Swell-Induced Surface Instability in Substrate-Confined Hydrogel Layer

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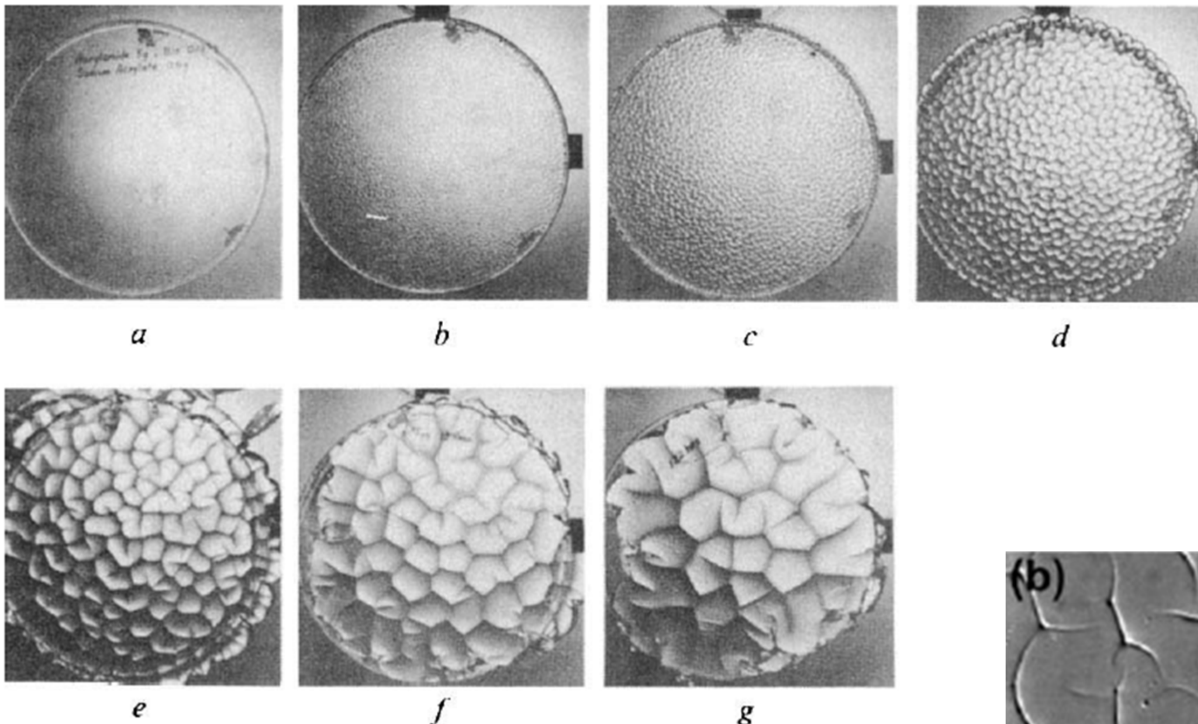
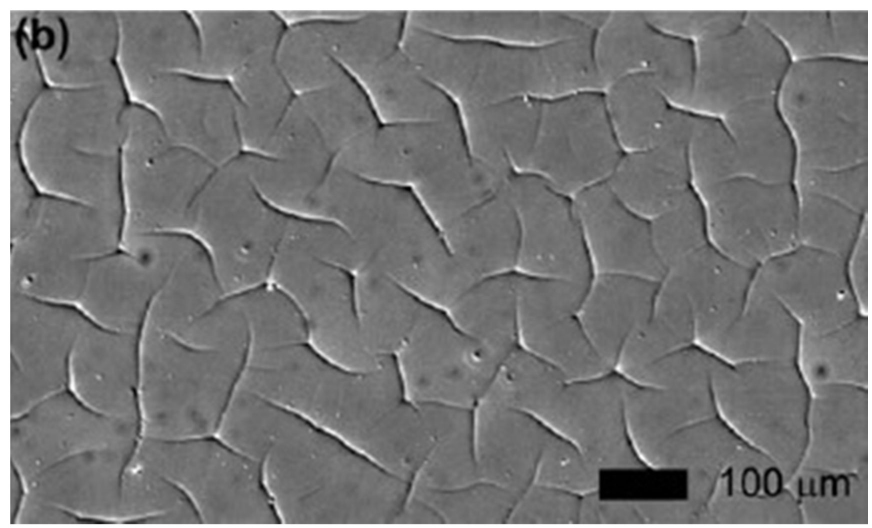
Swelling of rubber and gels



- Southern and Thomas, 1965
- Tanaka et al, 1987
- Trujillo et al., 2008



- ➢ Critical condition for the onset of surface instability?
- ➢ Any characteristic size?
- ➢ Effect of kinetics?

A theoretical framework for gels

Free energy density function $U(\mathbf{F}, C)$

Nominal stress $s_{iK} = \frac{\partial U}{\partial F_{iK}}$

Chemical potential $\mu = \frac{\partial U}{\partial C}$

Volume change

$\det(\mathbf{F}) = 1 + vC$

Equilibrium equations $\frac{\partial s_{iK}}{\partial X_K} + B_i = 0$ $\frac{\partial \mu}{\partial X_K} = 0$

Boundary conditions $T_i = s_{iK} N_K$ **or** $\delta x_i = 0$ $\mu = \mu_{ext}$

- Hong, Zhao, Zhou, and Suo, JMPS 2008

A specific material model

Free energy density function

$$U(\mathbf{F}, C) = U_e(\mathbf{F}) + U_m(C)$$

Neo-Hookeon rubber elasticity:

$$U_e(\mathbf{F}) = \frac{1}{2} N k_B T \left[F_{iK} F_{iK} - 3 - 2 \ln(\det(\mathbf{F})) \right]$$

Flory-Huggins polymer solution theory:

$$U_m(C) = \frac{k_B T}{v} \left[vC \ln\left(\frac{vC}{1+vC} \right) + \frac{\chi v C}{1+vC} \right]$$

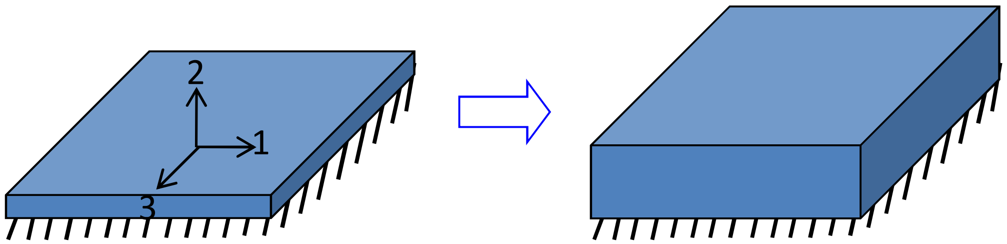
Nk_BT : initial shear modulus of the polymer network

N : No. of polymer chains per unit volume

ν : Volume of a solvent molecule

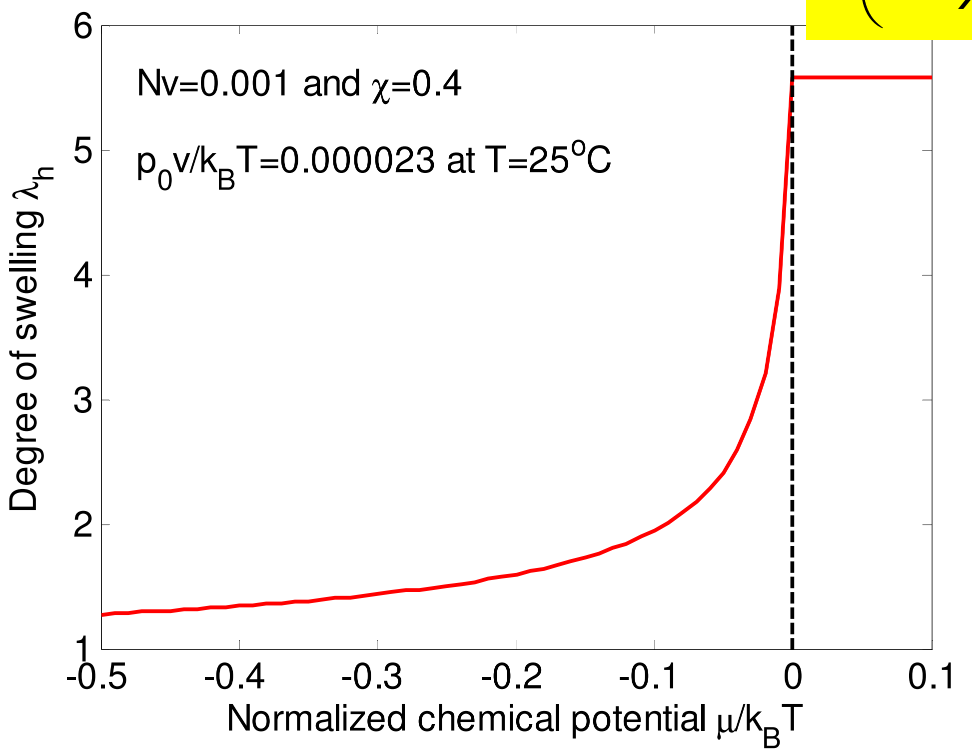
χ : Enthalpy of mixing parameter

Homogeneous swelling of a hydrogel layer



$$\lambda_1 = \lambda_3 = 1$$
$$\lambda_2 = \lambda_h > 1$$

$$\ln\left(1-\frac{1}{\lambda_h}\right)-\frac{1}{\lambda_h}+\frac{\chi}{\lambda_h^2}+Nv\left(\lambda_h-\frac{1}{\lambda_h}\right)=\frac{\mu_{ext}-pv}{k_BT}$$

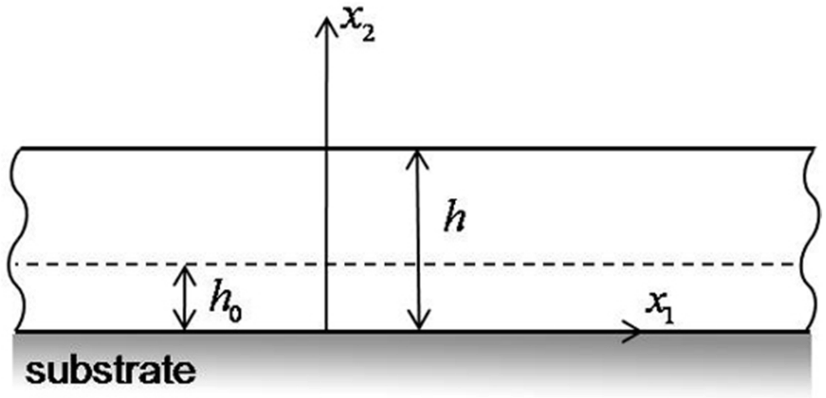


External chemical potential:

$$\mu_{ext} = k_B T \ln\left(p / p_0\right) \qquad p \le p_0$$

$$\mu_{ext} = (p - p_0)v \qquad p \ge p_0$$

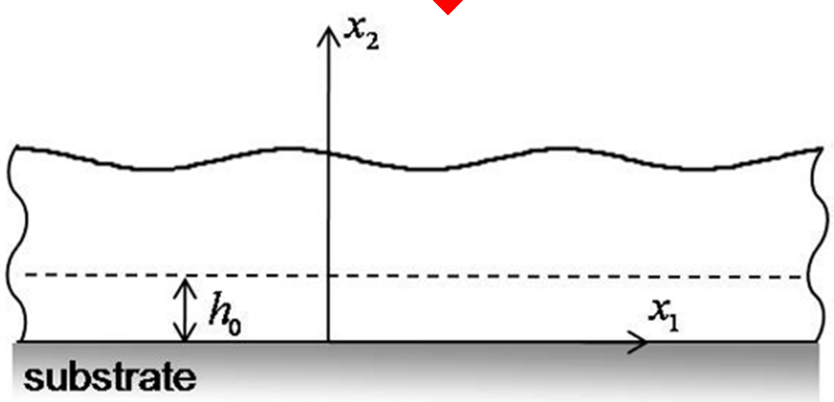
A linear perturbation analysis



Homogeneous swelling

$$\mathbf{F} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & \lambda_h & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

Linear perturbation: $u_1 = u_1(x_1, x_2),\ u_2 = u_2(x_1, x_2)$



$$\tilde{\mathbf{F}} = \begin{bmatrix} 1 + \frac{\partial u_1}{\partial x_1} & \lambda_h \frac{\partial u_1}{\partial x_2} & 0 \\ \frac{\partial u_2}{\partial x_1} & \lambda_h \left(1 + \frac{\partial u_2}{\partial x_2}\right) & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

Kang and Huang, J. Mech. Phys. Solids 58, 1582-1598 (2010).

Linearized equilibrium equations

$$\left(1+\lambda_h\xi_h\right)\frac{\partial^2 u_1}{\partial x_1^2}+\lambda_h^2\frac{\partial^2 u_1}{\partial x_2^2}+\lambda_h\xi_h\frac{\partial^2 u_2}{\partial x_1\partial x_2}=0$$

$$\frac{\partial^2 u_2}{\partial x_1^2}+\lambda_h\left(\xi_h+\lambda_h\right)\frac{\partial^2 u_2}{\partial x_2^2}+\lambda_h\xi_h\frac{\partial^2 u_1}{\partial x_1\partial x_2}=0$$

Solution by the method of Fourier transform

$$\begin{cases}\hat{u}_1\left(x_2;k\right)=\sum_{n=1}^{4}A_n\bar{u}_1^{(n)}\exp\left(q_n x_2\right)\\ \hat{u}_2\left(x_2;k\right)=\sum_{n=1}^{4}A_n\bar{u}_2^{(n)}\exp\left(q_n x_2\right)\end{cases}$$

Kang and Huang, J. Mech. Phys. Solids 58, 1582-1598 (2010).

Critical Conditions for Surface Instability

Boundary conditions

$$\begin{cases} s_{22} = -p\left(1+\dfrac{\partial u_1}{\partial x_1}\right) & \textbf{at } x_2 = h \\ s_{12} = p\dfrac{\partial u_2}{\partial x_1} & \textbf{at } x_2 = h \\ u_1 = u_2 = 0 & \textbf{at } x_2 = 0 \end{cases}$$

$$\Rightarrow \quad \boxed{\sum_{n=1}^{4} D_{mn} A_n = 0}$$

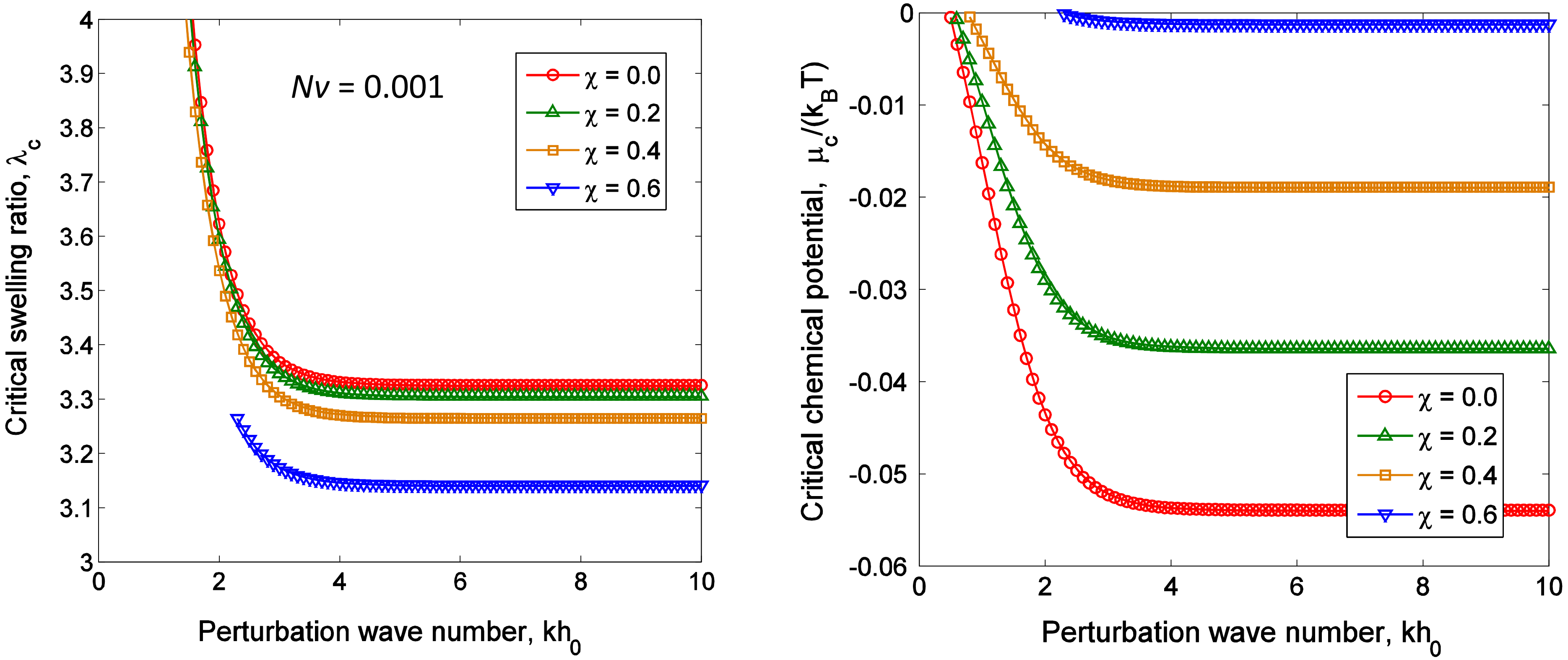
$$[D_{mn}] = \begin{bmatrix} 1 & 1 & 1 & 1 \\ -\lambda_h & \lambda_h & -\beta & \beta \\ 2\lambda_h e^{kh_0} & 2\lambda_h e^{-kh_0} & \left(\lambda_h + \dfrac{1}{\lambda_h}\right)e^{\beta kh} & \left(\lambda_h + \dfrac{1}{\lambda_h}\right)e^{-\beta kh} \\ \left(\lambda_h + \dfrac{1}{\lambda_h}\right)e^{kh_0} & -\left(\lambda_h + \dfrac{1}{\lambda_h}\right)e^{-kh_0} & 2\beta e^{\beta kh} & -2\beta e^{-\beta kh} \end{bmatrix}$$

Critical condition:

$$\det[D_{mn}] = f\left(kh_0, \lambda_h; Nv, \chi\right) = 0$$

Kang and Huang, J. Mech. Phys. Solids 58, 1582-1598 (2010).

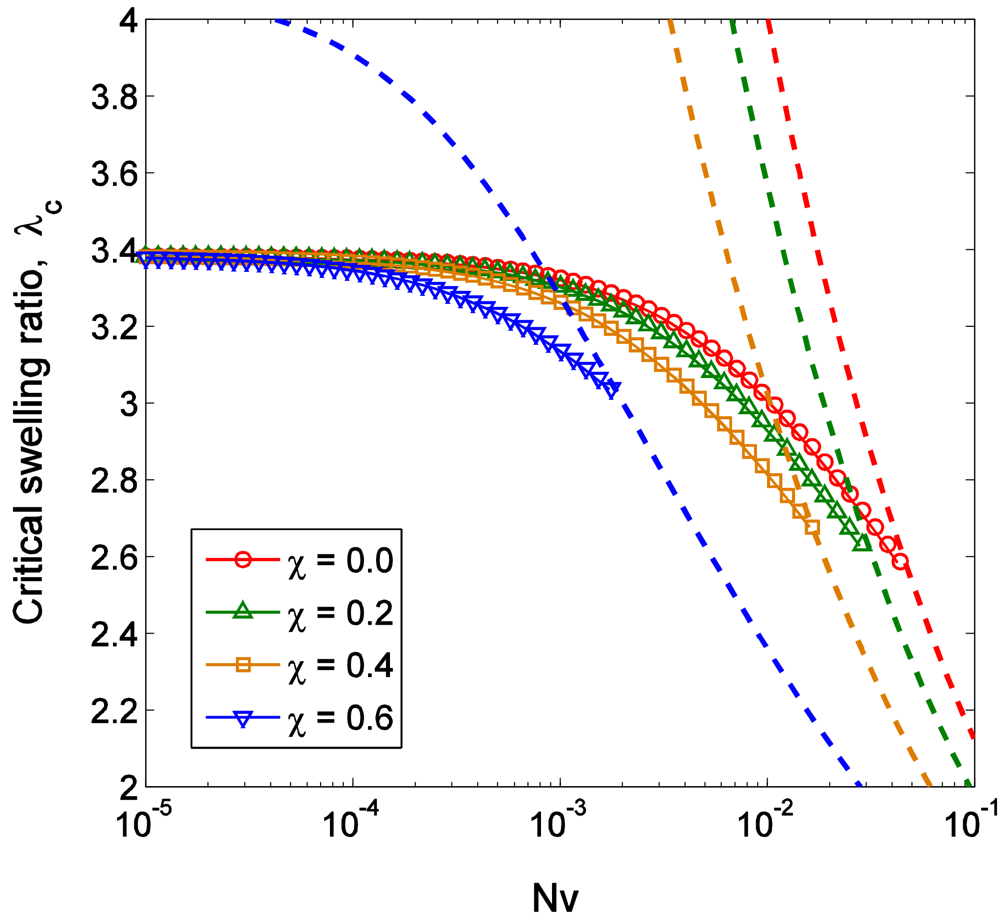
Effect of perturbation wave number



- Long wavelength perturbation is stabilized by the substrate effect.
- Short wavelength perturbation is unaffected.
- Thus the critical condition can be taken at the short-wavelength limit.

Kang and Huang, J. Mech. Phys. Solids 58, 1582-1598 (2010).

Short-wave limit ($kh_0 \to \infty$)

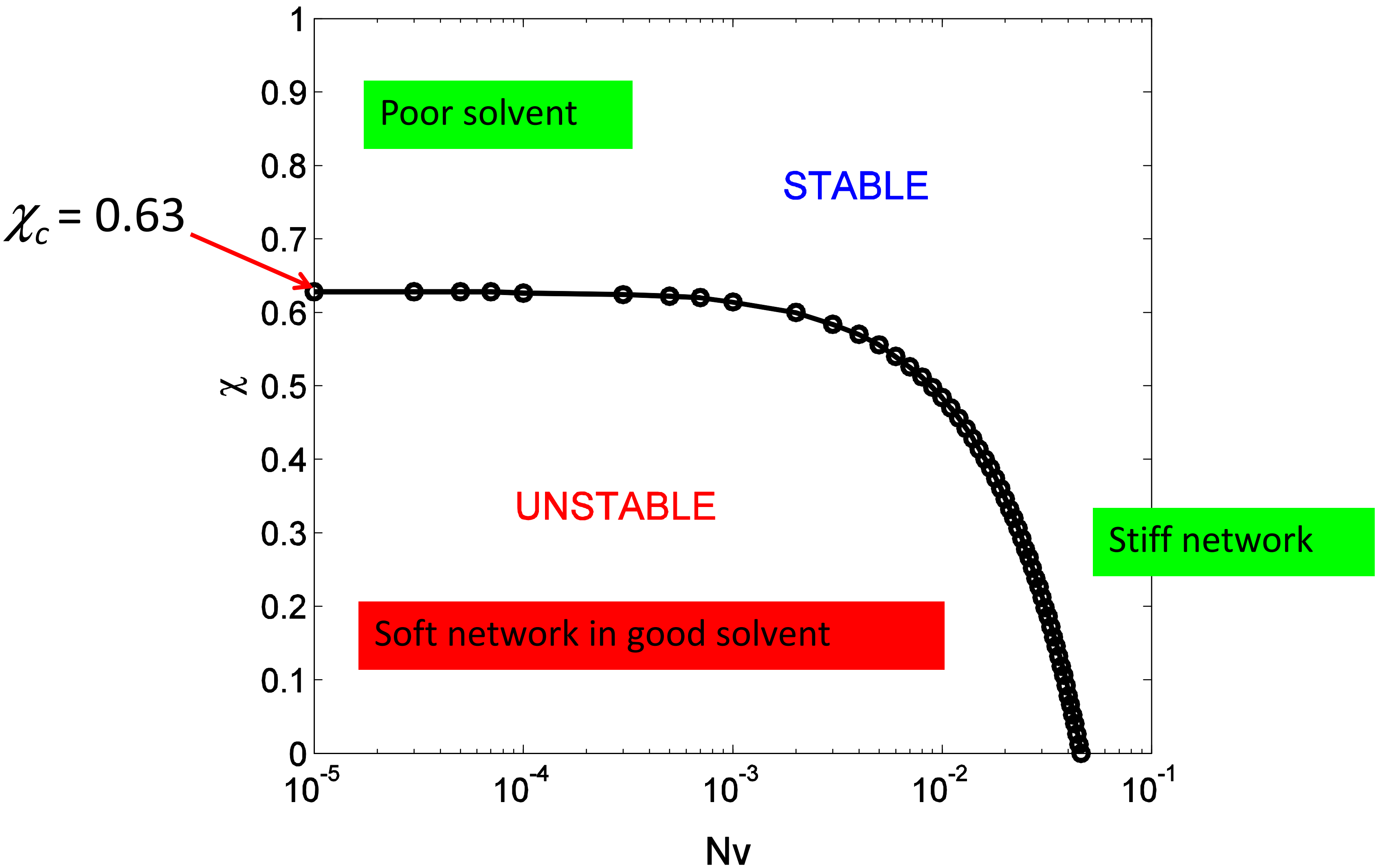


$$\left(\lambda_h + \frac{1}{\lambda_h}\right)^2 = 4\lambda_h \beta$$

- The critical swelling ratio depends on *Nv* and χ, ranging between 2.5 and 3.4.
- For each χ, there exists a critical value for *Nv*.
- For small *Nv* (< 10^{-4}), the critical swelling ratio is nearly a constant (~3.4).

Kang and Huang, J. Mech. Phys. Solids 58, 1582-1598 (2010).

A stability diagram



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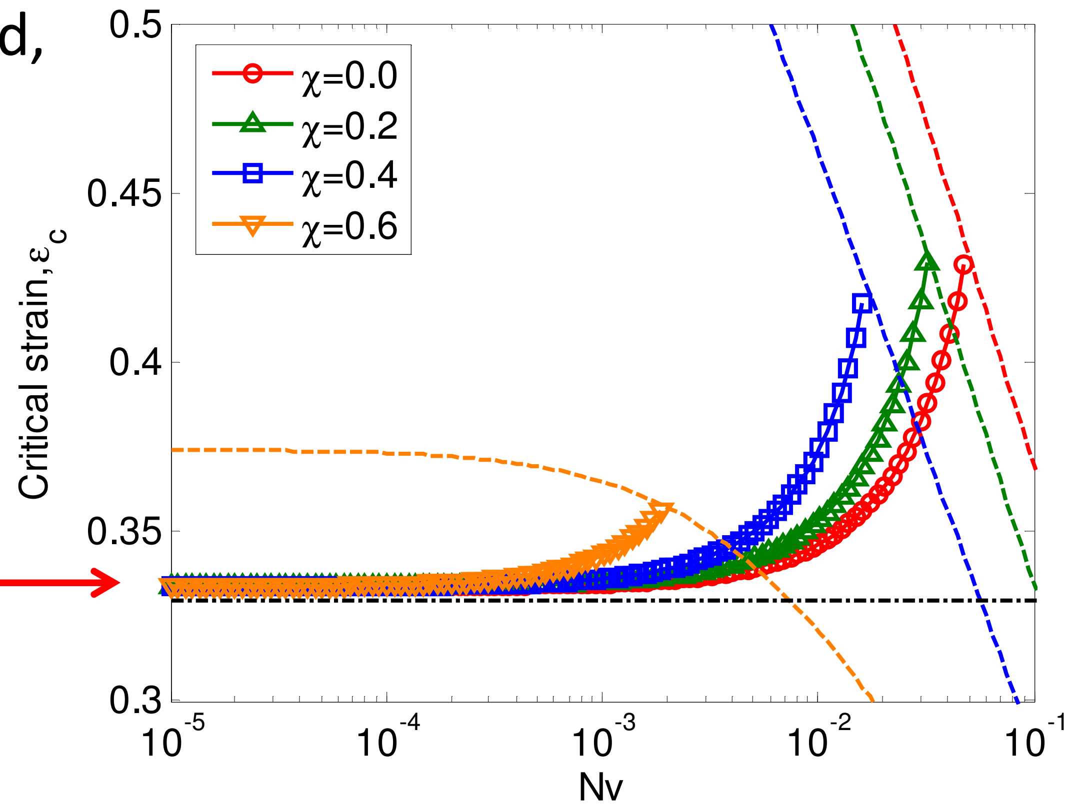
Critical linear strain

Relative to the unconstrained, free swelling in 3D:

$$\varepsilon = \frac{\lambda_{3D} - 1}{\lambda_{3D}}$$

$$\varepsilon_c = 0.33$$



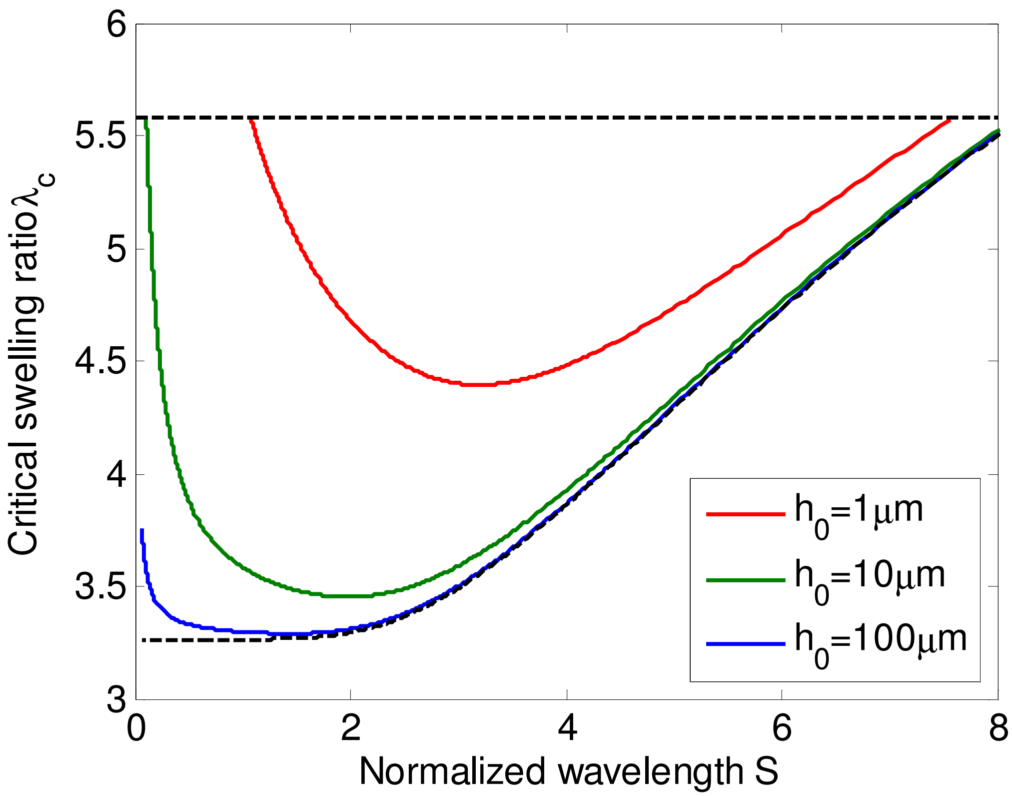
- Trujillo et al.'s experiments for a swelling hydrogel
- Biot's analysis for rubber under equi-biaxial compression

Kang and Huang, J. Mech. Phys. Solids 58, 1582-1598 (2010).

Effect of surface tension

A length scale:

$$L = \frac{\gamma}{Nk_B T} \sim \frac{0.53nm}{N\nu}$$

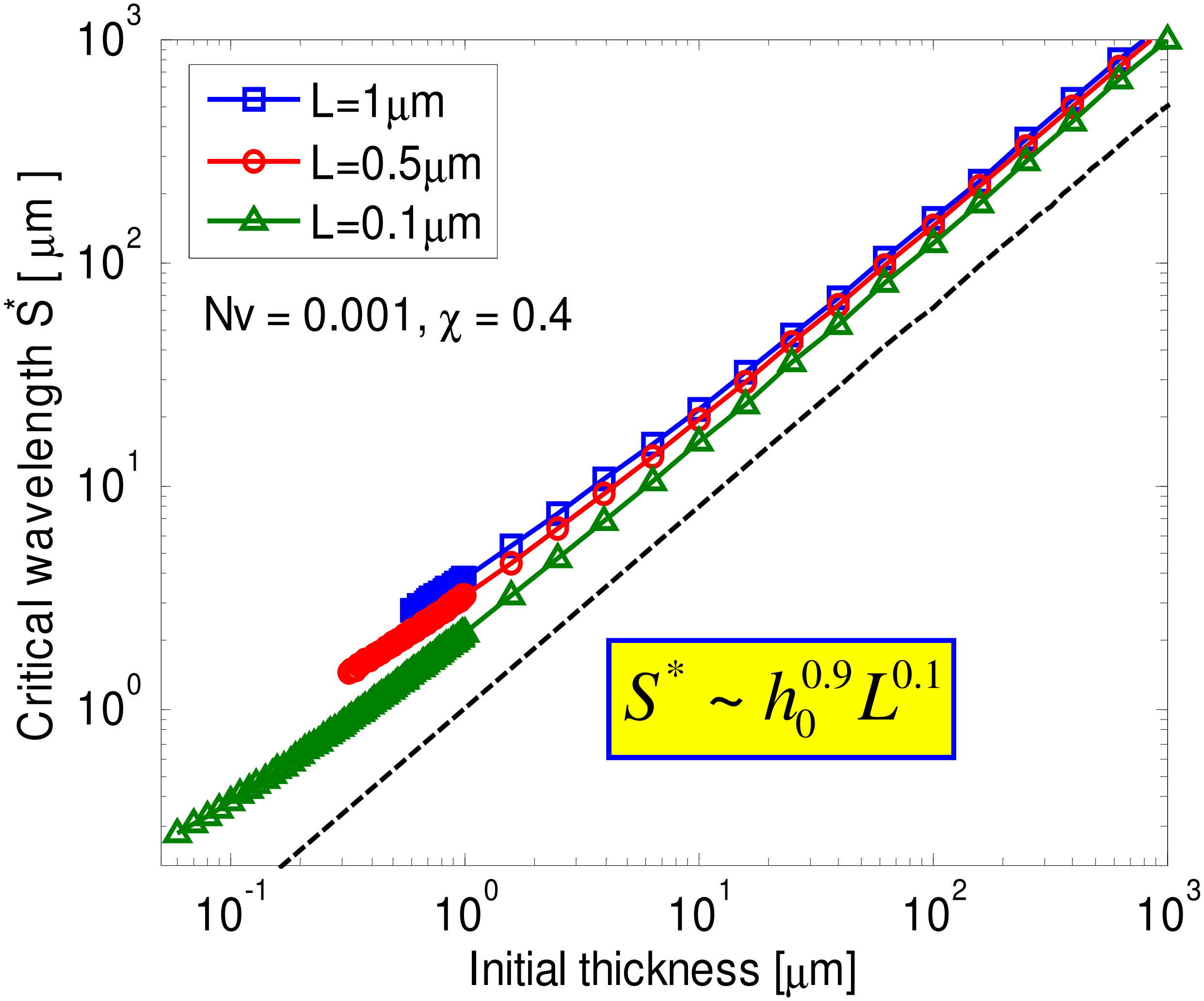


$N\nu = 0.001,\ \chi = 0.4$

- Long wavelength perturbation is stabilized by the substrate.
- Short wavelength perturbation is stabilized by surface tension.
- An intermediate characteristic wavelength emerges.
- The minimum critical swelling ratio depends on the layer thickness.

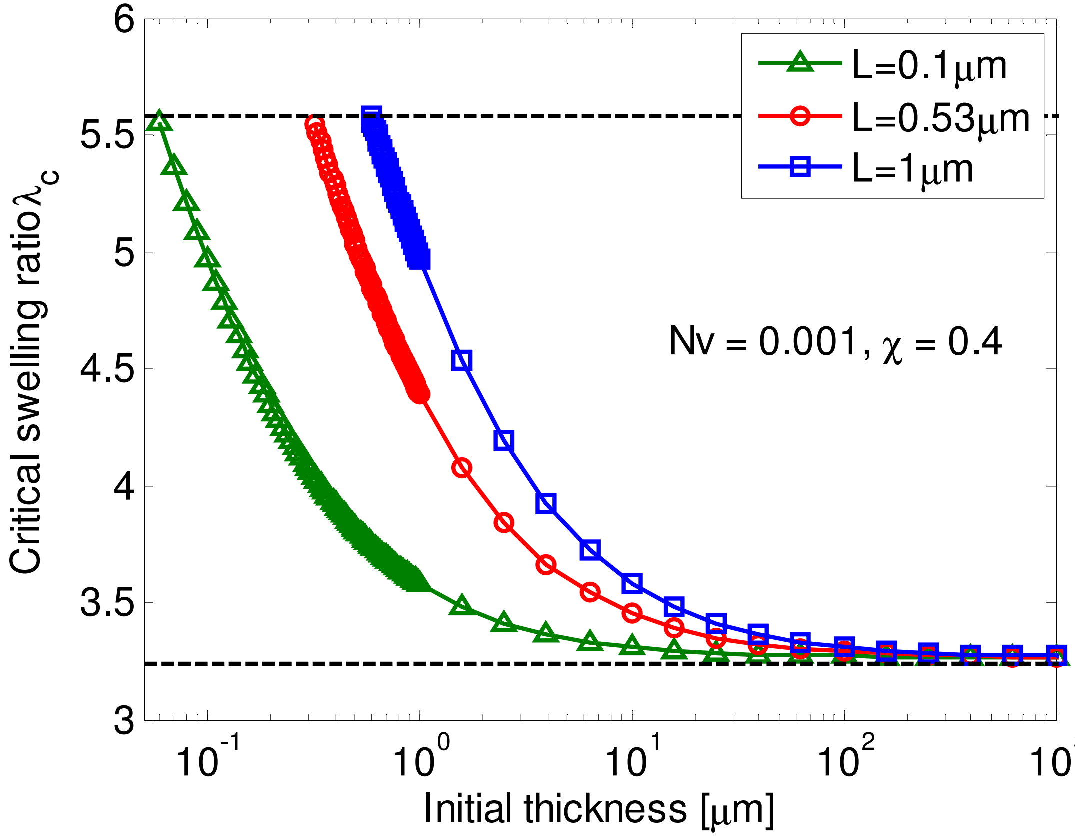
Kang and Huang, Soft Matter 6, 5736-5742 (2010).

Characteristic wavelength



Kang and Huang, Soft Matter 6, 5736-5742 (2010).

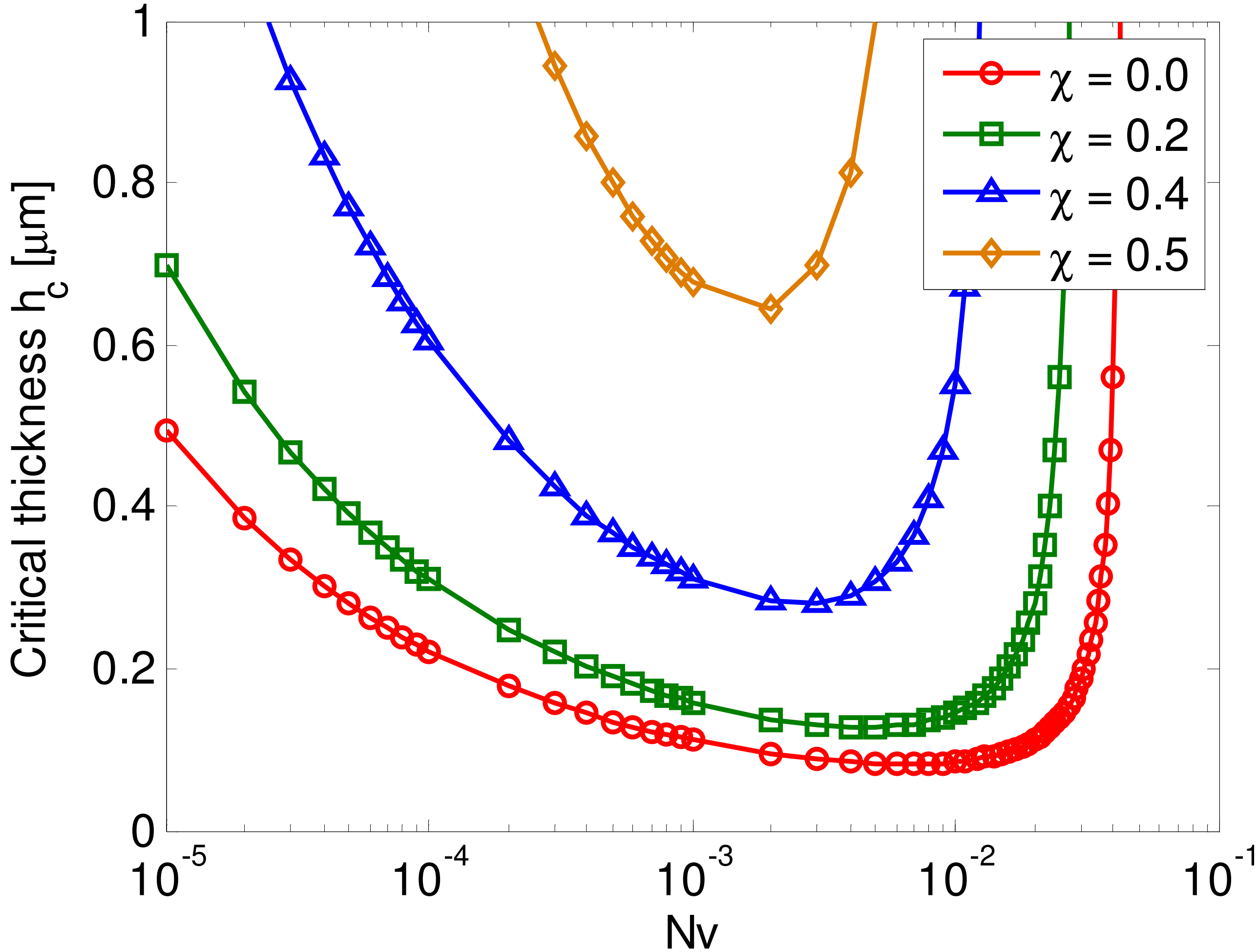
Thickness-dependent stability



- The hydrogel layer becomes increasingly stable as the initial layer decreases;
- Below a critical thickness (h_c), the hydrogel is stable at the equilibrium state.

Kang and Huang, Soft Matter 6, 5736-5742 (2010).

Critical thickness



$$L' = \frac{\gamma v}{k_B T} = 0.53nm$$

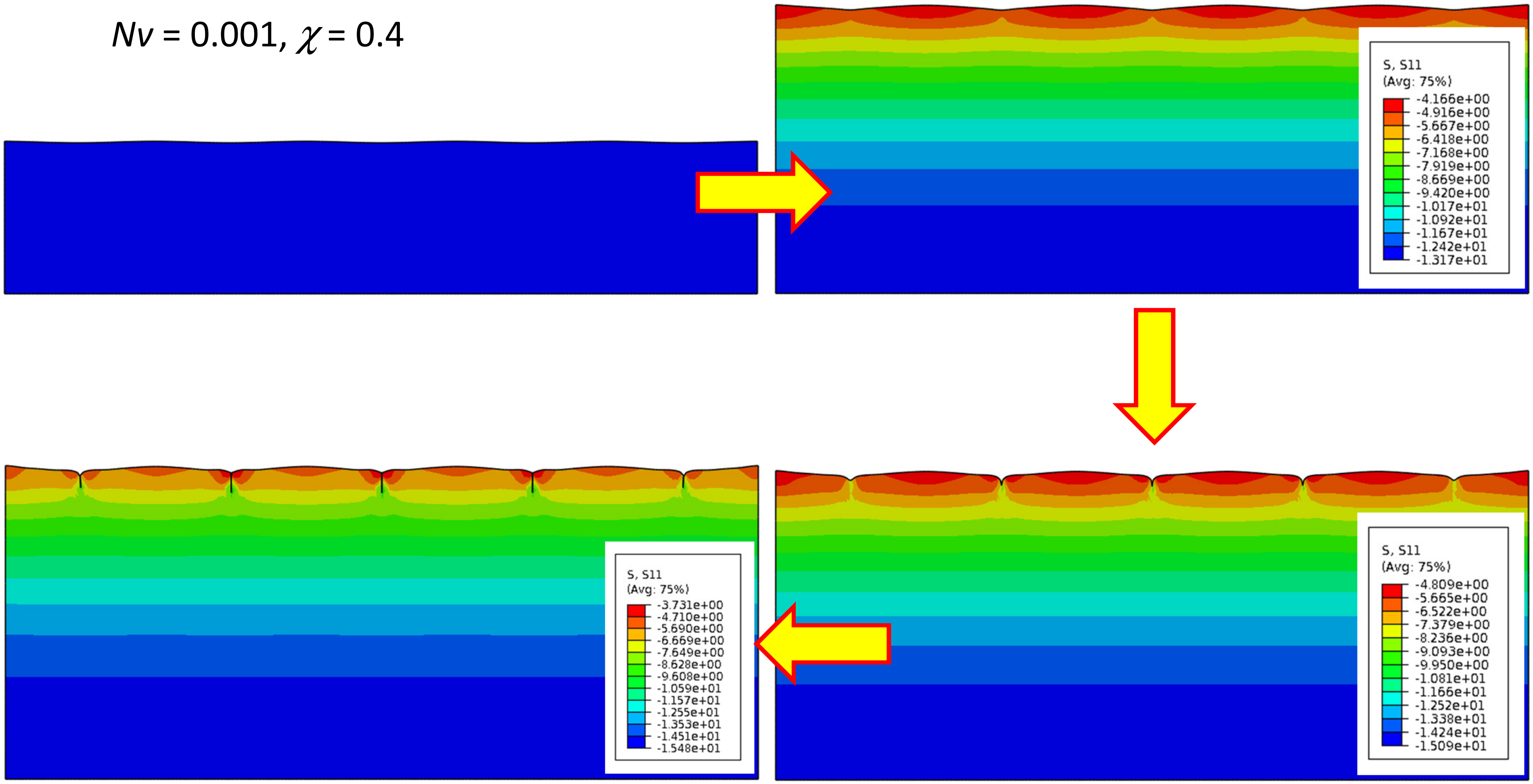
$$L = \frac{L'}{Nv}$$

- The critical thickness is linearly proportional to *L*, with the proportionality depending on *Nv* and χ.

Kang and Huang, Soft Matter 6, 5736-5742 (2010).

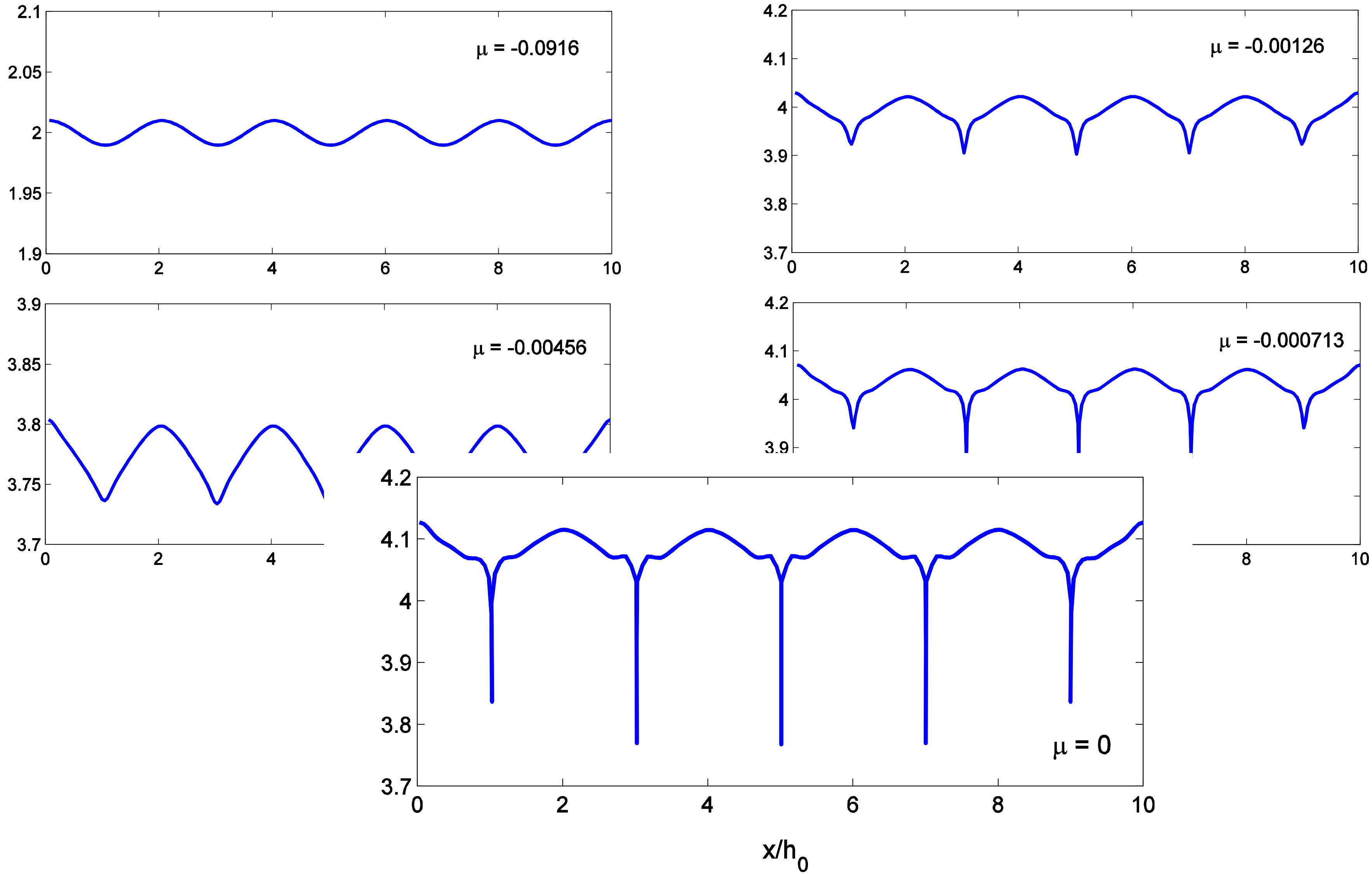
Finite element simulation

Nv = 0.001, χ = 0.4



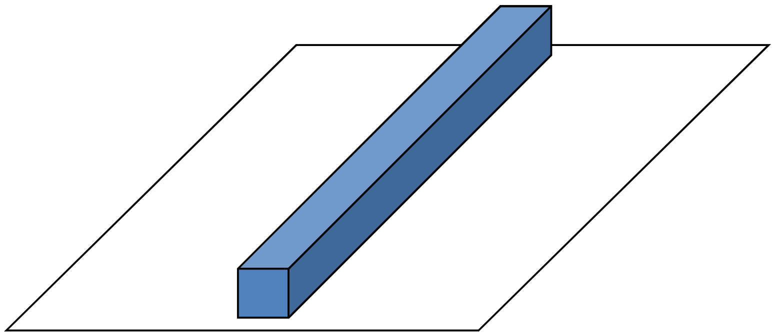
Kang and Huang, J. Mech. Phys. Solids 58, 1582-1598 (2010).

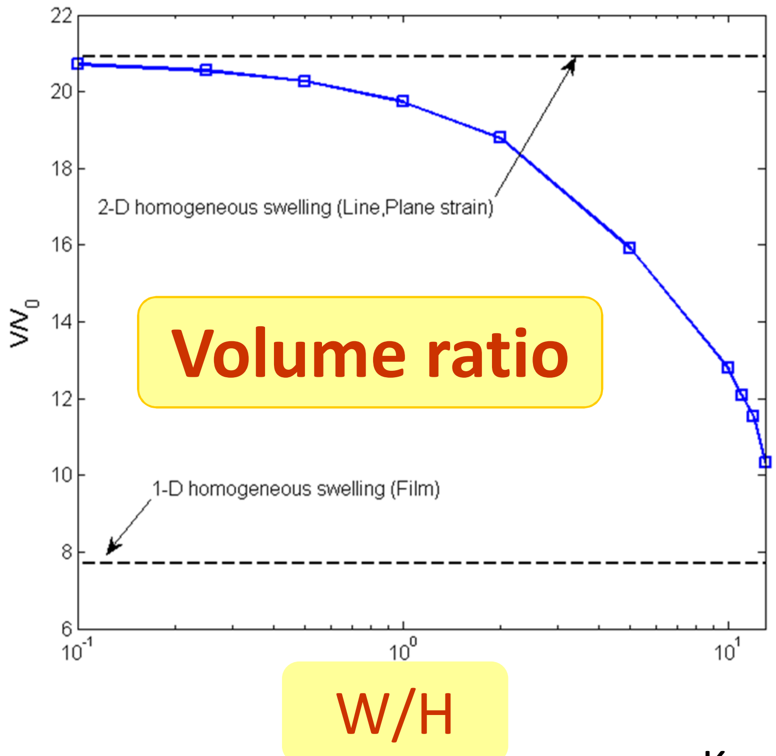
Surface Evolution

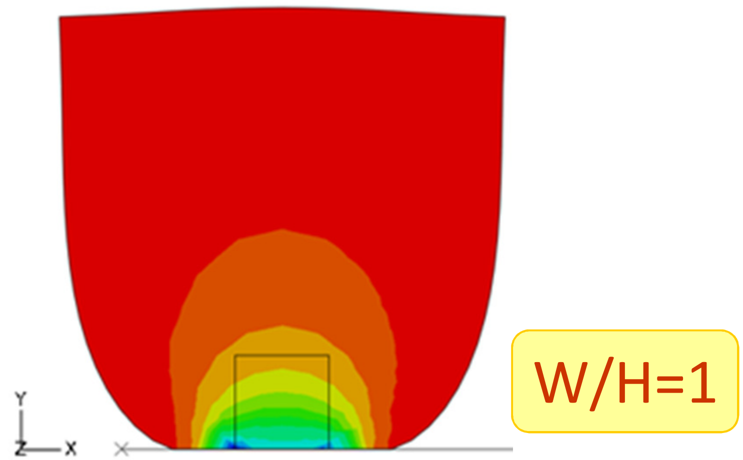


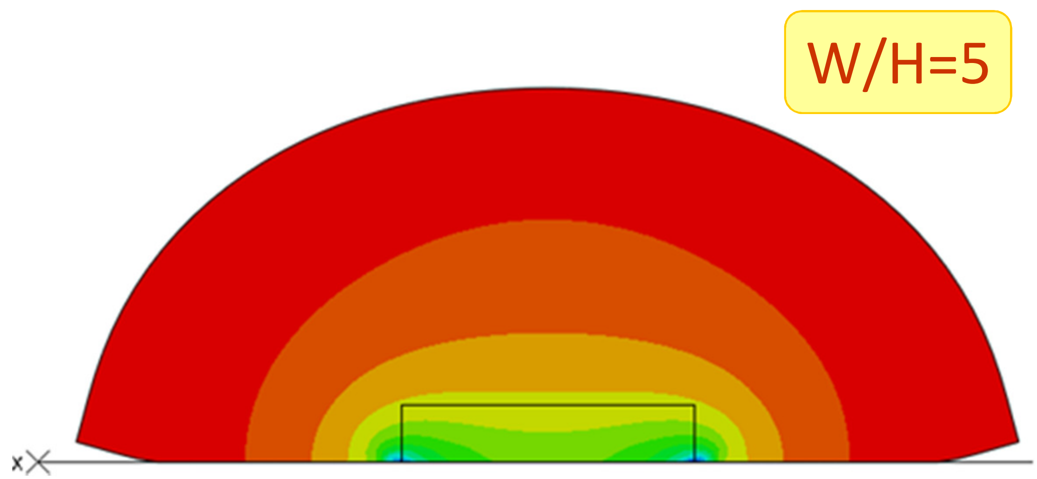
Kang and Huang, J. Mech. Phys. Solids 58, 1582-1598 (2010).

Inhomogeneous Swelling of Substrate-Supported Hydrogel Lines





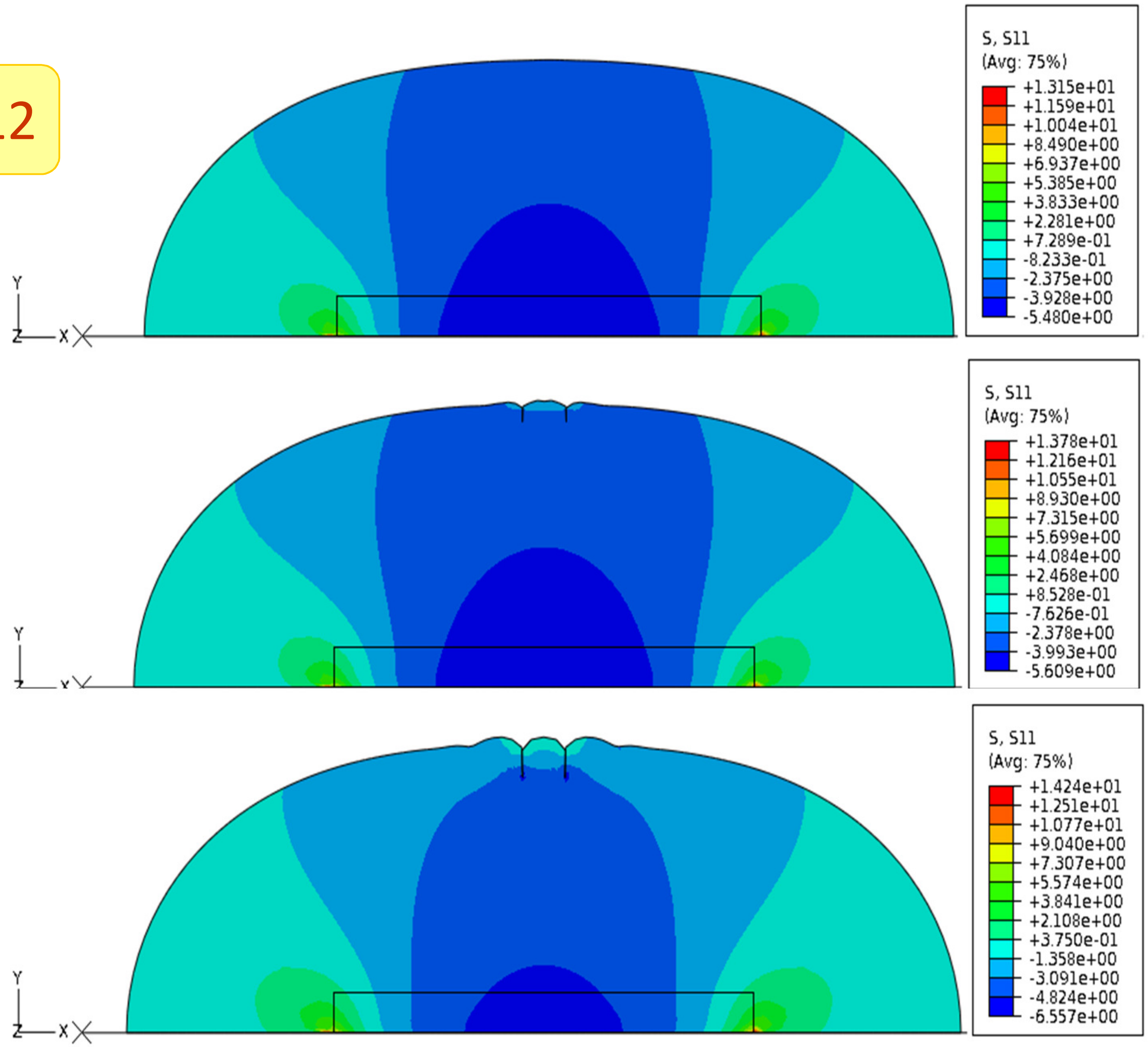




Kang and Huang, J. Applied Mechanics 77, 061004 (2010).

Spontaneous Formation of Creases

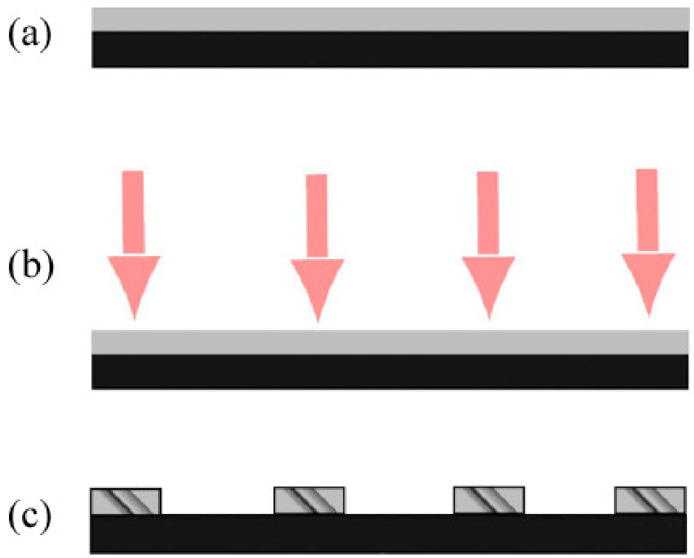
W/H=12

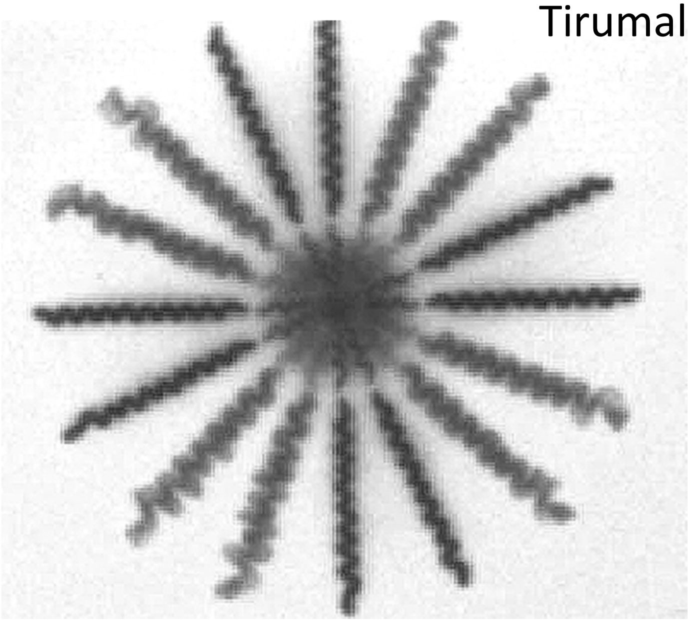


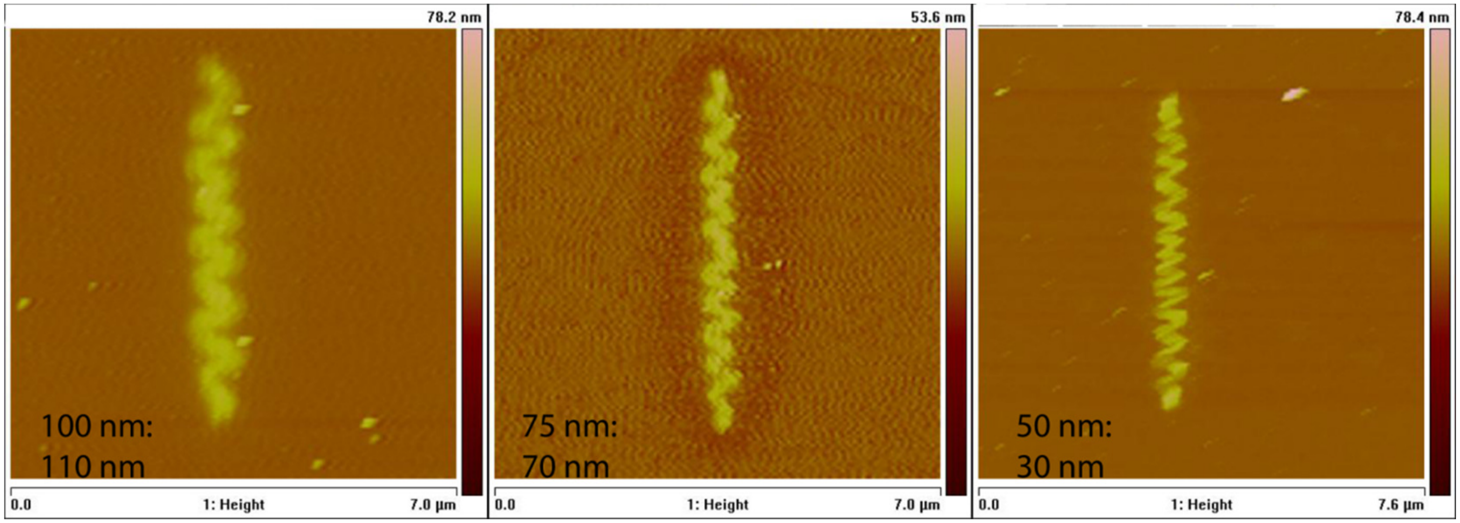
Kang and Huang, J. Applied Mechanics 77, 061004 (2010).

Swell-induced buckling

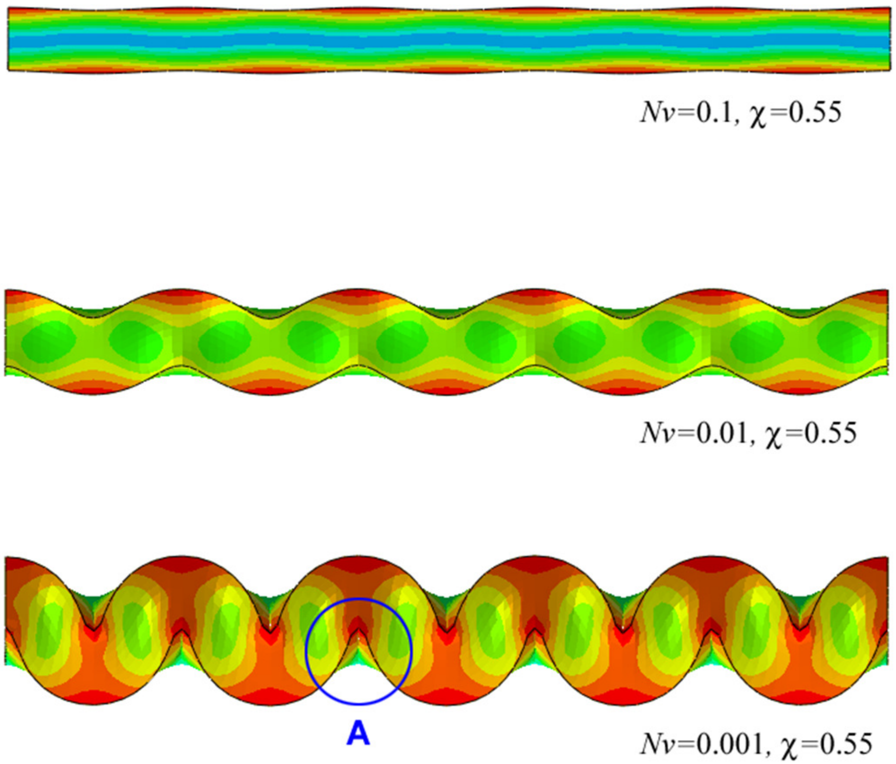
Tirumala et al., 2005

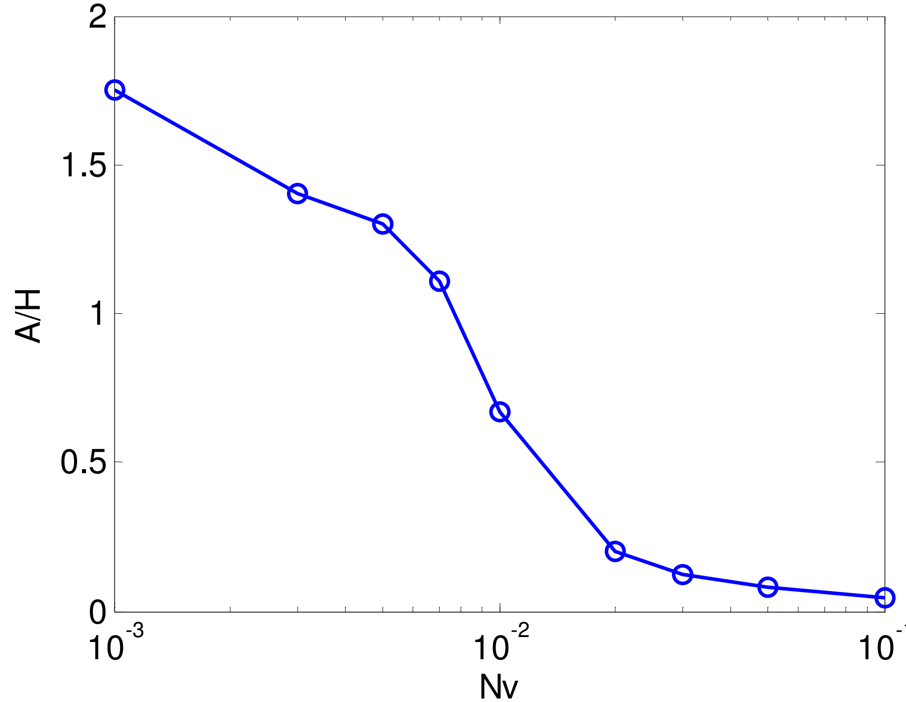






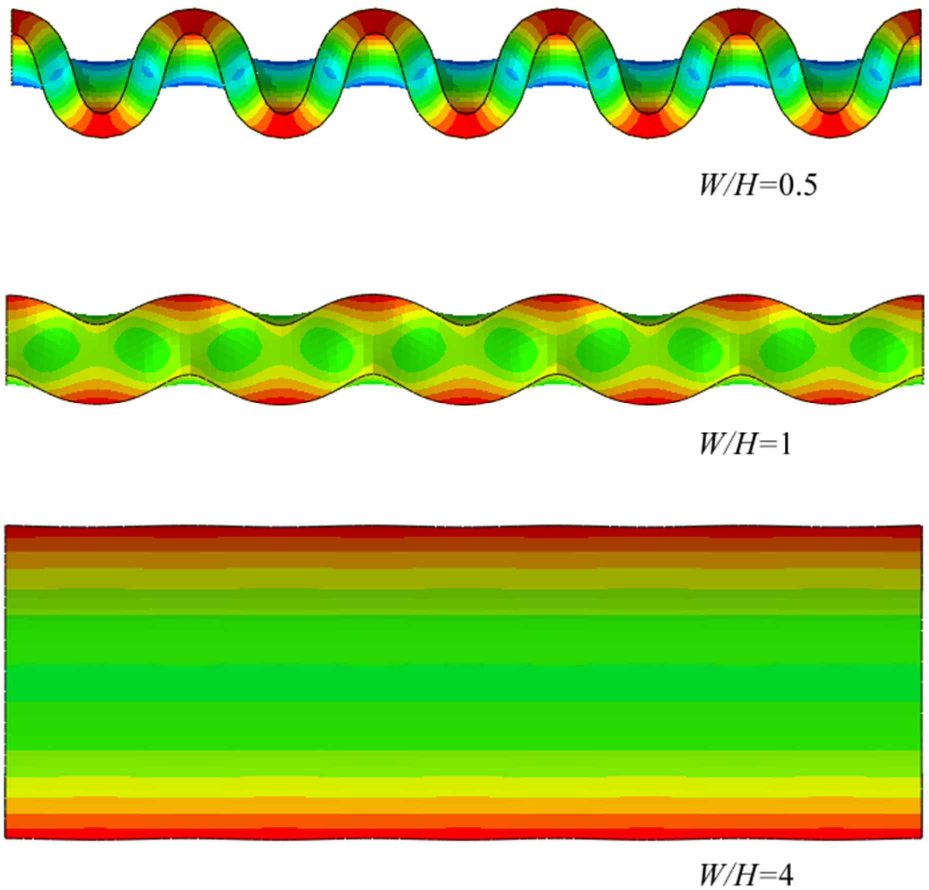
Effect of material parameters

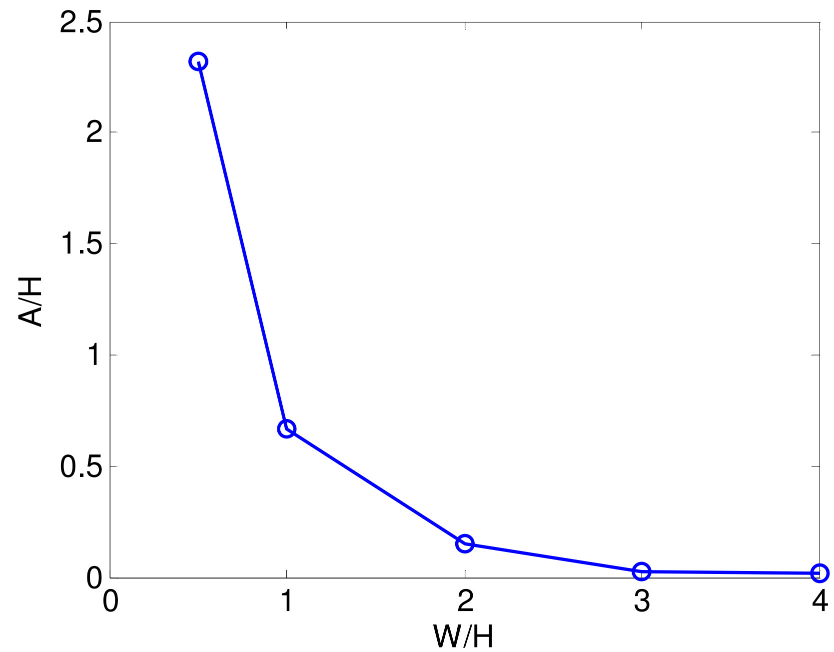




Kang and Huang, Int. J. Applied Mechanics, in press.

Effect of geometry (constraint)





Kang and Huang, Int. J. Applied Mechanics, in press.

Summary

- **Opportunity:** Within the general theoretical framework, instability of hydrogel-like soft material can be understood and exploited.
- **Challenge:** The highly nonlinear aspects in the material, geometry, and instability mechanics pose serious challenges for theoretical analysis and numerical simulations.
- **Strategy:** Collaborations between experimental and theoretical studies will be most successful.