \( \kappa \) is the curvature of the solvent-air interface and \( \Pi \) is the osmotic pressure in the gel. To observe osmocapillary phase separation, we need to reduce the magnitude of the osmotic pressure in the gel—that is, to bring the chemical potential of solvent in the gel to be sufficiently close to that in pure liquid solvent. An effective way to do so is to use a solvent of giant molecules.

Consider a network of polymer swollen with the liquid of the polymer of the same chemical structure. The enthalpy of mixing vanishes, and the mixing of the solvent and network is entirely driven by entropy. Let \( V \) be the volume of the networked polymer, \( N \) be the number of uncrosslinked polymer chains, and \( \Omega \) be the volume per chain. When the uncrosslinked chains form a pure liquid, the volume of the liquid is \( N \Omega \), and the number of configurations scales as \( W_0 \propto (N\Omega)^N \). When the uncrosslinked chains and the network form a gel, the volume of the gel is \( V + N\Omega \), and the number of configurations scales as \( W_{gel} \propto (V + N\Omega)^N \). Consequently, the entropy of mixing is \( S_{gel} - S_0 = k \log (W/W_0) \). The change in the chemical potential of solvent between the two states of aggregation obeys the thermodynamic relation

\[
\mu_{gel} - \mu_0 = -T \frac{\partial}{\partial N} (S_{gel} - S_0) / \partial N,
\]

giving

\[
\mu_{gel} = \mu_0 + kT \left( \log \frac{N\Omega}{V+N\Omega} + \frac{V}{V+N\Omega} \right).
\] (6.11)

Equation (6.11) corresponds to the entropy of mixing in the Flory-Huggins model [98, 99]; here we have neglected the change in the entropy due to the elasticity of the network. For a gel in which the volume of solvent is comparable to that of the networked polymer, the term in the parenthesis in (6.11) is of order unity, so that the osmotic pressure is on
the order of $\Pi \sim kT/\Omega$. For example, the density of a polymer is on the order of $10^3 \text{kg/m}^3$; for a polymer chain of molecular weight of 100,000 g/mol, the volume of the polymer is about $2 \times 10^{-25} \text{m}^3$ and the osmotic pressure is about 25 kPa. The osmotic pressure is greatly reduced for a gel with solvent of long-chain polymers. Taking a representative value of surface energy, $\gamma = 20 \text{mN/m}$, we obtain an osmocapillary length on the order of microns.

6.4 Phase separation along a three-phase contact line

In a recent experiment, Jensen et al. [100] observed the formation of a liquid phase along the contact line of three phases (air, a gel and a solid). In their experiment, spherical glass particle is dropped onto loosely crosslinked PDMS. The PDMS is so soft that it partially engulfs the glass particle. In the loosely crosslinked PDMS, some of the PDMS molecules are not crosslinked, and can migrate out as liquid PDMS. The experiment shows that uncrosslinked PDMS molecules extrude out from the gel and form a liquid phase near the contact line (Figure 6.3).

We now interpret this experimental observation in terms of osmocapillary phase separation. Liquid PDMS is nonvolatile and the possibility of condensation from vapor is excluded. The three-phase contact line has a singular curvature, which allows osmocapillary phase separation with at any finite $\Pi$. In the experiment, the PDMS network and the PDMS liquid consist of the identical molecular structure except for a tiny fraction of crosslinkers. Consequently, enthalpy of mixing vanishes. The reported molecular weight of the pre-crosslinked PDMS is 28000 g/mol, and the density of PDMS is 0.97 kg/m$^3$ [101]. The volume occupied by each polymer chain can be estimated based on the molar weight of the polymer, which gives $\Omega = 4.8 \times 10^{-26} \text{m}^3$. It was measured that the volume fraction of uncrosslinked PDMS is 62%, Equation (6.11) gives the osmotic pressure $\Pi \sim 15 \text{kPa}$. Taking the surface energy of the PDMS as 20 mN/m. The
corresponding osmocapillary length is $\gamma/\Pi = 1.3\mu m$. This estimate is comparable to the size of the liquid phase observed in the experiment. A full analysis of the experiment requires a theory that couples osmosis, capillarity and elasticity, which is beyond the scope of this paper.

Figure 6.3. When a glass particle is dropped on a soft PDMS gel swollen with liquid PDMS, liquid PDMS extrudes out near the three-phase contact line.

6.5 Osmocapillary phase separation vs. capillary condensation

When the surface of a solid is exposed to the ambient air, liquid water may condense out from humid air near small cavities on a solid surface (Figure 6.1b). This capillary condensation has important consequence for micro-electro-mechanical systems [102-104], self-assembly [105-107], and atomic force microscopes [108-110].

We now consider a polymer network swollen with a solvent and exposed to air (Figure 6.1d). The solvent is volatile, and a vapor of the solvent exists in the air. Consequently, capillary condensation and osmocapillary phase separation are concurrent processes. Thermodynamic equilibrium requires that the chemical potential of solvent be the same everywhere, $\mu_{gel} = \mu_l = \mu_f = \mu_v$, giving that
\[ \Pi = \sigma = \gamma k = -\frac{kT}{\Omega} \log \left( \frac{P}{P_0} \right). \] 

(6.12)

The last equation is the Kelvin relation commonly used to analyze capillary condensation.

Equation (6.12) shows that the condition of equilibrium for osmocapillary phase separation is identical to that for capillary condensation. However, the kinetics of the two processes are different. Capillary condensation is due to the condensation of solvent from the vapor, whereas osmocapillary phase separation is due to the diffusion of solvent in the gel.

We compare condensation from the vapor and diffusion in the gel using basic kinetic theory [111-113]. The average velocity of solvent molecules in the vapor is \( v = \sqrt{\frac{3kT}{m}} \), where \( m \) is the mass per molecule. The law of ideal gases gives the number of solvent molecules per unit volume of vapor, \( c = \frac{P_0}{kT} \), where \( P_0 \) is the equilibrium partial pressure of solvent in the vapor. The rate of condensation scales as \( \frac{dn}{dt} \sim cvL^2 \), where \( n \) is the number of solvent in the liquid phase, and \( L \) is the length scale of the liquid phase. Note that \( n \sim \frac{L^3}{\Omega} \). Consequently, the relaxation time for capillary condensation scales as \( \tau_{\text{cond}} \sim L\sqrt{mkT} / P_0\Omega \). On the other hand, the relaxation time for osmocapillary phase separation scales as \( \tau_{\text{osmo}} \sim \frac{L^3}{D} \), where \( D \) is the diffusivity of the solvent in the gel.

Equating the relaxation times of the two kinetic processes, \( \tau_{\text{cond}} = \tau_{\text{osmo}} \), we obtain a length scale \( L_{\text{cross}} = D\sqrt{mkT} / P_0\Omega \). Take orders of magnitude representative of water, \( m \sim 10^{-26}\text{kg}, \Omega \sim 10^{-29}\text{m}^3, kT \sim 10^{-21}\text{J} \) and \( P_0 \sim 1\text{kPa} \). The diffusivity of water in hydrogel is roughly \( D \sim 10^{-9}\text{m}^2/\text{s} \) [114]. The length scale is estimated as \( L_{\text{cross}} = 0.1\mu\text{m} \). This means that, for hydrogels, at sub-micron scale the osmocapillary phase separation dominates over capillary condensation. In the limit of a gel with a nonvolatile solvent, the crossover
length approaches infinity, and the formation of the liquid phase is due entirely to osmocapillary phase separation.

We have identified two length scales: the osmocapillary length $\gamma/\Pi$, and the kinetic crossover length $L_{\text{cross}} = D\sqrt{m/kT}/P_0\Omega$. Experimental observations of a cavity on a gel-air interface will depend on how the size of the cavity $L$ compares with these two length scales (Figure 6.4). When osmosis prevails over capillarity, no phase separation occurs. When capillarity prevails over osmosis, phase separation occurs, either by the diffusion of solvent in the gel, or by the condensation of solvent from the vapor.

Figure 6.4. Osmocapillary phase separation occurs when the size of the cavity $L$ is small compared to two lengths, the osmocapillary length $\gamma/\Pi$, and the kinetic crossover length $L_{\text{cross}} = D\sqrt{m/kT}/P_0\Omega$.

6.6 Osmocapillary phase separation in phenomena of practical significance

Like capillary condensation, osmocapillary phase separation is expected to be important in many applications. Here we briefly discuss several examples. Osmocapillary
phase separation may change the wettability of the gel surface (Figure 6.5a). The gel and its solvent can have different surface property if the gel has a low swelling ratio, or if the gel carries some functional particles like clay [115]. A droplet of liquid immiscible with the solvent may have different wettability towards the solvent and towards the gel. When the osmotic pressure inside the gel is low, osmocapillary phase separation covers most surface asperities with the solvent, and the wettability of the surface is close to that of the pure solvent. When the osmotic pressure inside the gel is high, osmocapillary phase separation only covers a tiny portion of the surface asperities, and the wettability of the surface is close to that of the gel.

Osmocapillary phase separation may also change the optical property of the gel (Figure 6.5b). Depending on the fabrication process, the surface of a gel can be rough and scatter light, resulting in a translucent material. Usually, the difference in refractive index between the gel and the solvent is much smaller than the difference between the gel and the air. With low osmotic pressure, osmocapillary phase separation covers all the asperities, and the material is transparent. With high osmotic pressure, the rough surface scatters light, and the material is translucent.

The examples of Figure 6.5a and Figure 6.5b show that osmocapillary phase separation enables switching of the surface property by tuning the osmotic pressure, which could be done by connecting the gel with a reservoir of solvent or applying stress. The same principle has been demonstrated in the “self-healing, slippery liquid infused porous surface” (SLIPS) [116, 117]. In that case, lubricant is infused into a porous material, and the wettability of the porous material is tuned by changing the pore pressure of the lubricant. If we accept pore pressure as an extension of osmotic pressure, these experiments fit into the theory of osmocapillary phase separation.

Osmocapillary phase separation may result in a liquid bridge at the tip of an atomic force microscope (Figure 6.5c). As discussed earlier, below the kinetic crossover
length, osmocapillary phase separation dominates over capillary condensation. Consequently, the liquid bridge draws liquid from the gel, rather than from the ambient air. The difference in kinetics can result in noticeable difference if the atomic force microscope works in the dynamic modes [118]. In addition, capillary condensation may be avoided by immersing the sample in a cover liquid. If the cover liquid is immiscible with the solvent, osmocapillary phase separation can still result in a liquid bridge. For a gel with nonvolatile solvent, test in vacuum can also avoid capillary condensation, but osmocapillary phase separation can still result in liquid bridge as well.

As demonstrated by Jensen et al [100], osmocapillary phase separation produce a liquid ring along the three-phase contact line (Figure 6.5d). It is known that liquid phase around contact line can strongly influence adhesion [119]. This implies that the osmocapillary phase separation will also affect adhesion.

When a soft material is compressed beyond a critical level, the surface of the material forms creases [15, 71]. Creases account for many naturally observed phenomena, including the creases on our skin and the sulci in the brain. If a crease happens on the surface of a gel, the self-contact leads to a singularity in the curvature of the gel-air interface. Such a singularity may cause osmocapillary phase separation (Figure 6.5e), although we are unaware of any experimental observations.

Singularity in the curvature may also happen at the tip of a crack, where osmocapillary phase separation is expected (Figure 6.5f). Depending on the size of the crack opening relative to the osmocapillary length, the solvent may propagate a long distance along the crack. If we think porous rock as a special case of gel and think crude oil as its solvent, such a phenomenon has been widely used in the production of tight oil through hydraulic fracture [120].
Figure 6.5. Osmocapillary phase separation may relate to a variety of phenomena. (a) Osmocapillary phase separation may change the wettability between a gel and an immiscible liquid. (b) Osmocapillary phase separation may switch a translucent material to a transparent material by covering the surface roughness. (c) Osmocapillary phase separation may result in a liquid bridge at the tip of an atomic force microscope. (d) Osmocapillary phase separation changes the adhesion between two materials. (d) Osmocapillary phase separation may happen near the tip of a crease. (e) Osmocapillary phase separation may happen near the tip of a crack, extracting liquid out along the crack.

6.7 Conclusion

For a pure liquid solvent in a cavity to coexist in equilibrium with a gel, the Laplace tension in the pure liquid solvent must equal the osmotic pressure in the gel. The competition between capillarity and osmosis defines the osmocapillary length. A cavity smaller than the osmocapillary length draws solvent from the gel and the vapor concurrently. Diffusion of the solvent in the gel prevails over the condensation of the solvent from the vapor when the cavity is smaller than a kinetic crossover length. Osmocapillary phase separation can still occur even when the gel is isolated from vapor
phase, or when the solvent of the gel is nonvolatile. Osmocapillary phase separation may be important in many applications, including the wettability of gels, the transparency of gels, the liquid bridge at the tip of an atomic force microscope, the adhesion on gel, the surface morphology of gels, and the production of tight oil.
Chapter 7.

Elastic leak of a seal

7.1 Elastomeric seals

Seals are ubiquitous. Familiar examples are those in plumbing joints, drinking bottles, and pressure cookers. Engines require seals to enable gas-tight, reciprocating motion of pistons in cylinders [121, 122]. Hydraulic fracture requires seals to isolate fluids in gaps between pipes and boreholes [123-126]. Seals, along with tires and bearings, are among the most significant applications of elastomers [127]. Seals are inexpensive, but their failure can be costly. The explosion of the space shuttle Challenger, for example, was traced to the failure of O-rings [128].

The softness of an elastomer is essential to both the function and failure of a seal. The elastomer seals a fluid in a gap between mating parts made of hard materials. The softness enables the seal to deform easily, adapting to unpredictable variations in its working environment, such as the height of the gap, the misalignment of the mating parts, the roughness of their surfaces, and changes in temperature. With this adaptation, neither the seal nor the mating parts need to be designed with high precision, which could be costly or impossible. The softness of the elastomer, however, also makes the seal prone to failure. The fluid pressure can cause the seal to deform and damage, leading to leak [121, 122].

Here we study a particular mode of failure, elastic leak. An elastomer seals a fluid by forming contact with surrounding hard materials. As the fluid pressure increases, the contact stress also increases but not as much. When the fluid pressure surpasses the contact stress in some part of the contact region, the seal and the hard materials lose contact in this region, forming a leaking path which eventually penetrates through the
whole contact region. This mode of failure is entirely due to elastic deformation: the seal leaks without any material damage. We construct a transparent experimental setup to watch the seal deform and leak, and compare experimental observations to theoretical predictions. We find that the critical fluid pressure for elastic leak depends on the geometry and constraint of the seal, but is insensitive to the rate at which the fluid is injected.

Whereas seals have been studied as boundary-value problems of elasticity (e.g., [129-131]), how the solutions of elasticity relate to the leak of seals is poorly understood. In postmortem examinations of failed seals, damage is often highly visible, but elastic deformation is not [121, 132]. Perhaps because of this biased evidence, the central significance of elastic deformation to the leak of seals is underappreciated. The object of this paper is to quantify elastic leak using a combination of experiment and modeling.

7.2 A model of elastic leak.

Prior to the injection of fluid, two rigid walls place an elastomer in a state of precompression (Figure 7.1a). On the right side of the elastomer, a step in the bottom wall defines the sealing site. For the time being, we neglect the adhesion and friction between the walls and the elastomer, and assume that the elastomer deforms elastically without damage. The elastomer and the two walls form contact. We focus on the distribution of the contact stress between the elastomer and the top wall. The contact stress peaks in the interior of the contact, and vanishes at the edges of the contact [129].
Figure 7.1. Elastic escape and elastic leak. (a) Prior to the injection of fluid, two rigid walls place an elastomer in a state of precompression. A step in the bottom wall defines the sealing site. Between the elastomer and the top wall is a distribution of contact stress. (b) When a fluid of quantity $Q$ is injected, the fluid pressure $p$ is applied on the elastomer and the elastomer deforms. The elastomer seals the gap when the contact stress rises above the fluid pressure. (c) The fluid pressure may cause the elastomer to squeeze into the tight space above the step, and escape from the sealing site. (d) The seal leaks when
the contact stress in the interior of the contact drops below the fluid pressure.  (e) A $p-Q$ diagram that characterizes elastic leak.

When a fluid of a small pressure $p$ is injected into the space on the left side of the seal, the elastomer deforms, pushes against the step, and extrudes a small part into the tight space above the step (Figure 7.1b). The fluid pressure changes the region of contact, and increases and redistributes the contact stress [130, 131]. When both the elastomer and the wall have smooth surfaces, the fluid pressure matches the contact stress at the edge of the contact. The edge of the contact would recede if the fluid pressure were above the contact stress at the edge of the contact, and would advance if the fluid pressure were below the contact stress at the edge of the contact. When the fluid pressure is low, the contact stress inside the contact rises above the fluid pressure. It is the rising contact stress in the interior of the contact that prevents the fluid from penetrating into the contact. The seal does not leak.

As the fluid pressure increases, the seal can fail in two modes. In one mode of failure, the whole elastomer squeezes into the tight space above the step, and escape from the sealing site [133](Figure 7.1c). Although the fluid pressure is still lower than the peak contact stress, the escaped seal is commonly considered a failure. This mode of failure, elastic escape, will not be studied in this paper. In the other mode of failure, as the fluid pressure increases, the peak contact stress also increases but not as much. When the fluid pressure reaches a critical value $p_c$, the contact stress peaks at the left edge of the contact and still matches the fluid pressure, whereas the contact stress in the interior of the contact drops below the fluid pressure (Figure 7.1d). Consequently, the fluid penetrates the contact, pulled by the lower and lower contact stress ahead. The elastomer and the top wall lose contact in some region, forming a leaking path. This mode of failure, elastic leak, will be the focus of the remainder of the paper.
The seal is a nonlinear system. We use the fluid pressure $p$ as the loading parameter, and use the quantity of injected fluid, $Q$, as a proxy for the state of the system. We characterize elastic leak using a $p$-$Q$ diagram (Figure 7.1e). As the quantity of injection $Q$ increases, the fluid pressure $p$ increases. When the fluid pressure reaches a critical level $p_c$, the seal leaks, and the quantity of injection can increase infinitely without increasing the fluid pressure. When the fluid pressure is reduced below the critical level, the leak stops, and the elastomer recovers toward its initial shape. When the fluid pressure is increased to $p_c$ again, the leak resumes. Since we have assumed that the elastomer is elastic and the contact is free of adhesion and friction, the system is perfectly reversible. Whenever the leak stops, the seal has no memory of the previous leak. Each recovering-reloading curve parallels the initial loading curve, shifted by the quantity of fluid that has leaked through the seal.

### 7.3 Visualizing elastic leak in experiments

The concept of elastic leak can be tested with any seal configuration. We study elastic leak with a desktop experiment. We use an adhesive to glue a layer of hydrogel, dimensions $l$, $w$ and $h$, to acrylic spacers and a sheet of glass (Figure 7.2a). A transparent acrylic sheet of thickness $\Delta h$ and width $w$ is attached to another sheet of glass, i.e. the cover glass sheet. When the cover glass sheet is glued on top of the acrylic spacers, the hydrogel is precompressed with a strain $\varepsilon = \Delta h / h$ (Figure 7.2b). No adhesive is applied between the cover sheet and the hydrogel. One side of the hydrogel is a sealed chamber, and the other side of the hydrogel is open to the air. We use a syringe pump to inject water into the chamber while a pressure gauge records the fluid pressure inside the chamber. A digital camera is used to monitor the movement of hydrogel and water, which are colored in red and blue. The setup is placed vertically during experiments so
that any leaked fluid can automatically drain out. See a photo of the experimental setup (Figure B.1).

Figure 7.2. A desktop experimental setup. (a) The hydrogel, of dimensions $h$, $l$ and $w$ in the undeformed state, is glued to a sheet of glass and to acrylic spacers. (b) An acrylic sheet of thickness $\Delta h$ is attached to another sheet of glass. When the cover sheet is glued to the spacer, the hydrogel is precompressed with a displacement $\Delta h$. The glass, acrylic and hydrogel define a chamber, which connects to a syringe pump and a pressure gauge. The setup is placed vertically so that any leaked fluid can automatically drain out.

Our experimental setup bears resemblance to seals commonly used in oilfields [125, 134], and is inspired by recent work employing soft and transparent system to study seal problem [134]. We design the setup with following considerations. First, the transparency of the glass allows us to watch the seal deforming and leak. Second, the design ensures that the seal leaks before the glass breaks. For the fluid to deform the seal, the pressure in the fluid scales with the elastic modulus of the seal. To lower the pressure in the desktop experiment, we make the seal using a hydrogel of a low elastic modulus (~kPa), which is much below the elastic modulus of an elastomer (~MPa).
Third, we design the seal to minimize the number of geometric parameters. We choose the rectangular shape with $w >> h$, so that the aspect ratio $l/h$ is the only dimensionless group describing the geometric effect of the seal. We prevent elastic escape not by a step in the bottom glass sheet, but by gluing the hydrogel to the bottom glass sheet. Fourth, the design allows us to vary the constraint of the seal by changing the strain of precompression, $\varepsilon$.

Figure 7.3. Experimental observations of elastic leak. (a) The fluid pressure as a function of time. A hydrogel, with shear modulus $\mu=1.03\text{kPa}$, and dimensions $h = 4.5$
mm, $l = 20$ mm, and $w = 120$ mm, is precompressed at a strain of $\varepsilon = 20\%$. The syringe pump injects water at a rate of 5 ml/min until the seal leaks. After steady state leak is achieved the force applied on the syringe pump is removed. Three loading-unloading cycles are plotted. (b) Five snapshots of the seal corresponding to states marked in the pressure-time curve in (a). (c) The $p$-$Q$ curves at several rates of injection. (d) The leak-stop pressure is insensitive to the rate of injection, and increases with the strain of precompression. (e) The effects of the length to thickness ratio and the strain of precompression on the leak-initiation pressure (dashed lines) and leak-stop pressure (solid lines).

As the syringe pump injects fluid at a constant rate into the chamber, we measure the fluid pressure (Figure 7.3a), and watch the seal deform and leak (Figure 7.3b). Initially, the fluid pressure rises, and the hydrogel deforms but does not leak. On reaching a peak value $p_i$, the fluid pressure drops precipitously, while a drop of water runs rapidly through the interface between the hydrogel and the cover sheet (Movie B.1). The fluid pressure then settles at a plateau $p_s$, and the seal leaks in a steady state. When we remove the force applied to the syringe pump, immediately the fluid pressure drops below the plateau and the leak stops (Movie B.2). It takes some time for the hydrogel to recover its initial configuration, and for the fluid pressure to vanish. No fracture or debris of hydrogels is observed. We will call $p_i$ the leak-initiation pressure, and $p_s$ the leak-stop pressure. On pushing the syringe pump again at the constant rate of injection, we record a somewhat lower leak-initiation pressure, but nearly identical leak-stop pressure. The behavior of the seal is repeatable from cycle to cycle.

We conduct the experiment with several variables: the rate of injection, the strain of precompression, and the length of the seal. The $p$-$Q$ diagram remains nearly identical
even though the rate of injection changes by two orders of magnitude (Figure 7.3c). The leak-stop pressure increases with the strain of precompression and with the length of the seal (Figure 7.3d, Figure 7.3e).

7.4 Comparison between theory and experiment

These experimental observations broadly confirm the model of elastic leak, but also show some significant differences. The model predicts that the leak initiates and stops at exactly the same pressure, $p_c$. The experiment, however, shows two distinct pressures: the peak (the leak-initiation pressure $p_i$), and the plateau (the leak-stop pressure $p_s$). This difference between the model and the experiment may result from friction and adhesion between the hydrogel and the cover glass. Friction and adhesion are neglected in the ideal model, but are present in the experiment. When the hydrogel deforms, additional fluid pressure is required to overcome the friction and adhesion (Figure B.2). When the leak reaches steady state, however, the hydrogel stops deforming, and the additional fluid pressure to overcome friction and adhesion is no longer necessary, so that a lower fluid pressure sustains the steady leak. We expect the seal during the steady leak to obey the elastic leak model, and $p_s$ to be quantitatively comparable to the $p_c$. In particular, we expect $p_s$ to depend only on the elastic and geometric properties of the system. Indeed, $p_s$ is highly repeatable across cycles (Figure 7.3a). By contrast, the leak-initiation is sensitive to friction and adhesion. After the initial cycle, the friction and adhesion may reduce if the interface between hydrogel and the glass traps water [135]. Consequently, subsequent cycles require lower leak-initiation pressures (Figure 7.3a).

Our model predicts that, on reaching the critical pressure, the fluid faces monotonically decreasing contact stress (Figure 7.1d). Thus, once the fluid enters the
contact, it will unstably propagate through the entire contact. This behavior is indeed observed in experiment (Movie B.1). The time scale for the unstable leak is very short comparing to the time scale of our experiment. This theoretical prediction explains why the fluid pressure drops precipitously after the seal starts to leak.

When a seal leaks, the fluid pressure keeps at a plateau pressure. This observation should not be surprising. There is not much resistance for the leaking path to spread, and the leaking path should be very thin so that the elastomer is only slightly perturbed from its configuration right before leak. The fluid pressure required to maintain the path is not much higher than \( p_c \), and is essentially unchanged when the rate of injection changes by two orders of magnitude.

Some variations in a seal are unavoidable, and the deformation is not perfectly uniform across the width of the hydrogel. The hydrogel and the cover glass lose contact in some region and form a leaking path. After the leak initiates, the fluid pressure drops, so that no other leaking path can form. In all experiments we observe only one leaking path in each seal. In the following cycles, the leaking path forms at the same place.

To compare the model and the experiment quantitatively, we analyze seals using the finite element software ABAQUS. The elastomer is modeled as an incompressible neo-Hookean material with shear modulus \( \mu [136] \), and is assumed to deform under the plane strain conditions. The elastomer is a rectangular block in the undeformed state, bonded to the bottom wall, in contact with the top wall with neither adhesion nor friction. A precompression of strain \( \varepsilon \) is applied by lowering the top wall. The system has three dimensionless parameters: the normalized fluid pressure \( p/\mu \) represents the load, the aspect ratio \( l/h \) represents the geometry of the seal, and the strain of precompression \( \varepsilon \) represents the constraint of the seal. At a given fluid pressure \( p/\mu \), we calculate the
shape of the elastomer, and the distribution of the contact stress between the elastomer and the top wall (Figure 7.4a-d).

As noted before, when the two smooth surfaces form a contact, the contact stress at the edge of the contact matches the fluid pressure outside. This continuity, however, does not apply if either one of the two surfaces is not smooth [137]. When the edge of the block of elastomer coincides with the edge of the contact, the contact stress at the edge of the contact in general differs from the fluid pressure.

In the absence of the fluid pressure, \( p / \mu = 0 \), the rigid walls place the elastomer in a state of precompression. Because the elastomer is bonded to the bottom wall and is in contact with the top wall with no friction and adhesion, the precompression causes the top part of the elastomer to bulge out. Small parts of the elastomer near its edges lose contact with the top wall—that is, the edges of the elastomer do not coincide with the edges of the contact. The contact stress is symmetrically distributed in the contact, peaks at the mid-point of the contact, and vanishes at the two edges of the contact.

At the fluid pressure of \( p / \mu = 4.9 \), the shape of the elastomer is asymmetric. At the right edge of the contact, additional area of the elastomer loses contact with the top wall, and the contact stress matches with the zero pressure outside. The left edge of the contact coincides with the edge of the elastomer, so that the contact stress does not match the fluid pressure. In this case, the contact pressure at the left edge of the contact exceeds the fluid pressure, and the seal does not leak. The fluid pressure raises the contact stress, and shifts the peak contact stress toward the left edge.

At the fluid pressure of \( p / \mu = 15.6 \), the elastomer shears even more, and a significant amount of material extrudes out at the right side. The distribution of contact stress becomes monotonic, peaks at the left edge of the contact, and vanishes at the right edge of the contact. The contact stress at the left edge remains above the fluid pressure,
and the seal does not leak. This behavior persists up to the fluid pressure $p/\mu = 32.5$, when the peak contact stress matches the fluid pressure, and the seal leaks.

![Figure 7.4](image.png)

**Figure 7.4.** Finite element analysis of elastic leak. (a)–(d) Snapshots of a deformed seal of ratio $l/h = 6$ and a precompression $\varepsilon = 10\%$ at four levels of the fluid pressure. The corresponding distributions of contact stress are also plotted. At each level of the fluid pressure, a black cross marks the position of the peak contact stress. The stress distribution in the interior of the seal is shown in Figure B.5. (e) The critical fluid
pressure predicted theoretically (solid curves) is compared with the leak-stop pressure measured experimentally (crosses).

Following the above procedure, we calculate the critical fluid pressure for various values of $l/h$ and $\varepsilon$ using the finite element method, and fit our result to an analytical expression (Figs. B.3, B.4):

$$\frac{p_c}{\mu} = \frac{A}{1-\varepsilon h} + \frac{B \varepsilon}{1-\varepsilon h} \left( \frac{l}{h} \right)^2,$$

(7.1)

with $A = 3.0$ and $B = 2.9$. We compare the theoretical predictions to the experimentally measured values of the leak-stop pressure (Figure 7.4e). The agreement is good for low precompression $\varepsilon = 10\%$ or small ratios of $l/h$. For high precompression and large aspect ratios, the theoretical predictions and the experimental results differ, but they are still well within a factor of two.

**Figure 7.5.** Elastic instability prior to the leak. (a) For a seal of low precompression ($\varepsilon = 10\%, l/h = 6.7$), prior to the leak, the edge of the hydrogel is nearly straight. (b) For a seal of moderate precompression ($\varepsilon = 30\%$) and a relatively small aspect ratio ($l/h = 2.2$), prior to the leak, the straight edge of the hydrogel becomes unstable and forms a wavy shape. (c) For a seal of high precompression ($\varepsilon = 37\%$) and a relatively large aspect ratio ($l/h = 4.4$), prior to the leak, the straight edge of the hydrogel becomes unstable but does not form a wavy shape.
The precise cause for the deviation between the theory and experiment is uncertain. One likely cause is the relaxation of the hydrogel. Prior to the injection of fluid, the hydrogel is in a state of precompression, and is stored for four hours to reach adequate adhesion. During this period, the contact stress due to precompression relaxes somewhat (Figure B.6). How this relaxation affects critical fluid pressure is a complex question, which we do not pursue here. Another likely cause is elastic instability prior to the leak. In a few cases, before the seal leaks, we observe that the straight edge of the hydrogel becomes unstable and forms a wavy shape (Figure 7.5b, Movie B.3). In some other cases, the pre-leak instability does not form waves, possibly because the ratio $w/l$ is too small (Figure 7.5c, Movie B.4). The pre-leak instability violates the assumption of the plane strain conditions, and conceivably lowers the critical fluid pressure for elastic leak. However, our simulation based on the plane strain conditions gives good prediction for some cases where instability is observed. For example, for the case of distinct fingering instability (Figure 5b, $ε = 30\%$, $l/h = 2.2$), the theoretical prediction agrees well with the experimentally measured critical pressure for elastic leak (Figure 7.4e). A wavelike instability has been studied recently for hydrogels bonded between two rigid walls [138-140], but the effect of this instability on elastic leak has not been studied.

7.5 Discussion.

Elastic deformation is of central significance to the leak of seals. For instance, in oilfields elastomers are widely used to block fluids, e.g., for testing rocks [141], completing boreholes [142], and preparing boreholes for multi-stage hydraulic fracture [124]. In contrast to many other applications, the sealing conditions in oilfields cannot be fully determined before operation. Seals may be insufficiently constrained due to the uncertainty of the sizes of boreholes, unexpected damage of the gauge rings, and
insufficient swelling of the elastomers [143]. Such seals can leak without appreciable
damage of the elastomer [144].

Even for seals subject to high constraint, where failure is commonly attributed to
the damage of elastomers [121, 145], damage by itself often does not create a leaking path.
Rather, damage is a precursor for leak, lowering the constraint, allowing the seal to
undergo excessive elastic deformation. Examples include fracture and abrasion of the
elastomer, and debonding between the elastomer and the rigid walls. After a certain
amount of damage, the seal leaks by the elastic deformation of the leftover material. In
some cases over 50% of the material is lost before the seal leaks [132]. A seal can also fail
because the properties of elastomer change with time. The elastomer may become brittle
due to aging, or soften because crosslinks break down, or develop irreversible
deformation due to the formation of crosslinks under heat and chemical attack, or swell
in the presence of solvent [121]. In most cases, a seal still leaks by forming a leaking path
in the contact with the hard materials. That is, elastic leak follows degradation.

In summary, we study elastic leak, a mode of failure in which seals leak by elastic
deformation without any material damage. We design an experiment to watch seals
deform and leak, and compare experimental observations with theoretical predictions.
We find that the critical fluid pressure for elastic leak depends on the geometry and
constraint of the seal, but not on the rate at which the fluid is injected. Our study points
to the significance of elastic deformation in modes of failure that also involve material
damage.
Chapter 8.

Elastic leak of a seal series

8.1 High pressure sealing in oil and gas industry

This chapter studies the mechanics of elastomeric seals in series. We demonstrate the fundamental significance of elastic leak in achieving high sealing capacity. The findings will have direct impact on the design of seals for applications under extreme conditions, such as seals used in hydraulic fracture. Seals are among the most significant applications of elastomers. Elastomeric seals have the advantages such as large sealing range, low cost, light weight and easy to manufacture. As a result, they are widely used in everyday life (e.g., plumbing joint, drinking bottle and pressure cooker) and various industrial applications (e.g., engine, pressure pump and packers).

We are particularly interested in the elastomeric seals (i.e., packers) used in oil and gas industry to block fluids of high pressure. Applications include water shut-off, inflow control, and multistage hydraulic fracture[123-126, 146]. It is now widely appreciated that hydraulic fracture is principally responsible for the boom in shale gas exploitation[147]. The essential parts of a packer are one or more elastomeric elements (individual seals), bonded around a metallic pipe, and protected at the ends by metallic gauge rings (Figure 1a, b). The elastomeric elements are either deformed by mechanical mechanisms[146] (e.g., mechanical packer), or swollen by imbibing fluids[94, 148, 149] (e.g., swellable packer). The elastomeric elements seal the gap between the pipe and the wellbore, and prevent the fluid from flowing from a zone of high pressure to a zone of low pressure. The difference in the pressures between the zones is called the differential pressure. The maximum differential pressure that a packer can seal defines its sealing capability. With the increase of hydraulic pressure used in fracturing a reservoir, the
sealing capability of packers also needs to be increased, i.e., the swellable packer needs to seal a differential pressure about 70 MPa during the fracture job[144]. (Recall that the elastic modulus of an elastomer is on the order of 1 MPa.)

To increase the sealing capability, one approach is to increase the length of elastomeric element, referred to as the continuous design (Figure 1a)[126, 150]. The other approach is to space several elements along the length, referred to as the spaced design (Figure 8.1b). Relative to the continuous design, the spaced design has advantages such as low cost of manufacture, easy transport, and low risk for downhole operation. When the downhole fluid filled between elements is nearly incompressible, e.g., water, the differential pressure is distributed to each element. In that case, the spaced design is anticipated to seal larger differential pressure than the continuous design, since more gauge rings are used to constrain the deformation of elastomer. When the downhole fluid is highly compressible, e.g., nature gas or oil/gas mixture[151, 152], external load may fail to transfer from the front element to sequential elements. As a result, the elements are damaged sequentially. For example, Nijhof et al[144] observed that with two swellable packers spaced along the pipeline, the differential pressure is mainly applied on the first element. When the differential pressure reached a critical value, the two elements were damaged one by one.

8.2 Elastic leak of a seal series

We have discussed elastic leak in the last chapter. Here we show that elastic leak is essential for the spaced design to achieve high sealing capacity when fluid in the spaces between them is compressible (Figures 8.1c-f). Initially, the space between the two sealing elements is filled with water/air mixture (Figure 8.1c). With the increasing of the external pressure $P_1$, the pressure in the middle chamber $P_2$ is nearly unchanged, because the initial change of pressure in air is negligible (Figure 8.1f). The external load is mainly
applied on the first element, which deforms. The second element, however, is nearly undeformed. When the differential pressure, $P_1 - P_2$, reaches a critical value, the first element loses the contact with wellbore in some regions, forming a very thin leaking path (Figure 8.1d). This leak, which we call elastic leak, is due to the elastic deformation of the elastomer and no material damage is involved. With water fully filling the middle region, differential pressure becomes evenly distributed to the two elements (Figure 8.1e). As a result, $P_2$, increases in association with the increase of $P_1$ (Figure 8.1f). These two spaced elements remain sealing until the fluid pressure $P_1$ reaches a higher critical value. (Figure 8.1f). With more elements spaced along the pipeline, the critical leaking pressure will be higher. In addition, the leaking path can be sealed whenever $P_1$ drops below the critical value since elastic leak is reversible. In contrast, $P_2$ will be identical to $P_1$ after the damage of the first element if the leak is due to material damage. Then the elements will fail sequentially and the critical leaking pressure cannot be increased by increasing the number of elements.

In this chapter, we modify the desktop experimental setup introduced in the last chapter to demonstrate that the spaced design seals larger fluid pressure than continuous design. We further show that when air (highly compressible) filled between elements, spaced sealing design is functional when elements leak elastically, and fails when elements leak due to material damage.
Figure 8.1. Elastic leak of individual seals amplifies the collective sealing capacity of multiple seals. (a) Schematic of a continuous sealing design. (b) Schematic of a spaced sealing design. (c) After sealing, the spaces between sealing elements are partially filled with water. The first element deforms under the external pressure $P_1$, but the second element is nearly undeformed. (d) As $P_1$ reaches a critical value, the first element leaks elastically and the water fills the space between elements. (e) After water fully fills the space between the two elements, both elements deform and resist the differential pressure collectively. (f) The fluid pressures $P_1$ and $P_2$ as functions of time in the process (c)-(e).

Our experimental setup uses a hydrogel as the sealing element (Figure 8.2). The low elastic modulus of the hydrogel allows us to perform the experiments at relatively low fluid pressure, on desktop. The transparency of the setup allows us to watch
deformation, leak and recovery in situ. We synthesize polyacrylamide hydrogel using the free-radical method[153]. Two identical blocks of the hydrogel, of the dimensions \( l, w \) and \( h \) in the undeformed state, are glued parallel to a glass sheet and an acrylic spacer (Figure 8.2a). We use acrylic steps with the height \( t \) to represent the effect of gauge rings and constrain the extrusion of sealing elements. Two steps are glued to the base glass sheet and in contact with the front side of hydrogel blocks. A transparent acrylic sheet of thickness \( \Delta h \) and width \( w \) is glued to the cover glass sheet. When the cover glass sheet is glued on the top of the spacer, the hydrogel is compressed with a strain \( \varepsilon = \Delta h/h \) (Figure 8.2b). No adhesive is applied between the cover glass sheet and hydrogel. The glass, spacer and hydrogels form two closed chambers. We use a syringe pump to inject water into the first chamber at a constant rate and measure the pressures in the first and second chambers using two separate pressure gauges. The second chamber is either filled with water or air to mimic nearly incompressible or highly compressible downhole fluid. A digital camera is used to monitor the movement of hydrogels (colored red) and water (colored blue). For comparison, we also replace two sealing elements in this setup with one sealing element with the dimensions \( 2l, w \) and \( h \) (Figure 8.2c).
Figure 8.2. Experimental setup. (a) Two blocks of a hydrogel, of dimensions $h$, $l$ and $w$ in the undeformed state, are glued to a sheet of glass and to an acrylic spacer. Two acrylic steps with height $t$ are glued to the base glass sheet and in contact with the front side of hydrogel blocks. An acrylic sheet of thickness $\Delta h$ is attached to the cover glass sheet. (b) When the cover glass sheet is glued to the spacer, the hydrogel is precompressed with a displacement $\Delta h$. The glass, spacer and hydrogels define two closed chambers. The first chamber connects to a syringe pump and a pressure gauge, and the second chamber connects to another pressure gauge. (c) For comparison, in the other setup, a hydrogel of dimensions $h$, $2l$ and $w$ in the undeformed state, is used.
First, we compare spaced and continuous sealing designs for an identical total length of sealing elements. In this case, water as a representative nearly-incompressible fluid is fully filled in regions between two sealing elements before loading. Associated with the syringe pump injecting water into the first chamber, the fluid pressure measured by gauges in spaced and continuous designs are plotted in Figure 8.3a and Figure 8.3b, respectively, and the snapshots for elements deforming and leaking are plotted in Figure 8.3c and Figure 8.3d, respectively. With water filled between elements, the fluid pressures in the first and second chamber, $P_1$ and $P_2$, respectively, increase simultaneously (Figure 8.3a), which indicates that the external load is distributed to both sealing elements. When $P_1$ reaches 64kPa and $P_2$ reaches 30kPa, both elements leak (Figure 8.3c). This observation demonstrates that both elements leak at the same differential pressure about 30kPa. For comparison, we measure the leak pressure of one continuous sealing element with the length doubled and other dimensions identical to the spaced sealing element (Figure 8.3b and 8.3d). With the same total length, this continuous block leaks at 46kPa, about 30% lower than the spaced design (Figure 8.3b). This difference is due to the extra step used in spaced design that can constrain the deformation of elastomer element.
Figure 8.3. Comparison between spaced and continuous sealing designs. In the spaced sealing design, two hydrogels (crosslinker (wt%) = 0.06%, water (wt%) = 88%) with dimensions of \( l = 15.00 \text{ mm} \), \( h = 6.00 \text{ mm} \), and \( w = 120.00 \text{ mm} \), is precompressed with a displacement \( \Delta h = 0.80 \text{ mm} \), i.e., \( \varepsilon = 13.3\% \). The height of the steps \( t = 2.60 \text{ mm} \). The two chambers are filled with water before loading. The syringe pump injects water at a constant rate of 2 ml/min until the seals leak steadily. In the continuous design, all the conditions are identical to spaced design except the sealing element becomes a continuous block with the dimensions \( 2l \times h \times w \). (a) The fluid pressures as functions of time for spaced design. (b) The fluid pressure as a function of time for continuous design. (c) and (d) show the snapshots of the seals at the unpressurized state and leaking state corresponding to (a) and (b), respectively.

Next, we show that elastic leak enables the spaced sealing design to function even when fluid filled between elements is highly compressible. We trap air in the second chamber initially. With the increase of \( P_1 \), \( P_2 \) is nearly zero at the beginning and slightly increased, which is caused by the compression of air in the second chamber (Figure 8.4a).
As a result, the first element undergoes large deformation while the second element is nearly undeformed (snapshot 1 in Figure 8.4b). Without water filled between elements, the external load cannot be evenly distributed among elements. When $P_1$ reaches 38.3kPa, the first element leaks elastically while the second element still seals (Figure 8.4a). With more water filled in the second chamber, the external load has distributed to two sealing elements, i.e., the increase of $P_2$ is proportional to the increase of $P_1$ (Figure 8.4a) and both sealing elements deform in this stage (snapshot 2 in Figure 8.4b). A nearly constant pressure difference between $P_1$ and $P_2$ is observed in this stage. This is consistent with our observations in the last chapter that upon elastic leak, the differential pressure applied on the elastomer is nearly a constant. In other words, the first element can carry a certain amount of differential pressure while the element is leaking. This behavior differentiates elastic leak and damaged leak. When $P_1$ increases to critical pressure 49.9 kPa, both elements leak. Both $P_1$ and $P_2$ reach a plateau after a precipitous drop (Figure 8.4a). The trapped air is expelled and replaced by injected water (snapshot 3 in Figure 8.4b).

These experimental results broadly confirm the mechanism illustrated in Figure 8.1. The difference between experiments and simplified mechanism is due to the effect of air pressure change in the second chamber, which is neglected in the idealized analysis. The fluid pressure applied on the first chamber is on the same order of magnitude of air pressure since the hydrogel blocks used in this experiment is relatively soft. (The modulus of the hydrogel is on the order of 1 kPa.) Therefore, the effect of air pressure is non-negligible. We anticipate the effect of air pressure will be less significant when elastomer is stiffer, e.g., the modulus for elastomer used in real application is on the order of 1 to 10MPa. The corresponding pressure-time curve will be closer to Figure 8.1f.
Figure 8.4. Spaced sealing design with air filled between elements before loading. Two blocks of a hydrogel with the identical dimensions to the previous test are precompressed with a displacement of $\Delta h = 0.75$ mm, i.e., $\varepsilon = 12.5\%$. The height of steps $t = 2.57$ mm. The syringe pump injects water at a constant rate of 2 ml/min. (a) The fluid pressures in the first and second chambers as functions of time. (b) Three snapshots of the seals corresponding to the states marked in the pressure-time curves in (a).

8.3 Damaged leak of a seal series

For comparison, we change the material of sealing element to be a relatively brittle hydrogel to study the consequence of damaged leak. In this mode of leak, the seal suffers material damage, and does not regain sealing capacity after leak. The second chamber is set to be empty of water before loading. The pressure-time curve for the first stage, where both elements seal, is similar to Figure 8.4a. Because the hydrogel is brittle, the seal leaks by forming a crack (snapshot 1 in Figure 8.5b). After this damaged leak, the seal cannot sustain any differential pressure, i.e., $P_1$ and $P_2$ are nearly identical after the first element leaks (Figure 8.5a). Consequently, the fluid pressure is entirely applied on the second element, which fails subsequently (snapshot 2 in Figure 8.5b). Consequently,
if individual seals suffer damaged leak, the critical leaking pressure cannot be increased by increasing the number of sealing elements. Our experiments demonstrate the central significance of elastic leak to achieving high sealing capacity of the spaced design.

Figure 8.5. The spaced hydrogels fail sequentially by material damage. Two blocks of a hydrogel (crosslinker (wt%) = 0.3%, water (wt%) = 92%) with dimensions of \( h = 6.00 \) mm, \( l = 15.00 \) mm and \( w = 120.00 \) mm, are precompressed with a displacement \( \Delta h = 1.50 \) mm, i.e., \( \varepsilon = 25\% \). The height of steps \( t = 3.00 \) mm. The syringe pump injects water at a constant rate of 5 ml/min until both the hydrogels fails. The high concentration of crosslinks makes the hydrogel brittle, so that the individual seal leaks by forming cracks.

(a) The fluid pressures in the first and second chambers as functions of time. (b) Two snapshots of the seals corresponding to states marked in the pressure-time curves in (a). (c) Schematic of sequential failing of spaced seals by material damage.
In conclusion, we use a desktop experimental setup to observe seals to deform and leak, and compare the spaced and continuous design. We find that with water between elements, spaced design can seal larger differential pressure than continuous design. We also study the case when air is filled between spaced elements before loading. We find that elastic leak enables the differential pressure to distribute to two spaced elements. By contrast, when seals leak by material damage, the differential pressure cannot be distributed and elements are damaged sequentially. The elastic leak of individual seals amplifies collective sealing capability of serial seals.
Chapter 9.

Summary

In this dissertation, we have looked at different aspects of the soft materials, including the viscosity, diffusivity, solubility, capillarity, elasticity, osmosis and compressibility. Although each aspect could be described by a relatively simple law, the combination different aspects constitute the extremely rich mechanics and physics of soft materials. In chapter 2 and 3 we focused on the coupling between viscosity and diffusivity. In chapter 4 we looked at the interaction between solubility and viscosity. In chapter 5 we looked at the competition between capillarity and elasticity. In chapter 6 studied the competition between capillarity and osmosis. In chapter 7 and 8 we studied the effect of elasticity and compressibility. There are certainly more aspects of soft materials that brings interesting mechanics and physics, like the electricity in dielectric elastomer [154], the magnetism in magnetorheological materials [155], the anisotropy in liquid crystal elastomers [156]. In principle, the coupling between any two of the above aspects can lead to interesting problems.

Potential applications of these problems are also rich. The elastomeric seal as discussed in the last two chapters is a well established example. The study of the influence of osmocapillary phase separation on adhesion has also emerged [100]. Crease is important in the morphology generation in many biological systems [71-73] and has potential engineering applications [74-78]. The idea of coupled diffusion and viscous flow has been applied in the design of lead-free solder [44] and Li-ion batteries [65]. It may also be important in the study of biological cells. Since both viscoelasticity and poroelasticity are known to be important in the cell mechanics [14, 157], a time and length scale where poroviscosity dominates seems unavoidable.
The mechanics and physics of soft materials are rich and important. It is hoped that this dissertation offers insight into a few fundamental problems and that the methodology used here may be generalized to other problems.
Appendix A. Supporting information for Chapter 5

A.1 Basic theory of elastocapillarity

Consider a body in three dimensions. When the body is in the reference state, a material particle occupies a place whose coordinate is \(X\). When the body deforms to the current state, and the material particle \(X\) moves to a place whose coordinate is \(x\). The deformation of the body is described by the mapping

\[
x = x(X).
\]

(A.1)

The domain of this function is the coordinates of material particles when the body is in the reference state. The range of this function is the coordinates of the places occupied by the material particles. Deformation gradient is given by

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

(A.2)

The field \(F(X)\) is the gradient of the field of deformation \(x(X)\). If the body is made of binary mixture, the composition at any location is specified by the concentration of the solute \(c(x)\). \(c(x)\) is defined as the number of solute molecules per unit current volume. Correspondingly, we could define the nominal concentration of the solute \(C(X)\) as the number of the solute molecules per unit reference volume, and the following relation holds:

\[
C(X) = c(x) \det(F)
\]

(A.3)

Consider a body of single phase in a binary mixture undergoes an inhomogeneous deformation. The free energy of the body is given by

\[
\int W(F, C) dV + \int \gamma(F, C, C') da.
\]

(A.4)
Here $dV$ is a volume element in the reference state while $da$ is an area element on in the current state. $W$ is the free energy of the bulk material per unit reference volume and $\gamma$ is the interfacial energy per unit current area. In general, the interfacial energy may depend on the composition of the bulk material on both sides of the interface. Here $C'$ denotes the concentration in contact with the surface outside the body. In addition, when a piece of material is deformed, the structure and composition of its surface may also change. Consequently, $\gamma$ would depend on the deformation gradient $\mathbf{F}$ as well.

For a pure liquid in contact with gas, when a new surface area is created, molecules from the bulk merge onto the surface. The structure and composition of the surface remain the same. As a result, $\gamma$ is a constant. For most gels the crosslink density is low so that individual chains largely preserve their configuration in a liquid state [8]. The liquid-like property has manifested itself in many different aspects, including the Neo-Hookean elasticity [158], the success of using Flory-Huggins solution model to predict the swelling of gel [159] and the liquid-like dielectric behavior in elastomers [160]. We thus expect the surface energy of a gel to have liquid-like behavior as well. In the following discussion, we will take $\gamma$ as a constant.

Consider a piece of hydrogel in air with applied surface traction. At equilibrium, the first order variation of the free energy of the whole system needs to vanish,

$$
\int \delta W dV + \gamma \delta a = \int T_i \delta x_i dA.
$$

(A.5)

Here $\delta a$ denotes the total variation of the interfacial area between hydrogel and air. $T_i$ is the $i$-th component of the traction per unit reference area. $dA$ is the area element in the reference configuration. For a continuous and smooth surface, the following geometric relation holds:

$$
\delta a = \int K n_i \delta x_i da.
$$

(A.6)
Here $K$ is the mean curvature related to the principal radii of the surface:

$$K = \frac{1}{R_1} + \frac{1}{R_2}, \quad (A.7)$$

and the curvature can be calculated from the current shape of the surface. The surface between hydrogel and air may not be continuous with respect to surface of the hydrogel if there is self-contact. The surface may not be smooth if there is a triple junction. Here we assume none of those situations happen.

Recall that the nominal stress and deformation gradient are work-conjugate,

$$\delta W = s_{ik} \delta F_{ik}. \quad (A.8)$$

Also recall the relation between the nominal stress and the true stress

$$\sigma_{ij} = s_{ik} F_{jk} / J, \quad (A.9)$$

and the relation between the areas in the reference state and the current state,

$$F_{ik} n_i da = J N_k dA. \quad (A.10)$$

We write

$$\int \delta W dV = \int s_{ik} \delta F_{ik} dV = \int s_{ik} \delta x_{i,k} dV$$

$$= \int \left[ (s_{ik} \delta x_i)_{,k} - s_{ik,k} \delta x_i \right] dV$$

$$= \int s_{ik} N_k \delta x_i da - \int s_{ik,k} \delta x_i dV$$

$$= \int \sigma_{ij} n_j \delta x_i da - \int s_{ik,k} \delta x_i dV \quad (A.11)$$

Now with (A.5) and (A.11), (A.4) could be rewritten as:

$$-\int s_{ik,k} \delta x_i dV + \int \left[ (\sigma_{ij} + \gamma K \delta_{ij}) n_j - t_i \right] \delta x_i da = 0. \quad (A.12)$$

The condition of equilibrium holds for arbitrary changes of the field of deformation, $\delta x_i$.

Consequently, the above condition of equilibrium is equivalent to

$$s_{ik,k} = 0 \quad (A.13)$$

in the interior of the body, and
on the surface of the body.

A.2 Linear perturbation for the critical strain of wrinkle

Since the deswelling of the hydrogel during the experiment is negligible, we model the hydrogel as an incompressible Neo-Hookean material. The free energy of the material per reference volume is:

$$ W(F) = \frac{\mu}{2} F_{ik} F_{ik} \cdot $$  \hspace{1cm} (A.15)

The nominal stress is:

$$ s_{ik} = \mu F_{ik} - \Pi H_{ik} \cdot $$  \hspace{1cm} (A.16)

Here $H_{ik} = \partial \det(F) / \partial F_{ik}$. $\Pi$ is the hydrostatic pressure. Due to the assumption of incompressibility, $\Pi$ is prescribed from force balance and the boundary condition but not from the constitutive model. The variation of the stress is:

$$ \delta s_{ik} = \mu \delta F_{ik} - \delta \Pi H_{ik} + \Pi \delta H_{ik} \delta F_{ik} \cdot $$  \hspace{1cm} (A.17)

The force balance requires:

$$ \delta F_{ik} = 0 \cdot $$  \hspace{1cm} (A.18)

The incompressibility requires:

$$ H_{ik} \delta F_{ik} = 0 \cdot $$  \hspace{1cm} (A.19)

(18) and (19) constitute a complete set of equations for $\delta x, \delta \Pi$.

Consider a chunk of hydrogel bounded on the substrate as shown in Figure A.1. At the free surface ($X_2 = 0$), the tangent traction should vanish. The normal traction should equate the Laplace pressure $\gamma K$. 

\[ \left( \sigma_{ij} + \gamma K \delta_{ij} \right) n_j = t_i \]  \hspace{1cm} (A.14)
At the bounded surface \((X_2 = H)\), the perturbed displacement should vanish:

\[
\begin{cases}
\delta x_1 = 0 \\
\delta x_2 = 0
\end{cases}
\]

(A.21)

(18-21) constitutes a complete boundary value problem which a valid perturbation field should satisfy.

**Figure A.1.** Consider a piece of elastomer compressed under generalized plane strain condition. The hydrogel has a free surface on one side and is bounded at the other side. Set up a Cartesian reference system with \(X_1\) along the surface of the hydrogel and \(X_2\) pointing from the free surface towards the bounded surface. The bounded surface locates at \(X_2 = H\), where \(H\) is the thickness of the hydrogel in the reference configuration.

Consider the generalized plane strain condition with unperturbed deformation gradient

\[
\mathbf{F} = \begin{bmatrix}
\lambda_1 \\
\left(\lambda_1 \lambda_3\right)^{-1} \\
\lambda_3
\end{bmatrix}
\]

(A.22)

and assume the perturbed field to be
The variational stress under these assumptions is:

\[ \begin{align*}
\delta s_{11} &= \mu \left(1 + \lambda_1^{-2} \lambda_3^{-2}\right) \delta x_{1,1} - \delta \Pi \left(\lambda_1\right)^{-1} \\
\delta s_{12} &= \mu \delta x_{1,2} + \mu \lambda_1^{-2} \lambda_3^{-1} \delta x_{2,1} \\
\delta s_{21} &= \mu \delta x_{2,1} + \mu \lambda_1^{-2} \lambda_3^{-1} \delta x_{1,2} \\
\delta s_{22} &= 2 \mu \delta x_{2,2} - \delta \Pi \lambda_1 \lambda_3
\end{align*} \]  

(A.24)

with the rest of the stress components vanish. Assume:

\[ \begin{align*}
\delta x_1 &= A \exp(kX) \cos \omega X \\
\delta x_2 &= B \exp(kX) \sin \omega X \\
\delta \Pi &= C \exp(kX) \sin \omega X
\end{align*} \]  

(A.25)

Plugging into the governing equations (18) and (19) we have:

\[ \begin{bmatrix}
\mu k^2 - \mu \left(1 + \frac{1}{\lambda_1^4 \lambda_3^2}\right) \omega^2 & \frac{\mu \omega k}{\lambda_1^2 \lambda_3} & -\frac{\omega}{\lambda_1} \\
-\frac{\mu \omega k}{\lambda_1^2 \lambda_3} & 2 \mu k^2 - \mu \omega^2 & -\lambda_1 \lambda_3 k \\
-\frac{\omega}{\lambda_1} & \lambda_1 \lambda_3 k & 0
\end{bmatrix} \begin{bmatrix}
A \\
B \\
C
\end{bmatrix} = 0 \]  

(A.26)

To have non-trivial solution we require the determinant of the coefficient matrix to vanish, which gives:

\[ \lambda_1^4 \lambda_3^2 k^4 - \left(1 + \lambda_1^4 \lambda_3^2\right) \omega^2 k^2 + \omega^4 = 0. \]  

(A.27)

The roots are \(k_1 = \omega, k_2 = -\omega, k_3 = \frac{\omega}{\lambda_1^2 \lambda_3}, k_4 = -\frac{\omega}{\lambda_1^2 \lambda_3}\). So the general solution can be expressed in the following form:
\[
\begin{bmatrix}
\delta x_1 & \delta x_2 & \delta \Pi
\end{bmatrix} =
\begin{bmatrix}
\cos \omega X_1 & \sin \omega X_1 & \sin \omega X_1
\end{bmatrix}
\begin{bmatrix}
\sum_i A_i \exp(k_i X_2) \\
\sum_i B_i \exp(k_i X_2) \\
\sum_i C_i \exp(k_i X_2)
\end{bmatrix}.
\] (A.28)

The general solution need to satisfy the governing equations (18) and (19) at every point in the field. As a result, coefficients \( A_i, B_i, C_i \) are constrained by the following condition:

\[
\begin{bmatrix}
A_i \\
B_i \\
C_i
\end{bmatrix} = B_i
\begin{bmatrix}
\frac{\lambda_1^2 \lambda_3 k}{\omega_i} \\
1 \\
\mu(k_i^2 - \omega^2)
\end{bmatrix}
\] (A.29)

Transform the boundary condition at \( X_2 = 0 \) (20) to the reference state:

\[
\begin{cases}
\delta s_{12} = 0 \\
\delta s_{22} = -\gamma \delta x_{2,1} \lambda_3 / \lambda_1
\end{cases}
\] (A.30)

Plug (28) and (29) into (21) and (30), we have the following coefficient matrix:

\[
\begin{bmatrix}
\lambda_1^4 \lambda_3^2 + 1 & \lambda_1^4 \lambda_3^2 + 1 & 2 \\
2 - \frac{\lambda_3 \gamma}{\lambda_1 \mu H} & -2 - \frac{\lambda_3 \gamma}{\lambda_1 \mu H} & -\frac{\lambda_3 \gamma}{\lambda_1 \mu H} \\
\lambda_1^2 \lambda_3 \exp(\bar{\omega}) & -\lambda_1^2 \lambda_3 \exp(-\bar{\omega}) & \exp\left(\frac{\bar{\omega}}{\lambda_1^2 \lambda_3}\right) - \exp\left(-\frac{\bar{\omega}}{\lambda_1^2 \lambda_3}\right)
\end{bmatrix}
\] (A.31)

Here \( \bar{\omega} = \omega H = \frac{2\pi}{H} / L \). To have non-trivial solution, the determinant of this matrix needs to vanish as well. Given \( \lambda_1, L \), this determines the critical \( \lambda_2 \).
A.3 Finite element simulation

Physically, interface is a thin layer of material of which the free energy density is different from the bulk. In finite element simulation, this could be represented by attaching a layer of shell element at the boundary of the bulk material. The material model of the shell element should reflect the free energy density of the surface.

In the case of constant surface tension $\gamma$, the effect of interfacial tension can be easily imitated by linear elastic shell, which is widely available in commercial finite element packages. To ensure that $\gamma$ is independent of deformation, we require the stress and the cross section of the section both to be constant. That means, the shear modulus, $\mu << \gamma$, and the Poisson’s ratio $\nu = 0$. The finite value of the surface tension could be achieved by prescribe a finite residue stress.

We simulated the postbuckling behavior of our model system (the green part of Figure A.1) using commercial finite element software ABAQUS. The simulation is done under plane strain condition. A rectangular area of Neo-Hookean material is created to represente the sample. A layer of beam element is bonded to the top boundary of the sample to imitate surface tension. The bottom of the sample is prescribed to be flat. A linear horizontal displacement field corresponding to the compression is applied. This imitates the effect of loading by a stiff substrate. For each $\gamma / \mu H$, the width of one half of the optimal wavelength for wrinkle is simulated. The left and right boundaries are prescribed to remain vertical. The material can slide up and down. The top-left corner of the sample is finely meshed so that the element size is at least one order of magnitude small than $\gamma / \mu$.

During the simulation, the material is first compressed above the critical strain of wrinkle. Since the initial surface is perfectly flat, the bifurcation point will not cause any problem in the simulation. Then the top-left corner is pulled downward with
displacement control. The displacement control is relaxed in the next step. The configuration is automatically relaxed towards the stable path. In the final step, Riks method is used to track the post-buckling path all the way to the bifurcation point.

A.4 Experimental method

The polyurethane (F-105, BJB enterprises) was used for the mounting layer of experiments. F-105A and F-105B were mixed with the ratio of 1:1, followed by degasing until bubbles disappeared. The degased sample was put at room temperature for 1 four and then in the oven around 70 °C over 16 h to fully cure it. Only for the stiff gels with shear modulus over 1000 Pa, PU mounting layer was further treated with methacryloxypropyltrichlorosilane (Gelest) at 70 °C overnight to make double bodings for the good adhesion to a hydrogel. The PAAm hydrogel was synthesized between a glass coverslip and the PU mounting later. The glass coverslip was washed in water, ethanol (PHARMCO-AAPER), and aceton (Fisher Scientific) with sonicator, followed by the oxygen plasma treatment for 15 min. Then, it was treated with 200 µl (tridecafluoro-1,1,2,2-tetrahydrooctyl)dimethylchlorosilane (Gelest) over 70 °C overnight for the clean detachment from the gel. The aqueous pre-gel solution was made with the different concentrations of acrylamide (Sigma-Aldrich) (AAm), bisacrylamide (Research Organics) (BisAAm) and 2.5 v/v% of 3.4 wt% photo initiator VA-086 (Wako Pure Chemical Industries, Ltd.) aqueous solution, and deionized water to tune the shear modulus: from the stiffest sample 7.7 w/v% crosslink 1.9 mol% (AAm 1043 mM and BisAAm 20.2 mM), 5.2 w/v% crosslink 2.9 mol% (AAm 681 mM and BisAAm 19.8 mM), 5.2 w/v% crosslink 0.48 mol% (AAm 718 mM and BisAAm 3.48 mM), 5.2 w/v% crosslink 0.29 mol% (AAm 721 mM and BisAAm 2.10 mM), and 5.2 w/v% crosslink 0.19 mol% (AAm 722 mM and BisAAm 1.40 mM). The shear modulus ranging from ~150 Pa to ~7800 Pa, one and half order difference, was achieved (Figure A.3 and Table A.1). The aqueous pre-gel solution
was degassed, followed by nitrogen backfill. Then the pre-gel solution was filtered with 0.45 µm pore size filter. After putting the solution inside a glove box filled with nitrogen for 30 min, it was injected between the glass slide and the stretched mounting layer with 1 mm glass slide spacers in the glove box filled with nitrogen, then exposed by UV light with wavelength of 365 nm for 20 min. The surface tension of each pre-gel solution was measured by the custom made tensiometer. Elastocapillary length (\( \gamma / \mu \)) and elastocapillary number (\( \gamma / \mu H \)) were calculated with the measured shear modulus and surface tension (Table A.1).

**Figure A.2.** Experimental setup and procedure: (a) stretching PU substrate, (b) synthesis of PAAm gel on the mounting layer, (c) compressing PAAm gel by releasing strain, and (d) experimental setup of high speed camera, humidity chamber, and motor controlled compression machine. The strain \( \varepsilon \) is calculated as \( \varepsilon = 1 - l / L \).
Figure A.3. The rheological measurements of PAAm gel with different concentrations and crosslink densities.

Table A.1. Sample properties

<table>
<thead>
<tr>
<th>PAAm gel concentration</th>
<th>7.7 w/v% crosslink 1.9 mol%</th>
<th>5.2 w/v% crosslink 2.9 mol%</th>
<th>5.2 w/v% crosslink 0.48 mol%</th>
<th>5.2 w/v% crosslink 0.29 mol%</th>
<th>5.2 w/v% crosslink 0.19 mol%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shear modulus (Pa)</td>
<td>7825 ± 338</td>
<td>1910 ± 38</td>
<td>580 ± 25</td>
<td>297 ± 12</td>
<td>156 ± 7</td>
</tr>
<tr>
<td>Surface tension (mN/m)</td>
<td>63.38 ± 0.59</td>
<td>64.81 ± 1.00</td>
<td>66.38 ± 0.81</td>
<td>65.50 ± 0.72</td>
<td>65.30 ± 0.67</td>
</tr>
<tr>
<td>Elastocapillary length (mm)</td>
<td>0.0081 ± 0.0004</td>
<td>0.0339 ± 0.0008</td>
<td>0.113 ± 0.005</td>
<td>0.217 ± 0.009</td>
<td>0.419 ± 0.02</td>
</tr>
<tr>
<td>Elastocapillary number</td>
<td>0.0081 ± 0.0004</td>
<td>0.0339 ± 0.0008</td>
<td>0.113 ± 0.005</td>
<td>0.217 ± 0.009</td>
<td>0.419 ± 0.02</td>
</tr>
</tbody>
</table>
**Figure A.4.** The weight change of PAAm gels with different concentrations and crosslink densities at 79 %RH.

**Figure A.5.** The nucleation strain shows no correlation with the strain rate.
Appendix B. Supporting information for Chapter 7

B.1 Experimental setup

We synthesize polyacrylamide hydrogel using the free-radical method. Acrylamide (AAM), N,N’-methylenebis(acrylamide) (MBAA), ammonium persulfate (APS) and N,N,N’,N’-tetramethylethylenediamine (TEMED) are acquired from Sigma Aldrich. We dissolve powder of AAM in deionized water with the weight fraction of AAM fixed at 0.12 that of the aqueous solution. We add MBAA (at 0.0006 the weight of AAM) as the crosslinker, TEMED (at 0.0025 the weight of AAM) as the crosslinker accelerator, and APS (at 0.0085 the weight of AAM) as initiator for free-radical polymerization. We color the hydrogel in red using a food dye (Shank’s Extracts, acquired from VWR International LLC.), at 0.002 the volume of aqueous solution. We pour the solution into plastic molds to form rectangular samples. After gelation, the samples are stored at room temperature for 1 day to complete polymerization. We glue the hydrogel to acrylic spacers and the glass using superglue (Loctite® Instant-Bonding Adhesive 409, acquired from McMaster-CARR). We store the sealed setup in a humid box for 4 hours to reach sufficient adhesion. We color water in blue using a food dye (Shank’s Extracts, acquired from VWR International LLC.).

The experimental setup consists of a seal device, a syringe, a pressure gauge, an Instron machine, and a camera. The chamber (blue part) in the seal device is connected to the syringe and pressure gauge by plastic tubes (Figure B.1). In experiment, the Instron machine compresses the syringe at a constant velocity to provide a constant rate of injection. The pressure gauge records the fluid pressure inside the chamber, and the camera monitors the movement of hydrogel and fluid.
Figure B.1. A photo of the experimental setup.

B.2 Pressure-injection diagram with hysteresis

In our experimental setup, some friction exists between the hydrogel and the cover glass. As the fluid pressure increases, in addition to the elasticity of the hydrogel, friction also resists the deformation. Consequently, the real loading curve will be higher than the elastic loading curve. After the leaking path is formed, the deformation stops and friction disappears. The resistance of the fluid itself is negligible in our experiment, and the behavior of the system is fully predicted by the elastic leak model. During recovering and reloading, friction will kick in and cause hysteresis. In principle the hysteretic loop could be different from cycle to cycle (Figure B.2).
Figure B.2. Pressure-injection diagram that includes effects of both elasticity and hysteresis.

B.3 Numerical analysis

We use the finite element software ABAQUS, and model the elastomer with the CPE4H element. We prescribe the bottom boundary of the elastomer with zero displacement, and allow all the other boundaries of the elastomer to form frictionless contact with the rigid walls. The contact is enforced with the augmented Lagrange method. The top wall is moved downward to apply the precompression. Uniform pressure is applied on the left boundary of the elastomer. When the strain precompression is greater than 20%, the top left tip will reach critical strain for the onset of a crease. To avoid this instability, a rounded corner with a radius of 1% of the sample thickness is added. This defect affects the contact stress somewhat and reduces $p_c$ by a small amount. To ease difficulty in simulating contact, for large aspect ratio and high precompression cases, the left portion of the top boundary that is expected to be in contact with the top wall has been applied with a sliding boundary condition instead of the contact condition. In all these cases, this part of the boundary is under compression, and will not detach from the wall.
We build an approximate model to fit the simulated critical fluid pressure for elastic leak (Figure B.3). On the deformed seal just before the leak, we mark the shear strains at the two ends of the seal, $\gamma_1$ and $\gamma_2$. When the seal shears uniformly, $\gamma_1 = \gamma_2$. The precompression, however, causes the elastomer to shear more on the right end than on the left end. Prior to the injection of fluid, the precompression causes the top part of the elastomer to bulge out by an area $lhe$ (Figure 7.4a).

![Diagram of the elastic leak model](image)

**Figure B.3.** The approximate model for the critical fluid pressure for elastic leak. The shear strain is assumed to be homogeneous perpendicular to the pressure gradient and linear along the pressure gradient.

When the fluid is injected, the elastomer shears, and the difference in the shear strains at the two ends gives an area scaled as $k(\gamma_2 - \gamma_1)h^2$, where factor $k$ is a constant. Incompressibility requires that the two areas be equal:

$$lhe = k(\gamma_2 - \gamma_1)h^2,$$

(B1)

The seal is in contact with the top wall without adhesion and friction, so that the force due to the fluid pressure balances the force due to the shear stress between the elastomer and bottom wall:

$$p(1-\varepsilon)h = \mu \int_0^l \left(\gamma_1 + \frac{(\gamma_2 - \gamma_1)x}{l}\right) dx.$$  

(B2)

Here we have assumed that the shear strain is linearly distributed between the two ends of the elastomer. The integration gives that
where $A$ and $B$ are two constants related to $\gamma$ and $k$. The formula is fitted to the critical pressure obtained from the finite element analysis (Figure B.4), giving $A = 3.0$ and $B = 2.9$.

**Figure B.4.** Fitting the formula of the critical fluid pressure. Fitted result is plotted as solid lines while the simulation results are drawn as circles.

**Figure B.5.** The distribution of hydrostatic pressure and shear stress in the interior of the seal. The hydrostatic pressure distribution inside the seal is in agreement with the
contact stress distribution on the top surface of the seal. The shear stress distribution roughly follows our assumption in Figure B.3.

**B.4 Relaxation of precompression**

Since hydrogel is poroelastic, storage may partially relax the contact stress of precompression. To test its effect, a layer of hydrogel, with dimensions \( w = 120 \text{ mm}, h = 4.5 \text{ mm}, l = 10 \text{ mm or 30 mm} \), is glued to a glass sheet, and compressed by the load cell of an Instron machine from the top surface of the hydrogel with a fixed strain, \( \varepsilon = 10\% \) or \( 37\% \). The strain is fixed for four hours while the contact force between hydrogel and the load cell of Instron is recorded. It is shown that the relaxation of contact stress is insignificant for low precompression (\( \varepsilon = 10\% \)), for different aspect ratio (\( l = 10 \text{ mm and } l = 30 \text{ mm} \)). For high precompression (\( \varepsilon = 37\% \)), however, the relaxation is much more significant and the effect is more severe for high aspect ratio case \( (l = 30 \text{ mm}) \) than for low aspect ratio case \( (l = 10 \text{ mm}) \), Figure B.6.

![Figure B.6](image)

**Figure B.6.** The relaxation of contact stress of precompression.
### B.5 Movies

**Movie B.1. Leak initiation.** When the fluid pressure reaches the peak (0.389 bar in this movie), a drop of fluid rapidly penetrates along the interface between the hydrogel and cover glass, and then a continuous fluid channel forms. The movie is first shown in the normal speed and then is shown eight times slower. (aspect ratio $l/h = 4.4$, strain of precompression $\varepsilon = 20\%$, and rate of injection $R = 5$ ml/min)

**Movie B.2. Steady state leak and leak stop.** When the seal leaks in steady state, the fluid pressure settles at a plateau (0.249 bar in this movie). When we reduce the fluid pressure below this plateau value, the leak stops immediately. (aspect ratio $l/h = 4.4$, strain of precompression $\varepsilon = 20\%$, and rate of injection $R = 15$ ml/min)

**Movie B.3. Formation of instability with wavy shape.** In some cases, before the seal leaks, the straight edge of the hydrogel becomes unstable, and forms a wavy shape. Then a leaking path forms at a trough of the wave. (aspect ratio $l/h = 2.2$, strain of precompression $\varepsilon = 30\%$, and rate of injection $R = 5$ ml/min)

**Movie B.4. Formation of instability without wavy shape.** In some cases, prior to the leak, the straight edge of the hydrogel becomes unstable, but does not form a wavy shape. The seal leaks through the tip of instability. (aspect ratio $l/h = 4.4$, strain of precompression $\varepsilon = 37\%$, and rate of injection $R = 5$ ml/min)
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