Polymer Properties
Quiz 12
April 12, 2017

Vilgis and Winter [Vilgis TA and Winter HH, *Colloid and Polymer Science* **266** 494-500 (1988).] describe a critical gel in Figure 2 as a gel where local clusters grow to span the entire sample. Vilgis states: *Directly at the percolation threshold, when the power law in G' and G" is observed, no length scale matters, in contrast to regimes below the gel point where the size of the typical cluster is the characteristic length scale and above the gel point where the size of weakly linked regions dominate.* At the percolation threshold the number of structures with relaxation times $\tau = 1/\omega$ is given by $N(\omega) = \omega^{ds-1}$ where d_s is the spectral dimension and in this case is equal to the connectivity dimension c. For percolation gels, at frequencies higher than a critical frequency, G' is proportional to G" and both scale with a power of frequency related to d_s. Consider that the dynamic strain is related to the dynamic stress by the response function

$\varepsilon(t) = \int_0^t \sigma(t')\mu(t-t')\,dt'$, and that

$$G^*(\omega, p_c) = a\,S\,(i\omega)^n \qquad (1)$$

$$\eta^* = (G'^2 + G''^2)^{1/2}/\omega \qquad (2)$$

For the critical percolation threshold gel, where η^* is the complex viscosity and G*is the complex modulus, and S is a complex function of frequency. Also, consider that for a simple system, such as a sphere in a viscous fluid $\tau \sim \eta/kT$,

a) Sketch the response function for a Hookean elastic, Newtonian fluid, and a damped harmonic oscillator.
b) Sketch the response function for a gel at the critical threshold that follows the behavior described by Vilgis and Winter.
c) Describe the relaxation time for a harmonic oscillator, Hookean elastic, a Newtonian fluid, and a diffusing colloidal particle (polymer).
d) What would be the characteristic of the relaxation time for the percolation gel?
e) Sketch the creep curve (elongation versus time) for a Hookean elastic, Newtonian fluid, and an anelastic material.
f) Sketch the creep curve you might expect for Vilgis/Winter gel at the percolation threshold. (How does it relate to the response function in part b?)
g) Explain why a percolation gel might be useful as a sound absorbing material.
h) Explain the behavior seen in Figure 1 below.

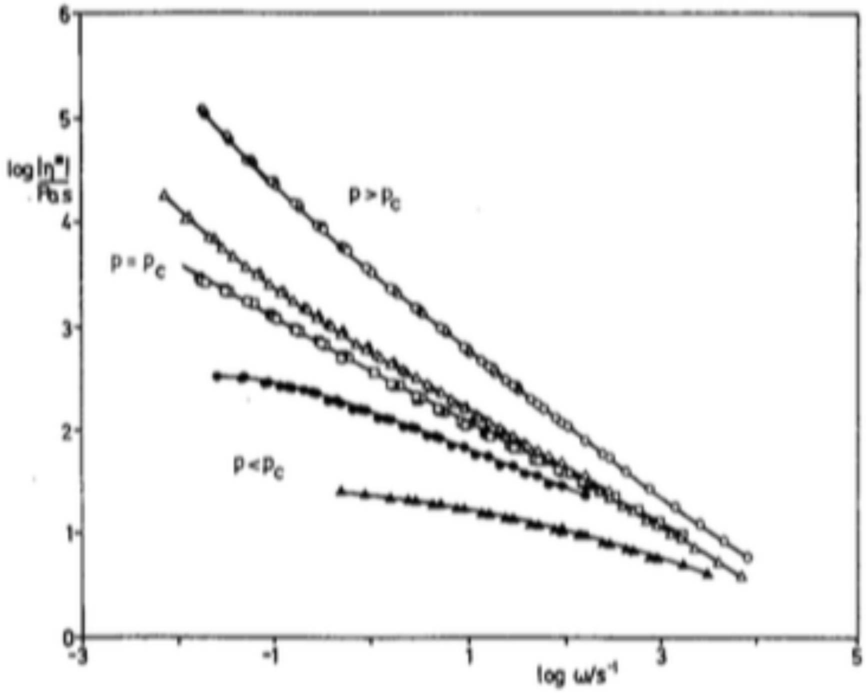


Fig. 1. Dynamic viscosity of a crosslinking polydimethylsiloxane near the gel point (data form Ref. [5]) for different extents of reaction. As described in the text, the power law is already established at frequencies larger than a crossover frequency. Above the percolation threshold (curves ○, △), the correlation length decreases again and the crossover freqency is again shifted to larger values. The viscosity at the gel point is given by the indicated straight line (□). The measurements for $p < p_c$ are indicated by ● and ▲

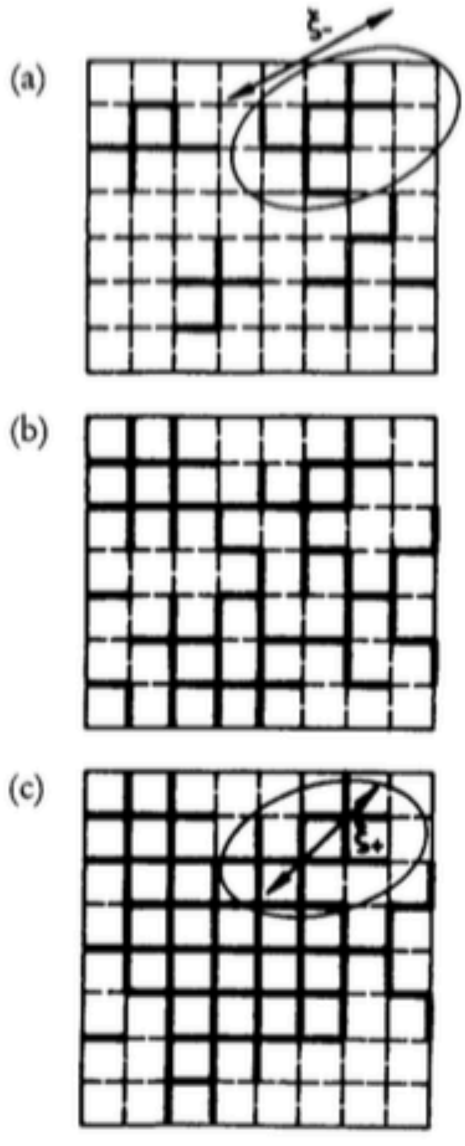
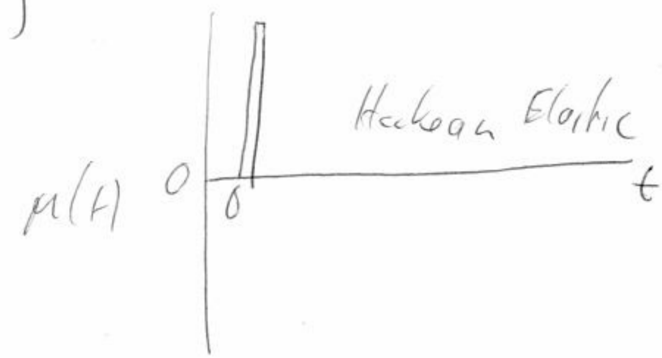


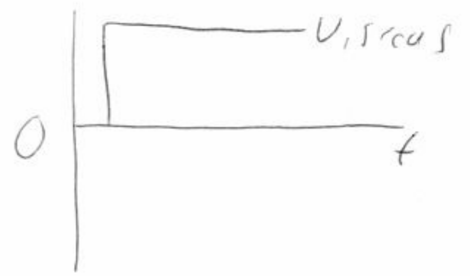
Fig. 2. Schematic sketches of three stages during percolation: (a) $p < p_c$: Only finite clusters are present; the correlation length is the size of a typical cluster. (b) $p = pc_c$: The correlation length is infinite. It extends over the entire size of the lattice. The size of the cluster is infinite. (c) $p > p_c$: The bonds are filling the lattice more and more. The correlation length decreases as the selfsimilar regions decrease

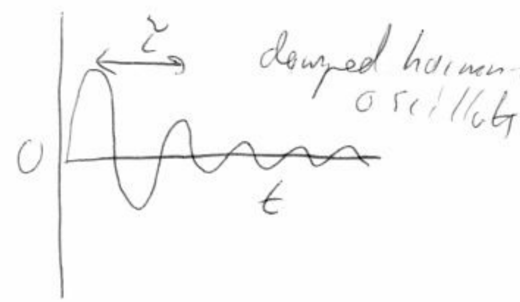
Vilgis TA and Winter HH, *Colloid and Polymer Science* **266** 494-500 (1988).

ANSWERS

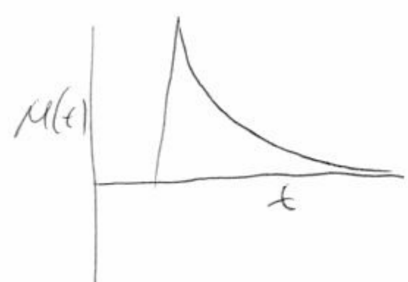
a)







b)



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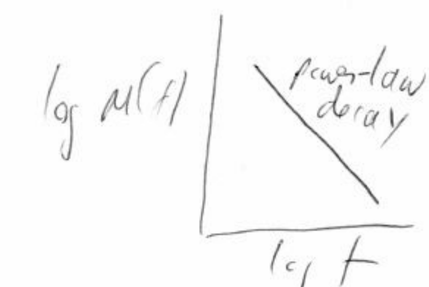


$$\mu(t) = \sum \omega^{(d_s-1)} \delta\left(\frac{1}{\omega}\right)$$

$$t = \frac{1}{\omega}$$

c) Hookean $\tau = 0$

Viscous fluid $\tau \sim \eta$

Harmonic Oscillator $\tau = \tau_0 \sin \omega t$

diffusing colloidal particle $\tau = \frac{v_{avr}}{\zeta} \sim 0$

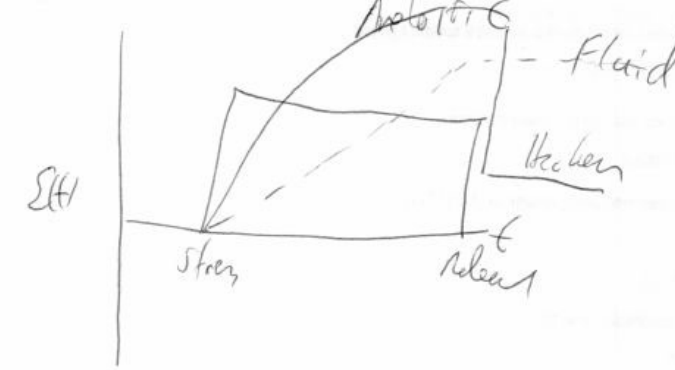
d) τ would have a power-law distribution

$$N(\tau) = \left(\frac{1}{t}\right)^{d_s - 1}$$

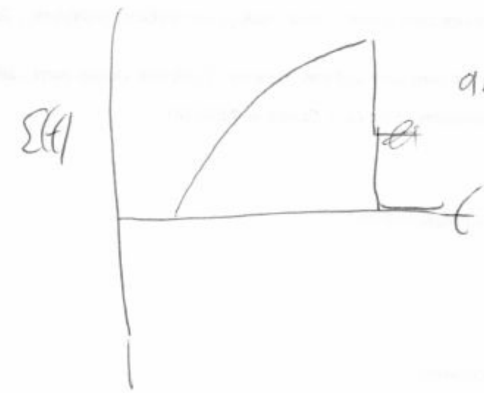
$$\langle \tau \rangle = \int_0^\infty \left(\frac{1}{t}\right)^{d_s - 1} t \, dt$$

$$\langle \tau \rangle = \int_0^\infty \left(\frac{1}{t}\right)^{d_s} dt$$

e)



f)



g) Maxwell at all frequencies
see answer 'd'

h) $\eta^* \sim \frac{(G'^2 + G''^2)^{1/2}}{\omega} \sim \tau$

so it is a power law decay
for the percolation threshold

below threshold it is a viscous
shear thinning fluid
above a viscoelastic solid