P.G. de Gennes,

PERCOLATION

AND GELATION

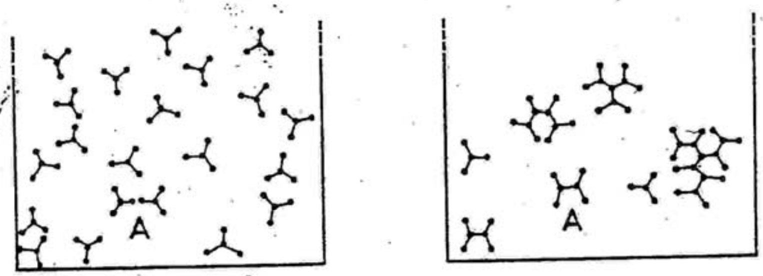
de Gennes - P. Lafore- J.P. Millot J. Phys. 20, 624, 1959

- **Mixture of active A + inactive B on propagation (impurity band in semi cond.; spin waves in ferromagnetic mixture)**

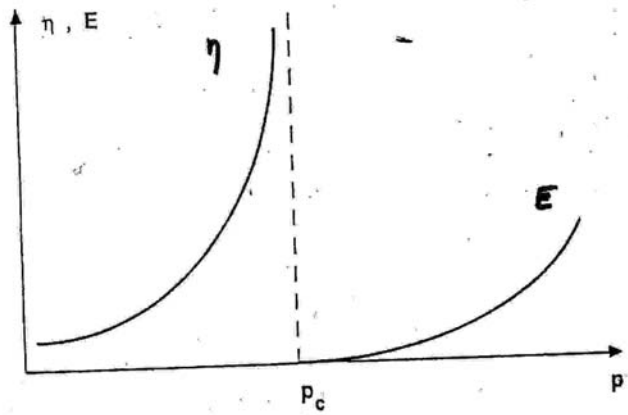
$\longrightarrow$

- **Critical concentration resulting from pure geometrical effect separating**

2 regimes



(a) (b)

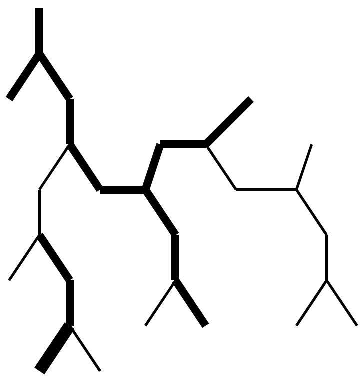


$$\eta \sim \varepsilon^{-s} \qquad E \sim \varepsilon^{\mu} \qquad \varepsilon \equiv |p - p_c| .$$

Flory- Stockmayer- Zimm

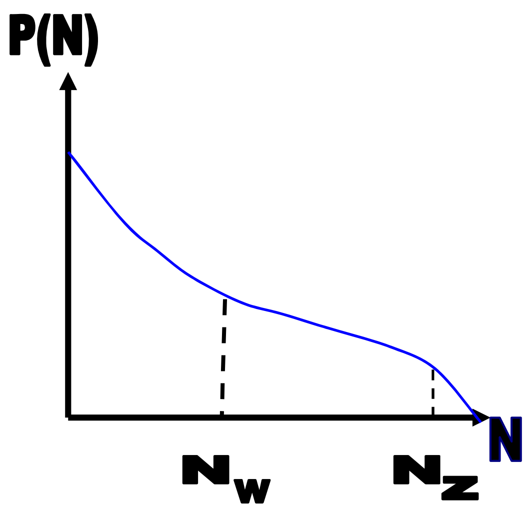
-no loops

- 1 linear path between any 2 points.

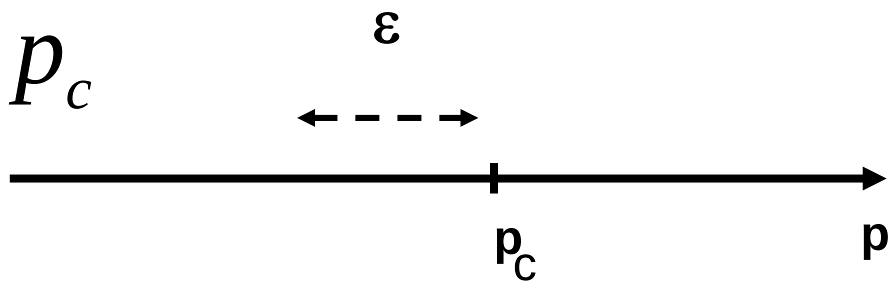


$$P(N) \propto N^{-\tau} f(N/N_z)$$

$$\tau = 5/2$$



$$\varepsilon = p - p_c$$



$$N_w \propto \varepsilon^{-1}$$

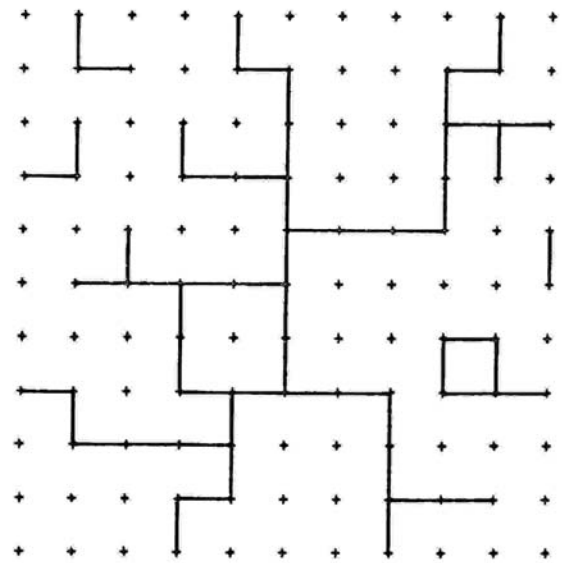
$$N_z \propto \varepsilon^{-2}$$

$$R \propto N^{1/4}$$

$$\xi \propto \varepsilon^{-1/2}$$

D= 4

de Gennes- Stauffer (76)



- Percolation

  bonds at random
- probability p

- p << pc finite
- p > pc infinite mol
  = GEL

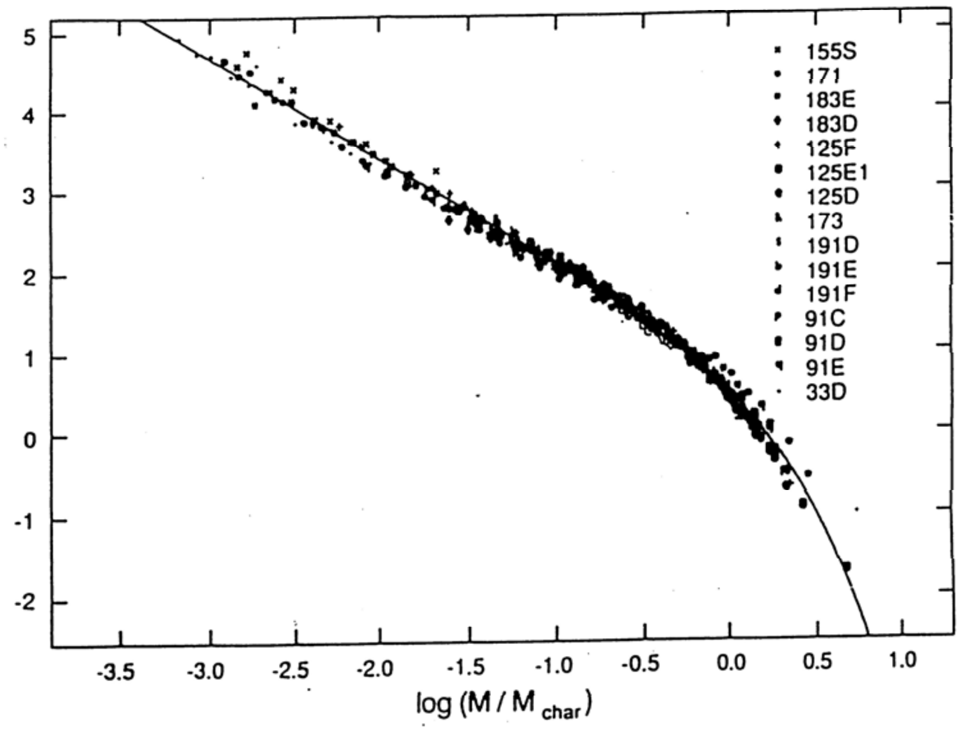
$$P(N) \propto N^{-\tau} f(N/N_z)$$

$\tau = 1 + d/D$

$C^*(N)$

- Gelation = percolation
- Exp: Leibler et al.; Rubinstein- Colby; Schaefer, Martin et al. Adam, Bouchaud et al.

$\tau = 2.2 \pm 0.05$



Difference with animals. PGG(1980)

Flory theory: **Animals:**

$$F = \frac{R^2}{N^{1/2}} + v\frac{N^2}{R^d}$$

$d_c = 8$

D = 2(d+2)/5

Percolation:

$$F = \frac{R^2}{N^{1/2}} + v\frac{N^2}{N_w R^d}$$

$d_c = 6$

$$MF: N_w \propto N^{1/2}$$

D= (d+2)/2

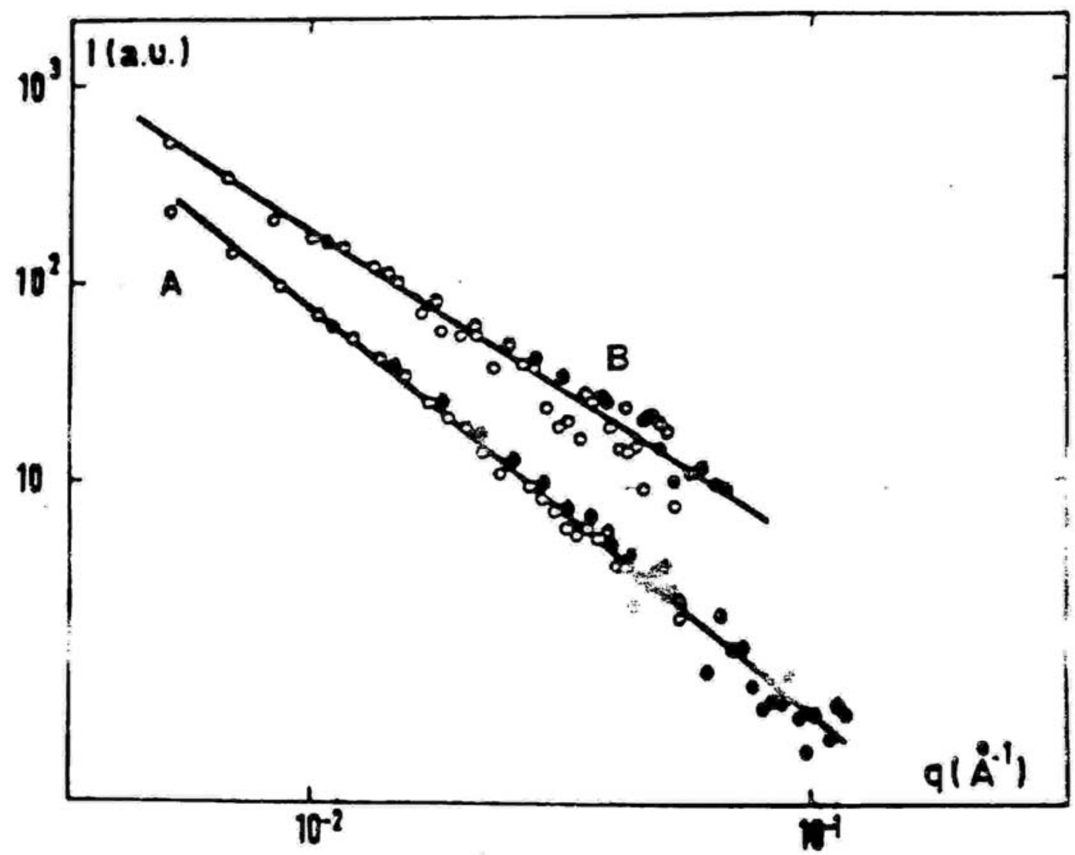
- **Dilute polydisperse:**

$$S(q) = q^{-D(3-\tau)}$$ **polydisperse**

$$S_1(q) = q^{-D}$$ **monodisperse**

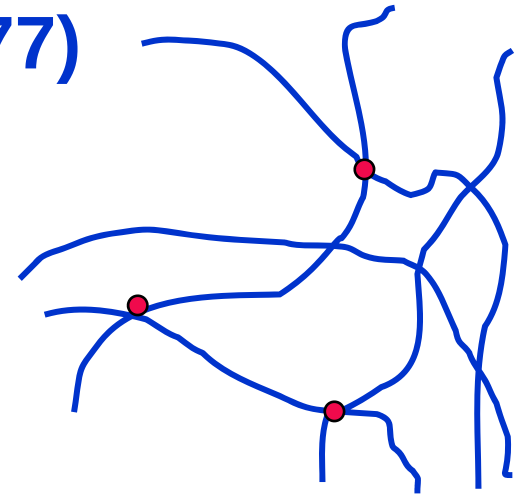
D = 1.98± 0.05

$\tau = 2.2$ **± 0.05**



I (a.u.)
10^3
10^2
10
A
B
q (Å^{-1})
10^{-2}
10^{-1}

Vulcanization PGG (1977)

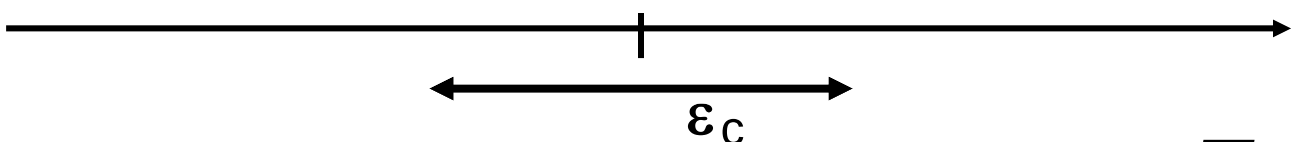


- Cross-linking of linear chains Z
- Unit mass is Z Unit length is $\sqrt{Z}$

$$F_{\mathrm{int}} = \frac{N^2}{N_w R^d} = \frac{\varepsilon^{-4} Z^2}{\varepsilon^{-1} Z \varepsilon^{-d/2} Z^{d/2}} = \varepsilon^{-3+d/2} Z^{1-d/2}$$

d = 3

Critical region is very small



$$\varepsilon_c \propto Z^{-1/3}$$

Exp: Colby- Lusignan

Viscosity (PGG 1978)

- no hydrodynamics; no entanglements

Longitudinal flow: $u_x = sx$ $u_y = -sy$

Dissipation per molecule: $T\overset{\circ}{S} = \varsigma s^2 \sum (x_n^2 + y_n^2)$

$\eta \propto R_{Gw}^2$ **Viscosity exponent:** $s = 2\nu - \beta$

$D(N) \propto D_0 / N$

$G \propto 1/\xi^3$

$T(N) \propto \xi^2 / D \propto N\xi^2$

$\eta \propto GT \propto N/\xi$ (Id)

$s = \beta + \gamma - \nu$

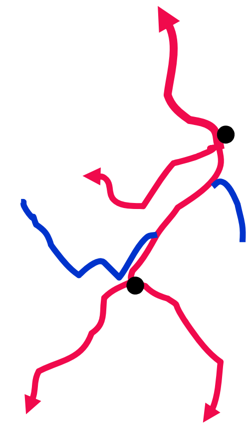
$\eta \propto N_w^{3/4}$

Modulus PGG (1976)

- Conductance σ proba p; 0 proba 1-p

$$\sigma_{nm} = \sigma / N_{nm}$$

Active path



Current through surf ξ^{d-1} $$\frac{\sigma \xi E}{\bar{N}} = \Sigma \xi^{d-1}$$

$$\Sigma \propto \xi^{2-d} / \bar{N} \propto \varepsilon^{1+(d-2)\nu}$$

$t = 1+(d-2)\nu$

$t = \varsigma+(d-2)\nu$

($t = \nu d$)

Rheology

$$\eta \propto \varepsilon^{-s}$$

$$G \propto \varepsilon^{t}$$

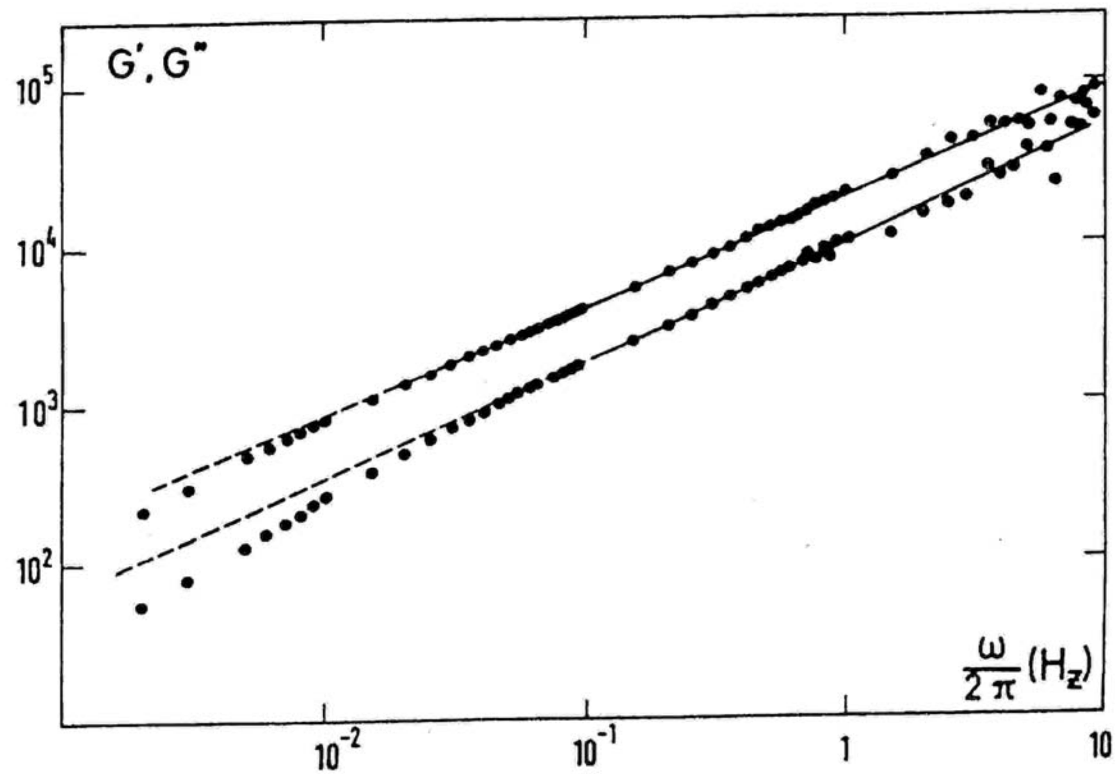
$$\bar{E}(\omega) = E(\omega) + j\omega\eta(\omega)$$

$$\bar{E}(\omega) = \varepsilon^{t} f(j\omega\varepsilon^{-s-t})$$

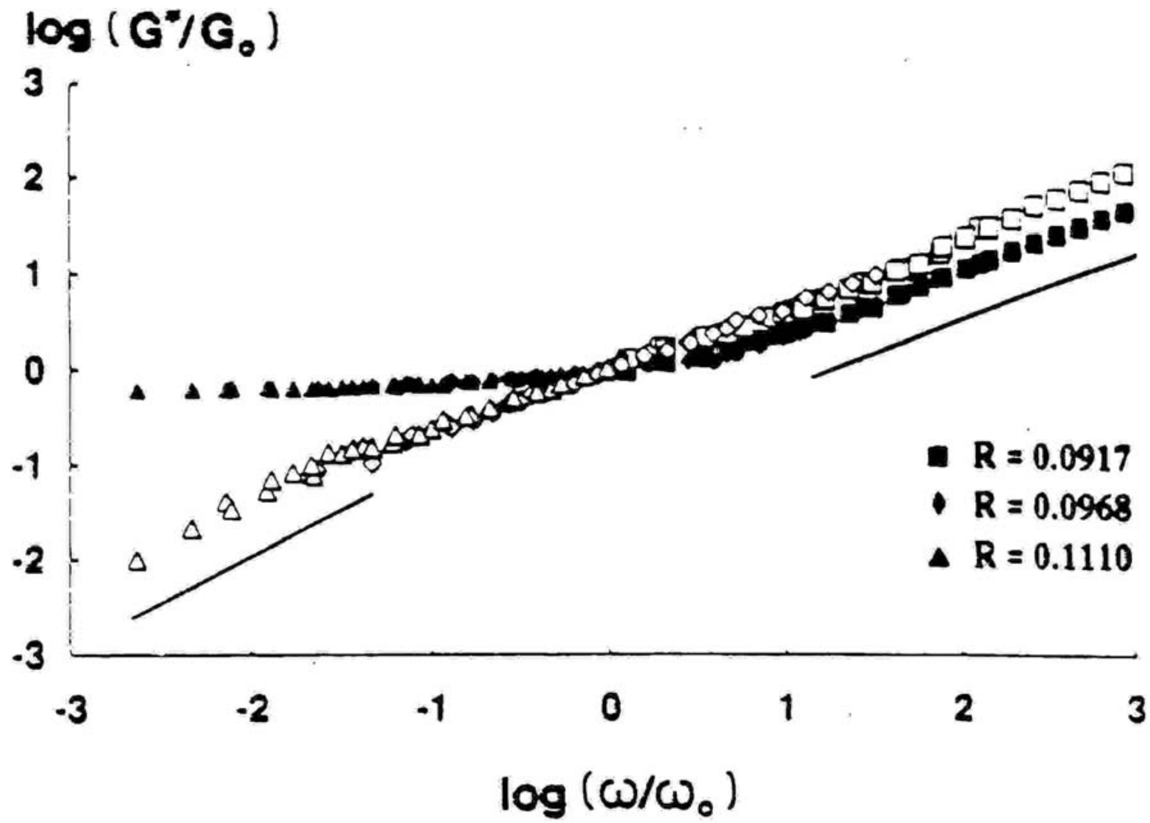
$$T \propto \varepsilon^{s+t}$$

$$\bar{E}(\omega T \geq 1) \propto (j\omega)^{t/(s+t)}$$

Exp t/(s+t) = 0.66



G', G"
10^5
10^4
10^3
10^2
$\frac{\omega}{2\pi}$ (Hz)
10^{-2}
10^{-1}
1
10



log (G"/G$_o$)
3
2
1
0
-1
-2
-3
-3
-2
-1
0
1
2
3
log (ω/ω$_o$)
R = 0.0917
R = 0.0968
R = 0.1110

Incoherent scattering
Dilute system of labelled monomers

$$I(q,\omega) = \int dt e^{i\omega t} < \exp[iq(r(t) - r(0))] >$$

For small q, < > ~ exp(-Dq^{2}t)

D(n,t) ~ kT/6πη(r)r

$$\eta(r) \approx r^{s/\upsilon}$$

$$D = D_0 n^{-a}$$

a =(s+ν)/(β+γ)

$$P(n) = n^{-(1+\beta/(\beta+\gamma))}$$

$$I(x = Dq^2 t) = x^{-\beta/(\nu+s)}$$

$$I(q,\omega) \propto \omega^{-1+\beta/(\nu+s)} q^{-2\beta/(\nu+s)}$$

- **Incoherent scattering(1979)**
- **Microphase separation (1979)**
- **Diffusion of ants and termites on branched structures (1983)**

- **Reversible gels**
- **Glass transition**
- **Polyelectrolyte gels**
- **Fractured gels**
- **Rubber- Rubber adhesion**
- **Competition between diffusion and cross- linking at Pol.-Pol. Interface.**
- **…..**