Physical Gels

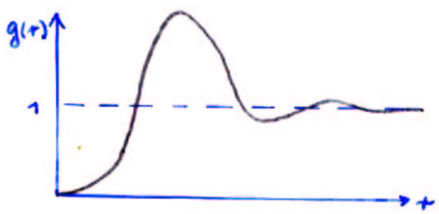
- dissolve powder in milk
- bring it to a boil
- let it cool down

} reversible

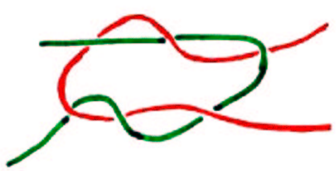
fluid becomes more and more viscous; depending on concentration and temperature

Sol	Gel
highly viscous fluid	amorphous solid
Vanilla sauce	pudding

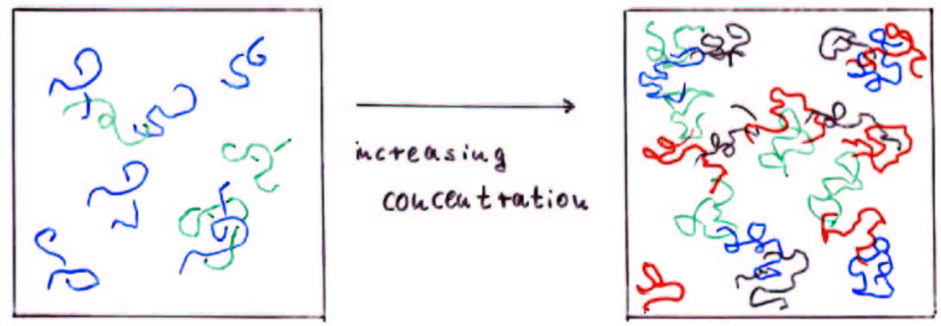
pair-correlation



interactions:
van der Waals attraction
entanglements



Possible Scenario for the Gel Transition



low concentration of macromolecules	high concentration of macromolecules
small clusters	macroscopic cluster of entangled mol.

entanglements are reversible

which molecule belongs to which cluster? changes with time

→ structural glasses

Chemical Gelation

epoxy resin, wallpaper paste

two components < long polymer chains; hardening molecule, bi- (or more) valent reaction

polymers form permanent clusters

which polymer belongs to which cluster? quenched variable

separation of timescales

random connectivity is quenched

motion of the monomers is thermal

chemical gelation is percolation transition

Flory, Stockmayer '41-'48

de Gennes, Stauffer '78-'82

controlparameter: $c := \frac{\#\text{ of crosslinks}}{\#\text{ of chains}}$

$c < c_{crit}$

sol: fluid

no macroscopic cluster

$c > c_{crit}$

gel: amorphous solid

macroscopic cluster

Applications in Biophysics

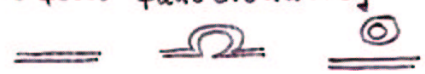
- cell locomotion: generated by actin cytoskeleton

  actin filaments are linked into networks (treelike)

  cell motion: polymerization at front end, dissociation at rear end

- endocytoses

  molecule with either 5- or 6 fold functionality

  regulates curvature 

Outline

I. Experimental findings in near-critical gels

II. Edwards model of a gel

III. Models of Dynamics

IV. Stress Relaxation

V. Density Fluctuations

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Density fluctuations as measured by inelastic light scattering

Martin et al., 1991 (TMOS)

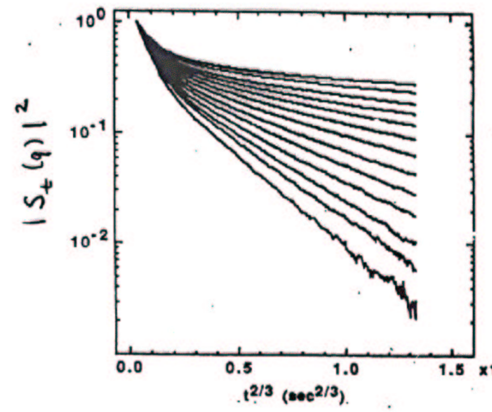
$$S_t(q) = \langle \overline{e^{i\vec{q}(\vec{R}_i(t)-\vec{R}_i(0))}} \rangle$$

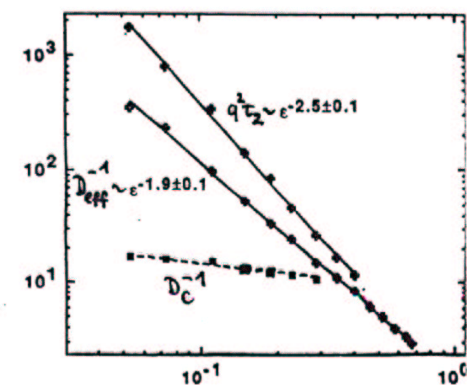
$$\sim e^{-(t/\tau(q))^{\beta}}$$

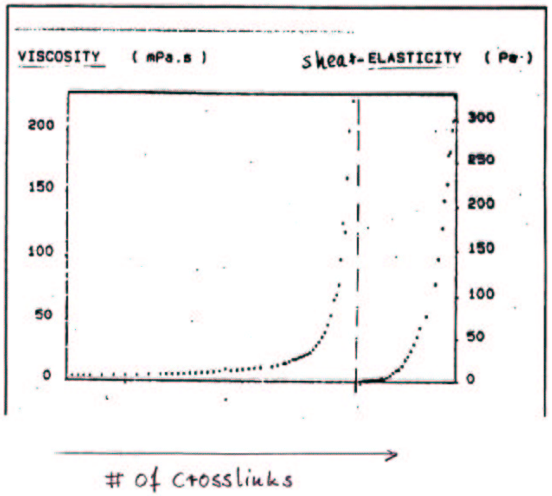
$$\beta \sim 2/3$$

$$\tau(q) \sim q^2 \varepsilon^{-s}$$

$$D_{eff}^{-1} \sim \varepsilon^{-x}$$







Gauthier-Manuel et al.
J. Physique 48, 869 (87)

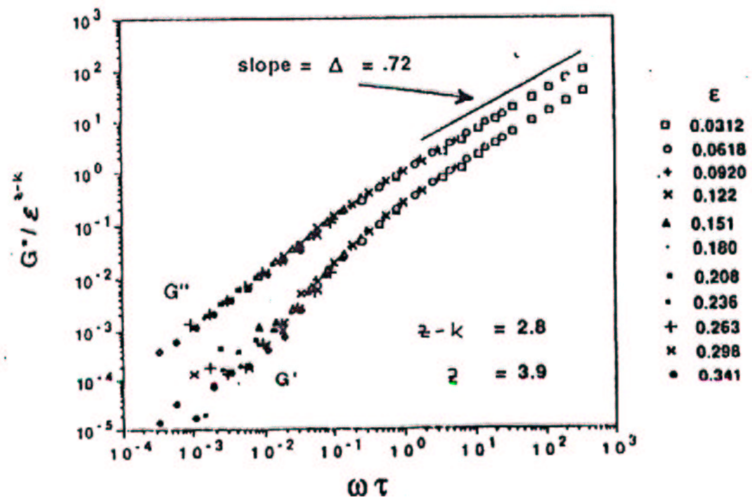
silica gels

$\eta \sim \varepsilon^{-k}$, $k \sim 1.0 \pm 0.1$

scaling ansatz:

$$G(t) \sim \frac{\eta}{\tau}\left(\frac{\tau}{t}\right)^{\Delta} e^{-(t/\tau)^{\beta}}$$

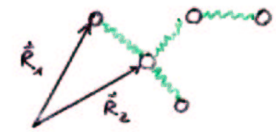
Adolf & Martin, Macromolecules 23, 1999



II Edwards Model of a Gel

- degrees of freedom

$$\{\vec{R}_i\}_{i=1,2..N}$$



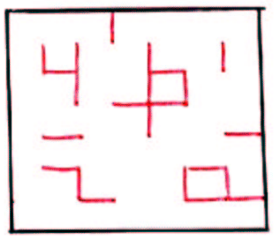
- Hamiltonian

$$\boxed{H_0 = \sum_{ij} J_{ij} (\vec{R}_i - \vec{R}_j)^2 / a^2 = \sum_{ij} \Gamma_{ij}\, \vec{R}_i \cdot \vec{R}_j / a^2}$$

quenched random connectivity

Random Graphs: $P(J_{ij}) = (1 - \frac{2c}{N})\,\delta(J_{ij}) + \frac{2c}{N}\,\delta(J_{ij} - 1)$

d-dim. percolation, e.g.



cluster size distribution

$$\boxed{\tilde{\tau}_n(c) \sim n^{-\tau} e^{-n/n^*(c)}}$$

$n^*(c) \sim \varepsilon^{-1/\sigma}$, $\varepsilon = |c - c_{crit}|$

percolation threshold c_{crit}

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excluded volume $\quad v(\hat{R}_i - \hat{R}_j)$

$$\boxed{H = \sum_{ij} \Gamma_{ij} (\hat{R}_i \cdot \hat{R}_j)/a^2 + \sum_{ij} v(\hat{R}_i - \hat{R}_j)}$$

Ball, Deam, Edwards
Goldbart, Goldenfeld
Goldbart, Castillo, A.Z. $\quad$ Adv. Phys. 45, 393, '96

III Models of Dynamics

Doi & Edwards "Theory of Polymer Dynamics"
Bird et al. "Dynamics of polymeric Liquids"

A) Rouse Model

$$\boxed{\zeta \dot{\vec{R}}_i(t) = -\frac{\partial H_0}{\partial \vec{R}_i(t)} + \hat{f}_i(t)}$$

friction const. $\quad$ spring forces $\quad$ thermal noise

no excluded volume, no hydrodynamic interactions

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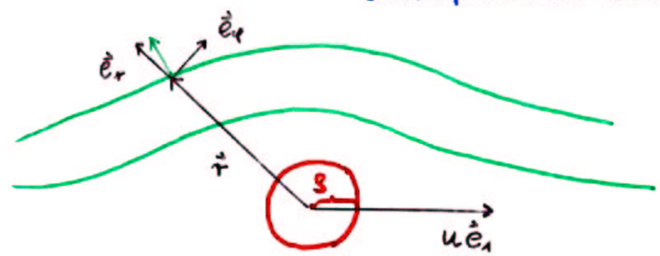
B) Zimm Model

uniform motion of a sphere of Radius ϱ in solvent (incompressible and low Reynolds #)



far field

$$\boxed{\vec{v}_s(\vec{r}) = \frac{3}{4}\frac{\varrho}{r} u \left(2\cos\varphi\, \vec{e}_r - \sin\varphi\, \hat{e}_\varphi\right) + \mathcal{O}\left(\frac{\varrho^3}{r^3}\right)}$$

force on sphere $\quad \vec{F} = 6\pi\eta_s \varrho u \vec{e}_1$

$$\vec{v}_s(\vec{r}) = \Omega(\vec{r})\, \vec{F}$$

Oseen tensor

$$\boxed{\Omega(\vec{r}) := \frac{1}{8\pi\eta_s r}\left(\mathbb{1} + \hat{e}_r \vec{e}_r^{\,t}\right)}$$

Relaxation Dynamics in the solvent

$$\zeta\left(\dot{\vec{R}}_i(t) - \vec{v}_s\right) = -\frac{\partial H_0}{\partial \vec{R}_i(t)} + \vec{f}_i(t)$$

$$\vec{v}_s(\vec{R}_i) = \sum_{j(\neq i)} \Omega(\vec{R}_i - \vec{R}_j)\left(-\frac{\partial H_0}{\partial \vec{R}_j} + \vec{f}_j\right)$$

preaveraging : $\Omega \rightarrow \langle\Omega\rangle_{eq} \rightarrow$ linear eq. of motion

C) Excluded volume : $H_0 \rightarrow H$

D) Phenomenological Dynamics

polymer confined to a tube

Reptation

contour fluctuations

constraint release ...

Tube theory of entangled polymer dynamics 1385

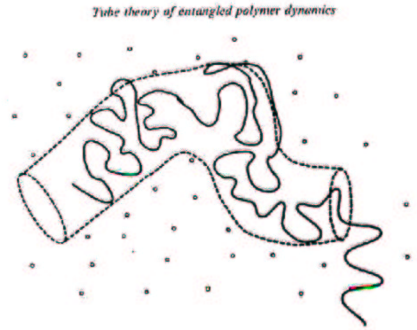
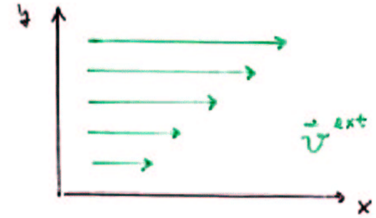


Figure 4. A tube-like region of constraint arises around any selected polymer chain in a melt due to the topological constraints of other chains (small circles) in its neighbourhood. [Diagram courtesy of R. Blackwell.]

Review by T. McLeish

Adv. Phys. 51, 1379, 2002

IV Stress Relaxation (Rouse m.)



$$\vec{v}^{ext}(t) = y\,\vec{e}_x\,\varkappa(t)$$

$\downarrow$

$$\boxed{\zeta\left(\dot{\vec{R}}_i(t) - \vec{v}^{ext}\right) = -\sum_j \Gamma_{ij}\,\vec{R}_j(t) + \vec{f}_i(t)}$$

$\downarrow$

$R_i^y\,\vec{e}_x\,\varkappa$ linear eq. of motion

Random connectivity matrix Γ

- Γ is blockdiagonal ; block $\triangleq$ cluster
- Γ has zero eigenvalues, one for each cl.

  EV: constant within one cluster

  E_0: projector onto nullspace of Γ

$$\boxed{\Gamma = E_0\Gamma + (1-E_0)\Gamma} = E_0\Gamma + \tilde{\Gamma}$$

↙ long time decay of density fluctuations

↘ stress relaxation

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shear stress $\sigma_{xy}(t) = \int^{t} dt' \, G(t-t') \, \varkappa(t')$

$$\boxed{G(t) = \int_0^\infty d\gamma \, D(\gamma) \, e^{-\gamma t}}$$

$$\boxed{D(\gamma) = \frac{1}{N} \overline{\mathrm{Tr}\,\delta(\gamma - \tilde{\Gamma})}}$$

Random graphs (Bray & Rodgers '88)

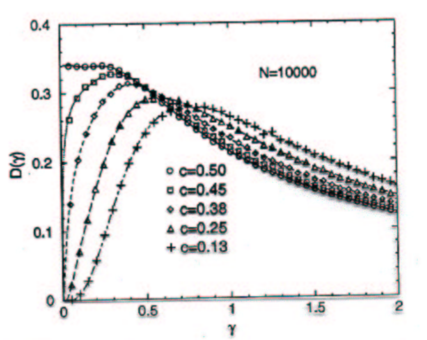
Lifshitz tails of $D(\gamma)$ for $\gamma \to 0$: $D(\gamma) \sim e^{-\left(\frac{h(c)}{\gamma}\right)^{1/2}}$

$h(c) \sim (1-2c)^3$

→ stretched exponential for large t

$$\boxed{\begin{array}{c} G(t) \sim e^{-(t/\tau^*)^{1/3}} \\ \tau^* \sim \varepsilon^{-3} \end{array}}$$

PHYSICAL REVIEW E64 021404



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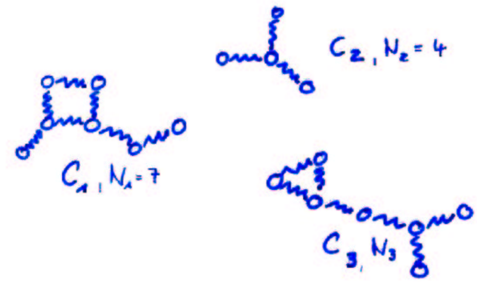
static shear viscosity $\sigma_{xy} = \eta \, \varkappa$

$$\boxed{\eta = \frac{\varepsilon}{2N} \mathrm{Tr} \, \frac{1-E_0}{\Gamma}}$$

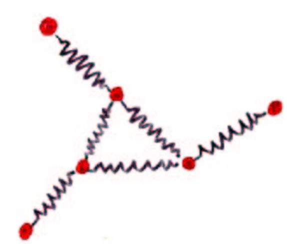
Cluster decomposition

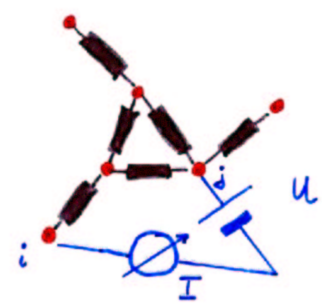
Γ is block diagonal



$$\frac{2}{\varepsilon} \quad \boxed{\eta = \sum_{k=1}^{K} \frac{N_k}{N} \, \eta(C_k)}$$

Viscosity of a cluster with n sites





resistance $R(i,j) = \frac{U}{I}$

Klein & Randić 1993 $\frac{2n}{\varepsilon}\eta = \boxed{\frac{1}{n} \sum_{i,j} R(i,j) = \mathrm{Tr} \, \frac{1-E_0}{\Gamma}}$

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average over all cluster sizes : $\tau_n \sim n^{-\tau} e^{-n/n^*}$, $n^* \sim \varepsilon^{-1/\sigma}$

critical behaviour of resistance

Lubensky, Wang
Harris, Lubensky

$$\boxed{\bar{\eta} \sim \varepsilon^{-k} \qquad k = \left(1 + \tau + \frac{2}{d_s}\right)/\sigma}$$

spectral dimension d_s

characteristic of the connectivity of percolating cluster

Return probability of a random walker $P(s) \sim s^{-d_s/2}$

$\varepsilon = d-6$ expansion for d_s
numerical data in $d=3$ by Gingold & Lobb '90

random graphs : logarithmic divergence

3d percolation : $k \sim 0.7$

$G(t) \sim t^{-\Delta}\, g(t/\tau^*)$ $\qquad \tau^* \sim \varepsilon^{-z}$

$$\boxed{\Delta = \frac{d_s}{2}(\tau - 1)} \qquad \boxed{z = \frac{2}{d_s \sigma}}$$

	z	Δ	k
2d	3.8	0.70	1.2
3d	3.3	0.79	0.71
RG	3	1	0

simulations : M. Plischke et al.
$k \sim 0.7 \quad \Delta \sim 0.76$

Del Gado et al. : $k \sim 1.3$