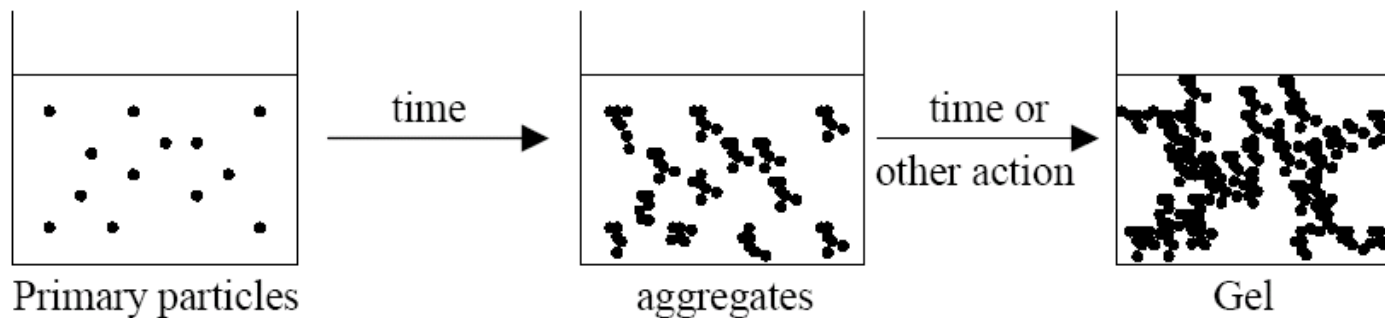


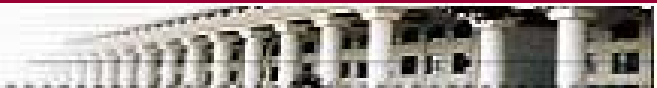
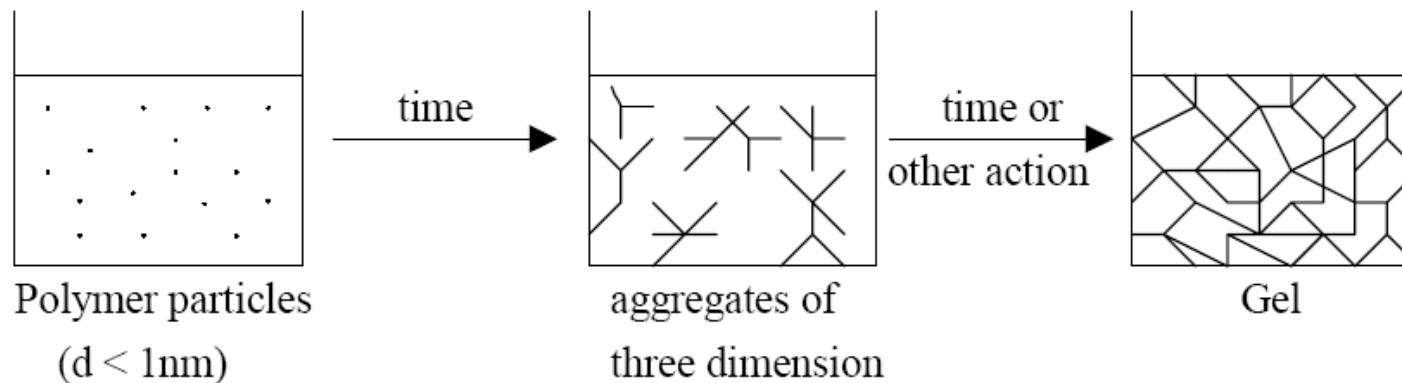
V. Gelation Phenomena

The hydrolysis and condensation reactions lead to the growth of clusters that eventually collide and link together into a gel.

◆ Gelation of Particulate Sol



◆ Gelation of Polymeric Sol

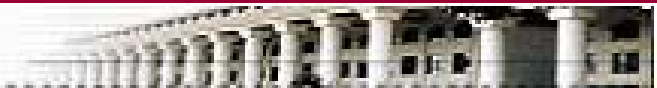
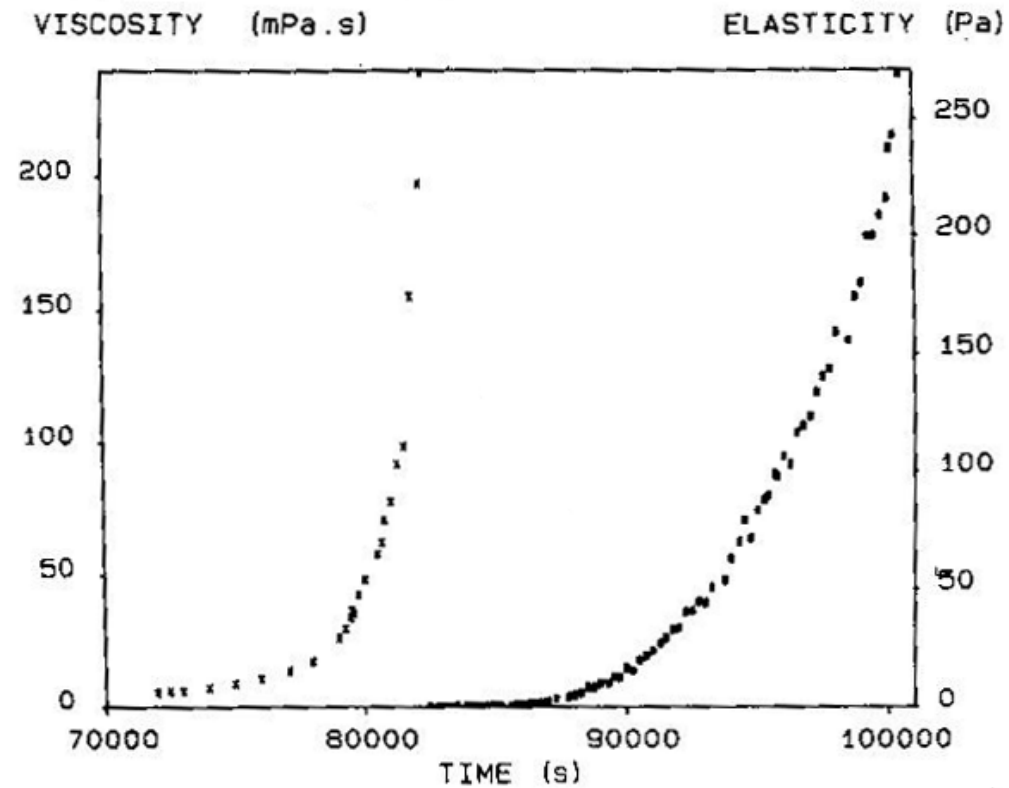


◆ Change in Rheological Behavior during Gelation Process

$$\tau_x = \mu \frac{du_x}{dy} = \mu \dot{\gamma}$$

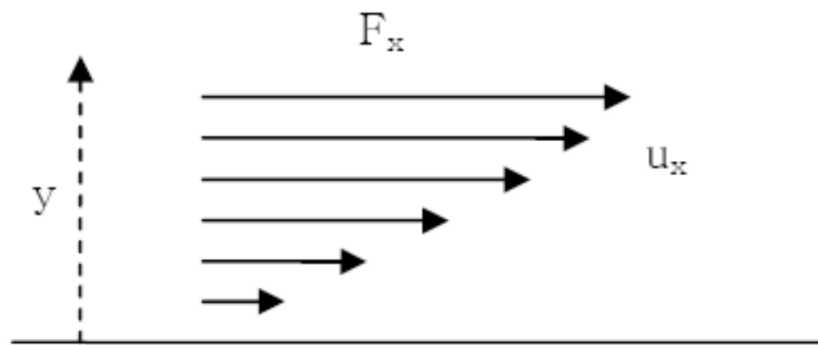
τ_x : shear stress

$\dot{\gamma}$: shear rate



◆ Viscous/Elastic Materials

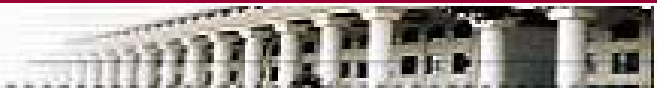
Viscous Materials



$$(F_x / A) = -\mu \left(\frac{du_x}{dy} \right)$$

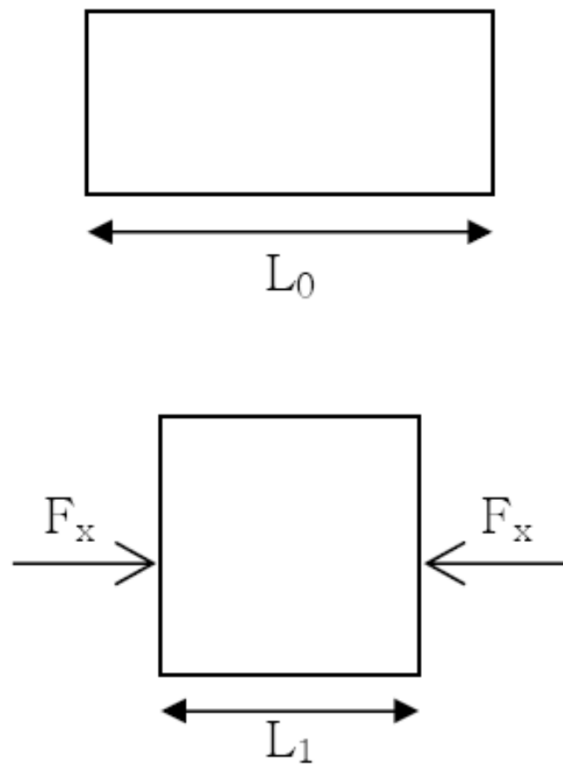
\uparrow Shear stress \downarrow viscosity \swarrow Shear rate

The larger the μ , the more solid-like is the viscous materials



Elastic Materials

For incompressible materials



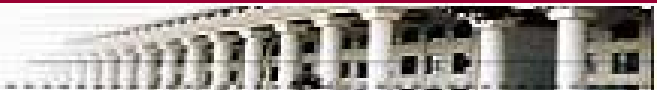
Elasticity

$$(F_x / A) = 3G \left[-\frac{(L_1 - L_0)}{L_0} \right]$$

Stress *Strain*

Detailed description: The equation relates stress to strain for an incompressible material. A dashed arrow labeled 'Elasticity' points down to the coefficient '3G'. A dashed arrow labeled 'Stress' points up to the term '(F_x / A)'. A dashed arrow labeled 'Strain' points up to the term '-(L_1 - L_0) / L_0'.

The larger the G, the more rigid is the material



Shear Modulus

$$G = G'' + G'$$

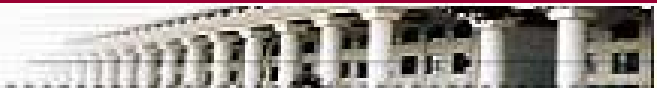
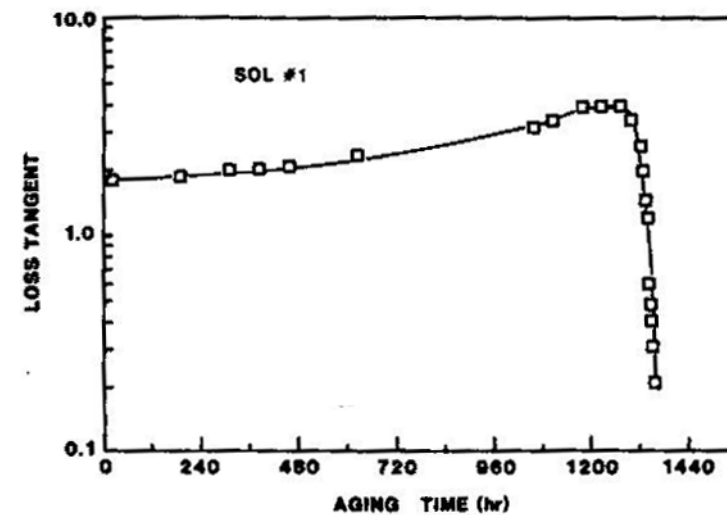
↗ Elastic contribution (storage modulus)

↘ Viscous contribution (loss modulus)

Loss Tangent

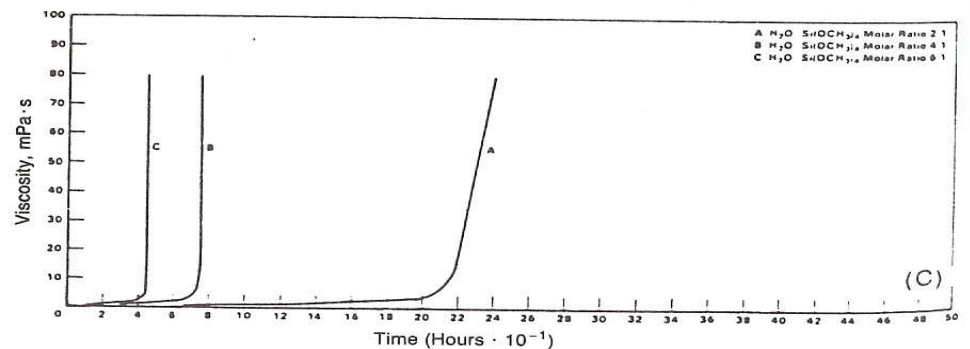
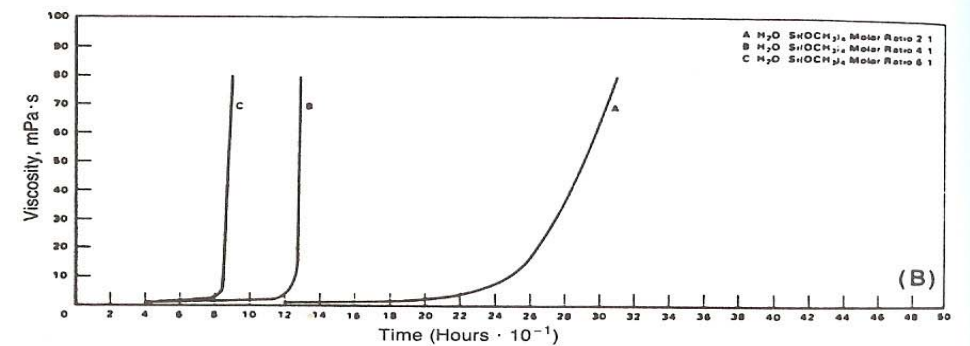
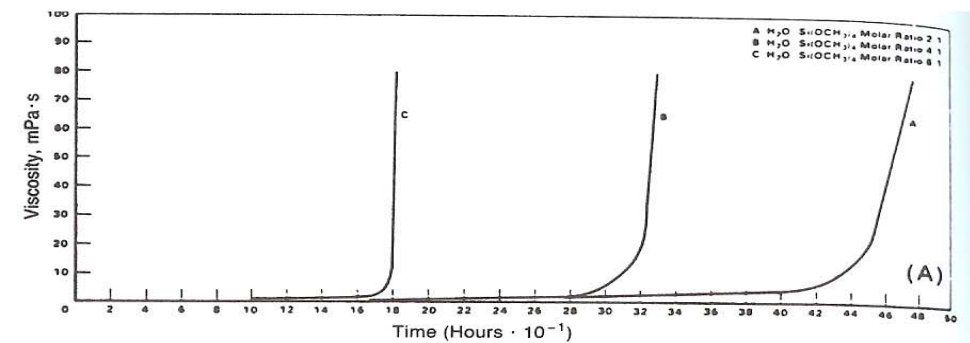
$$\tan \delta = G'' / G'$$

- ◆ Definition of the time of Gelation, t_{gel}
- time at which the viscosity suddenly increases (at certain value of the viscosity)
- time at which the loss tangent is maximum

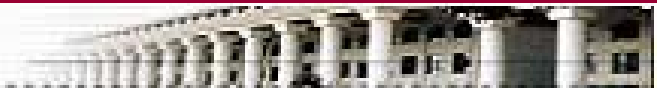


◆ Effect of Experimental Factors on t_{gel}
For SiO_2 gel from alkoxide (polymeric sol)

- type of acid, pH
- type of salt
- $[\text{H}_2\text{O}]/[\text{MOR}]$ ratio
- size of alkoxy group



Effect of solution concentration on viscosity change during the sol-gel transition of TMOS solutions with $R = (\text{moles H}_2\text{O})/(\text{moles TMOS}) = 2$ (curve A), 4 (curve B), and 6 (curve C) in sols containing (A) 100, (B) 75, (C) 50 g/l SiO_2 . From Debsikdar [11]. Reprinted by permission of the American Ceramic Society.



◆ Effects of Size of Alkoxy Group on Gelation Time

Steric (Spatial) Effects

Any complication of OR group retards the rate of hydrolysis and condensation, and therefore gelation rate.

Longer, more branched alkoxy group \Rightarrow slower hydrolysis and condensation rates
 \Rightarrow longer t_{gel}

Inductive Effects

Under the acidic condition (electrophilic attack hydrolysis)

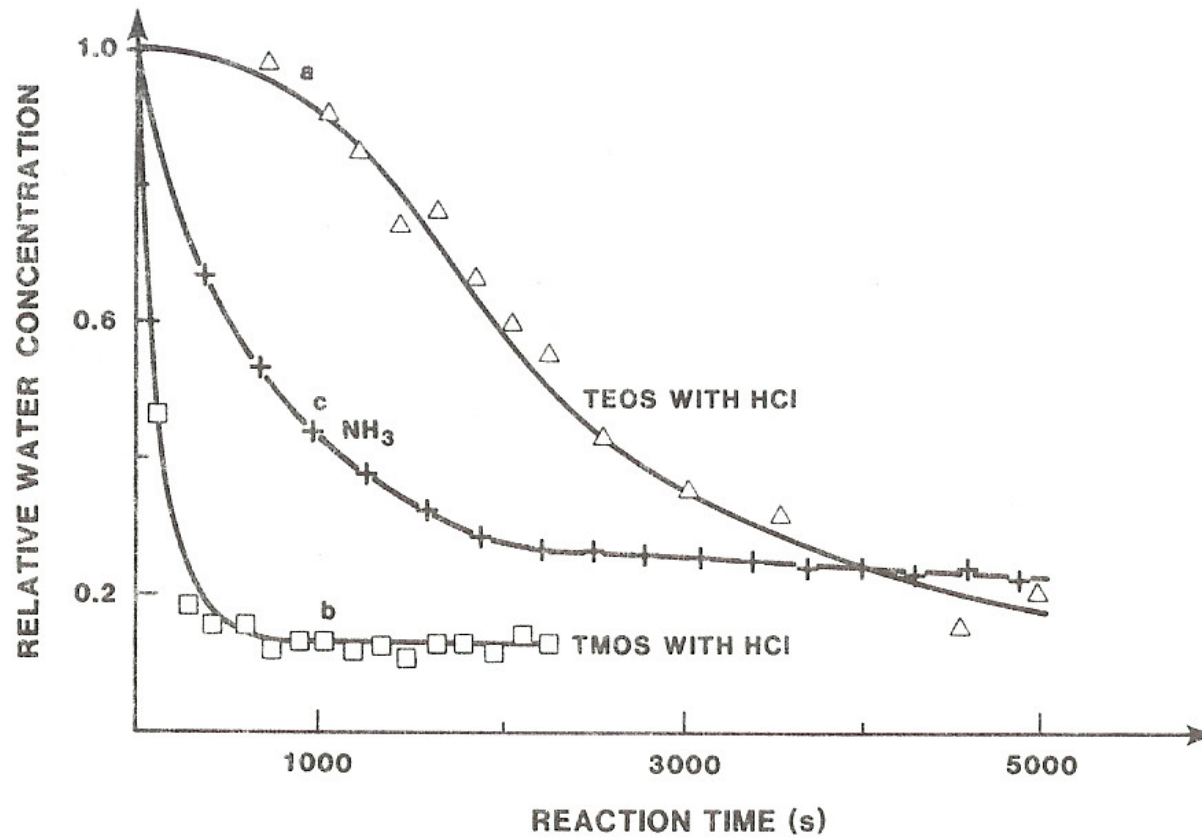
Shorter OR group \Rightarrow more electronegative of Si in $\text{Si}(\text{OR})_4$
 \Rightarrow larger hydrolysis rate

Under basic conditions (nucleophilic attack hydrolysis)

Shorter OR group \Rightarrow lower hydrolysis rate

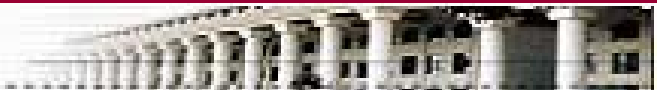


Fig. 11.



Relative water concentration versus time during acid-or base-catalyzed hydrolysis of TEOS or TMOS [58].

Longer or more branched PR \Rightarrow longer t_{gel}



CLASSICAL THEORY FOR GELATION

◆ Basic Concepts and Assumptions

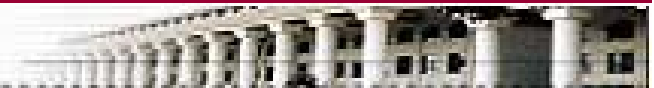
P : fraction of all possible bonds already formed

P_c : fraction P at the gelation point

z : functionality of a monomer

Assumptions

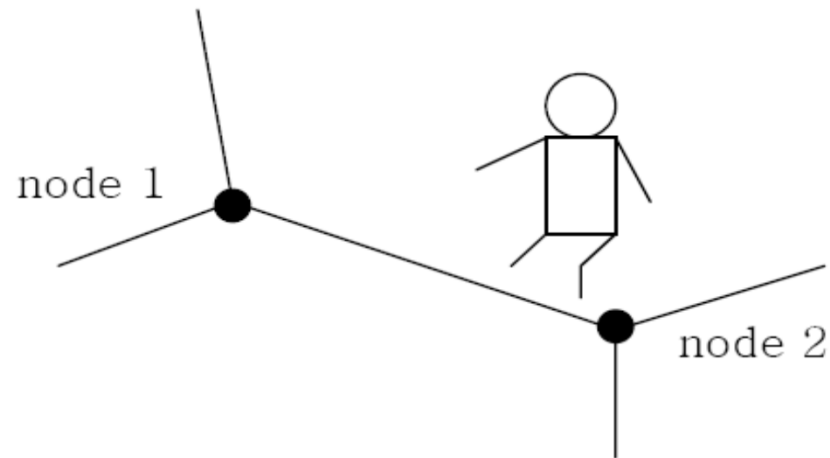
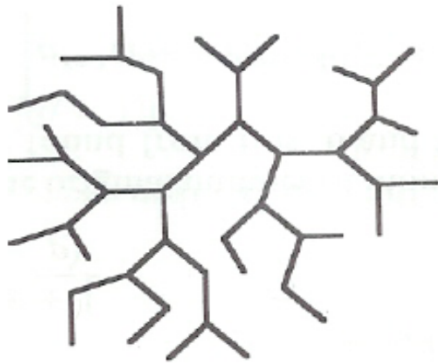
1. The reactivity of all functional groups on a monomer is equal, regardless the difference of the functional groups or whether or not other bond has formed.
2. The bonds form only between polymers (and monomer), not within the polymers, so that the polymers contain no closed loops



◆ Bethe Lattice (Cayley Tree)

A (polymeric or particulate) cluster which branches without ever forming rings (as a result of those two assumptions).

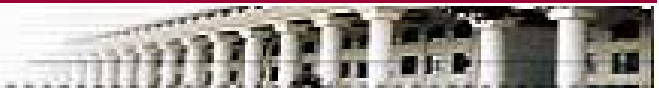
A Cayley tree with $z = 3$



A guy traveling along a path of completed bonds, and at each node (e.g. node 1), he finds $(z-1)$ opportunities to continue his journey.

The possibility that one of these possible paths to continue his journey in a completed bond is

$$(z-1)P$$



For a polymer or particle network to continue indefinitely, there must be at least one completed path (bond) from each node, i.e.:

$$(z-1)P \geq 1$$

The critical condition for gelation is then:

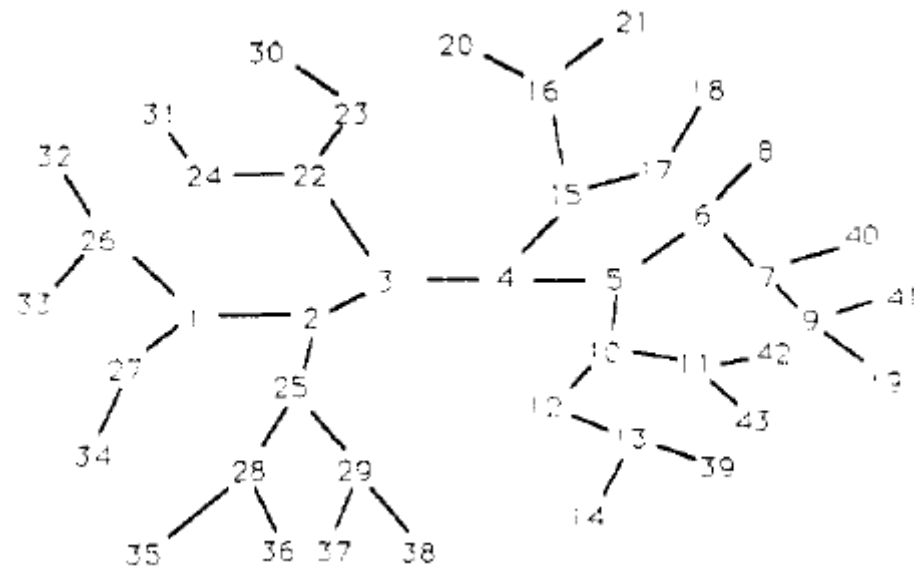
$$P_c = 1/(z-1)$$

E.g. for monomer with $z = 2$,

$$P_c = 1/(2-1) = 1$$

Physically it means that all bonds should be completed for gelation.





$z=3$ (functionality)

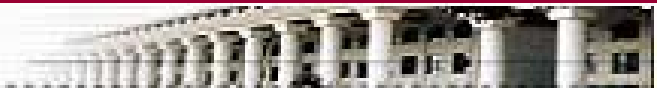
$N=43$

(total number of bond sites)

$n=84$

(total number of node bonds)

$$P=n/(Nz)$$



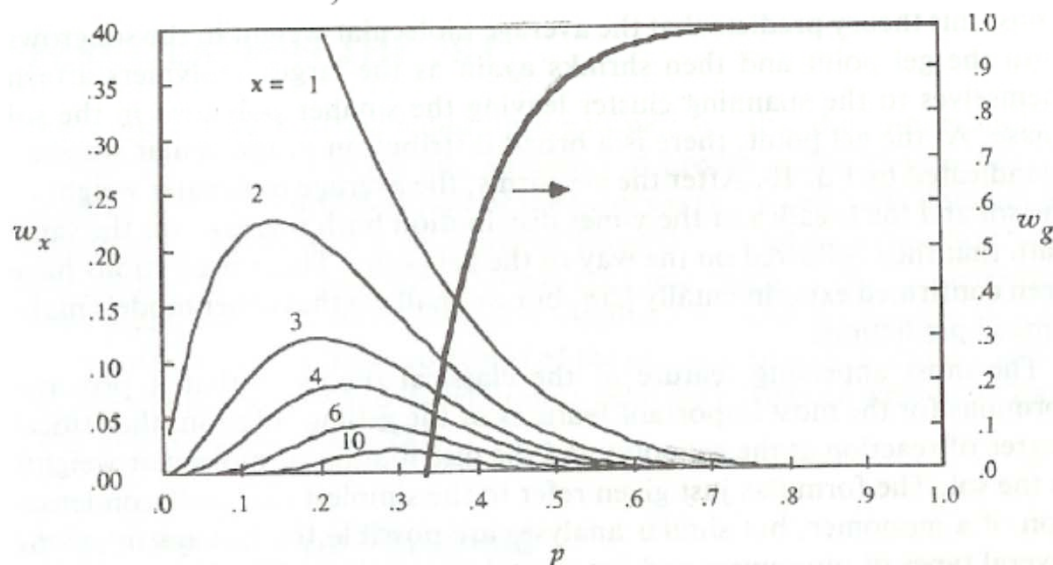
◆ The Weight fraction of X-mers

X-mers: a polymer made up of X monomer or a particle cluster made up of X particles

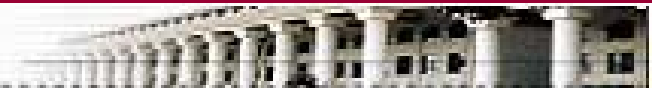
$$w_x = \left[\frac{zx(zx - x)!}{(zx - 2x + 2)!x!} \right] p^{x-1} (1 - p)^{2+(z-2)x}$$

P also means degree of reaction (or time). E.g., P=0 means the beginning of gelation process.

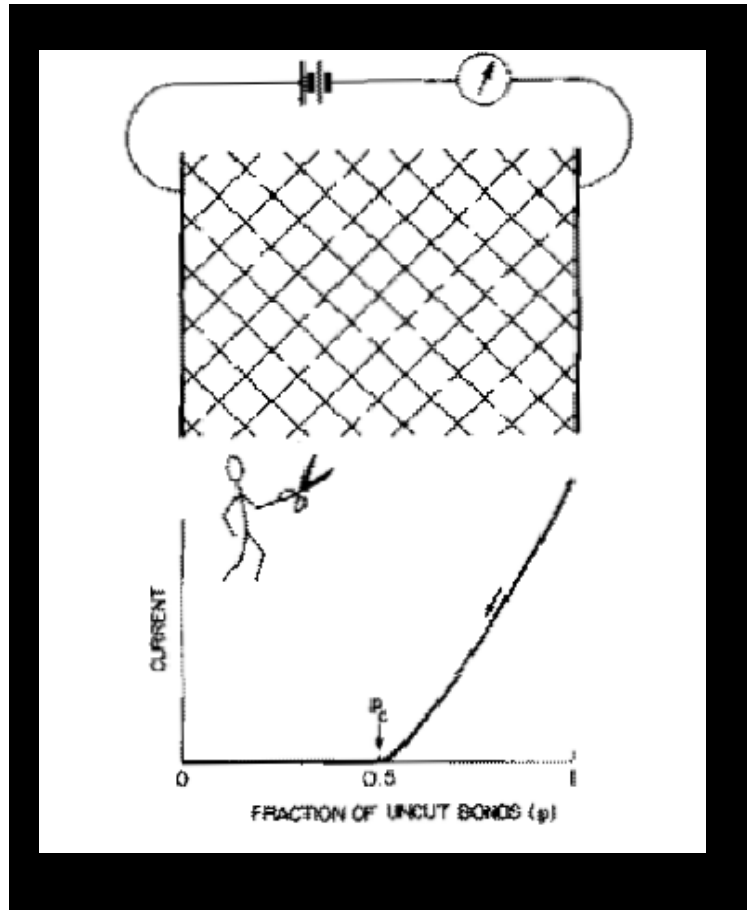
for $z = 4, Pc = 0.333$



Weight fractions of various finite species (w_x) and of gel (w_g) in tetrafunctional ($z=4$) condensation as function of degree of reaction, p .



Percolation Theory

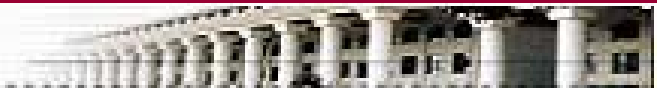


Let's consider a 2D grid made of a network resistors forming a regular lattice.

The network, represented by a very large square-lattice network of interconnections, is attacked by a crazed saboteur who, armed with wire cutters, proceeds to cut the connecting links at random.

Q. What fraction of the links(or bonds) must be cut in order to electrically isolate the two boundary bars?

A. 50%



PERCOLATION THEORY

◆ Site Percolation

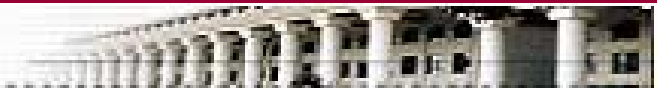
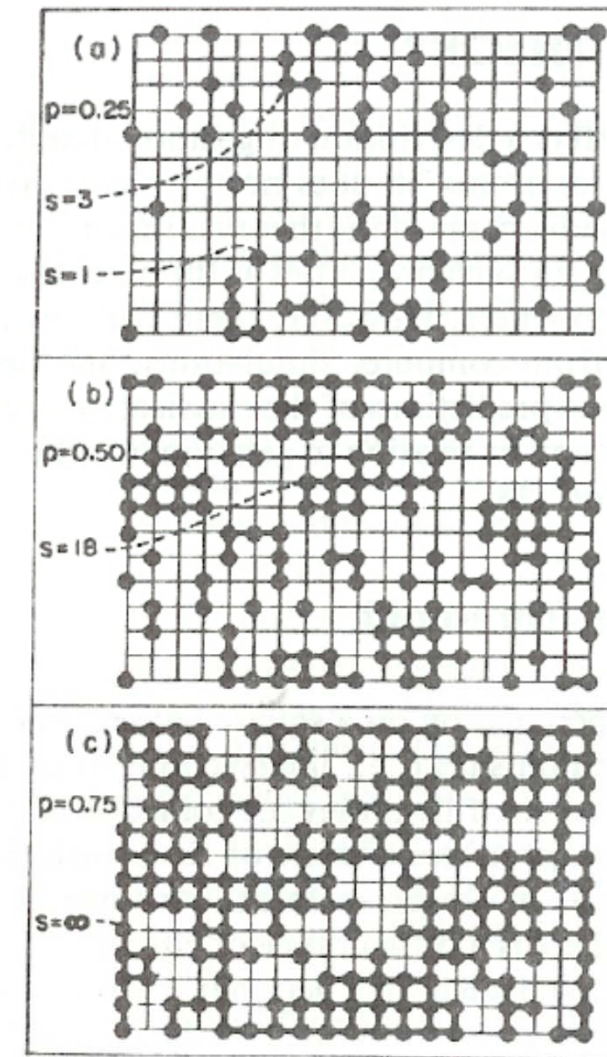
s : number of sites in a cluster (size)

n_s : frequency of clusters with size s

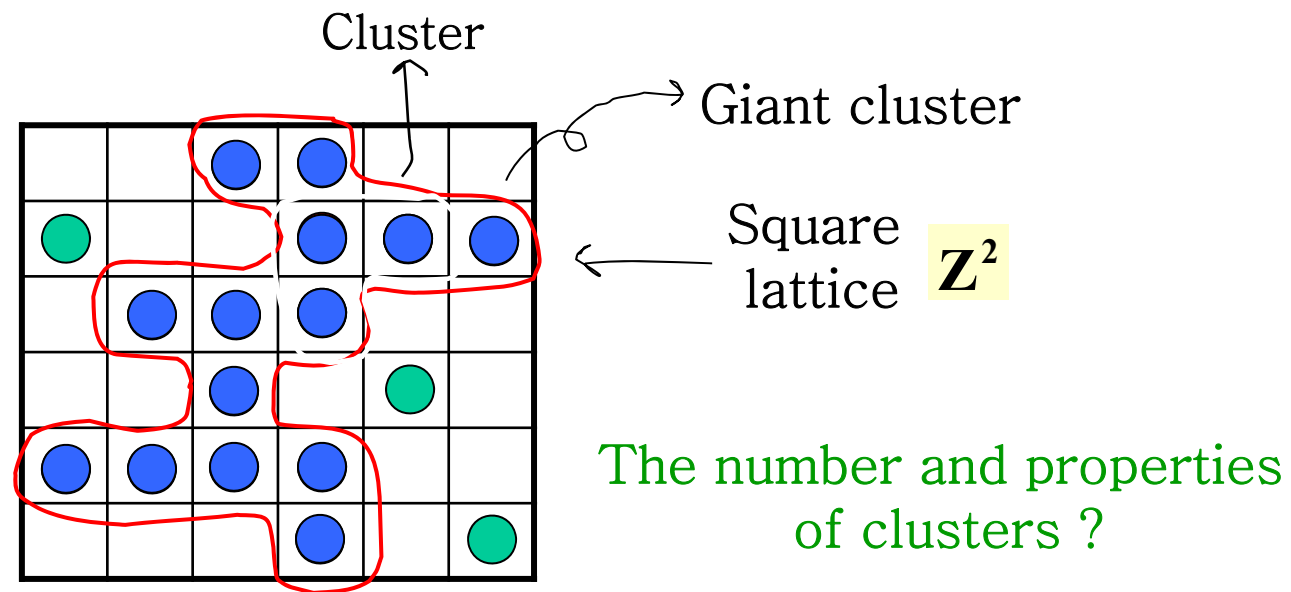
P : fraction of filled sites

P_c : percolation threshold, a critical value of P at which the spanning cluster first appears

Site percolation on the square lattice, illustrating various cluster sizes (s) for three values of p , the fraction of filled sites.



What is Percolation?



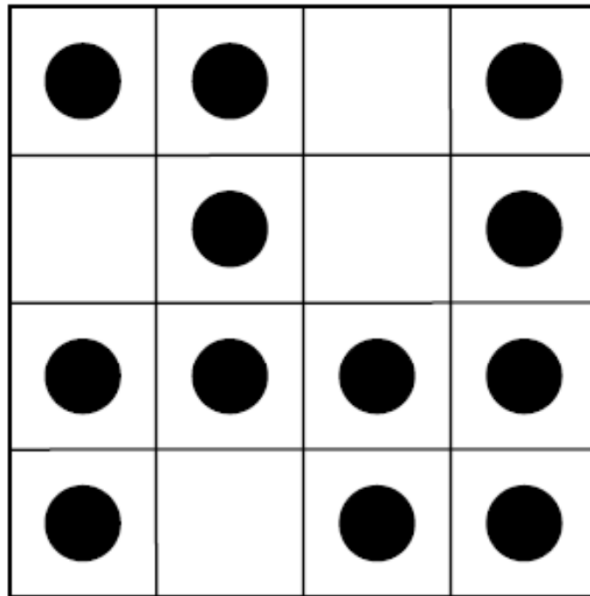
Percolation



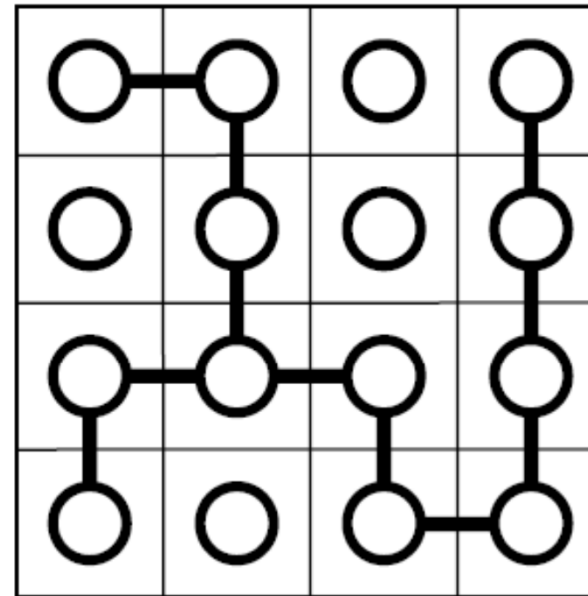
◆ Bond Percolation

The sites are already filled (with monomers or particles) and the bonds are filled at random.

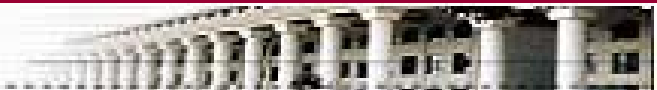
Site Percolation



Bond Percolation



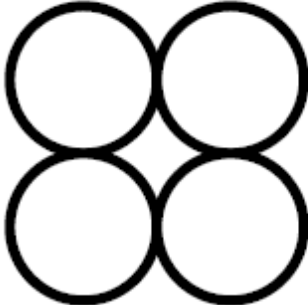
$$P_c^{\text{SITE}} > P_c^{\text{BOND}}$$



◆ Volume Fraction at Percolation Threshold

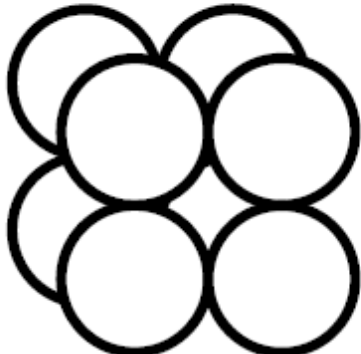
v : Filling factor, the fraction of volume (or area) that would be occupied if every sites were covered with spheres (or circles).

2d

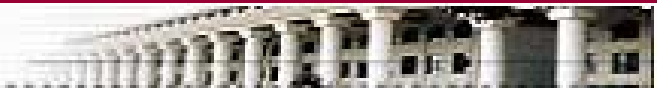


$$v = \frac{4(\pi R)^2}{4(2R)^2} = 0.785$$

3d



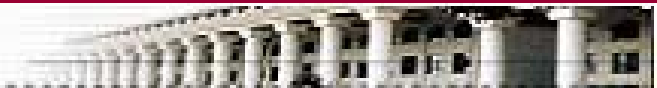
$$v = \frac{8(4/3\pi R^3)}{8(2R)^3} = 0.524$$



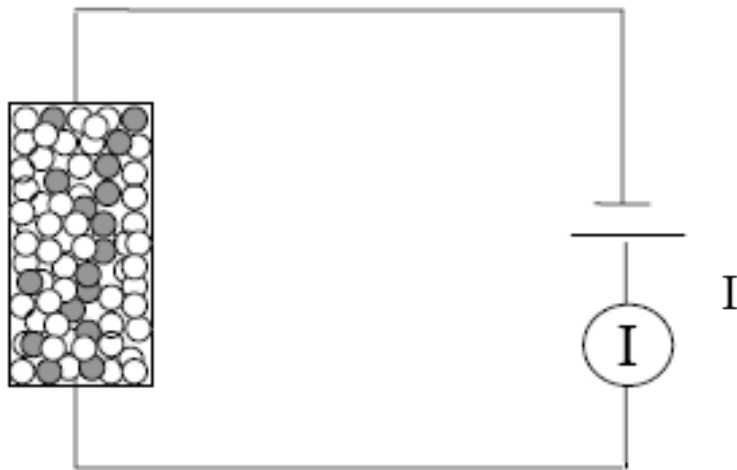
Φ_c : volume fraction at percolation threshold ($\Phi_c = vP_c$)

Percolation Threshold for Some Lattice

Dimen- sionality	Type of Lattice	z	$1/(z-1)$	P_c^{BOND}	P_c^{SITE}	v	Φ_c^{SIZE}
1	chain	2	1	1	1	1	1
2	triangle	6	0.20	0.35	0.50	0.90	0.45
2	square	4	0.33	0.50	0.59	0.79	0.47
3	simple cubic	6	0.20	0.25	0.31	0.52	0.16

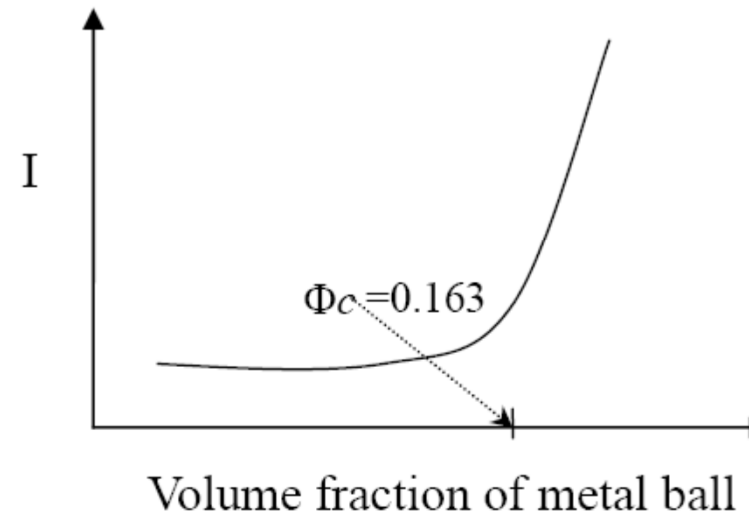


◆ Properties of Material around Percolation Threshold



- - Metal balls
- - Glass balls

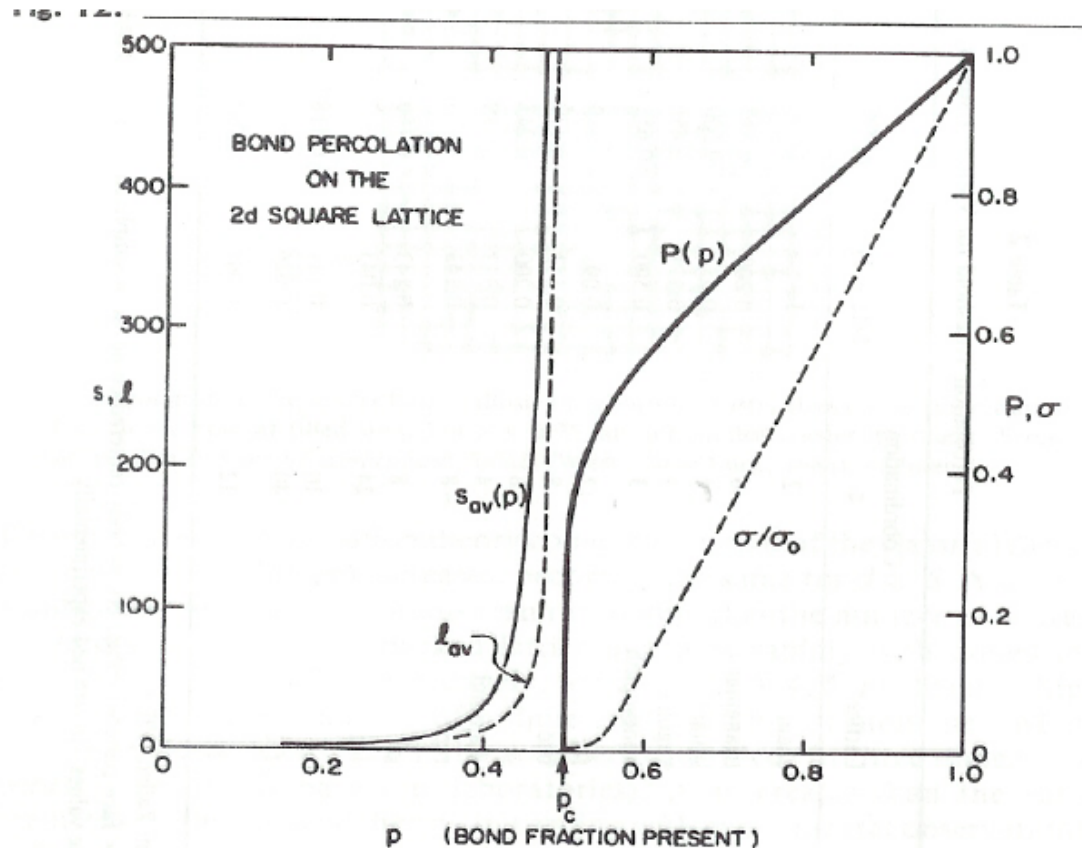
filled with glass(insulator) and metal(conductor) balls of equal size



In general, properties of the system change dramatically in the vicinity of the percolation threshold, as shown below (the result of computer simulation).

l_{av} - spanning length, the distance between two sites (or bond centers) in a cluster, rough estimate of cluster size

P - the probability that a given site (or bond) is attached to the spanning cluster



The behavior, as a function of the fraction (p) of filled bonds, of key properties that characterize bond percolation on the square lattice in two dimensions. The percolation probability $P(p)$, the average cluster size $s_{av}(p)$, and conductivity σ are results of computer studies; the spanning length l_{av} is schematic. From Zallen, *The Physics of Amorphous Solids* (Wiley, New York, 1983), chapter 4.



KINETICS OF AGGREGATION PROCESS

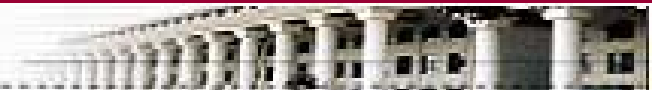
◆ Smoluchowski's Equation

The rate at which the number of clusters of size s changes with time:

$$\frac{dn_s}{dt} = \underbrace{\left(\frac{1}{2}\right) \sum_{i+j=s} K(i, j) n_i n_j}_{\text{Term 1}} - \underbrace{n_s \sum_{j=1}^{\infty} K(s, j) n_j}_{\text{Term 2}}$$

n_i, n_j - the numbers of clusters with size i or j

$K(i, j)$ - coagulation kernel (equivalent to rate constant)



Term 1 – the rate of creation of clusters of size s by aggregation of two smaller clusters of size i and j , respectively, $i+j=s$

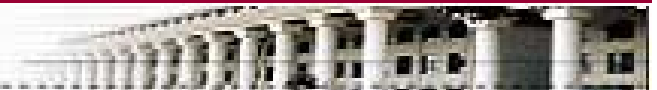
e.g. formation rate of cluster with $s=4$ from smaller clusters is a summation of the following

$$\text{Term 1} = \frac{1}{2}(K(1,3)n_1n_3 + K(2,2)n_2n_2 + K(3,1)n_3n_1) = K(1,3)n_1n_3 + \frac{1}{2}K(2,2)n_2n_2$$

Term 2 – the rate at which clusters of size s are eliminated by further aggregation with other clusters with size from $j=1$ to ∞

e.g. for $s=2$

$$\text{Term 2} = n_2 \sum_{j=1}^{\infty} K(2, j)n_j$$



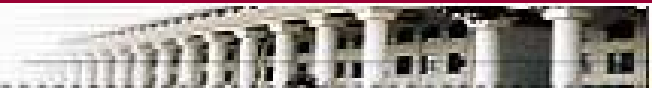
The coagulation kernel is a homogeneous function and related to the size of the clusters

$$K(ai, aj) = a^\lambda K(i, j) = a^\lambda K(j, i)$$

$$K(i, j) \approx i^\mu j^\nu \quad \text{for } j \gg i$$

$$\text{with } \nu \leq 1$$

$$\lambda = \mu + \nu \leq 2$$



◆ Three Different Classes of Gelation Process

Class I ($\mu > 0$), gelation is dominated by collisions between large clusters

e.g. for $\nu = 1, \mu = 1$ $K(i, j) = ij$; and for $s = 4$

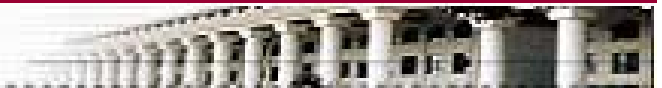
	i	1	2	3
j	K			
1				3
2			4	
3		3		

K is the largest for $i=2$ and $j=2$

Class II ($\mu=0$), frequency for collision of large-with-large clusters is the same as that for large-with-small clusters

e.g. for $\nu = 1, \mu = 0$ $K(i, j) = j$; and for $s = 4$

	i	1	2	3
j	K			
1				1
2			2	
3		3		



Class III ($\mu < 0$), Gelation is dominated by collisions of large-with-small clusters.

◆ Properties of Growing Clusters According to Smoluchowski's Theory

	λ	$M_w(t)$ or $n_{av}(t)$	Gelling
Class I	$\nu < \lambda < 1$	t^z , with $z=1/(1-\lambda)$	No
Class I	$1 < \lambda \leq 2$	$ t_{gel} - t ^{-z}$, with $z=1/(1-\lambda)$	Yes
Class II	$\lambda = \nu \leq 1$	Same as Class I	No
Class III	$\lambda < \nu$	Same as Class I	No

