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Diffusion and swelling in finitely deforming elastomers

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Outline

1. Physical Description of Swelling
2. Theory
   - Assumptions
   - Balance Laws
   - Mean Stress Theorem : Existence of a Free Swelling Solution
   - Polyconvexity : Existence of energy minimizers
3. Our Results/Contribution

Diffusion and Swelling

Diffusion motion of a fluid through a solid due to

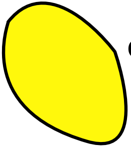
- chemical affinity, *Flory-Huggins model*
- motion of the solid, *stress-assisted diffusion*

Swelling deformation of a solid due to change in fluid content

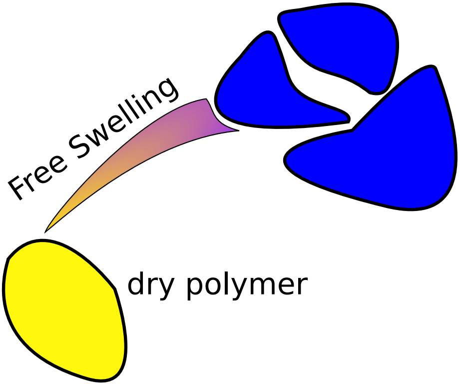
co-located materials allow for a number of complex behaviors

- biological systems : *growth*, *resorption*, *remodeling [5]*
  - nutrient transport
  - waste removal
- engineering materials : solvent/diffusion interactions
  - scission [7]
  - polymerization

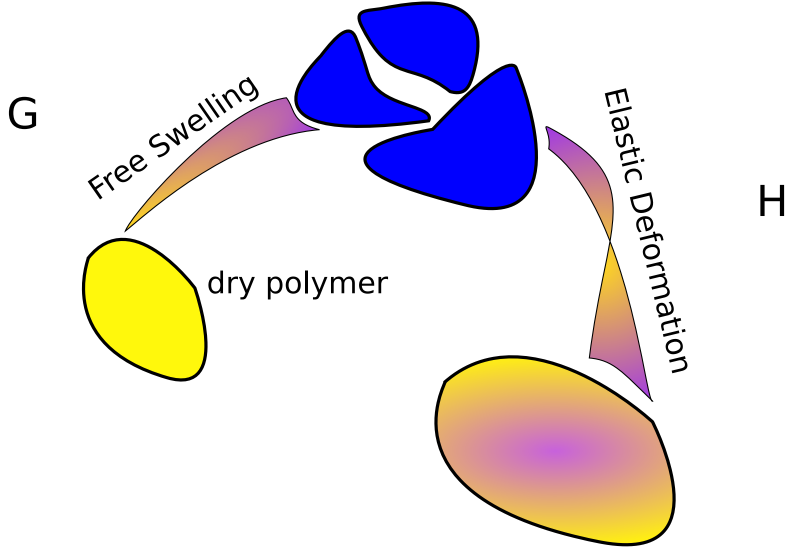
Reference State : Dry Polymer



Free-Swelling

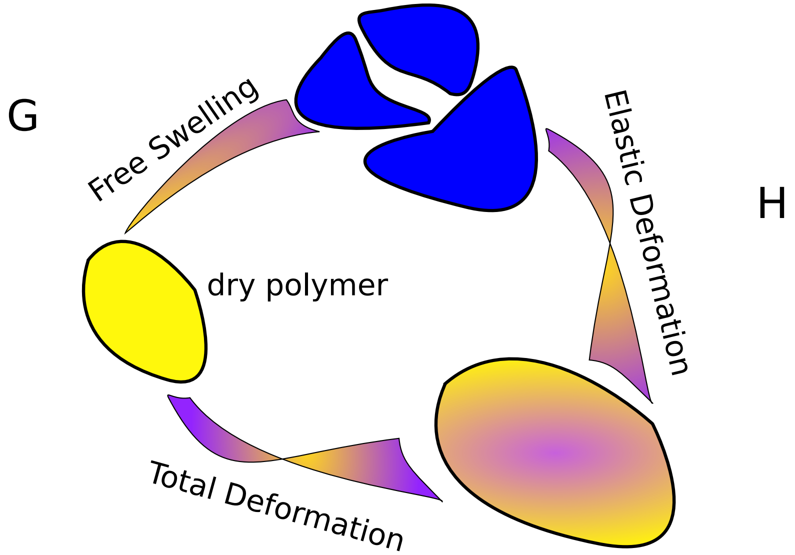


Elastic Deformation



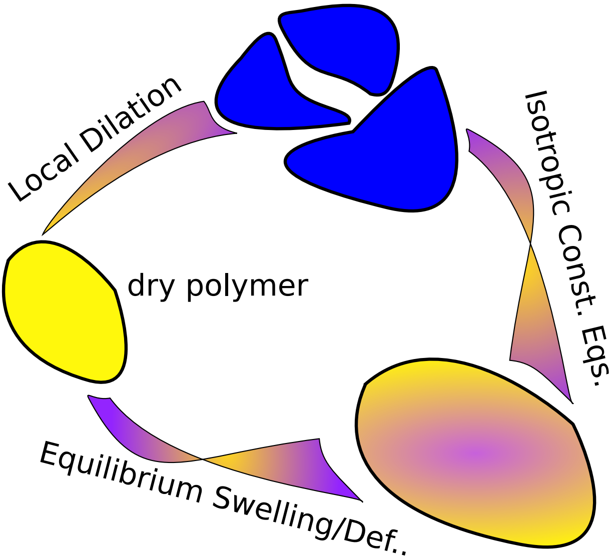
F=HG

Multiplicative Decomposition



F=HG

Mechanics



Local Dilation
Isotropic Const. Eqs.
dry polymer
Equilibrium Swelling/Def..

Continuum Mechanics approaches for isotropic swelling

- researchers generally decompose the total deformation into an isotropic free swelling deformation and an elastic isochoric deformation, see Pence [6], Anand [2]
    - the reference frame for the isotropic swelling portion is the dry elastomer
    - the reference frame for the elastic problem is the free swollen state
    - define concentration as mass of the diffusant per unit volume of the reference frame of the dry polymer
- this decomposition is justified : we show
    - the existence of a dilational deformation solution to the free swelling problem
    - this solution is *locally* energetically optimal since free-swelling provides for a polyconvex strain energy
    - constitutive equations need only be made isotropic w.r.t. the swollen state

Diffusive Balance : Global Form

- π is an arbitrary material subset of the dry polymer
- diffusant content is changed only through flux

$$\frac{d}{dt}\int_{\pi}\sigma dV = -\int_{\partial\pi}\mathbf{m}\cdot\mathbf{N}dA \ \forall\ \pi\subset\kappa \tag{1}$$

Diffusive Balance : Local Form

$$\dot{\sigma} + Div\mathbf{m} = 0 \text{ in } \kappa \tag{2}$$

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Dissipation Inequality

- Statement of the 2nd law in the absence of heat flux
- Power is supplied via tractions and fluid flux

$$\mathscr{D}(\pi,t) = \underbrace{\int_{\partial\pi} (\mathbf{p}\cdot\dot{\mathbf{x}} - \mathbf{q}\cdot\mathbf{N})\, dA}_{\mathscr{P}\ :\ \text{power supplied}} - \underbrace{\frac{d}{dt}\int_{\pi} \Psi\, dV}_{\dot{\mathscr{E}}} \geq 0 \ \forall\ \pi \subset \kappa \tag{3}$$

Dissipation Inequality : Local Form

$$(\Psi_{\mathbf{F}} - \mathbf{P})\cdot\dot{\mathbf{F}} + (\Psi_{\sigma} - \mu)\dot{\sigma} + \mathbf{m}\cdot D\mu \leq 0 \text{ in } \kappa \tag{4}$$

- Two rate terms $\dot{\mathbf{F}}$ and $\dot{\sigma}$

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Total Volume

$$\int_{\pi} J_F dv = \int_{\pi} (J_{F_e} + J_{F_d})\, dV \;\forall\; \pi \subset \kappa \quad (5)$$

Total Volume : Local Form

$$J_F = J_{F_e} + J_{F_d} \text{ in } \kappa \quad (6)$$

Assumption : *fluid volume is due solely to fluid flux.*

$$J_{F_d} = \sigma = \sigma_d v_d \text{ in } \kappa \quad (7)$$

Swelling Constraint

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Connects the energetic rate terms

Theory

For an isochoric elastic deformation, $J_{F_e} = 1$

$$J_F = 1 + \sigma = 1 + \sigma_d v_d \ \forall \ \pi \subset \kappa \tag{8}$$

Relate the Energetic Rates

$$\dot{\overline{J_F}} = \mathbf{F}^\star \cdot \dot{\mathbf{F}} = \dot{\sigma} = \dot{\sigma}_d v_d \text{ in } \kappa \tag{9}$$

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Simplifies the local dissipation inequality

Dissipation Inequality : Local Form

$$[\Psi_{\mathbf{F}} - \mathbf{P} + (\Psi_\sigma - \mu)\,\mathbf{F}^\star] \cdot \dot{\mathbf{F}} + \mathbf{m} \cdot D\mu \leq 0 \text{ in } \kappa \tag{10}$$

- Here $\dot{\mathbf{F}}$ and $\mathbf{m}$ are unrestricted

$$\mathbf{P} = \Psi_{\mathbf{F}} + \underbrace{(\Psi_\sigma - \mu)}_{q}\mathbf{F}^\star \text{ in } \kappa \tag{11}$$

$$\mathbf{m} \cdot D\mu \leq 0 \text{ in } \kappa \tag{12}$$

Constitutive structure of the flux

$$\mathbf{m} = \mathbf{M}(\mathbf{F}, \sigma, D\mu)\, D\mu \tag{13}$$

Mobility Tensor Satisfies

$$D\mu \cdot \mathbf{M}(\mathbf{F}, \sigma, D\mu)\, D\mu \leq 0 \tag{14}$$

Representation Theorem

$$\mathbf{M} = \alpha_0 \mathbf{I} + \alpha_1 \mathbf{U} + \alpha_2 \mathbf{U}^2 \tag{15}$$

$$\mathbf{m} = \left(\gamma_0 \mathbf{I} + \gamma_1 \mathbf{U} + \gamma_2 \mathbf{U}^2\right) \mathbf{H}^t (grad\, \mu) \tag{16}$$

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Isotropy and Noll's Rule

Isotropic Material

- Material whose *symmetry group* w.r.t. some reference configuration is the *proper orthogonal group*

$$\mathbf{G}\left(\mathbf{QHQ}^T\right) = \mathbf{QG}(\mathbf{H})\mathbf{Q}^T \tag{17}$$

$$\mathbf{m}\left(\mathbf{QUQ}^T\right) = \alpha_0\mathbf{QIQ}^T + \alpha_1\mathbf{QUQ}^T + \alpha_2\mathbf{QU}^2\mathbf{Q}^T = \mathbf{Qm}(\mathbf{U})\mathbf{Q}^T \tag{18}$$

Noll's Rule

$$\mathbf{H}_1 = \mathbf{FH}_0\mathbf{F}^{-1} \tag{19}$$

Isotropy and Noll's Rule

Noll's Rule applied to flux

$$\mathbf{m}_1 = \mathbf{G}\mathbf{m}_0\mathbf{G}^{-1} \tag{20}$$

$$\mathbf{m}_1 = (\lambda\mathbf{I})\,\mathbf{m}_0\,(\lambda\mathbf{I})^{-1} = \mathbf{m}_0 \tag{21}$$

- *if constitutive response is isotropic w.r.t. the swollen state, it is also isotropics w.r.t. the dry polymer.*

Mean Stress Theorem

- The mean value of the stress in a body is

$$MV(\mathbf{P}) = \frac{1}{Vol(\pi)} Sym\left[\int_{\partial\pi} \mathbf{p} \otimes \mathbf{x} dA + \int_{\pi} \mathbf{b} \otimes \mathbf{x} dV\right] \tag{22}$$

- As body force **b** and tractions **p** vanish the mean stress approaches zero.
- As $Vol(\pi) \to 0$, $\mathbf{P}(\mathbf{x}) \to MV(\mathbf{P}) = \mathbf{0}$
- also applies to $\mu\dot{\sigma} \leq 0$

Stress Free Reference

- The mean value of the stress approaches zero as the size of an arbitrary subregion approaches zero.
- The Mean Stress theorem establishes the existence of a stress free reference state, generally not continuous.

Existence of a Free Swelling Solution

- As the polymer undergoes local, isotropic swelling, a dilation deformation, to a stress-free local state

$$\mathbf{P} = \mathbf{R}\sigma = 0 \tag{23}$$

- $\sigma = \left(\frac{\partial \psi}{\partial i_1} + i_1 \frac{\partial \psi}{\partial i_2}\right)\mathbf{I} - \frac{\partial \psi}{\partial i_2}\mathbf{U} - q\mathbf{U}^{\star}$
- Taking the trace, obtain the equilibrium condition for free swelling with $i_1 = 3\lambda$, and $i_2 = 3\lambda^2$ and the swelling

$$q i_2 = 3\frac{\partial \psi}{\partial i_1} + 2\frac{\partial \psi}{\partial i_2} \tag{24}$$

$$\lambda^3 = 1 + \sigma \tag{25}$$

Strain Energy in terms of Stretch Tensor

- If the strain energy is insensitive to SPRBM and isotropic w.r.t. it is a function of the invariants of $\mathbf{U}$, $i_1,\ i_2,\ i_3$.
- These are related to the invariants of $\mathbf{C}$

$$I_1 = i_1^2 - 2i_2,\ I_2 = i_2^2 - 2i_1 i_3,\ I_3 = i_3^2 \tag{26}$$

- The i_k can be obtained from the I_k by inverting $I_1 = i_1^2 - 2i_2$, $I_2 = i_2^2 - 2i_1 i_2,\ I_3 = i_3^2$
  - Iterative techniques
  - essentially a 2x2 matrix inversion problem
  - SVD
- The strain energy formulation in terms of the stretch tensors is helpful in proving polyconvexity since it provides convenient formulations of the derivatives [4]

$$(i_1)_{\mathbf{F}} = (i_2)_{\mathbf{F}^\star} = \mathbf{R},\ \Phi_{\mathbf{F}} = \frac{\partial \varphi}{\partial i_1}\mathbf{R}\ \Phi_{\mathbf{F}^\star} = \frac{\partial \varphi}{\partial i_2}\mathbf{R} \tag{27}$$

Polyconvexity requires the existence of a function Φ such that

$$\Psi'(\mathbf{F}) = \varphi(\mathbf{F}, \mathbf{F}^\star, J_F) \tag{28}$$

is jointly convex in its arguments. This implies non-local Quasi-convexity which assure an energy minimizers and hence a solution for a specific deformation.

For polyconvexity

$$\begin{aligned} \Psi'(\overline{\mathbf{F}}) - \Psi'(\mathbf{F}) \geq \; & \varphi_{\mathbf{F}}(\mathbf{F}, \mathbf{F}^\star, J_F) \cdot (\overline{\mathbf{F}} - \mathbf{F}) \\ + \; & \varphi_{\mathbf{F}^\star}(\mathbf{F}, \mathbf{F}^\star, J_F) \cdot \left(\overline{\mathbf{F}}^\star - \mathbf{F}^\star\right) \\ + \; & \varphi_{J_F}(\mathbf{F}, \mathbf{F}^\star, J_F) \cdot (J_{\overline{F}} - J_F) \quad \forall \; \mathbf{F} \text{ and } \overline{\mathbf{F}} \end{aligned} \tag{29}$$

invariants of **U**

Here we show that isotropic swelling, since it is a dilational deformation, is polyconvex for any strain energy

B

all 1976 [1]

- A polyconvex strain energy function provides the existence of a energy minimizer
- not unique

Choose the function

$$\Phi\left(\mathbf{F},\mathbf{F}^{\star},J_F\right)=\varphi\left(\sqrt{\mathbf{F}^t\mathbf{F}},\sqrt{\left(\mathbf{F}^{\star}\right)^t\mathbf{F}^{\star}},J_F\right) \quad (30)$$

work with i_k and it's derivatives w.r.t. $\mathbf{F}$, $\mathbf{F}^*$ as it simplifies the calculations.

Polyconvexity of a Free Swelling Solution

For free swelling $\mathbf{F} = \lambda \mathbf{I}$, and the i_k formulation, polyconvexity simplifies to :

$$\psi\left(\overline{i_1}, \overline{i_2}, \sigma^*\right) - \psi\left(i_1, i_2, \sigma^*\right) \leq \left(\overline{i_1} - i_1\right) \frac{\partial \psi}{\partial i_1} + \left(\overline{i_2} - i_2\right) \frac{\partial \psi}{\partial i_2} \qquad (31)$$

- We know $\frac{\partial \psi}{\partial i_1} \geq 0$, $\frac{\partial \psi}{\partial i_2} \geq 0$ by definition of polyconvexity
- Require a suitable formulation of $\bar{i}_1, \bar{i}_2$ to show that this holds for a given deformation
- Ogden provides a decomposition of a dilation into a *pure shear* and a *isochoric extension with lateral compression.*

Polyconvexity for Free Swelling : I

Ogden [3](pg. 110) : any dilation can be decomposed into a *pure shear* and an *isochoric axial extension*

$$\overline{\mathbf{F}} = \overline{\mathbf{U}} = \left(\overline{\lambda}\mathbf{I}\right)\mathbf{SE} \tag{32}$$

where

$$\mathbf{S} = s\mathbf{u}_1 \otimes \mathbf{u}_1 + s^{-1}\mathbf{u}_2 \otimes \mathbf{u}_2 + \mathbf{u}_3 \otimes \mathbf{u}_3 \tag{33}$$

$$\mathbf{E} = t^{-\frac{1}{2}}\left(\mathbf{u}_1 \otimes \mathbf{u}_1 + \mathbf{u}_2 \otimes \mathbf{u}_2\right) + t\mathbf{u}_3 \otimes \mathbf{u}_3 \tag{34}$$

leading to

$$\bar{i}_1 = \overline{\lambda}\left[\left(s + s^{-1}\right)t^{-\frac{1}{2}} + t\right],\ \bar{i}_2 = \overline{\lambda}^2\left[\left(s + s^{-1}\right)t^{\frac{1}{2}} + t^{-1}\right],\ \bar{i}_3 = \overline{\lambda}^3 \tag{35}$$

Polyconvexity for Free Swelling : II

$$\Psi_{(\sigma^\star)}\left(\overline{\mathbf{F}}\right) - \Psi_{(\sigma^\star)}\left(\mathbf{F}\right) \geq \lambda f\left(s,t\right)\frac{\partial \psi}{\partial i_1} + \lambda^2 f\left(s,t^{-\frac{1}{2}}\right)\frac{\partial \psi}{\partial i_2} \quad (36)$$

- $\lambda \geq 0$ by choice of reference frame
- $\frac{\partial \psi}{\partial i_1} \geq 0$, $\frac{\partial \psi}{\partial i_2} \geq 0$ by definition of polyconvexity
- $f\left(s,t\right) = \left(s + s^{-1}\right)t^{-\frac{1}{2}} + t^1 - 3 \geq 0$
- $f\left(s,t^{-\frac{1}{2}}\right) = \left(s + s^{-1}\right)t + t^{-1} - 3 \geq 0$

$$f\left(x,y\right) \geq 0 \iff g\left(x\right) \geq h(y) \quad (37)$$

$$x + x^{-1} \geq \left(3 - y\right)t^{-\frac{1}{2}} \quad (38)$$

$g\left(x\right)$ has a strict global *minimum* equal to 2 at $(1,1)$
$h(x)$ has a strict global *maximum* equal to 2 at $(1,1)$

Summary

- Taking the dry polymer as a reference simplifies polyconvexity calculations
- The Mean Stress Theorem suggests the existence of a stress-free and flux-free local swollen reference state
- A dilational deformation is a solution to the Free Swelling problem for an arbitrary swelling field.
- A strain energy function that is isotropic w.r.t. the swollen frame is isotropic w.r.t. the dry reference due to Noll's Rule, i.e. dilational deformations preserves the symmetry group.
- This justifies using a multiplicative decomposition of the total deformation such that it is composed of an point-wise dilational swelling and an elastic deformation.

- Outlook
  - Analytical and Computational results
  - Growth, remodeling, resorption driven by diffusion
  - Time-dependent diffusion
  - Anisotropy

For Further Reading I

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Piola Stress

$$\mathbf{P} = \mathbf{R}\sigma \tag{39}$$

$$\sigma = \left(\frac{\partial\psi}{\partial i_1} + i_1\frac{\partial\psi}{\partial i_2}\right)\mathbf{I} - \frac{\partial\psi}{\partial i_2}\mathbf{U} - q\mathbf{U}^{\star} \tag{40}$$

$$\mu = \frac{\partial\psi}{\partial\sigma} + q \tag{41}$$

Piola Stress in terms of principal stretches

$$\mathbf{R} = \mathbf{v}_i \otimes \mathbf{u}_i \tag{42}$$

$$\sigma = \sum \left(\frac{\partial W}{\partial \lambda_i} - q u_i \right) \mathbf{u}_i \otimes \mathbf{u}_i \tag{43}$$

$$\lambda_i \text{ evals of } \mathbf{U} \tag{44}$$

$$\frac{J_F}{\lambda_i} \text{ evals of } \mathbf{U}^\star \tag{45}$$

$$\mathbf{u}_i \text{ evectors of } \mathbf{U} \text{ and } \mathbf{U}^\star \tag{46}$$

$$W(\lambda_i, \sigma) = \psi(\lambda_1 + \lambda_2 + \lambda_3, \lambda_1\lambda_2 + \lambda_1\lambda_3 + \lambda_3\lambda_2, \sigma) \tag{47}$$