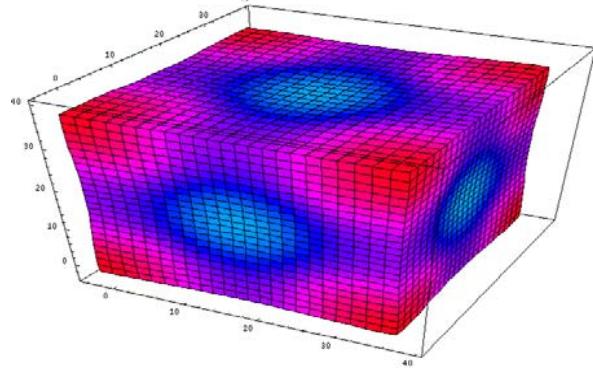
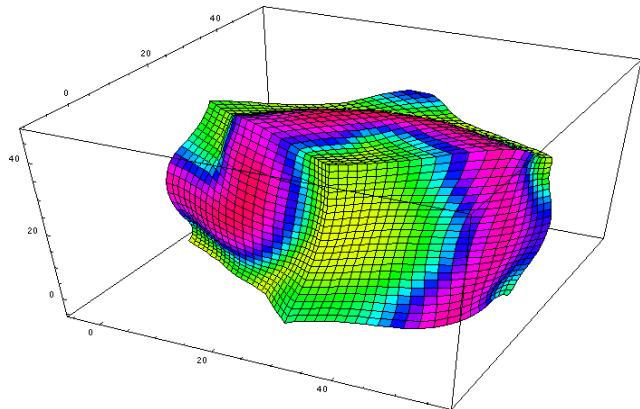


# **Three-dimensional model for chemoresponsive polymer gels**

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## ● Chemo-Responsive BZ Gels: Introduction

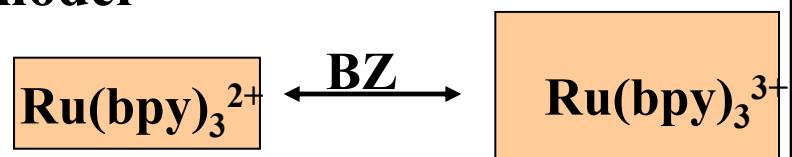
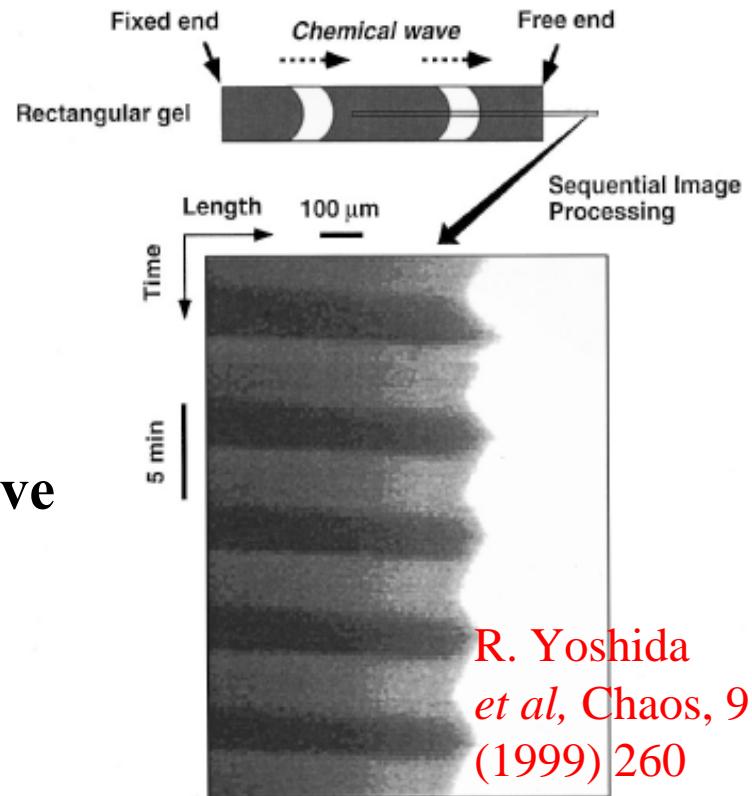
### □ Inspiration: experiments on BZ responsive gel:

- ☞ N-isopropylacrylamide (NIPAAm)
- ☞ Covalently bonded Ru(bpy)<sub>3</sub>
- ☞ Swollen in water solution of MA, NaBrO<sub>3</sub> and HNO<sub>3</sub>
- ☞ BZ reaction causes periodic swelling-deswelling

### □ Aim: design gel-based system sensitive to mechanical impact

- ☞ Mechanical energy is converted into chemical signal

### □ Challenge: develop an efficient 3D model for BZ chemo-responsive gels



## ● Model (V. Yashin, A. Balazs, Science 314, 798, 2006)

### □ Evolution equations

$$\begin{aligned}\frac{d\nu}{dt} &= -\nu \nabla \cdot \mathbf{v}^{(p)} + \varepsilon G(u, \nu, \phi); & \frac{d\phi}{dt} &= -\phi \nabla \cdot \mathbf{v}^{(p)}; \\ \frac{du}{dt} &= -u \nabla \cdot \mathbf{v}^{(p)} + \nabla \cdot \left[ \mathbf{v}^{(p)} \frac{u}{1-\phi} \right] + \nabla \cdot \left[ (1-\phi) \nabla \frac{u}{1-\phi} \right] + F(u, \nu, \phi).\end{aligned}$$

☞  $\phi$  volume fraction of polymer,  $u$  concentration of dissolved reagent,

☞  $\nu$  concentration of oxidized metal-ion catalyst

$$\phi \mathbf{v}^{(p)} + (1-\phi) \mathbf{v}^{(s)} \equiv 0$$

↑                      ↙  
Polymer velocity      Solvent velocity

☞  $\frac{d}{dt} \equiv \frac{\partial}{\partial t} + \mathbf{v}^{(p)} \cdot \nabla$

### □ Reaction kinetics : modified Oregonator

$$F = (1-\phi)^2 u - u^2 - f \nu (1-\phi) \frac{u - q(1-\phi)^2}{u + q(1-\phi)^2}; \quad G = (1-\phi)^2 u - (1-\phi)\nu$$

## ➊ Model: Calculate Energy and Stress Tensor

### □ Define energy density of deformed gel

☞  $U = U_{el}(I_1, I_3) + U_{FH}(I_3)$

☞ Elastic energy  $U_{el} = \frac{c_0 v_0}{2} (I_1 - 3 - \ln I_3^{1/2})$

☞ Interaction energy  $U_{FH} = \frac{2}{\sqrt{I_3}} [(1-\phi) \ln(1-\phi) + \chi_{FH}(\phi) \phi (1-\phi) - \chi^* v (1-\phi)]$

☞ Strain invariants  $I_1 = \text{tr } \hat{\mathbf{B}}$ ;  $I_3 = \det \hat{\mathbf{B}}$ ; where  $\hat{\mathbf{B}} = \hat{\mathbf{F}} \cdot \hat{\mathbf{F}}^T$ .

☞  $c_0$  is crosslink density,  $\chi^* > 0$ : hydrating effect of oxidized catalyst

### □ Define stress tensor

☞ 
$$\hat{\boldsymbol{\sigma}} = -P(\phi, v) \hat{\mathbf{I}} + c_0 v_0 \frac{\phi}{\phi_0} \hat{\mathbf{B}}$$

☞  $P(\phi, v) = \pi_{osm}(\phi, v) + c_0 v_0 \phi / 2\phi_0$ ,  $\pi_{osm} = -(\phi + \ln(1-\phi) + (\chi_0 + \chi_1 \phi) \phi^2) + \chi^* v \phi$

### □ Force balance equation

☞  $\nabla \cdot \hat{\boldsymbol{\sigma}} = v_0 T^{-1} D_u \zeta(\phi) (\mathbf{v}^{(p)} - \mathbf{v}^{(s)})$

☞  $\zeta(\phi) = \zeta(\phi_0) (\phi / \phi_0)^{3/2}$  is polymer-solvent friction coefficient

## ➊ 3D gLSM Model: Define Elements

### □ Define 3D element

$$(\mathbf{m}) = (i, j, k)$$

☞ Define local coordinate

$$\text{system } (\xi, \eta, \zeta)$$

☞ Define shape functions

$$N_n = \frac{1}{8}(1 + \xi\xi_n)(1 + \eta\eta_n)(1 + \zeta\zeta_n)$$

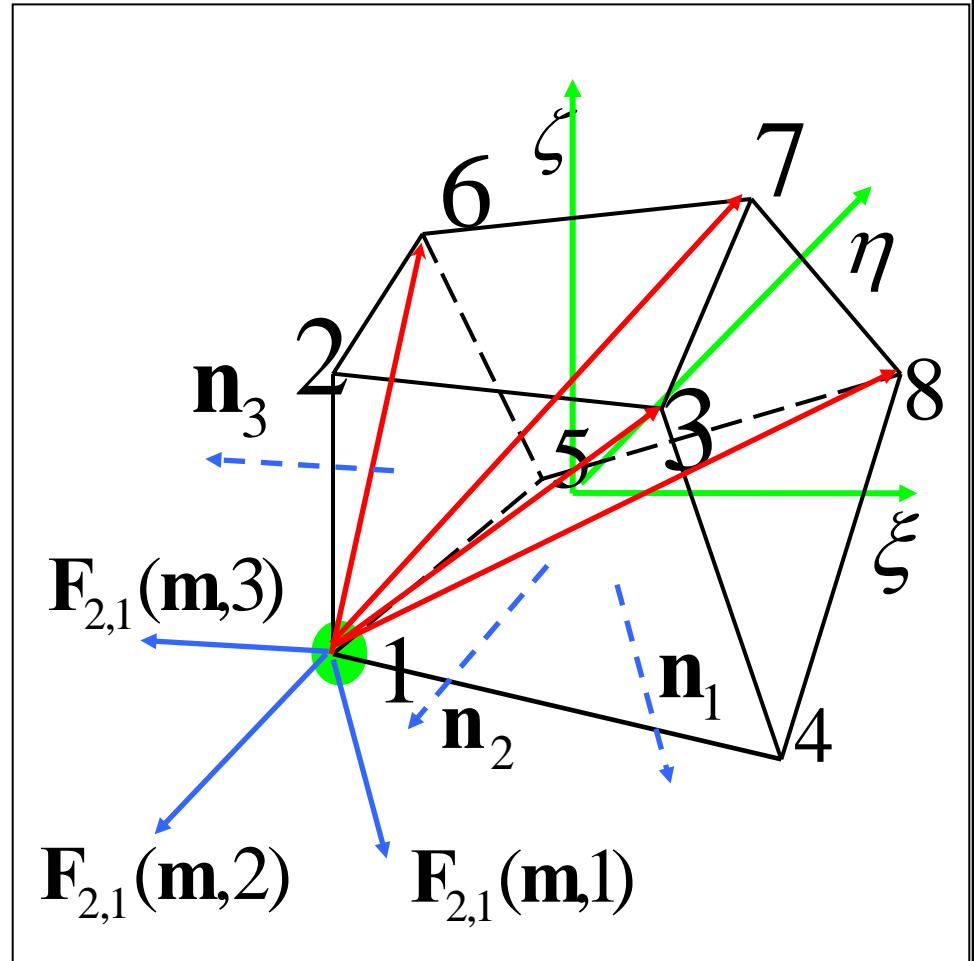
☞ Faces at  $\xi = \pm 1, \eta = \pm 1, \zeta = \pm 1$

☞ Coordinates within

$$\text{element } \mathbf{r}(\mathbf{m}) = \sum_{n=1}^8 N_n \mathbf{r}_n(\mathbf{m})$$

☞  $\mathbf{r}_n(\mathbf{m})$  :coordinates  
of node  $n = 1..8$

☞ Perform all integration in  
local coordinate system



### □ Sample consists of $(L-1) \times (L-1) \times (L-1)$ elements

## ➊ 3D gLSM model: Calculate Forces

### □ Total force acting on node n of element m



$$F_{TOTAL,n}(\mathbf{m}) = F_{1,n}(\mathbf{m}) + F_{2,n}(\mathbf{m})$$

### □ Calculate spring-like forces $\mathbf{F}_{1,n}(\mathbf{m})$



$$\mathbf{F}_{1,n}(\mathbf{m}) = -\partial U_1 / \partial \mathbf{r}_n(\mathbf{m}); \quad U_1 = \Delta^3 \sum U_1(\mathbf{m}).$$

$$\mathbb{H} U_1(\mathbf{m}) = \frac{c_0 v_0}{16} \int_{-1}^1 \int_{-1}^1 \int_{-1}^1 I_1(\xi, \eta, \zeta, \mathbf{r}(\mathbf{m})) d\xi d\eta d\zeta = \frac{c_0 v_0}{24 \Delta^2} \left( \sum_{NN} (\mathbf{r}_n(\mathbf{m}) - \mathbf{r}_{n'}(\mathbf{m}))^2 + \sum_{NNN} (\mathbf{r}_n(\mathbf{m}) - \mathbf{r}_{n''}(\mathbf{m}))^2 \right)$$



$$\mathbf{F}_{1,n}(\mathbf{m}) = \frac{c_0 v_0 \Delta}{12} \left( \sum_{NN(\mathbf{m}')} w(n', n) (\mathbf{r}_{n'}(\mathbf{m}') - \mathbf{r}_n(\mathbf{m})) + \sum_{NNN(\mathbf{m}')} (\mathbf{r}_{n'}(\mathbf{m}') - \mathbf{r}_n(\mathbf{m})) \right)$$

$\mathbb{H} w(n', n) = 1$  if boundary face,  $w(n', n) = 2$  if internal face



Elastic energy stored in springs between NN and NNN nodes

## ➊ 3D gLSM model (Cont.)

### □ Calculate force $F_{2,n}(\mathbf{m})$ acting on node $n$ due to isotropic pressure

☞ 
$$\mathbf{F}_{2,n}(\mathbf{m}) = \frac{1}{4} \sum_{\mathbf{m}'} P(\phi(\mathbf{m}'), v(\mathbf{m}')) (\mathbf{n}_1(\mathbf{m}') S_1(\mathbf{m}') + \mathbf{n}_2(\mathbf{m}') S_2(\mathbf{m}') + \mathbf{n}_3(\mathbf{m}') S_3(\mathbf{m}'))$$

- ☞ Summation over elements  $\mathbf{m}'$  containing node  $n$
- ☞ Pressure within element

$$P(\phi(\mathbf{m}'), v(\mathbf{m}')) = \pi_{osm}(\phi(\mathbf{m}'), v(\mathbf{m}')) + c_0 v_0 \phi(\mathbf{m}') / 2\phi_0$$

☞ Osmotic and elastic contributions

### □ Calculate nodal velocities

☞ 
$$\frac{d\mathbf{r}_n(\mathbf{m})}{dt} = M_n(\mathbf{m}) [F_{1,n}(\mathbf{m}) + F_{2,n}(\mathbf{m})]$$

- ☞ Update nodal coordinates  $\mathbf{r}_n(\mathbf{m})$
- ☞ Calculate new volumes of elements  $V(\mathbf{m}) = \int_{-1}^1 \int_{-1}^1 \int_{-1}^1 \det J(\mathbf{m}) d\xi d\eta d\zeta$

## ➊ 3D gLSM model

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### □ Update polymer volume fraction within element

$$\Leftrightarrow \phi(\mathbf{m}, t + \Delta t) = \Delta^3 \phi_0 / V(\mathbf{m})$$

### □ Update values of $u$ and $v$

$$\Leftrightarrow v(\mathbf{m}, t + \Delta t) = v(\mathbf{m}) + \Delta t [-v(\mathbf{m})T_0(\mathbf{m}) + \varepsilon G(u(\mathbf{m}), v(\mathbf{m}), \phi(\mathbf{m}))]$$

$$\Leftrightarrow u(\mathbf{m}, t + \Delta t) = u(\mathbf{m}) + \Delta t [-u(\mathbf{m})T_0(\mathbf{m}) + T_1(\mathbf{m}) + T_2(\mathbf{m}) + F(u(\mathbf{m}), v(\mathbf{m}), \phi(\mathbf{m}))]$$

$$\Leftrightarrow T_0(\mathbf{m}) = (1 - \phi(\mathbf{m}, t + \Delta t) / \phi(\mathbf{m})) / \Delta t$$

$$\Leftrightarrow T_1(\mathbf{m}) = \frac{1}{V(\mathbf{m})} \int_{\mathbf{r} \in V(\mathbf{m})} d\mathbf{r} \nabla \cdot [\mathbf{v}^{(p)}(\mathbf{m}) u(\mathbf{m}) / (1 - \phi(\mathbf{m}))] \quad (\text{Use finite element})$$

$$\Leftrightarrow T_2(\mathbf{m}) = \sum_{l=i,j,k} \left[ -\nabla_l \phi(\mathbf{m}) \nabla_l \tilde{u}(\mathbf{m}) + (1 - \phi(\mathbf{m})) \nabla_l^2 \tilde{u}(\mathbf{m}) \right] \quad (\text{Use finite difference})$$

☞ More details in “Three-dimensional Model for Chemo-responsive Polymer Gels Undergoing the BZ Reaction, O. Kuksenok, V.V.Yashin and A. C. Balazs, PRE (2008)

## ➊ Model Validation

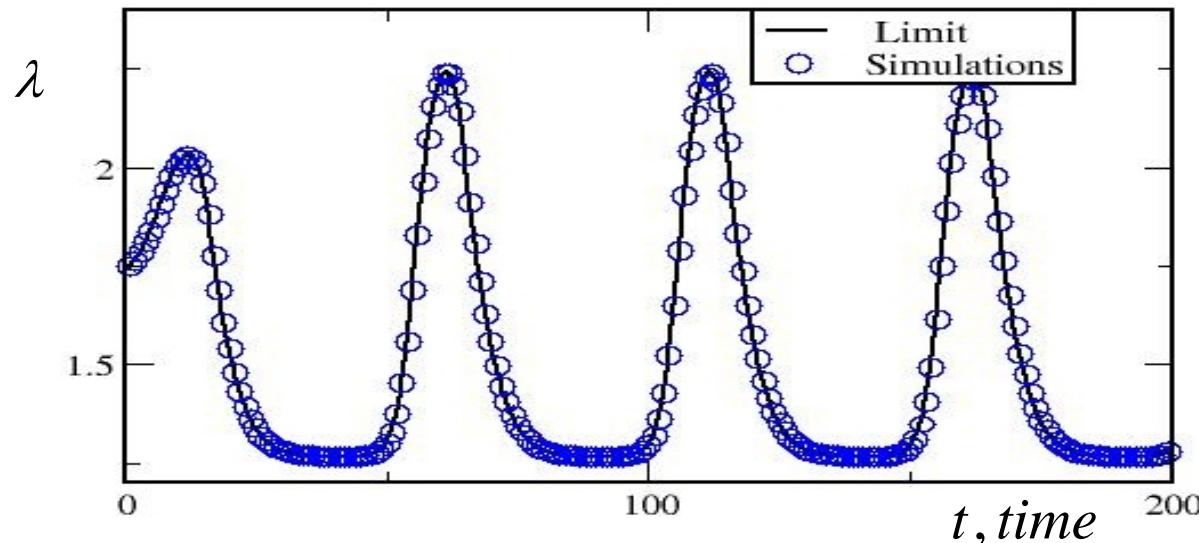
### □ No-diffusion and instantaneous pressure equilibration limit

☞ Simplified equations: 2 variables

$$c_0 v_0 \left[ \left( \frac{\phi}{\phi_0} \right)^{1/3} - \frac{\phi}{2\phi_0} \right] = \pi_{osm}(\phi, v_{lim})$$

$$\begin{aligned} \frac{du}{dt} &= - \frac{u}{1-\phi} \frac{d\phi}{dt} + F \Big|_{v=v_{lim}(\phi)} \\ \frac{d\phi}{dt} &= \frac{\phi}{v_{lim}(\phi)} \left[ \frac{dv_{lim}(\phi)}{dt} - \varepsilon G \Big|_{v=v_{lim}(\phi)} \right] \end{aligned}$$

### □ Evolution of degree of swelling $\lambda = (\phi_0 / \phi)^{1/3}$



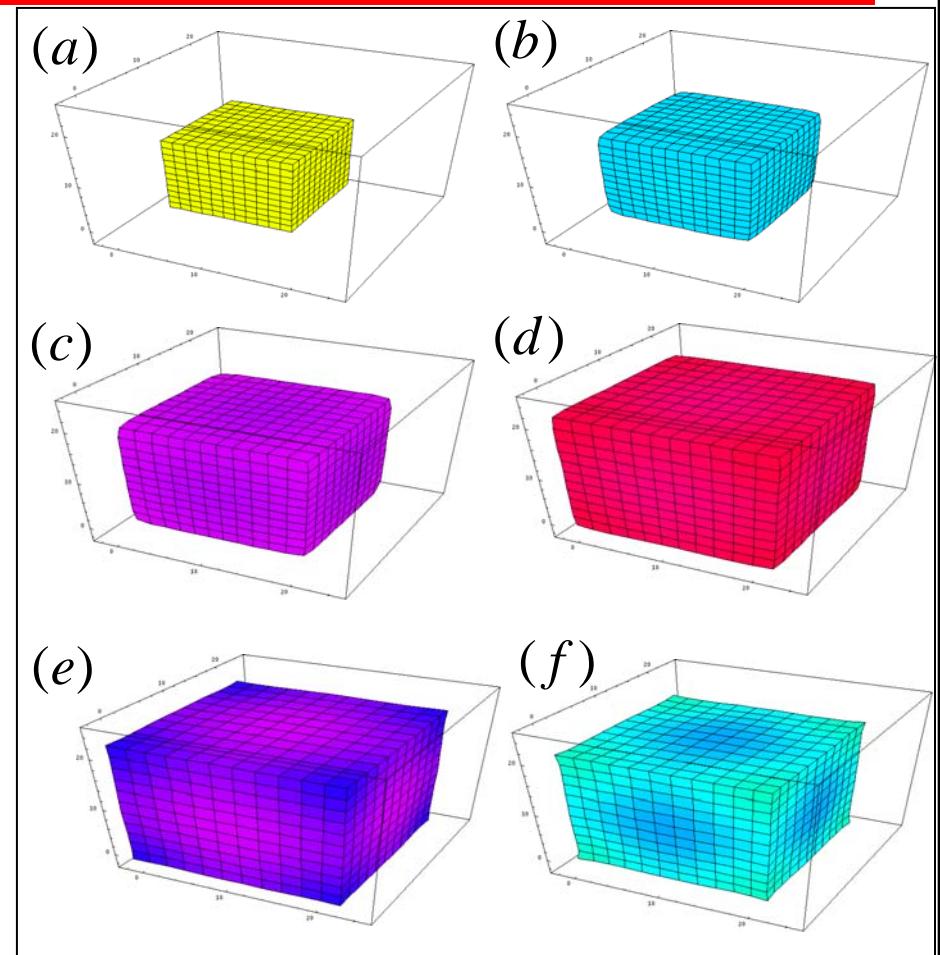
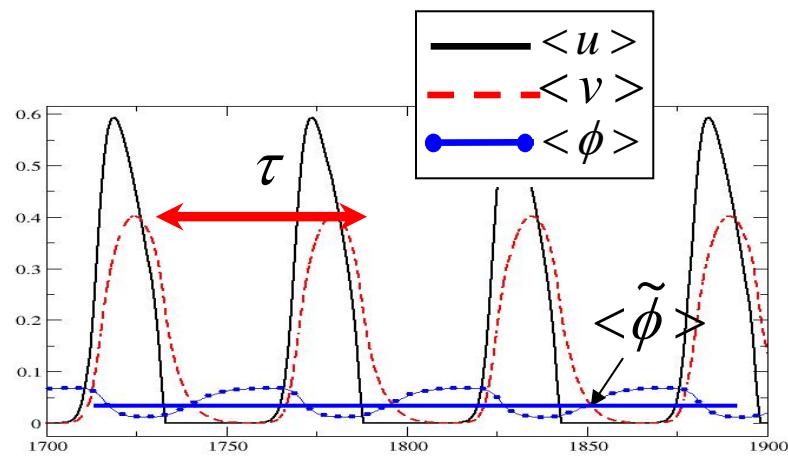
Parameters:  
 ☞  $f=0.8, L=2$   
 ☞ Same i.c.  
 ☞  $A_0 = 1000$

## ● 3D gLSM: Example of Regular Periodic Oscillations

- Sample size 12 X12 X 12, f=0.68

☞ No-flux b. c

- Time evolution of average characteristics

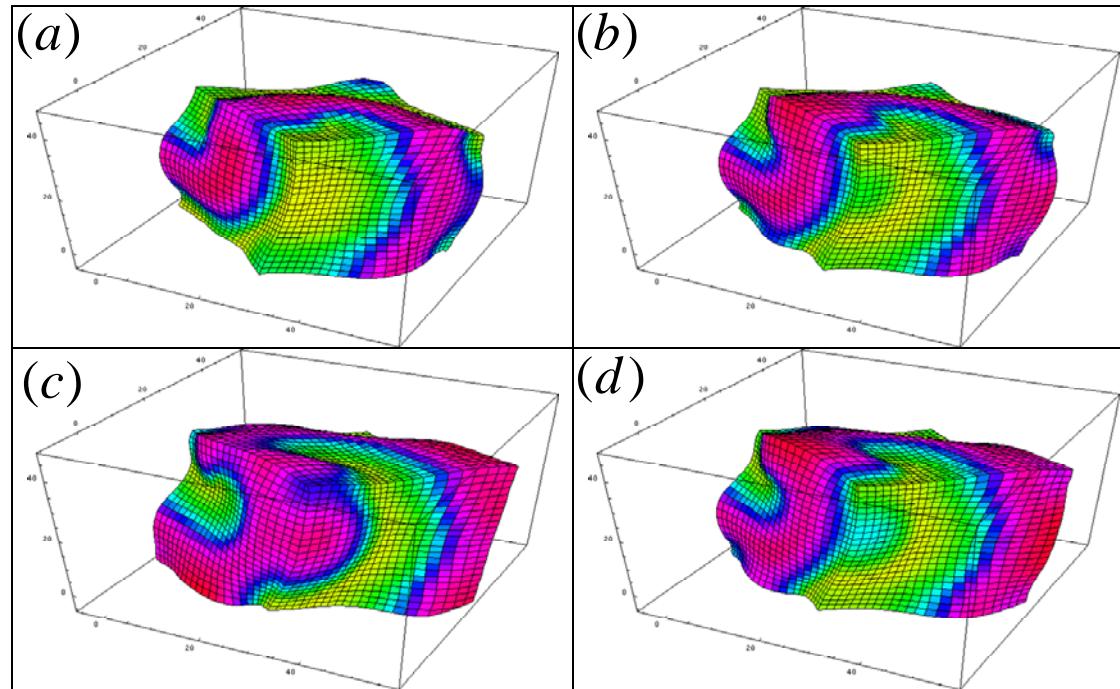


☞ Largest swelling corresponds to maximum  $\langle v \rangle$

$$v_{\min} = 0.0008 \quad v_{\max} = 0.4166$$

## ➊ 3D gLSM: Example of Non-Regular Oscillations

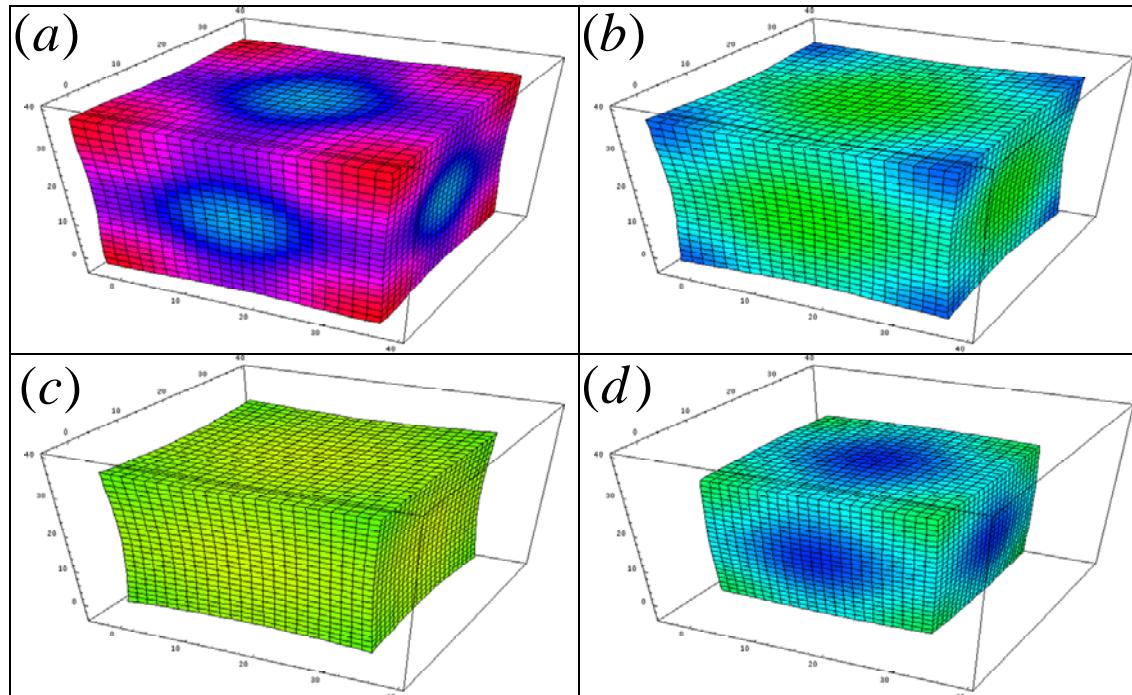
- Larger sample size ( $24 \times 24 \times 24$ ),  $f=0.68$



- ☞ Strong effect of diffusion
- ☞ Non-regular oscillations
- ☞ Realization depends on initial perturbation

## ● Effect of Increasing Stoichiometric Factor f

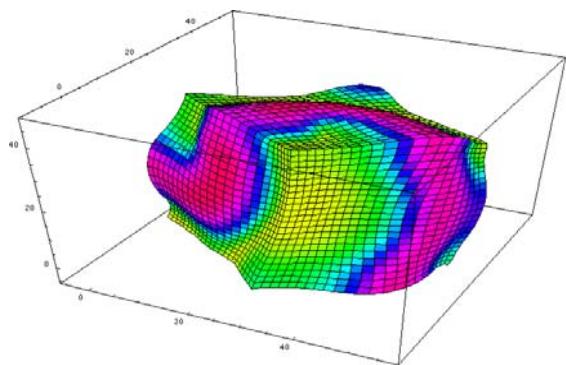
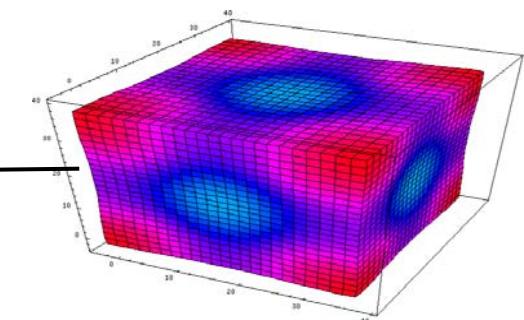
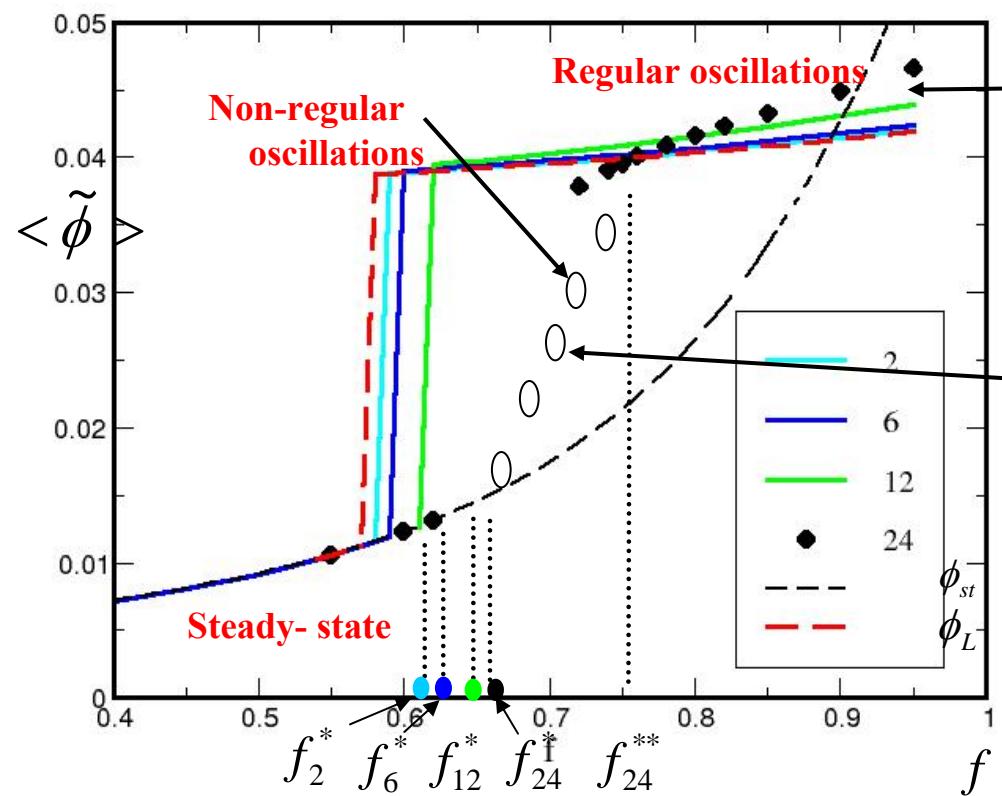
- Larger sample size (24 X 24 X 24 ), f=0.9



- ☞ Strong effect of diffusion
- ☞ Oscillations become regular
- ☞ Oscillations do not depend on initial perturbation

## ● Diagram of States

- Three possible cases: steady state, regular and non-regular oscillations



## ➊ Diagram of States (Cont'd).

**□ For smaller samples ( $L \leq 12$ ) :**

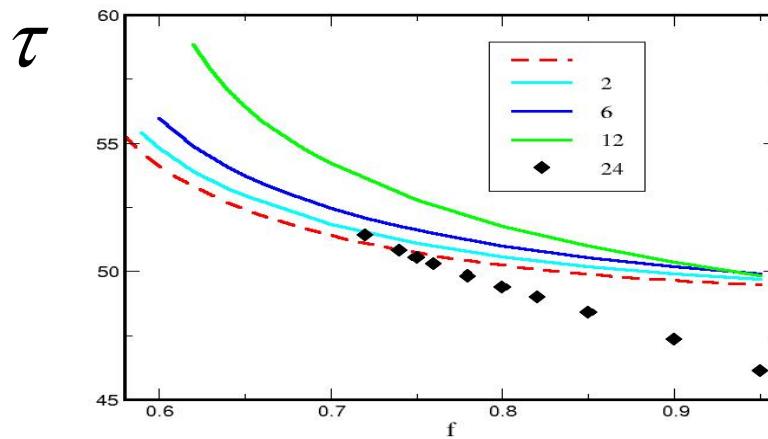
- ☞ If  $f \leq f_L^*$  steady-state; if  $f > f_L^*$  regular oscillations
- ☞  $f_L^*$  increases with increase in size  $L \times L \times L$

**□ For larger samples ( $L = 24$ ) :**

- ☞ If  $f \leq f_L^*$  steady-state; if  $f > f_L^{**}$  regular oscillations
- ☞ For  $f_L^* < f < f_L^{**}$  non-regular oscillations

**□ Period  $\tau$  (regular oscill.)**

- ☞ For smaller samples ( $L \leq 12$ )
  - ☞  $\tau$  increases with increase in  $L$
- ☞ For larger samples ( $L = 24$ )
  - ☞  $\tau$  is smaller

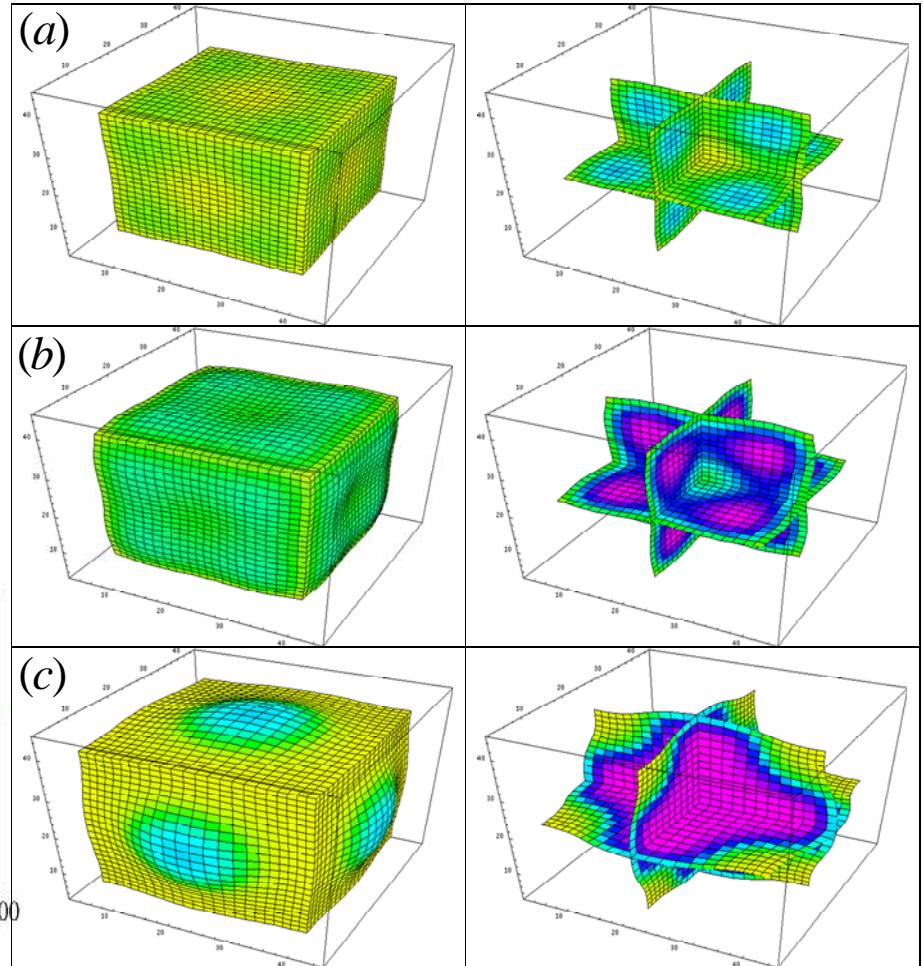
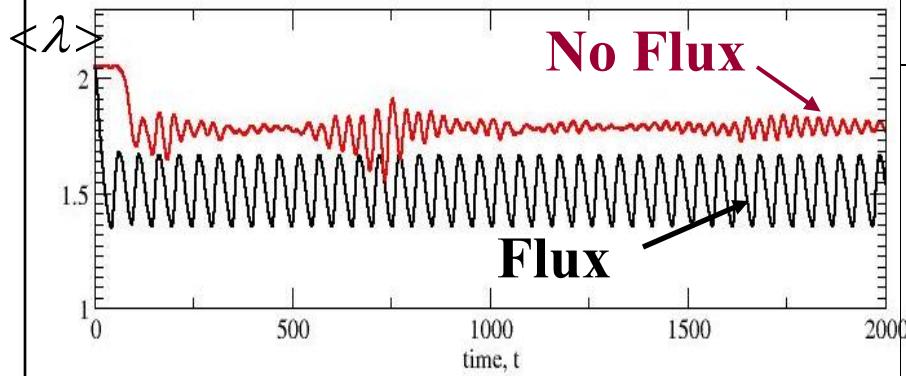


## ● Effect of Flux of $u$ through Surface, $f=0.68$

### □ Larger sample ( $L = 24$ )

- ☞ Flux of  $u$  through boundary
- ☞ Outside sample  $u = 0$
- ☞ Oscillations are regular

### □ Evolution of average swelling



- ☞ Dramatic effect of flux through the boundaries

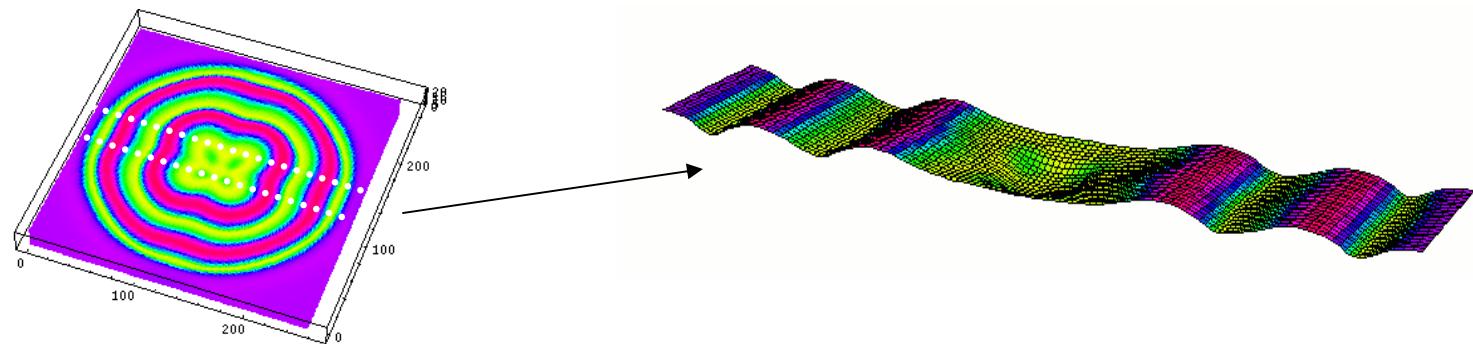
## ● Conclusions

- Developed first 3D computational model to study dynamics of chemo-responsive gels in three dimensions

- ☞ Performed first simulations of BZ gels in 3D

- Future plans

- ☞ Mechano-chemical transduction in BZ gels in 3D



- ☞ BZ gel coating sends global signal of local impact