“A new interpretation for the dynamic behavior of complex fluids at the sol-gel transition using the fractional calculus”

By Stephane Warlus and Alain Ponton

Rheol. Acta (2009) 48:51-58

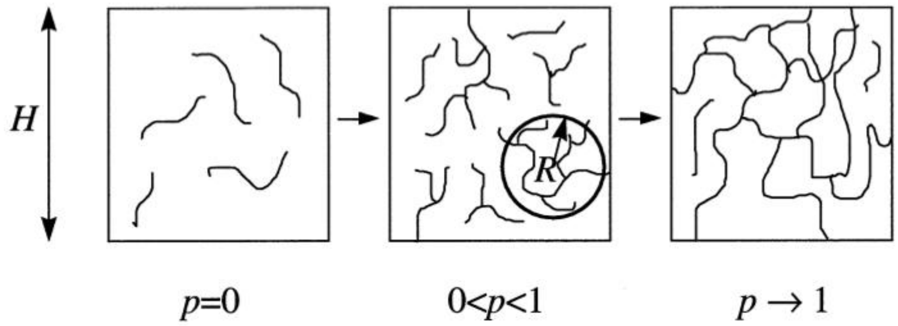
Chris Dimitriou

NNF Summer Reading Group

7/21/2010

The Critical Gel

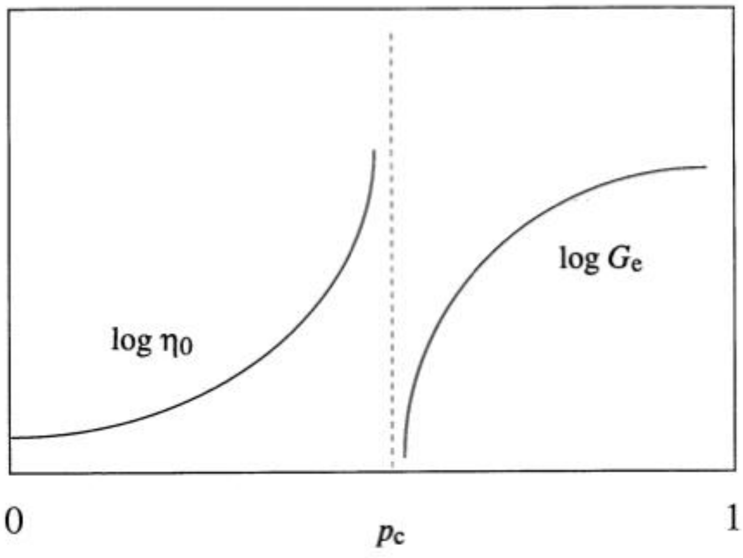
- Terminology
  - Liquid Solid Transition (LST)
  - Sol-Gel Trasition (SGT)
  - Critical Gel



- For a polymer, as crosslinking increases, the material approaches a gel
  - Idea of p

p is the “ratio of the number of chemical bonds to the total number of possible bonds”*

- As R→H we have a critical gel, I.e. the whole network is interconnected
  - $p = p_c$



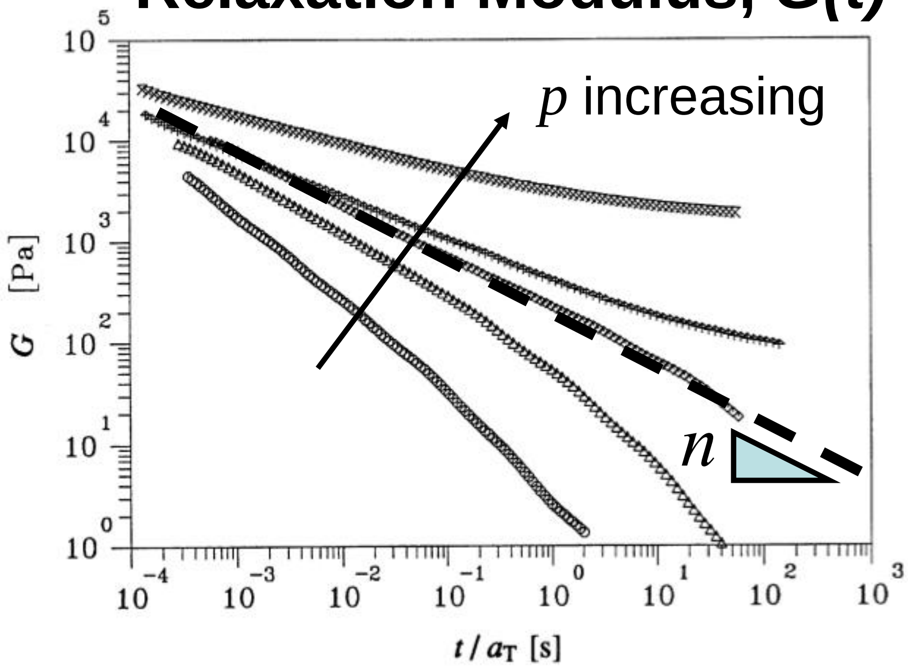
- Idea can be extended to physical gels ⇒ not restricted to crosslinking in polymers

*Winter and Mours, Rheology of Polymers near Liquid-Solid Transitions, *Advances in Polymer Science*, 1997

When do we have a critical gel?

- The material transitions from behaving like a fluid (relaxes completely) to a solid (has a non zero equilibrium modulus)

Relaxation Modulus, *G(t)*

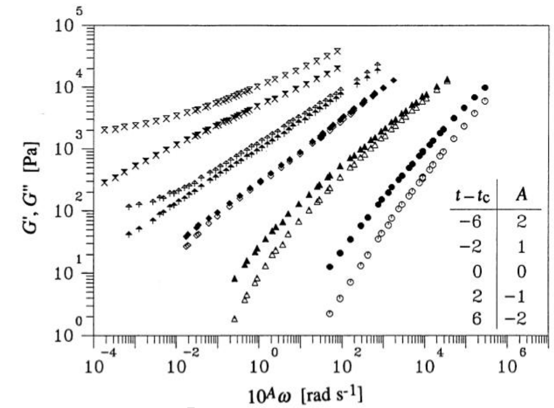


Relaxation modulus $\sigma(p,t)=\int_{-\infty}^{t} G(t-t')\dot{\gamma}(t')dt'$

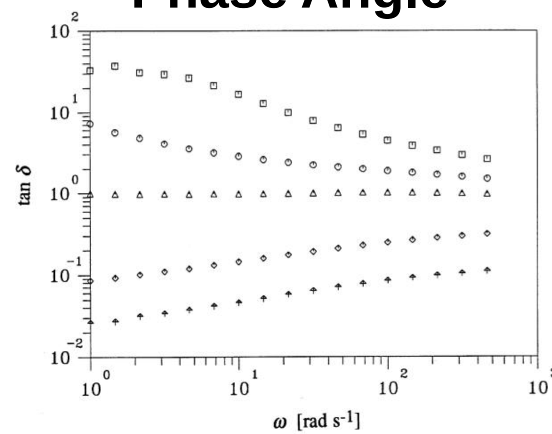
Winter & Mours $G(t)=St^{-n}$

Warlus & Ponton $G(t,p_c)=S_{p_c}t^{-\Delta_{pc}}$

Viscoelastic Moduli



Phase Angle



*Winter and Mours, Rheology of Polymers near Liquid-Solid Transitions, *Advances in Polymer Science*, 1997

Contribution of Warlus & Ponton

- Use of Riemann-Liouville integral operator to solve for constitutive model of a critical gel:

$$\sigma(p,t) = \int_{-\infty}^{t} G(t-t')\dot{\gamma}(t')dt' \longrightarrow \sigma(p_c,t) = S_{p_c}\int_{-\infty}^{t}(t-t')^{-\Delta_{pc}}\dot{\gamma}(t')dt'$$

$$G(t,p_c) = S_{p_c} t^{-\Delta_{pc}}$$

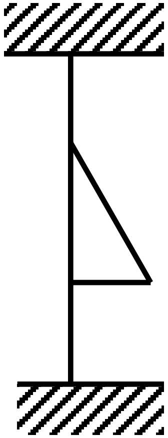
$$D^{\Delta} f(t) = \frac{1}{\Gamma(\Delta)}\int_0^t \frac{f(t')}{(t-t')^{1-\Delta}}dt'$$

$$D^{\Delta} f(t) \equiv \frac{d^{-\Delta} f(t)}{dt^{-\Delta}}$$

$$\sigma(p_c,t) = S_{pc}\Gamma(1-\Delta_{pc})\frac{d^{\Delta_{pc}}\gamma(t)}{dt^{\Delta_{pc}}}$$

Fractional Element!

Fractional Element (spring pot)



Behavior intermediate between elastic solid and Newtonian fluid, described by following:

$$\Delta_{pc}$$

$$\Lambda = S_{pc}\Gamma(1-\Delta_{pc})$$

What does the springpot predict for G’, G’’ and tan(δ)?

- As expected, a power law relaxation modulus:

$$G_{FE}(t) = \frac{\Lambda}{\Gamma(1-\Delta)} t^{-\Delta}$$

- G’ ,G’’ and tan(δ) are given by:

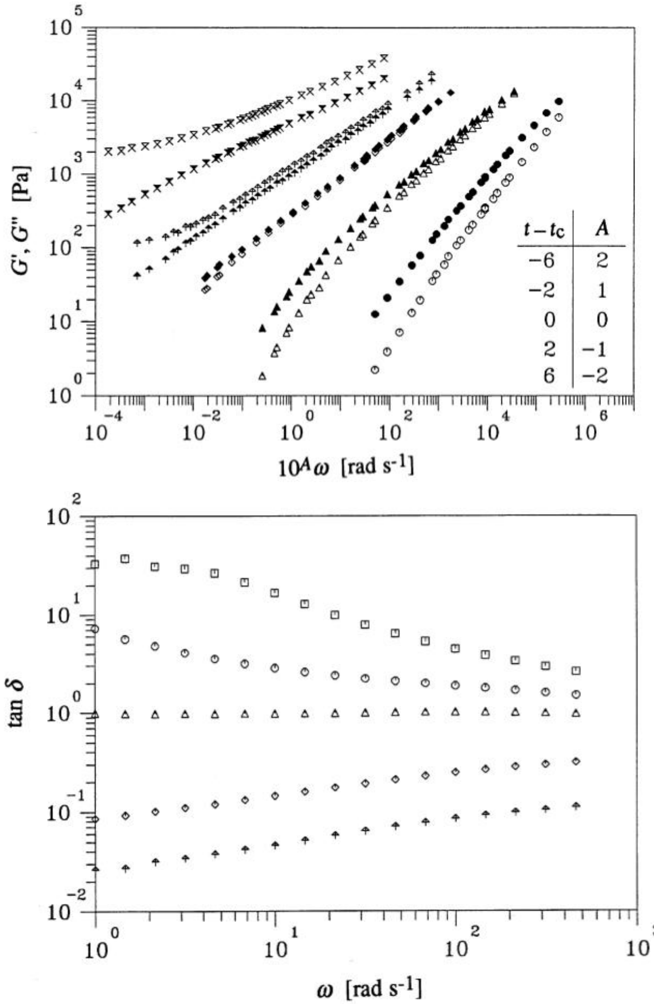
$$\sigma = \Lambda \frac{d^{\Delta}}{dt^{\Delta}}\left(\gamma_0 \sin \omega t\right)$$

$$\sigma = \gamma_0\left(\Lambda\omega^{\Delta} \sin\left(\omega t + \frac{\Delta\pi}{2}\right)\right)$$

$$G'(\omega) = \Lambda\omega^{\Delta} \cos\left(\frac{\Delta\pi}{2}\right)$$

$$G''(\omega) = \Lambda\omega^{\Delta} \sin\left(\frac{\Delta\pi}{2}\right)$$

$$\tan(\delta) = \tan\left(\frac{\Delta\pi}{2}\right)$$



Friedrich vs. Warlus

- 2 Different ways to extract viscoelasti moduli

Friedrich, Schiessel and Blumen:

$$\tau = E\lambda^{\beta} \frac{d^{\beta}\gamma(t)}{dt^{\beta}}$$

$$G^{*}(\omega) \equiv \tilde{\tau}(\omega) / \tilde{\gamma}(\omega)$$

"Multiplication rule"

$$\tilde{\tau}(\omega) = \int_{-\infty}^{\infty} E\lambda^{\beta} \frac{d^{\beta}\gamma(t)}{dt^{\beta}} e^{-i\omega t} dt = E\lambda^{\beta}(i\omega)^{\beta}\tilde{\gamma}(\omega)$$

$$\Rightarrow G^{*}(\omega) = E\lambda^{\beta}(i\omega)^{\beta}; \text{ where:}$$

$$\Lambda = E\lambda^{\beta}$$

$$\beta = \Delta$$

Warlus and Ponton:

$$\sigma = \Lambda \frac{d^{\Delta}}{dt^{\Delta}} (\gamma_0 \sin \omega t)$$

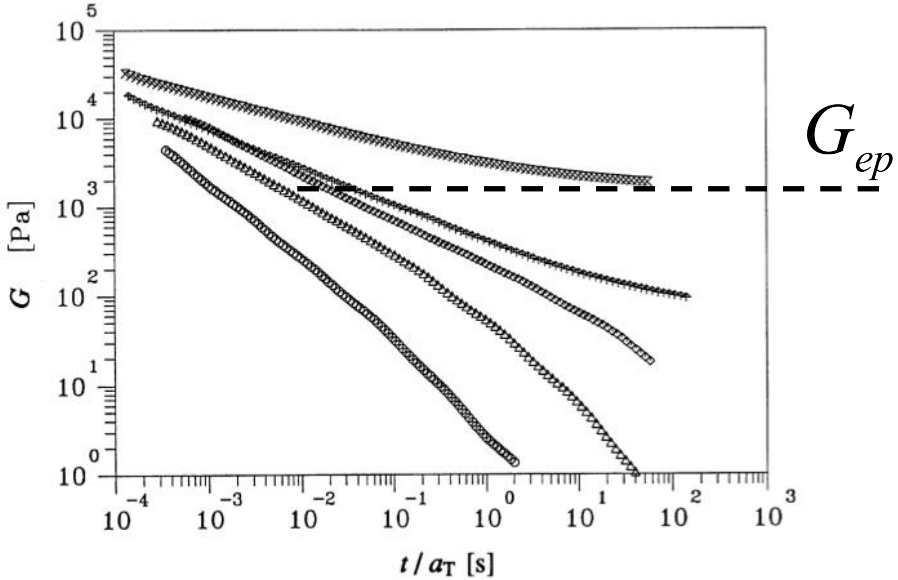
$$\sigma = \gamma_0 \left(\Lambda \omega^{\Delta} \sin \left(\omega t + \frac{\Delta \pi}{2} \right) \right)$$

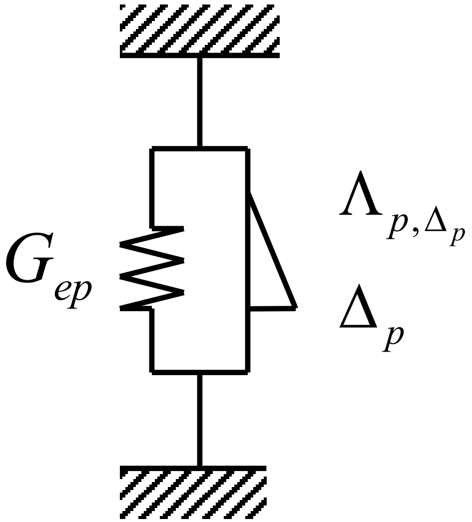
$$G'(\omega) = \Lambda \omega^{\Delta} \cos \left(\frac{\Delta \pi}{2} \right)$$

$$G''(\omega) = \Lambda \omega^{\Delta} \sin \left(\frac{\Delta \pi}{2} \right)$$

The Post-SGT State

- Warlus and Ponton argue that the behavior in the post SGT state can be described by the fractional Kelvin-Voigt model (KVF)





Shear stress relationship:

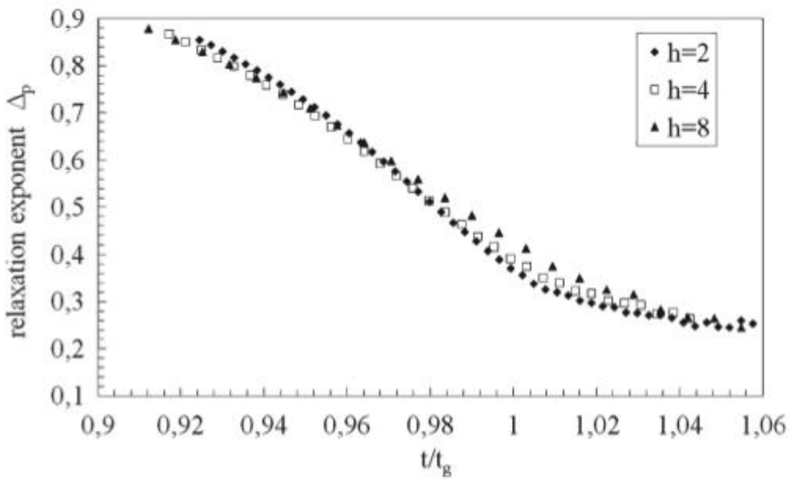
$$\sigma_{KVF}(p,t) = \Lambda_{p,\Delta_p} \frac{d^{\Delta_p}\gamma(t)}{dt^{\Delta_p}} + G_{ep}\gamma(t)$$

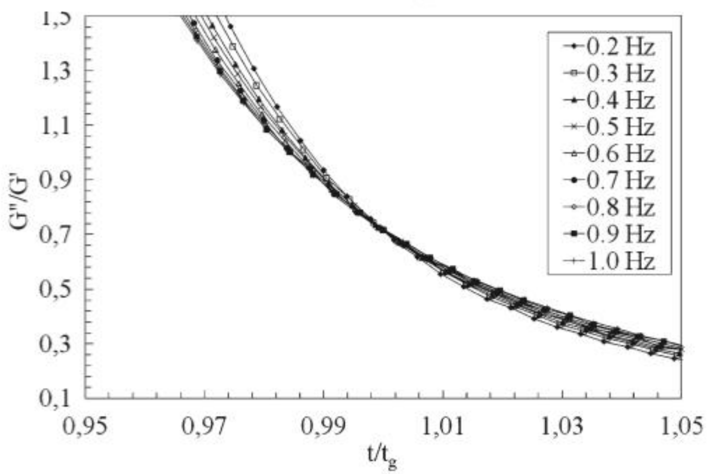
Shear stress relaxation modulus:

$$G_{KVF}(p,t) = \frac{\Lambda_{p,\Delta_p}}{\Gamma(1-\Delta_p)} t^{-\Delta_p} + G_{ep}$$

The Pre-SGT state

- Although not written in their 2009 paper, the authors have used expressions for the relaxation modulus in the pre SGT state





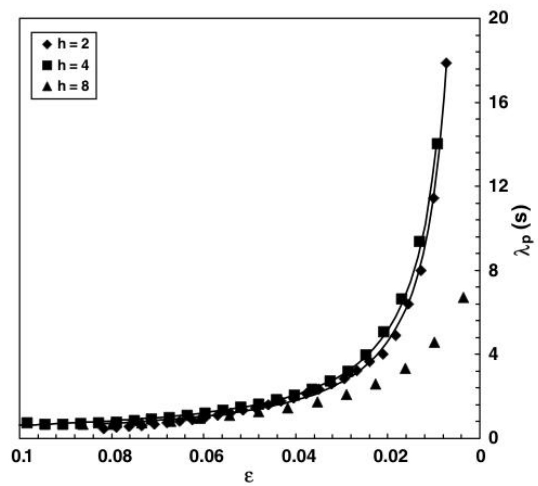
Extended relaxation modulus expression*:

$$G(p<p_c,t)=S_p t^{-\Delta_p}\exp(-t/\lambda_p)+G_{ep}$$

Pre SGT: $G(p<p_c,t)=S_p t^{-\Delta_p}\exp(-t/\lambda_p)$

CG: $G(p=p_c,t)=S_{p_c} t^{-\Delta_{pc}}$

Post SGT: $G(p>p_c,t)=S_p t^{-\Delta_p}+G_{ep}$



- This expression allows the parameters to have relevance in regions not directly at the SGT

*Warlus et. al., *Eur. Phys. E*, 2003

Massachusetts Institute of Technology

The fractional derivative order and fractal dimension

- Warlus states that dynamic light scattering (DLS) experiments show power law relaxation in the dynamic structure factor of some systems
- Structure and the critical exponent can be related as follows:

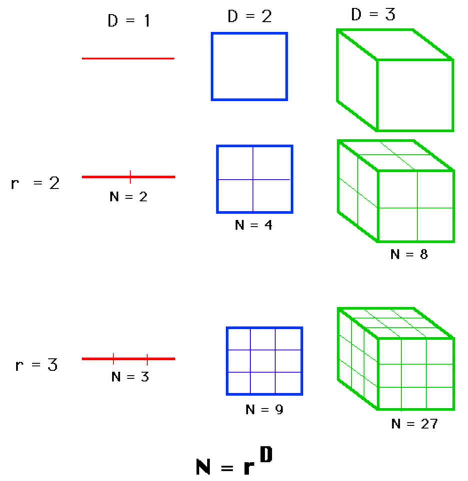
$$M \sim R^{d_f}$$

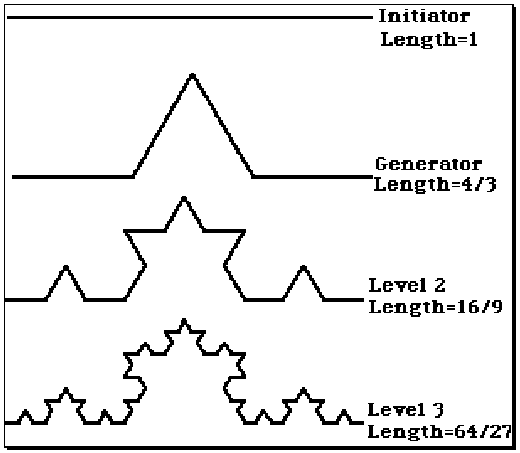
$$\Delta = \frac{d\left(d+2-2d_f\right)}{2\left(d+2-d_f\right)}$$

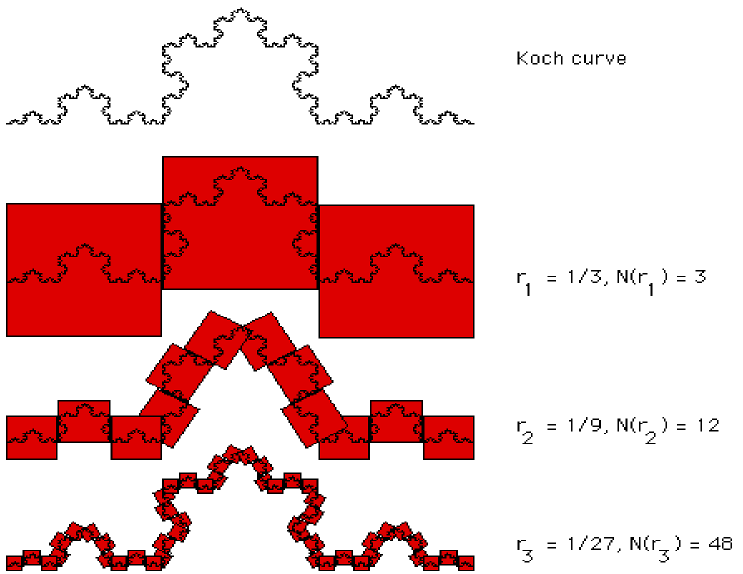
M. Muthukumar, *Macromolecules* 1989

M	Molecular Mass of clusters
R	Size of clusters
d_f	Fractal Hausdorff Dimension
d	Dimension of space (3d space)

- The fractal dimension can be understood by considering the Koch curve:





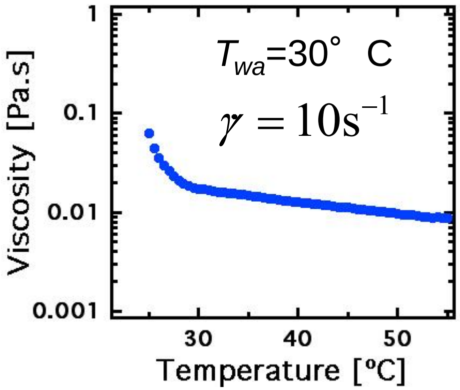


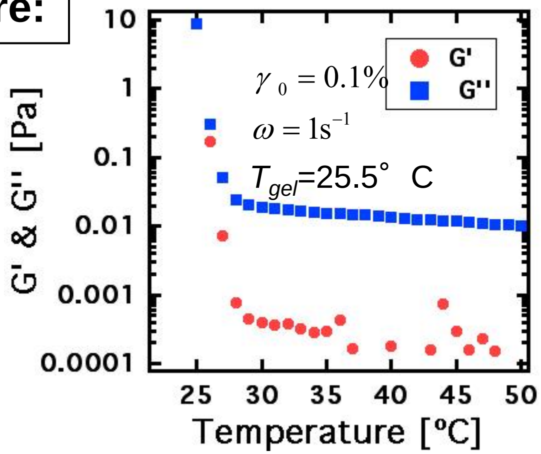
- Box counting is a common method used to determine the fractal dimension of a particular shape

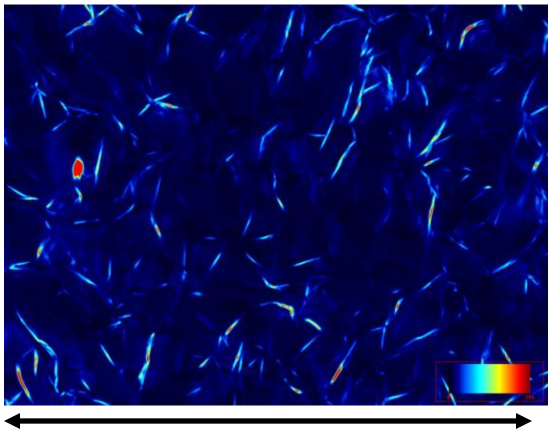
Connection to physical gels: wax-oil mixtures

- Wax-Oil gels are formed when wax precipitates out of the solution at lowered temperatures. A clear gelation point can be identified

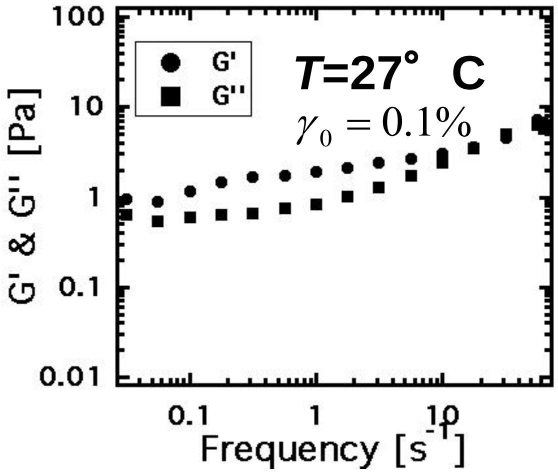
A 5% wax in oil mixture:

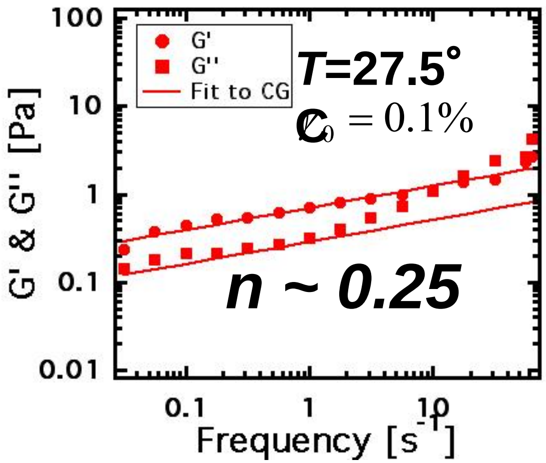


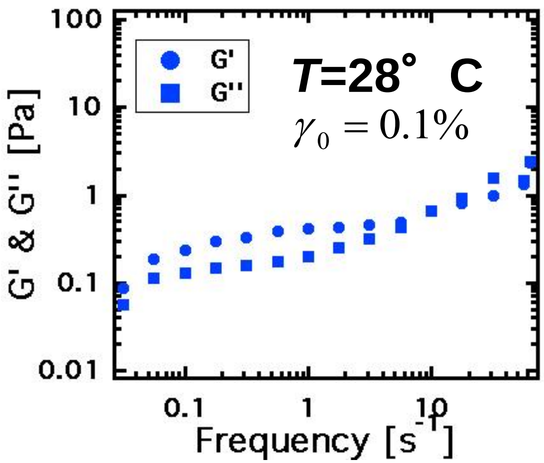




0.4mm







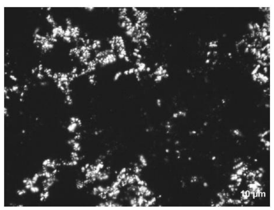
Relating slope of G'(ω) to fractal dimension

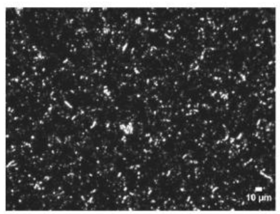
- Warlus and Ponton (*Rheol. Acta* 2009) give the following relation:

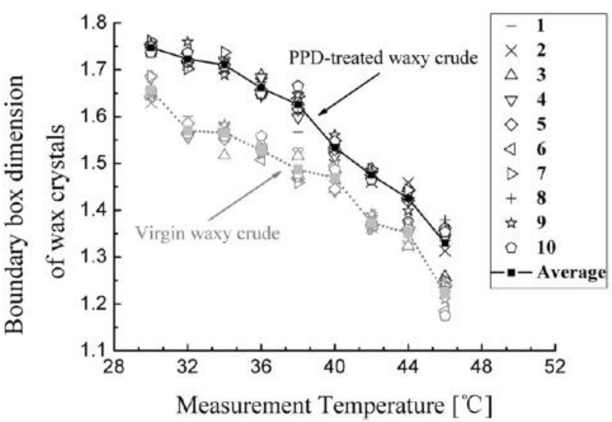
$$n = \frac{d\left(d + 2 - 2d_f\right)}{2\left(d + 2 - d_f\right)}$$

Where d_f is the fractal dimension

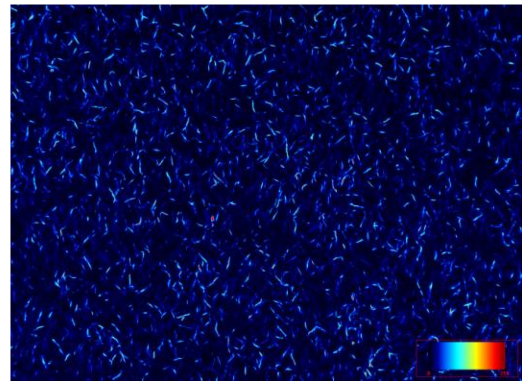
Study by Gao (*J Phys. Cond. Matter* 2006)

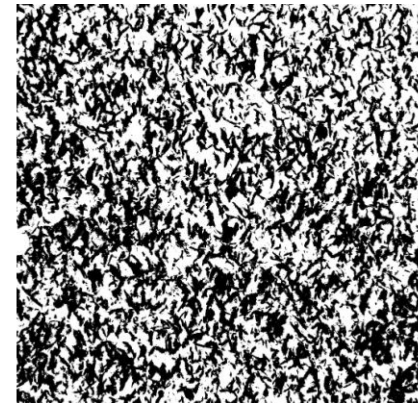


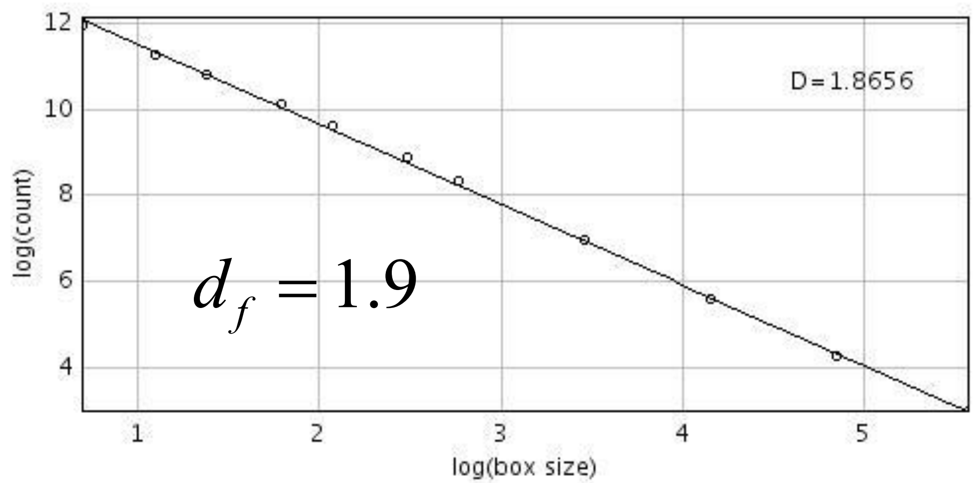




10% Wax Oil System (25° C):



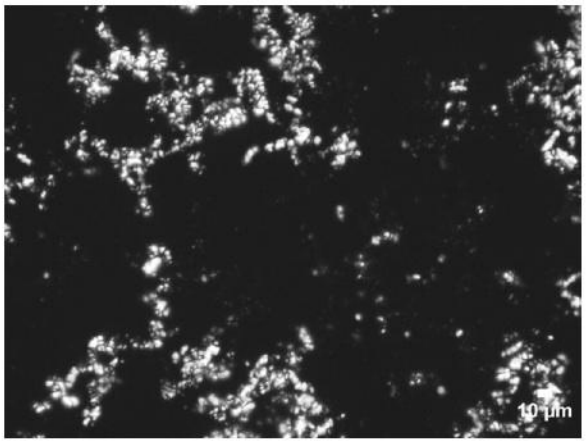




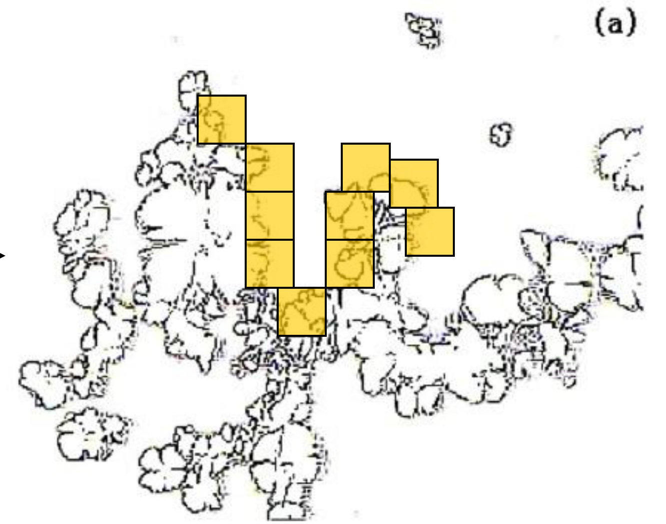
Box Counting Algorithm

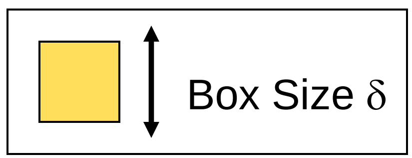
- The box counting algorithm is an simple algorithm to implement so as to determine the fractal dimension from digital images

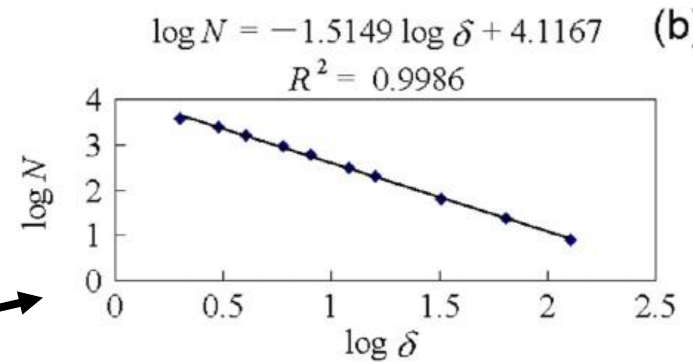
Begin with raw image:



Threshold/Extract boundary:







- With boxes of varying size (δ), measure how many are required to cover the boundary (N boxes)
- Plot log(N) vs log(δ) and the slope is equal to the box counting fractal dimension

Conclusion

- Critical gel: Terminology and behavior
- Using fractional calculus and fractional elements to understand behavior at the critical gel point
  - Viscoelastic moduli, relaxation modulus
- Pre and post SGT state according to Warlus and Ponton
- Connection between fractional derivative order and fractal dimension
- Connecting Warlus' work with a physical gel

Thank you for your attention!
Questions?