

Project: Surface Tension on Sphere

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1 Reformulation

References:

A. Javili and P. Steinmann titled *A finite element framework for continua with boundary energies. Part I: The two-dimensional case*

A. Javili and P. Steinmann titled *A finite element framework for continua with boundary energies. Part II: The three-dimensional case*

1.1 Kinematics and energies of continua with boundaries

Surfaces of bodies and interfaces between bodies exhibit different properties from the bulk. These effects can be modeled in terms of surface tension or an added term to the total potential energy, denoted by a bar

$$\begin{aligned} \text{Bulk : } U &= U_e + U_m - \mu C \\ \text{Surface : } &u_o \end{aligned}$$

Just as the deformation gradient is described by 2.1, there is a term to describe the surface deformation gradient:

$$\begin{aligned} \bar{\mathbf{F}} &= \frac{\partial x_i}{\partial X_K} \cdot \bar{\mathbf{I}} \\ \bar{\mathbf{F}} &= \mathbf{F} \cdot \bar{\mathbf{I}} \end{aligned} \tag{1.1}$$

where the mixed-variant surface unit tensor in the material configuration is:

$$\bar{\mathbf{I}} = \mathbf{I} - \mathbf{N} \otimes \mathbf{N} \tag{1.2}$$

Just as how the Jacobian is related to the volume, the surface J is related to the surface:

$$\begin{aligned} J &= \frac{dv}{dV} = \det \mathbf{F} \\ \bar{J} &= \frac{da}{dA} \end{aligned}$$

Can use the Nanson operator to define the surface jacobian, \bar{J}

$$\begin{aligned} \bar{J} &= |J \mathbf{F}^{-T} \mathbf{N}| \\ \bar{J} &= |\underbrace{\det \mathbf{F} \mathbf{F}^{-T}}_{\text{cofactor}} \mathbf{N}| \end{aligned} \tag{1.3}$$

1.1.1 Neo-Hookean type boundary potential

The internal potential energy can be expressed as:

$$w_0(\bar{\mathbf{F}}) = \frac{\bar{\lambda}}{2} \log^2 \bar{J} + \frac{\bar{\mu}}{2} (\bar{\mathbf{F}} : \bar{\mathbf{F}} - 2 - 2 \log \bar{J}) \tag{1.4}$$

1.1.2 Surface tension boundary potential

The internal potential energy can be expressed as:

$$w_0(\bar{\mathbf{F}}) = \gamma \bar{J} \tag{1.5}$$

1.2 Equilibrium Equations (Strong Forms)

Mechanical equilibrium equation:

$$\begin{aligned}\nabla \cdot \mathbf{P} + \mathbf{b}_o &= 0 & \text{in } V_o \\ \mathbf{P} \cdot \mathbf{N} - \bar{\nabla} \cdot \bar{\mathbf{P}} - \bar{\mathbf{b}}_o &= 0 & \text{on } S_o \\ \bar{\mathbf{P}} \cdot \mathbf{M} &= 0 & \text{on } L_o\end{aligned}$$

Mass conservation equation:

$$\begin{aligned}\dot{C} + \nabla \cdot \mathbf{J} &= r & \text{in } V_o \\ \mathbf{J} \cdot \mathbf{N} &= -i & \text{on } S_o\end{aligned}$$

1.2.1 Mechanical Equilibrium

Rearrange and multiply with a test function $\delta\varphi$ and integrate over domain

$$\begin{aligned}\int (\nabla \cdot \mathbf{P}) \cdot \delta\varphi dV + \int \mathbf{b}_o \cdot \delta\varphi dV &= 0 & \text{Int by Parts} \\ \int \nabla \cdot (\mathbf{P}^T \cdot \delta\varphi) dV - \int \mathbf{P} \cdot \nabla \delta\varphi dV + \int \mathbf{b}_o \cdot \delta\varphi dV &= 0 & \text{Divergence} \\ \int (\mathbf{P} \cdot \mathbf{N}) \cdot \delta\varphi dS - \int \mathbf{P} \cdot \nabla \delta\varphi dV + \int \mathbf{b}_o \cdot \delta\varphi dV &= 0 & \rightarrow \mathbf{P} \cdot \mathbf{N} = \bar{\nabla} \cdot \bar{\mathbf{P}} + \bar{\mathbf{b}}_o \\ \int (\bar{\nabla} \cdot \bar{\mathbf{P}}) \cdot \delta\varphi dS + \int \bar{\mathbf{b}}_o \cdot \delta\varphi dS - \int \mathbf{P} \cdot \nabla \delta\varphi dV + \int \mathbf{b}_o \cdot \delta\varphi dV &= 0 & \text{Int by Parts} \\ \int \bar{\nabla} \cdot (\bar{\mathbf{P}}^T \cdot \delta\varphi) dS - \int \bar{\mathbf{P}} \cdot \bar{\nabla} \delta\varphi dS + \int \bar{\mathbf{b}}_o \cdot \delta\varphi dS - \int \mathbf{P} \cdot \nabla \delta\varphi dV + \int \mathbf{b}_o \cdot \delta\varphi dV &= 0 & \text{Divergence} \\ \int (\bar{\mathbf{P}} \cdot \mathbf{M}) \cdot \delta\varphi dL - \int \bar{\mathbf{P}} \cdot \bar{\nabla} \delta\varphi dS + \int \bar{\mathbf{b}}_o \cdot \delta\varphi dS - \int \mathbf{P} \cdot \nabla \delta\varphi dV + \int \mathbf{b}_o \cdot \delta\varphi dV &= 0 \\ - \int \bar{\mathbf{P}} \cdot \bar{\nabla} \delta\varphi dS + \int \bar{\mathbf{b}}_o \cdot \delta\varphi dS - \int \mathbf{P} \cdot \nabla \delta\varphi dV + \int \mathbf{b}_o \cdot \delta\varphi dV &= 0\end{aligned}$$

Rearrange

$$\int \bar{\mathbf{P}} \cdot \bar{\nabla} \delta\varphi dS + \int \mathbf{P} \cdot \nabla \delta\varphi dV = \int \bar{\mathbf{b}}_o \cdot \delta\varphi dS + \int \mathbf{b}_o \cdot \delta\varphi dV \quad (1.6)$$

1.2.2 Mass Conservation

Multiply Eq. 2.4 with a test function μ and follow the same steps as above:

$$\begin{aligned}\int \dot{C} \delta\mu dV + \int (\nabla \cdot \mathbf{J}) \delta\mu dV &= \int r \delta\mu dV & \text{Int by Parts} \\ \int \dot{C} \delta\mu dV + \int \nabla \cdot (\mathbf{J}^T \delta\mu) dV - \int \mathbf{J} \cdot \nabla \delta\mu dV &= \int r \delta\mu dV & \text{Divergence} \\ \int \dot{C} \delta\mu dV + \int (\mathbf{J} \cdot \mathbf{N}) \delta\mu dV - \int \mathbf{J} \cdot \nabla \delta\mu dV &= \int r \delta\mu dV \\ \int \dot{C} \delta\mu dV - \int i \delta\mu dS - \int \mathbf{J} \cdot \nabla \delta\mu dV &= \int r \delta\mu dV \\ \int \dot{C} \delta\mu dV - \int \mathbf{J} \cdot \nabla \delta\mu dV &= \int r \delta\mu dV + \int i \delta\mu dS\end{aligned}$$

1.3 Weak Forms

$$\begin{aligned}\int \bar{\mathbf{P}} \cdot \bar{\nabla} \delta \boldsymbol{\varphi} dS &= \int \bar{\mathbf{b}}_{\mathbf{o}} \cdot \delta \boldsymbol{\varphi} dS \\ \int \mathbf{P} \cdot \nabla \delta \boldsymbol{\varphi} dV &= \int \mathbf{b}_{\mathbf{o}} \cdot \delta \boldsymbol{\varphi} dV \\ \int \dot{C} \delta \mu dV - \int \mathbf{J} \cdot \nabla \delta \mu dV &= \int r \delta \mu dV + \int i \delta \mu dS\end{aligned}$$

1.4 Free Energy

Free energy density

$$\begin{aligned}U(\mathbf{F}, \mu) &= U_e(\mathbf{F}) + U_m(C) - \mu C \\ u(\bar{\mathbf{F}})\end{aligned}$$

The free energy density of the system changes at the rate:

$$\begin{aligned}\delta U(\mathbf{F}, \mu) &= \frac{\partial U(\mathbf{F}, \mu)}{\partial \mathbf{F}} \delta \mathbf{F} + \frac{\partial U(\mathbf{F}, \mu)}{\partial \mu} \delta \mu \\ \delta u(\bar{\mathbf{F}}) &= \frac{\partial u(\bar{\mathbf{F}})}{\partial \bar{\mathbf{F}}} \delta \bar{\mathbf{F}}\end{aligned}$$

Together the gel and field of weights and pumps form a thermodynamic system

$$\begin{aligned}\frac{\delta G}{\delta t} &= \frac{\delta G_{bulk}}{\delta t} + \frac{\delta G_{surf}}{\delta t} \\ \frac{\delta G_{bulk}}{\delta t} &= \int \frac{\delta U}{\delta t} dV - \int \mathbf{b}_{\mathbf{o}} \cdot \frac{\delta \mathbf{x}}{\delta t} dV - \int \mu r dV - \int \mu i dS \\ \frac{\delta G_{surf}}{\delta t} &= \int \frac{\delta u}{\delta t} dS - \int \bar{\mathbf{b}}_{\mathbf{o}} \cdot \frac{\delta \bar{\mathbf{x}}}{\delta t} dS\end{aligned}$$

The change in free energy density over time

$$\begin{aligned}\frac{\partial U}{\partial t} &= \frac{\partial U}{\partial \mathbf{F}} \frac{\delta \mathbf{F}}{\delta t} + \frac{\partial U}{\partial \mu} \frac{\delta \mu}{\delta t} + \frac{\delta(\mu C)}{\delta t} \\ \frac{\partial u}{\partial t} &= \frac{\partial u}{\partial \bar{\mathbf{F}}} \frac{\delta \bar{\mathbf{F}}}{\delta t}\end{aligned}$$

Rephrase the two weak forms where δu is equivalent to $\delta \mathbf{x}/\delta t$ or $\delta \bar{\mathbf{x}}/\delta t$

$$\begin{aligned}\int \bar{\mathbf{P}} \cdot \bar{\nabla} \frac{\delta \bar{\mathbf{x}}}{\delta t} dS &= \int \bar{\mathbf{b}}_{\mathbf{o}} \cdot \frac{\delta \bar{\mathbf{x}}}{\delta t} dS \quad \rightarrow \quad \int \bar{\mathbf{P}} \cdot \frac{\delta \bar{\mathbf{F}}}{\delta t} dS = \int \bar{\mathbf{b}}_{\mathbf{o}} \cdot \frac{\delta \bar{\mathbf{x}}}{\delta t} dS \\ \int \mathbf{P} \cdot \nabla \frac{\delta \mathbf{x}}{\delta t} dV &= \int \mathbf{b}_{\mathbf{o}} \cdot \frac{\delta \mathbf{x}}{\delta t} dV \quad \rightarrow \quad \int \mathbf{P} \cdot \frac{\delta \mathbf{F}}{\delta t} dV = \int \mathbf{b}_{\mathbf{o}} \cdot \frac{\delta \mathbf{x}}{\delta t} dV\end{aligned}$$

Rewrite the weak form from $\delta \mu$ is μ

$$\int \frac{\partial C}{\partial t} \mu dV - \int r \mu dV - \int i \mu dS = \int \mathbf{J} \cdot \nabla \mu dV$$

Bulk

$$\begin{aligned}
\frac{\delta G_{bulk}}{\delta t} &= \int \frac{\delta U}{\delta t} dV - \int \mathbf{b}_o \frac{\delta \mathbf{x}}{\delta t} dV - \int \mu r dV - \int \mu i dS \\
&= \int \frac{\partial U}{\partial \mathbf{F}} \frac{\delta \mathbf{F}}{\delta t} dV + \int \frac{\partial U}{\partial \mu} \frac{\delta \mu}{\delta t} dV + \int \frac{\delta(\mu C)}{\delta t} dV - \int \mathbf{b}_o \frac{\delta \mathbf{x}}{\delta t} dV - \int \mu r dV - \int \mu i dS \\
&= \int \frac{\partial U}{\partial \mathbf{F}} \frac{\delta \mathbf{F}}{\delta t} dV + \int \frac{\partial U}{\partial \mu} \frac{\delta \mu}{\delta t} dV + \int \frac{\delta \mu}{\delta t} C dV + \int \mu \frac{\delta C}{\delta t} dV - \int \mathbf{P} \cdot \frac{\delta \mathbf{F}}{\delta t} dV - \int \mu r dV - \int \mu i dS \\
&= \int \left(\frac{\partial U}{\partial \mathbf{F}} - \mathbf{P} \right) \frac{\delta \mathbf{F}}{\delta t} dV + \int \left(\frac{\partial U}{\partial \mu} + C \right) \frac{\delta \mu}{\delta t} dV + \int \mu \frac{\delta C}{\delta t} dV - \int \mu r dV - \int \mu i dS \\
\frac{\delta G_{bulk}}{\delta t} &= \int \left(\frac{\partial U}{\partial \mathbf{F}} - \mathbf{P} \right) \frac{\delta \mathbf{F}}{\delta t} dV + \int \left(\frac{\partial U}{\partial \mu} + C \right) \frac{\delta \mu}{\delta t} dV + \int \mathbf{J} \cdot \nabla \mu dV
\end{aligned}$$

Surface

$$\begin{aligned}
\frac{\delta G_{surf}}{\delta t} &= \int \frac{\delta u}{\delta t} dS - \int \bar{\mathbf{b}}_o \frac{\delta \bar{x}}{\delta t} dS \\
&= \int \frac{\partial u}{\partial \bar{\mathbf{F}}} \frac{\delta \bar{\mathbf{F}}}{\delta t} dS - \int \bar{\mathbf{b}}_o \frac{\delta \bar{x}}{\delta t} dS \\
&= \int \frac{\partial u}{\partial \bar{\mathbf{F}}} \frac{\delta \bar{\mathbf{F}}}{\delta t} dS - \int \bar{\mathbf{P}} \cdot \frac{\delta \bar{\mathbf{F}}}{\delta t} dS \\
\frac{\delta G_{surf}}{\delta t} &= \int \left(\frac{\partial u}{\partial \bar{\mathbf{F}}} - \bar{\mathbf{P}} \right) \frac{\delta \bar{\mathbf{F}}}{\delta t} dS
\end{aligned}$$

Therefore

$$\frac{\delta G}{\delta t} = \int \left(\frac{\partial U}{\partial \mathbf{F}} - \mathbf{P} \right) \frac{\delta \mathbf{F}}{\delta t} dV + \int \left(\frac{\partial u}{\partial \bar{\mathbf{F}}} - \bar{\mathbf{P}} \right) \frac{\delta \bar{\mathbf{F}}}{\delta t} dS + \int \left(\frac{\partial U}{\partial \mu} + C \right) \frac{\delta \mu}{\delta t} dV + \int \mathbf{J} \cdot \frac{\partial \mu}{\partial X} dV$$

Thermodynamics dictates that the free energy of the system should never increase:

$$\frac{\delta G}{\delta t} \leq 0 \tag{1.7}$$

This leads to

$$\begin{aligned}
\mathbf{P} &= \frac{\partial U}{\partial \mathbf{F}} \\
\bar{\mathbf{P}} &= \frac{\partial u}{\partial \bar{\mathbf{F}}} \\
C &= -\frac{\partial U}{\partial \mu}
\end{aligned}$$

We enforce the negative definite structure of the last integrand by adopting a kinetic law

$$\mathbf{J} = -\mathbf{M} \cdot \frac{\partial \mu}{\partial X} = -\mathbf{M} \cdot \nabla \mu \tag{1.8}$$

1.5 Kinetic Law

The flux relates to the gradient of the chemical potential

$$\mathbf{j} = -\frac{cD}{kT} \frac{\partial \mu}{\partial x} \tag{1.9}$$

The true concentration relates to the nominal concentration as:

$$c = \frac{C}{\det \mathbf{F}} \quad (1.10)$$

Recall an identity

$$\det(\mathbf{F})\mathbf{N}dA = \mathbf{F}\mathbf{n}da \rightarrow \frac{\mathbf{N}dA}{\mathbf{n}da} = \frac{\mathbf{F}}{\det \mathbf{F}} \quad (1.11)$$

The number of molecules crossing the material element per unit time can be written:

$$\mathbf{j} \cdot \mathbf{n}da = \mathbf{J} \cdot \mathbf{N}dA \quad (1.12)$$

Consequently, relate the true flux to the nominal flux.

$$\begin{aligned} \mathbf{j} &= \mathbf{J} \cdot \frac{\mathbf{N}dA}{\mathbf{n}da} \quad \text{substitute Eq. 2.14} \\ &= \mathbf{J} \frac{\mathbf{F}}{\det \mathbf{F}} \quad \text{substitute Eq. 2.11} \\ &= -\mathbf{M} \cdot \frac{\partial \mu}{\partial X} \frac{\mathbf{F}}{\det \mathbf{F}} \quad \text{use chain rule} \\ &= -\mathbf{M} \frac{\partial \mu}{\partial x} \frac{\partial x}{\partial X} \frac{\mathbf{F}}{\det \mathbf{F}} \quad \text{use Eq. 2.12} \\ -\frac{cD}{k_B T} \frac{\partial \mu}{\partial x} &= -\mathbf{M} \frac{\partial \mu}{\partial x} \frac{\partial x}{\partial X} \cdot \frac{\partial x}{\partial X} \frac{1}{\det \mathbf{F}} \\ -\frac{cD}{k_B T} \det \mathbf{F} &= -\mathbf{M} \frac{\partial x}{\partial X} \cdot \frac{\partial x}{\partial X} \\ -\frac{CD}{k_B T} &= -\mathbf{M} \frac{\partial x}{\partial X} \cdot \frac{\partial x}{\partial X} \end{aligned}$$

Rearrange in terms of M_{KL} , use Eq. 2.13 and invoke incompressibility

$$\mathbf{M} = \frac{CD}{k_B T} \mathbf{F}^{-1} \mathbf{F}^{-T}$$

2 Formulation

This follows the formulation in "Effect of Solvent Diffusion on Crack-Tip Fields and Driving Force for Fracture of Hydrogels" which simplifies the free energy formulation in "A nonlinear, transient finite element method for coupled solvent diffusion and large deformation of hydrogels".

2.1 Equilibrium Equations (Strong Forms)

Deformation gradient of the polymer network:

$$F_{iK}(\mathbf{X}, t) = \frac{\partial x_i(\mathbf{X}, t)}{\partial X_K} \quad (2.1)$$

Mechanical equilibrium equation:

$$\frac{\partial S_{iJ}(\mathbf{X}, t)}{\partial X_J} + f_i(\mathbf{X}, t) = 0 \quad \text{in } V_o \quad (2.2)$$

$$S_{iJ}N_J = T_i \quad \text{or } u_i = \bar{u}_i \quad \text{on } S_o \quad (2.3)$$

Mass conservation equation:

$$\frac{\partial C(\mathbf{X}, t)}{\partial t} + \frac{\partial J_K(\mathbf{X}, t)}{\partial X_K} = r(\mathbf{X}, t) \quad \text{in } V_o \quad (2.4)$$

$$J_K N_K = -i \quad \text{or } \mu = \bar{\mu} \quad \text{on } S_o$$

2.2 Weak Forms

To convert an equation to a weak form, 1) Multiply by a test function, 2) integrate over domain, and 3) integration by parts.

$$(fg)' = f'g + fg' \rightarrow f'g = (fg)' - fg' \quad (2.5)$$

2.2.1 Mechanical Equilibrium

Rearrange and multiply Eq. 2.2 with a test function ξ_i

$$\begin{aligned} \frac{\partial S_{iK}}{\partial X_K} \xi_i &= -B_i \xi_i \quad \text{Integrate over domain} \\ \int \frac{\partial S_{iK}}{\partial X_K} \xi_i dV &= - \int B_i \xi_i dV \quad \text{Integration by parts} \\ \int (S_{iK} \xi_i)_{,K} dV - \int S_{iK} \frac{\partial \xi_i}{\partial X_K} dV &= - \int B_i \xi_i dV \quad \text{Use divergence theorem} \\ \int S_{iK} N_K \xi_i dA - \int S_{iK} \frac{\partial \xi_i}{\partial X_K} dV &= - \int B_i \xi_i dV \quad \text{Recognize } S_{iK} N_K = T_i \\ \int T_i \xi_i dA - \int S_{iK} \frac{\partial \xi_i}{\partial X_K} dV &= - \int B_i \xi_i dV \end{aligned}$$

Rearrange

$$\int T_i \xi_i dA + \int B_i \xi_i dV = \int S_{iK} \frac{\partial \xi_i}{\partial X_K} dV \quad (2.6)$$

2.2.2 Mass Conservation

Multiply Eq. 2.4 with a test function ζ and follow the same steps as above:

$$\begin{aligned}
& \frac{\partial C}{\partial t} \zeta + \frac{\partial J_K}{\partial X_K} \zeta = r \zeta \quad \text{Integrate over domain} \\
& \int \frac{\partial C}{\partial t} \zeta dV + \int \frac{\partial J_K}{\partial X_K} \zeta dV = \int r \zeta dV \quad \text{Integration by parts on 2nd term} \\
& \int \frac{\partial C}{\partial t} \zeta dV + \int (J_K \zeta)_{,K} dV - \int J_K \frac{\partial \zeta}{\partial X_K} dV = \int r \zeta dV \quad \text{Use divergence theorem} \\
& \int \frac{\partial C}{\partial t} \zeta dV + \int J_K N_K \zeta dA - \int J_K \frac{\partial \zeta}{\partial X_K} dV = \int r \zeta dV \quad \text{where } J_K N_K = i \\
& \int \frac{\partial C}{\partial t} \zeta dV + \int i \zeta dA - \int J_K \frac{\partial \zeta}{\partial X_K} dV = \int r \zeta dV
\end{aligned}$$

Rearrange

$$\int \frac{\partial C}{\partial t} \zeta dV = \int J_K \frac{\partial \zeta}{\partial X_K} dV + \int r \zeta dV + \int i \zeta dA \quad (2.7)$$

2.3 Free Energy

Free energy of the gel where the Legendre transform reformulates the free energy in terms of chemical potential instead of concentration:

$$\begin{aligned}
U(\mathbf{F}, C) &= U_e(\mathbf{F}) + U_m(C) \quad \text{Legendre Transform} \\
\hat{U}(\mathbf{F}, \mu) &= U_e(\mathbf{F}) + U_m(C) - \mu C
\end{aligned}$$

The free energy density of the system changes at the rate:

$$\delta U(\mathbf{F}, \mu) = \frac{\partial U(\mathbf{F}, \mu)}{\partial F_{iK}} \delta F_{iK} + \frac{\partial U(\mathbf{F}, \mu)}{\partial \mu} \delta \mu \quad (2.8)$$

The weights and pumps (Hong 2008) do work at the following rates:

$$\begin{aligned}
\text{Weights : } & \int B_i \frac{\delta x_i}{\delta t} dV + \int T_i \frac{\delta x_i}{\delta t} dA \\
\text{Pumps : } & \int \mu r dV + \int \mu i dA
\end{aligned}$$

Together the gel and field of weights and pumps form a thermodynamic system

$$\frac{\delta G}{\delta t} = \int \frac{\delta U}{\delta t} dV - \int B_i \frac{\delta x_i}{\delta t} dV - \int T_i \frac{\delta x_i}{\delta t} dA - \int \mu r dV - \int \mu i dA \quad (2.9)$$

Using Eq. 2.8

$$\frac{\partial U}{\partial t} = \frac{\partial U}{\partial F_{iK}} \frac{\delta F_{iK}}{\delta t} + \frac{\partial U}{\partial \mu} \frac{\delta \mu}{\delta t}$$

Substitute along with the weak forms where ξ, ζ are equivalent to $\frac{\delta x_i}{\delta t}, \mu$

$$\begin{aligned}
\frac{\delta G}{\delta t} &= \int \left(\frac{\partial U}{\partial F_{iK}} \frac{\delta F_{iK}}{\delta t} + \frac{\partial U}{\partial \mu} \frac{\delta \mu}{\delta t} \right) dV - \int B_i \frac{\delta x_i}{\delta t} dV - \int T_i \frac{\delta x_i}{\delta t} dA - \int \mu r dV - \int \mu i dA \\
&= \int \frac{\partial U}{\partial F_{iK}} \frac{\delta F_{iK}}{\delta t} dV + \int \frac{\partial U}{\partial \mu} \frac{\delta \mu}{\delta t} dV - \int S_{iK} \frac{\delta F_{iK}}{\delta t} dV - \int \mu r dV - \int \mu i dA \\
&= \int \left(\frac{\partial U}{\partial F_{iK}} - S_{iK} \right) \frac{\delta F_{iK}}{\delta t} dV + \int \frac{\partial U}{\partial \mu} \frac{\delta \mu}{\delta t} dV - \int \frac{\partial C}{\partial t} \mu dV + \int J_K \frac{\partial \mu}{\partial X_K} dV \\
&= \int \left(\frac{\partial U}{\partial F_{iK}} - S_{iK} \right) \frac{\delta F_{iK}}{\delta t} dV + \int \left(\frac{\partial U}{\partial \mu} \frac{\delta \mu}{\delta t} - \frac{\partial C}{\partial t} \mu \right) dV + \int J_K \frac{\partial \mu}{\partial X_K} dV \\
&= \int \left(\frac{\partial U}{\partial F_{iK}} - S_{iK} \right) \frac{\delta F_{iK}}{\delta t} dV + \int \left(\frac{\partial U}{\partial \mu} \frac{\delta \mu}{\delta t} - \frac{\partial C}{\partial \mu} \frac{\delta \mu}{\delta t} \mu \right) dV + \int J_K \frac{\partial \mu}{\partial X_K} dV \\
\frac{\delta G}{\delta t} &= \int \left(\frac{\partial U}{\partial F_{iK}} - S_{iK} \right) \frac{\delta F_{iK}}{\delta t} dV + \int \left(\frac{\partial U}{\partial \mu} - \frac{\partial C}{\partial \mu} \mu \right) \frac{\delta \mu}{\delta t} dV + \int J_K \frac{\partial \mu}{\partial X_K} dV
\end{aligned}$$

Check step leading to:

$$\frac{\delta G}{\delta t} = \int \left(\frac{\partial U}{\partial F_{iK}} - S_{iK} \right) \frac{\delta F_{iK}}{\delta t} dV + \int \left(\frac{\partial U}{\partial \mu} + C \right) \frac{\delta \mu}{\delta t} dV + \int J_K \frac{\partial \mu}{\partial X_K} dV$$

Thermodynamics dictates that the free energy of the system should never increase:

$$\frac{\delta G}{\delta t} \leq 0 \tag{2.10}$$

This leads to

$$\begin{aligned}
S_{iK} &= \frac{\partial U}{\partial F_{iK}} \\
C &= -\frac{\partial U}{\partial \mu}
\end{aligned}$$

We enforce the negative definite structure of the last integrand by adopting a kinetic law

$$J_K = -M_{KL} \frac{\partial \mu(\mathbf{X}, t)}{\partial X_L} \tag{2.11}$$

2.4 Kinetic Law

The flux relates to the gradient of the chemical potential by a well-known equation (Feynman et al. 1963)

$$j_i = -\frac{cD}{kT} \frac{\partial \mu}{\partial x_i} \tag{2.12}$$

The true concentration relates to the nominal concentration as:

$$c = \frac{C}{\det \mathbf{F}} \tag{2.13}$$

Recall an identity

$$\det(\mathbf{F}) N_K dA = F_{iK} n_i da \rightarrow \frac{N_K dA}{n_i da} = \frac{F_{iK}}{\det \mathbf{F}} \tag{2.14}$$

The number of molecules crossing the material element per unit time can be written:

$$j_i n_i da = J_K N_K dA \tag{2.15}$$

Consequently, relate the true flux to the nominal flux, starting with rearranging Eq. 2.15

$$\begin{aligned}
j_i &= J_K \frac{N_K dA}{n_i da} \quad \text{substitute Eq. 2.14} \\
&= J_K \frac{F_{iK}}{\det \mathbf{F}} \quad \text{substitute Eq. 2.11} \\
&= -M_{KL} \frac{\partial \mu}{\partial X_L} \frac{F_{iK}}{\det \mathbf{F}} \quad \text{use chain rule} \\
&= -M_{KL} \frac{\partial \mu}{\partial x_i} \frac{\partial x_i}{\partial X_L} \frac{F_{iK}}{\det \mathbf{F}} \quad \text{use Eq. 2.12} \\
-\frac{cD}{kT} \frac{\partial \mu}{\partial x_i} &= -M_{KL} \frac{\partial \mu}{\partial x_i} F_{iL} F_{iK} \frac{1}{\det \mathbf{F}}
\end{aligned}$$

Rearrange in terms of M_{KL} , use Eq. 2.13 and invoke incompressibility

$$\begin{aligned}
M_{KL} &= \frac{cD}{kT} F_{iK}^{-1} F_{iL}^{-1} \det \mathbf{F} \quad \text{substitute Eq. 2.13} \\
&= \frac{CD}{kT} \frac{1}{\det \mathbf{F}} F_{iK}^{-1} F_{iL}^{-1} \det \mathbf{F} \\
M_{KL} &= \frac{CD}{kT} F_{iK}^{-1} F_{iL}^{-1}
\end{aligned} \tag{2.16}$$

Substitute this result into Eq. 2.11

$$J_K = -\frac{CD}{kT} \frac{\partial X_K}{\partial x_i} \frac{\partial X_L}{\partial x_i} \frac{\partial \mu(\mathbf{X}, t)}{\partial X_L} \tag{2.17}$$

2.5 Strain Energy Density

The constituents of the hydrogel are assumed to be incompressible:

$$\det \mathbf{F} = 1 + \Omega C \tag{2.18}$$

Free energy due to stretching (Flory, 1953)

$$\begin{aligned}
U_e(\mathbf{F}) &= \frac{1}{2} N k_B T [F_{iK} F_{iK} - 3 - 2 \log(\det \mathbf{F})] \quad \text{Right Cauchy-Green tensor } C = F^T F \\
&= \frac{1}{2} N k_B T [\text{tr } \mathbf{C} - 3 - 2 \log(\det \mathbf{F})]
\end{aligned} \tag{2.19}$$

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

$$\begin{aligned}
U_m(C) &= -\frac{k_B T}{\Omega} \left[\Omega C \log \left(\frac{1 + \Omega C}{\Omega C} \right) + \frac{\chi}{1 + \Omega C} \right] \quad \text{Use. Eq. 2.18} \\
U_m(C) &= -\frac{k_B T}{\Omega} \left[(\det \mathbf{F} - 1) \log \left(\frac{\det \mathbf{F}}{\det \mathbf{F} - 1} \right) + \frac{\chi}{\det \mathbf{F}} \right] \quad \text{Use log property} \\
U_m(C) &= \frac{k_B T}{\Omega} \left[(\det \mathbf{F} - 1) \log \left(\frac{\det \mathbf{F} - 1}{\det \mathbf{F}} \right) - \frac{\chi}{\det \mathbf{F}} \right]
\end{aligned} \tag{2.20}$$

Total strain energy in terms of the deformation gradient:

$$\hat{U}(\mathbf{F}, \mu) = \frac{1}{2} N k_B T [\text{tr } \mathbf{C} - 3 - 2 \log(\det \mathbf{F})] + \frac{k_B T}{\Omega} \left[(\det \mathbf{F} - 1) \log \left(\frac{\det \mathbf{F} - 1}{\det \mathbf{F}} \right) - \frac{\chi}{\det \mathbf{F}} \right] - \mu \left(\frac{\det \mathbf{F} - 1}{\Omega} \right)$$

2.6 Nominal Stress and Concentration

The nominal stress and the concentration of the solvent can be obtained from the free energy density:

2.6.1 Nominal Stress

$$S_{iJ} = \frac{\partial \hat{U}}{\partial F_{iJ}}$$

$$S_{iJ} = \frac{\partial \hat{U}}{\partial I_1} \frac{\partial I_1}{\partial F_{iJ}} + \frac{\partial \hat{U}}{\partial I_3} \frac{\partial I_3}{\partial F_{iJ}}$$

where $I_1 = \text{tr } \mathbf{C}$ and $I_3 = \det \mathbf{F}$; therefore,

First Term:

$$\begin{aligned} \frac{\partial \hat{U}}{\partial I_1} &= \frac{\partial \hat{U}}{\partial \text{tr } \mathbf{C}} \\ &= \frac{\partial}{\partial \text{tr } \mathbf{C}} \left[\frac{1}{2} N k_B T [\text{tr } \mathbf{C} - 3 - 2 \log(\det \mathbf{F})] \right] \\ \frac{\partial \hat{U}}{\partial I_1} &= \frac{1}{2} N k_B T \end{aligned}$$

Second Term:

$$\begin{aligned} \frac{\partial I_1}{\partial F_{iJ}} &= \frac{\partial I_1}{\partial C_{KL}} \frac{\partial C_{KL}}{\partial F_{iJ}} \quad \text{where } C_{KL} = F_{mK} F_{mL} \\ &= \frac{\partial \text{tr } \mathbf{C}}{\partial \mathbf{C}} \frac{\partial (F_{mK} F_{mL})}{\partial F_{iJ}} \quad \text{where } \frac{\partial \text{tr } \mathbf{A}}{\partial \mathbf{A}} = I \\ &= \delta_{KL} \left[\frac{\partial F_{mK}}{\partial F_{iJ}} F_{mL} + F_{mK} \frac{\partial F_{mL}}{\partial F_{iJ}} \right] \\ &= \delta_{KL} [\delta_{mi} \delta_{KJ} F_{mL} + F_{mK} \delta_{mi} \delta_{LJ}] \\ \frac{\partial I_1}{\partial F_{iJ}} &= F_{iJ} + F_{iJ} = 2F_{iJ} \end{aligned}$$

Third Term:

$$\begin{aligned} \frac{\partial \hat{U}}{\partial I_3} &= \frac{\partial \hat{U}}{\partial \det \mathbf{F}} \\ &= \frac{\partial}{\partial \det \mathbf{F}} \left[\frac{1}{2} N k_B T [\text{tr}(\mathbf{C}) - 3 - 2 \log(\det \mathbf{F})] + \frac{k_B T}{\Omega} [(\det \mathbf{F} - 1) \log \left(\frac{\det \mathbf{F} - 1}{\det \mathbf{F}} \right) - \frac{\chi}{\det \mathbf{F}}] - \mu \left(\frac{\det \mathbf{F} - 1}{\Omega} \right) \right] \\ &= \frac{1}{2} N k_B T \left(-2 \frac{\partial \log(\det \mathbf{F})}{\partial \det \mathbf{F}} \right) + \frac{k_B T}{\Omega} \left[\frac{1}{\det \mathbf{F}} + \log \left(\frac{\det \mathbf{F} - 1}{\det \mathbf{F}} \right) + \frac{\chi}{(\det \mathbf{F})^2} \right] - \frac{\mu}{\Omega} \left(\frac{\partial \det \mathbf{F}}{\partial \det \mathbf{F}} \right) \\ &= -N k_B T \frac{1}{\det \mathbf{F}} + \frac{k_B T}{\Omega} \left[\frac{1}{\det \mathbf{F}} + \log \left(\frac{\det \mathbf{F} - 1}{\det \mathbf{F}} \right) + \frac{\chi}{(\det \mathbf{F})^2} \right] - \frac{\mu}{\Omega} \\ &= N k_B T \left\{ -\frac{1}{\det \mathbf{F}} + \frac{1}{N \Omega} \left[\frac{1}{\det \mathbf{F}} + \log \left(\frac{\det \mathbf{F} - 1}{\det \mathbf{F}} \right) + \frac{\chi}{(\det \mathbf{F})^2} \right] - \frac{\mu}{N \Omega k_B T} \right\} \\ \frac{\partial \hat{U}}{\partial I_3} &= N k_B T \left\{ -\frac{1}{\det \mathbf{F}} + \frac{1}{N \Omega} \left[\frac{1}{\det \mathbf{F}} + \log \left(\frac{\det \mathbf{F} - 1}{\det \mathbf{F}} \right) + \frac{\chi}{(\det \mathbf{F})^2} - \frac{\mu}{k_B T} \right] \right\} \end{aligned}$$

Fourth Term:

$$\begin{aligned}\frac{\partial I_3}{\partial F_{iJ}} &= \frac{\partial \det \mathbf{F}}{\partial F_{iJ}} \quad \text{where} \quad \frac{\partial \det \mathbf{F}}{\partial F} = (\det \mathbf{F}) \mathbf{F}^{-T} \\ &= \det \mathbf{F} F_{iJ}^{-T}\end{aligned}$$

Therefore:

$$\begin{aligned}S_{iJ} &= \frac{\partial \hat{U}}{\partial I_1} \frac{\partial I_1}{\partial F_{iJ}} + \frac{\partial \hat{U}}{\partial I_3} \frac{\partial I_3}{\partial F_{iJ}} \\ &= \frac{1}{2} N k_B T (2 F_{iJ}) + N k_B T \left\{ -\frac{1}{\det \mathbf{F}} + \frac{1}{N \Omega} \left[\frac{1}{\det \mathbf{F}} + \log \left(\frac{\det \mathbf{F} - 1}{\det \mathbf{F}} \right) + \frac{\chi}{(\det \mathbf{F})^2} - \frac{\mu}{k_B T} \right] \right\} \det \mathbf{F} F_{iJ}^{-T} \\ S_{iJ} &= N k_B T \left\langle F_{iJ} + \left\{ -\frac{1}{\det \mathbf{F}} + \frac{1}{N \Omega} \left[\frac{1}{\det \mathbf{F}} + \log \left(\frac{\det \mathbf{F} - 1}{\det \mathbf{F}} \right) + \frac{\chi}{(\det \mathbf{F})^2} - \frac{\mu}{k_B T} \right] \right\} \det \mathbf{F} F_{iJ}^{-T} \right\rangle\end{aligned}$$

2.6.2 Concentration

$$\begin{aligned}C(\mathbf{F}, \mu) &= -\frac{\delta \hat{U}}{\delta \mu} = -\left(-\frac{\det \mathbf{F} - 1}{\Omega} \right) \\ C(\mathbf{F}, \mu) &= \frac{\det \mathbf{F} - 1}{\Omega}\end{aligned}\tag{2.21}$$

2.7 Weak Forms and Time Integration

The weak forms are as followed:

$$\begin{aligned}\int S_{iJ} \frac{\delta u_i}{\delta X_J} dV - \int T_i \delta u_i dS - \int f_i \delta u_i dV &= 0 \\ \int \frac{\partial C}{\partial t} \delta \mu dV - \int J_K \frac{\delta \mu}{\delta X_K} dV - \int i \delta \mu dS - \int r \delta \mu dV &= 0\end{aligned}\tag{2.22}$$

The first weak form is not time-dependent (all in current time step)

Backward Euler Scheme on the second weak form where **superscript t indicates previous time step** and no superscript indicates current time step

$$\begin{aligned}\int \frac{C - C^t}{\Delta t} \delta \mu dV - \int J_K \frac{\delta \mu}{\delta X_K} dV - \int i \delta \mu dS - \int r \delta \mu dV &= 0 \\ \int (C - C^t) \delta \mu dV - \int J_K \frac{\delta \mu}{\delta X_K} \Delta t dV - \int i \delta \mu \Delta t dS - \int r \delta \mu \Delta t dV &= 0\end{aligned}$$

Leaving the following equations

$$\begin{aligned}\int (C - C^t) \delta \mu dV - \int J_K \frac{\delta \mu}{\delta X_K} \Delta t dV - \int i \delta \mu \Delta t dS - \int r \delta \mu \Delta t dV &= 0 \\ \int S_{iJ} \frac{\delta u_i}{\delta X_J} dV - \int T_i \delta u_i dS - \int f_i \delta u_i dV &= 0\end{aligned}$$

3 Normalization

Normalization parameters below:

Lengths normalized by thickness (dry) : $l = \tilde{l}H$

Surfaces normalized by : $dA = d\tilde{A}H^2$

Volumes normalized by : $dV = d\tilde{V}H^3$ or $dV = d\tilde{V}\Omega$

Time normalized by : $t = \tilde{t}\tau$ where $\tau = \frac{H^2}{D}$

Chemical Potential normalized by : $\mu = \tilde{\mu}k_B T$

Stress normalized by : $S = \tilde{S}Nk_B T$ $\gamma = \tilde{\gamma}Nk_B T$

Concentration normalized by : $\Omega C = \tilde{C} \rightarrow C = \frac{\tilde{C}}{\Omega}$

Normalization of nominal stress

$$\begin{aligned} S_{iJ} &= Nk_B T \left\langle F_{iJ} + \left\{ -\frac{1}{\det \mathbf{F}} + \frac{1}{N\Omega} \left[\frac{1}{\det \mathbf{F}} + \log \left(\frac{\det \mathbf{F} - 1}{\det \mathbf{F}} \right) + \frac{\chi}{(\det \mathbf{F})^2} - \frac{\mu}{k_B T} \right] \right\} \det \mathbf{F} F_{iJ}^{-T} \right\rangle \\ \tilde{S}Nk_B T &= Nk_B T \left\langle F_{iJ} + \left\{ -\frac{1}{\det \mathbf{F}} + \frac{1}{N\Omega} \left[\frac{1}{\det \mathbf{F}} + \log \left(\frac{\det \mathbf{F} - 1}{\det \mathbf{F}} \right) + \frac{\chi}{(\det \mathbf{F})^2} - \frac{\tilde{\mu}k_B T}{k_B T} \right] \right\} \det \mathbf{F} F_{iJ}^{-T} \right\rangle \\ \tilde{S} &= F_{iJ} + \left\{ -\frac{1}{\det \mathbf{F}} + \frac{1}{N\Omega} \left[\frac{1}{\det \mathbf{F}} + \log \left(\frac{\det \mathbf{F} - 1}{\det \mathbf{F}} \right) + \frac{\chi}{(\det \mathbf{F})^2} - \tilde{\mu} \right] \right\} \det \mathbf{F} F_{iJ}^{-T} \\ \tilde{S} &= F_{iJ} + \left\{ -\frac{1}{J} + \frac{1}{N\Omega} \left[\frac{1}{J} + \log \left(\frac{J - 1}{J} \right) + \frac{\chi}{J^2} - \tilde{\mu} \right] \right\} J F_{iJ}^{-T} \end{aligned}$$

Normalization of concentration

$$\begin{aligned} C &= \frac{(\det \mathbf{F} - 1)}{\Omega} \\ \frac{\tilde{C}}{\Omega} &= \frac{(\det \mathbf{F} - 1)}{\Omega} \\ \tilde{C} &= \det \mathbf{F} - 1 = J - 1 \end{aligned}$$

3.1 Normalization of Weak Forms

These normalizations are done with the assumption that $\Omega = H^3$ where $H = 1$.

3.1.1 Mechanical Equilibrium

$$\begin{aligned} \int S_{iJ} \frac{\delta u_i}{\delta X_J} dV - \int T_i \delta u_i dS - \int f_i \delta u_i dV &= 0 \\ \int \tilde{S}_{iJ} Nk_B T \frac{\delta \tilde{u}_i H}{\delta \tilde{X}_J H} d\tilde{V} \Omega - \int \tilde{T}_i Nk_B T (\delta \tilde{u}_i H) (d\tilde{S} H^2) - \int f_i \frac{Nk_B T}{H} \delta \tilde{u}_i H d\tilde{V} \Omega &= 0 \quad \Omega = H^3 \\ N\Omega k_B T \left[\int \tilde{S}_{iJ} \frac{\delta \tilde{u}_i}{\delta \tilde{X}_J} d\tilde{V} - \int \tilde{T}_i \delta \tilde{u}_i d\tilde{S} - \int f_i \delta \tilde{u}_i d\tilde{V} \right] &= 0 \end{aligned}$$

3.1.2 Mass Conservation

Normalize kinetic law Eq. 2.17

$$\begin{aligned}
J_K &= -\frac{CD}{vkT} \frac{\partial X_K}{\partial x_i} \frac{\partial \mu(\mathbf{X}, t)}{\partial x_i} \\
&= -\frac{CD}{k_B T} \frac{\partial X_K}{\partial x_i} \frac{\partial X_L}{\partial x_i} \frac{\partial \mu(\mathbf{X}, t)}{\partial X_L} \\
&= \frac{1}{k_B T} \frac{\tilde{C}}{\Omega} \frac{H^2}{\tau} \frac{\partial \tilde{X}_K}{\partial \tilde{x}_i} \frac{\partial \tilde{X}_L}{\partial \tilde{x}_i} \frac{\partial (\tilde{\mu} k_B T)}{\partial (\tilde{X}_L H)} \\
\tilde{J}_K &= \frac{\tilde{C}}{\Omega} \frac{H}{\tau} \frac{\partial \tilde{X}_K}{\partial \tilde{x}_i} \frac{\partial \tilde{X}_L}{\partial \tilde{x}_i} \frac{\partial \tilde{\mu}}{\partial \tilde{X}_L}
\end{aligned} \tag{3.1}$$

Using the normalized Flux equation, Eq. 3.1 in the first step

$$\begin{aligned}
&\int (C - C^t) \delta \mu dV - \int J_K \frac{\delta \mu}{\delta X_K} \Delta t dV - \int i \delta \mu \Delta t dS - \int r \delta \mu \Delta t dV = 0 \\
&\int (C - C^t) \delta \mu dV + \int \frac{\tilde{C}}{\Omega} \frac{H}{\tau} \frac{\partial \tilde{X}_K}{\partial \tilde{x}_i} \frac{\partial \tilde{X}_L}{\partial \tilde{x}_i} \frac{\partial \tilde{\mu}}{\partial \tilde{X}_L} \frac{\partial (\tilde{\mu} k_B T)}{\partial (\tilde{X}_K H)} \Delta \tilde{t} \tau d\tilde{V} \Omega - \int i \delta \mu \Delta t dS - \int r \delta \mu \Delta t dV = 0 \\
&\int \frac{1}{\Omega} (\tilde{C} - \tilde{C}^t) \delta \tilde{\mu} k_B T (d\tilde{V} \Omega) + \int \tilde{C} k_B T \frac{\partial \tilde{X}_K}{\partial \tilde{x}_i} \frac{\partial \tilde{X}_L}{\partial \tilde{x}_i} \frac{\partial \tilde{\mu}}{\partial \tilde{X}_L} \frac{\partial \tilde{\mu}}{\partial \tilde{X}_K} \Delta \tilde{t} d\tilde{V} \\
&\quad - \int \frac{\tilde{i}}{H^2 \tau} \delta \tilde{\mu} k_B T \Delta \tilde{t} \tau (d\tilde{S} H^2) - \int \frac{\tilde{r}}{\Omega \tau} \delta \tilde{\mu} k_B T \Delta \tilde{t} \tau (d\tilde{V} \Omega) = 0 \\
&k_B T \int (\tilde{C} - \tilde{C}^t) \delta \tilde{\mu} d\tilde{V} + k_B T \int \tilde{C} \frac{\partial \tilde{X}_K}{\partial \tilde{x}_i} \frac{\partial \tilde{X}_L}{\partial \tilde{x}_i} \frac{\partial \tilde{\mu}}{\partial \tilde{X}_L} \frac{\partial \tilde{\mu}}{\partial \tilde{X}_K} \Delta \tilde{t} d\tilde{V} - k_B T \int \tilde{i} \delta \tilde{\mu} \Delta \tilde{t} d\tilde{S} - k_B T \int \tilde{r} \delta \tilde{\mu} \Delta \tilde{t} d\tilde{V} = 0 \\
&k_B T \left[\int (\tilde{C} - \tilde{C}^t) \delta \tilde{\mu} d\tilde{V} + \int \tilde{C} \frac{\partial \tilde{X}_K}{\partial \tilde{x}_i} \frac{\partial \tilde{X}_L}{\partial \tilde{x}_i} \frac{\partial \tilde{\mu}}{\partial \tilde{X}_L} \frac{\partial \tilde{\mu}}{\partial \tilde{X}_K} \Delta \tilde{t} d\tilde{V} - \int \tilde{i} \delta \tilde{\mu} \Delta \tilde{t} d\tilde{S} - \int \tilde{r} \delta \tilde{\mu} \Delta \tilde{t} d\tilde{V} \right] = 0
\end{aligned}$$

Combine the weak forms together

$$\begin{aligned}
N \Omega k_B T \left[- \right] + k_B T \left[- \right] &= 0 \quad \text{Divide by } k_B T \\
N \Omega \left[- \right] + \left[- \right] &= 0 \rightarrow \left[- \right] + \frac{1}{N \Omega} \left[- \right] = 0 \\
\int \tilde{S}_{iJ} \frac{\delta \tilde{u}_i}{\delta \tilde{X}_J} d\tilde{V} - \int \tilde{T}_i \delta \tilde{u}_i d\tilde{S} - \int f_i \delta \tilde{u}_i d\tilde{V} + \frac{1}{N \Omega} \left[- \right] &= 0
\end{aligned}$$

Leaving the final weak normalized weak form:

$$\begin{aligned}
&\int \tilde{S}_{iJ} \frac{\delta \tilde{u}_i}{\delta \tilde{X}_J} d\tilde{V} - \int \tilde{T}_i \delta \tilde{u}_i d\tilde{S} - \int f_i \delta \tilde{u}_i d\tilde{V} = 0 \\
\frac{1}{N \Omega} \left[\int (\tilde{C} - \tilde{C}^t) \delta \tilde{\mu} d\tilde{V} + \int \tilde{C} \frac{\partial \tilde{X}_K}{\partial \tilde{x}_i} \frac{\partial \tilde{X}_L}{\partial \tilde{x}_i} \frac{\partial \tilde{\mu}}{\partial \tilde{X}_L} \frac{\partial \tilde{\mu}}{\partial \tilde{X}_K} \Delta \tilde{t} d\tilde{V} - \int \tilde{i} \delta \tilde{\mu} \Delta \tilde{t} d\tilde{S} - \int \tilde{r} \delta \tilde{\mu} \Delta \tilde{t} d\tilde{V} \right] &= 0
\end{aligned}$$

where the previous time step is \tilde{C}^t

4 Initial Conditions

4.1 Initial Condition for Chemical Potential without Surface Tension

Initially stress free gel:

$$\begin{aligned}
\tilde{S} = F_{iJ} + \left\{ -\frac{1}{\det \mathbf{F}} + \frac{1}{N\Omega} \left[\frac{1}{\det \mathbf{F}} + \log \left(\frac{\det \mathbf{F} - 1}{\det \mathbf{F}} \right) + \frac{\chi}{(\det \mathbf{F})^2} - \tilde{\mu} \right] \right\} \det \mathbf{F} F_{iJ}^{-T} &= 0 \\
F_{iJ} - F_{iJ}^{-T} + \frac{1}{N\Omega} \left[\frac{1}{\det \mathbf{F}} + \log \left(\frac{\det \mathbf{F} - 1}{\det \mathbf{F}} \right) + \frac{\chi}{(\det \mathbf{F})^2} - \tilde{\mu} \right] \det \mathbf{F} F_{iJ}^{-T} &= 0 \\
F_{iJ} - F_{iJ}^{-T} + \frac{1}{N\Omega} \left[F_{iJ}^{-T} + \det \mathbf{F} F_{iJ}^{-T} \log \left(\frac{\det \mathbf{F} - 1}{\det \mathbf{F}} \right) + \frac{\chi}{\det \mathbf{F}} F_{iJ}^{-T} \right] &= \tilde{\mu} \frac{1}{N\Omega} \det \mathbf{F} F_{iJ}^{-T} \\
\frac{N\Omega}{\det \mathbf{F} F_{iJ}^{-T}} \left(F_{iJ} - F_{iJ}^{-T} \right) + \frac{1}{\det \mathbf{F} F_{iJ}^{-T}} \left[F_{iJ}^{-T} + \det \mathbf{F} F_{iJ}^{-T} \log \left(\frac{\det \mathbf{F} - 1}{\det \mathbf{F}} \right) + \frac{\chi}{\det \mathbf{F}} F_{iJ}^{-T} \right] &= \tilde{\mu} \\
\frac{N\Omega}{\det \mathbf{F} F_{iJ}^{-T}} \left(F_{iJ} - F_{iJ}^{-T} \right) + \frac{1}{\det \mathbf{F}} + \log \left(\frac{\det \mathbf{F} - 1}{\det \mathbf{F}} \right) + \frac{\chi}{(\det \mathbf{F})^2} &= \tilde{\mu} \quad \text{where } \det \mathbf{F} = \lambda_o^3 \\
N\Omega \frac{\lambda_o}{\lambda_o^3} \left(\lambda_o - \frac{1}{\lambda_o} \right) + \frac{1}{\lambda_o^3} + \log \left(\frac{\lambda_o^3 - 1}{\lambda_o^3} \right) + \frac{\chi}{\lambda_o^6} &= \tilde{\mu}
\end{aligned}$$

This gives the initial normalized chemical potential

$$\tilde{\mu} = N\Omega \left(\frac{1}{\lambda_o} - \frac{1}{\lambda_o^3} \right) + \frac{1}{\lambda_o^3} + \log \left(\frac{\lambda_o^3 - 1}{\lambda_o^3} \right) + \frac{\chi}{\lambda_o^6}$$

4.2 Initial Condition for Chemical Potential with Surface Tension

Paper Reference: *Elatocapillarity: Surface Tension and the Mechanics of Soft Solids* by Style, Jagota, Hui, and Dufresne.

The essential idea is a connection between surface stress and bulk stress at the interface. The governing interfacial equation is a condition for static equilibrium.

$$\int_S \boldsymbol{\sigma}_1 \cdot \mathbf{n} dS - \int_S \boldsymbol{\sigma}_2 \cdot \mathbf{n} dS + \oint_C \boldsymbol{\Upsilon} \cdot \mathbf{b} dl = 0$$

Using the surface divergence theorem, we can obtain the generalization of Laplace's Law

$$\begin{aligned}
\boldsymbol{\sigma} \cdot \mathbf{n} + \tilde{\nabla} \cdot \boldsymbol{\Upsilon} &= 0 \quad \text{Assume surface stress is isotropic} \\
\boldsymbol{\sigma} \cdot \mathbf{n} + \tilde{\nabla} \cdot (\gamma \mathbf{I}) &= 0 \\
\boldsymbol{\sigma} \cdot \mathbf{n} + \gamma \tilde{\nabla} \cdot \mathbf{I} &= 0 \\
\boldsymbol{\sigma} \cdot \mathbf{n} + \gamma (\tilde{\nabla} \cdot \mathbf{n}) \mathbf{n} &= 0 \\
\boldsymbol{\sigma} \cdot \mathbf{n} + \gamma \kappa \mathbf{n} &= 0
\end{aligned}$$

Written in spherical coordinates

$$\begin{bmatrix} \sigma_{rr} & 0 & 0 \\ 0 & \sigma_{\theta\theta} & 0 \\ 0 & 0 & \sigma_{\varphi\varphi} \end{bmatrix} \begin{bmatrix} 1 \\ 0 \\ 0 \end{bmatrix} + \gamma \kappa \begin{bmatrix} 1 \\ 0 \\ 0 \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \\ 0 \end{bmatrix}$$

$$\sigma_{rr} + \gamma \kappa = 0$$

What is κ in the case of a sphere?

$$\begin{aligned}\text{Principal/Mean : } \kappa &= \frac{1}{r} \\ \text{Gaussian : } \kappa &= \frac{1}{r^2}\end{aligned}$$

Here we use two times the mean curvature

$$\begin{aligned}\sigma_r &= -\frac{2\gamma}{r_{out}} \quad \text{where } \lambda_r = \frac{r_{out}}{R_{out}} \rightarrow r_{out} = \lambda_r R_{out} \\ \sigma_r &= -\frac{2\gamma}{\lambda_r R_{out}} \quad \text{where } R_{out} = 1.0 \\ \sigma_r &= -\frac{2\gamma}{\lambda_r}\end{aligned}$$

Another way to think about this derivation is in terms of the Young-Laplace Equation, where we have two mediums α and β .

$$\gamma = (P^\beta - P^\alpha) \frac{\partial V^\beta}{\partial A^\beta}$$

The volume and surface area of a sphere are given as:

$$\begin{aligned}\text{Volume: } V^\beta &= \frac{4}{3}\pi r^3 \\ \text{Surface Area: } A^\beta &= 4\pi r^2\end{aligned}$$

Therefore

$$\begin{aligned}\gamma &= (P^\beta - P^\alpha) \frac{r}{2} \\ \frac{2\gamma}{r} &= \Delta P\end{aligned}$$

The constitutive expression given is (spherical coordinates)

$$\begin{aligned}\sigma_i &= \frac{\lambda_i}{J} \frac{\partial}{\partial \lambda_i} U_e + \frac{d}{dJ} U_m - \frac{\mu}{\Omega} \\ \sigma_r &= \frac{\lambda_r}{J} \frac{\partial}{\partial \lambda_r} U_e + \frac{d}{dJ} U_m - \frac{\mu}{\Omega}\end{aligned}$$

Free energy due to stretching (Flory, 1953) and mixing:

$$\begin{aligned}U_e(\mathbf{F}) &= \frac{1}{2} N k_B T [F_{iK} F_{iK} - 3 - 2 \log(\det \mathbf{F})] \\ U_e(\lambda_r, \lambda_\theta, \lambda_\varphi) &= \frac{1}{2} N k_B T [\lambda_r^2 + \lambda_\theta^2 + \lambda_\varphi^2 - 3 - 2 \log(\lambda_r \lambda_\theta \lambda_\varphi)]\end{aligned}$$

$$\begin{aligned}U_m(\mathbf{F}) &= \frac{k_B T}{\Omega} \left[(\det \mathbf{F} - 1) \log \left(\frac{\det \mathbf{F} - 1}{\det \mathbf{F}} \right) - \frac{\chi}{\det \mathbf{F}} \right] \\ U_m(J) &= \frac{k_B T}{\Omega} \left[(J - 1) \log \left(\frac{J - 1}{J} \right) - \frac{\chi}{J} \right]\end{aligned}$$

Calculate the derivatives

$$\begin{aligned}\frac{\partial U_e}{\partial \lambda_r} &= \frac{1}{2} N k_B T \frac{\partial}{\partial \lambda_r} [\lambda_r^2 + \lambda_\theta^2 + \lambda_\varphi^2 - 3 - 2 \log(\lambda_r \lambda_\theta \lambda_\varphi)] \\ &= \frac{1}{2} N k_B T [2\lambda_r - 2 \frac{\lambda_\theta \lambda_\varphi}{\lambda_r \lambda_\theta \lambda_\varphi}] \\ \frac{\partial U_e}{\partial \lambda_r} &= N k_B T [\lambda_r - \frac{1}{\lambda_r}]\end{aligned}$$

$$\begin{aligned}\frac{dU_m}{dJ} &= \frac{k_B T}{\Omega} \frac{d}{dJ} \left[(J-1) \log \left(\frac{J-1}{J} \right) - \frac{\chi}{J} \right] \\ \frac{dU_m}{dJ} &= \frac{k_B T}{\Omega} \left[\frac{1}{J} + \log \left(1 - \frac{1}{J} \right) + \frac{\chi}{J^2} \right]\end{aligned}$$

Substitute into constitutive relationship:

$$\begin{aligned}\sigma_r &= \frac{\lambda_r}{J} \frac{\partial}{\partial \lambda_r} U_e + \frac{d}{dJ} U_m - \frac{\mu}{\Omega} \\ \sigma_r &= N k_B T \frac{\lambda_r}{J} [\lambda_r - \frac{1}{\lambda_r}] + \frac{k_B T}{\Omega} \left[\frac{1}{J} + \log \left(1 - \frac{1}{J} \right) + \frac{\chi}{J^2} \right] - \frac{\mu}{\Omega} \\ \tilde{\sigma}_r N k_B T &= N k_B T \frac{\lambda_r}{J} [\lambda_r - \frac{1}{\lambda_r}] + \frac{k_B T}{\Omega} \left[\frac{1}{J} + \log \left(1 - \frac{1}{J} \right) + \frac{\chi}{J^2} \right] - \frac{\tilde{\mu} k_B T}{\Omega} \\ \tilde{\sigma}_r &= \frac{1}{\lambda_r} - \frac{1}{\lambda_r^3} + \frac{1}{N \Omega} \left[\frac{1}{\lambda_r^3} + \log \left(1 - \frac{1}{\lambda_r^3} \right) + \frac{\chi}{\lambda_r^6} \right] - \frac{\tilde{\mu}}{N \Omega} \\ \frac{\tilde{\mu}}{N \Omega} &= \frac{1}{\lambda_r} - \frac{1}{\lambda_r^3} + \frac{1}{N \Omega} \left[\frac{1}{\lambda_r^3} + \log \left(1 - \frac{1}{\lambda_r^3} \right) + \frac{\chi}{\lambda_r^6} \right] - \tilde{\sigma}_r \\ \tilde{\mu} &= N \Omega \left(\frac{1}{\lambda_r} - \frac{1}{\lambda_r^3} \right) + \frac{1}{\lambda_r^3} + \log \left(1 - \frac{1}{\lambda_r^3} \right) + \frac{\chi}{\lambda_r^6} - N \Omega \tilde{\sigma}_r \quad \text{Substitute } \sigma_r = -\frac{2\gamma}{\lambda_r} \\ \tilde{\mu} &= N \Omega \left(\frac{1}{\lambda_r} - \frac{1}{\lambda_r^3} \right) + \frac{1}{\lambda_r^3} + \log \left(1 - \frac{1}{\lambda_r^3} \right) + \frac{\chi}{\lambda_r^6} + N \Omega \frac{2\gamma}{\lambda_r}\end{aligned}$$

5 Length-Scales

5.1 Elastocapillary Length Scale

Refer to the paper *Elastocapillarity: Surface Tension and the Mechanics of Soft Solids* by Style, Jagota, Hui, and Dufresne

The length scale is given by:

$$l_e = \frac{\gamma}{E} \tag{5.1}$$

Recalling the definition for shear modulus:

$$G = \frac{E}{2(1+\nu)}$$

In Bouklas and Huang

$$G_0 = \frac{N k_B T}{\lambda_0} \quad G_\infty = \frac{N k_B T}{\lambda_\infty^f}$$

Considering instantaneous length scale, we can derive the elastocapillary length scale with respect to the constants we define:

$$\begin{aligned}
l_e &= \frac{\gamma}{E} \\
&= \frac{\gamma}{2(1 + \nu_0)G} \\
l_e &= \frac{\gamma}{2(1 + \nu_0)} \frac{\lambda_0}{Nk_B T}
\end{aligned}$$

Normalized

$$\begin{aligned}
l_e &= \frac{\lambda_0}{2(1 + \nu_0)} \frac{\gamma}{Nk_B T} \\
\tilde{l}_e &= \frac{\lambda_0}{2(1 + \nu_0)} \frac{\tilde{\gamma} Nk_B T}{Nk_B T} \\
\tilde{l}_e &= \frac{\lambda_0}{2(1 + \nu_0)} \tilde{\gamma}
\end{aligned}$$