Glass Transition as the Rheological Inverse of Gelation

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H Henning Winter

Department of Chemical Engineering and Department of Polymer Science and Engineering, University of Massachusetts, Amherst, Massachusetts 01003, United States

Supplemental reading:

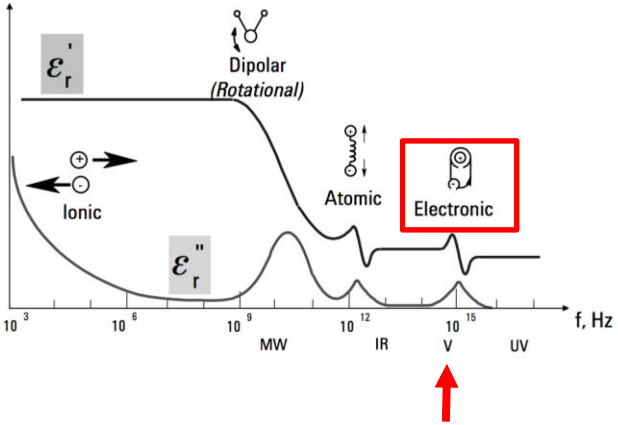
1. H. H. Winter, *Can the Gel Point of a Cross-linking Polymer be Detected by the G’-G’’ Crossover?* Polymer Engineering and Science **27**(22), 1698 (1987).
2. H. H. Winter et al. Rheology of Polymers Near Liquid-Solid Transitions. Advances in Polymer Science **134**, 165-234 (1997).
3. A. Negi et al. *Viscoelasticity of a colloidal gel during dynamical arrest: Evolution through the critical gel and comparison with a soft colloidal glass*. J. Rheol. **58**(5), 1557-1579 (2014).
4. Debenedetti PG et al. *Supercooled liquids and the glass transition.* Nature **410**, 259-267 (2001).
5. Martin JE, Adolf D, Wilcoxon JP. *Viscoelasticity of Near-Critical Gels.* Phys. Rev. Lett. **61,** 2620-2623 (1988).

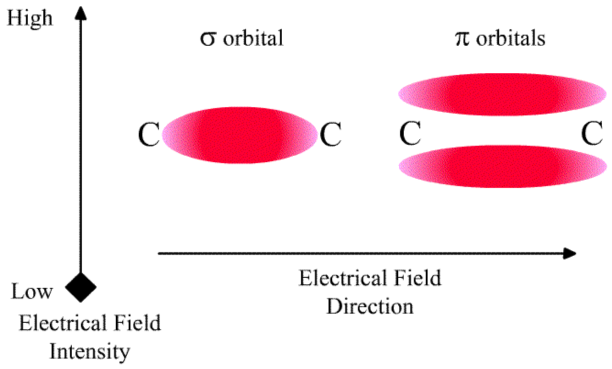
Refractive index and polarizability

Lorentz-Lorenz equation:

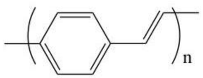
$$\frac{4\pi N\alpha_e}{3} = \frac{n^2 - 1}{n^2 + 2}$$

α_e=Electronic polarizability

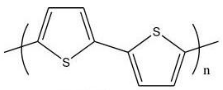




polyacetylene (PA)



polyphenylenevinylene (PPV)

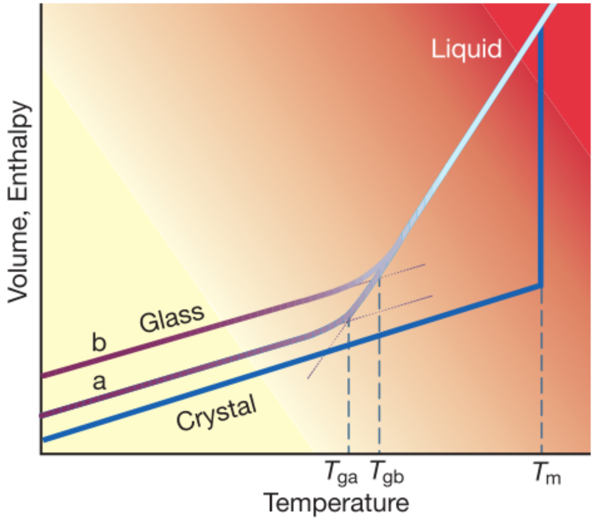


polythiophene (PT)

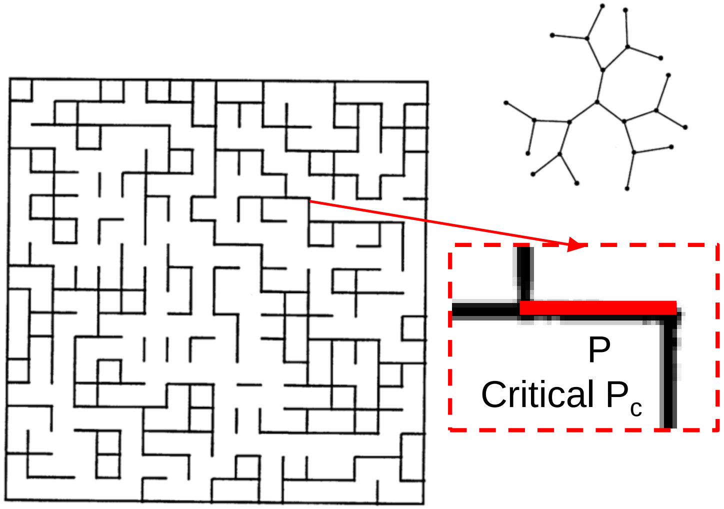
Glass Transition (GT) v. Gelation

To slow material dynamics of amorphous materials
***What we focus on:** Liquid-to-solid transition from the liquid side (LSTLS)*

- Glass Transition / vitrification:
  - Viscous liquid to “glassy” state
  - Abrupt, but continuous change of material properties[3]
  - Cooling rate dependent
- Gelation:
  - Network forming
  - Gel point (chemical gelation): weight average MW diverges to infinity[1,2]
  - Definition based on different theories[4, 5]
    - Percolation model with critical P_c



Debenedetti PG et al. Nature **410**, 259-267 (2001)



Winter, H et al. Advances in Polymer Science **134**, 165-234 (1997)

1. Flory, PJ (1941), J. Am. Chem. Soc. **63**: 3083.
2. Winter, H, Polymer Engineering and Science **27**(22), 1698 (1987).
3. Debenedetti PG et al. Nature **410**, 259-267 (2001).
4. Djabourov M. Polymer International, **25,** 135-143 (1991).
5. Winter, H et al. Advances in Polymer Science **134**, 165-234 (1997).

Background Knowledge

In the paper, Winter distinguished two transitions based on **relaxation time spectrum**.

Measure Relaxation modulus from Boltzmann constitutive equation

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

ϵ_i is defined as the "distance" from the transition

- Colloid suspension (analog to glass transition) $\epsilon = |\phi - \phi_c|/\phi_c$
- Molecular glass former $\epsilon = \left|T - T_g\right|/T_g$
- Gel $\epsilon = p_c - p$

Relaxation modulus from different relaxation modes

$$G(t, \epsilon_i) = G_e(= 0 \; if \; liquid) + \int_0^{\tau_{max}} \frac{d\tau}{\tau} H(\tau, \epsilon_i) e^{-t/\tau}$$

From small-amplitude oscillatory shear (SAOS)

$$G' = G_e + \int_0^{\tau_{max}} \frac{d\tau}{\tau} H(\tau) \frac{(\omega\tau)^2}{1 + (\omega\tau)^2}$$

$$G'' = \int_0^{\tau_{max}} \frac{d\tau}{\tau} H(\tau) \frac{(\omega\tau)}{1 + (\omega\tau)^2}$$

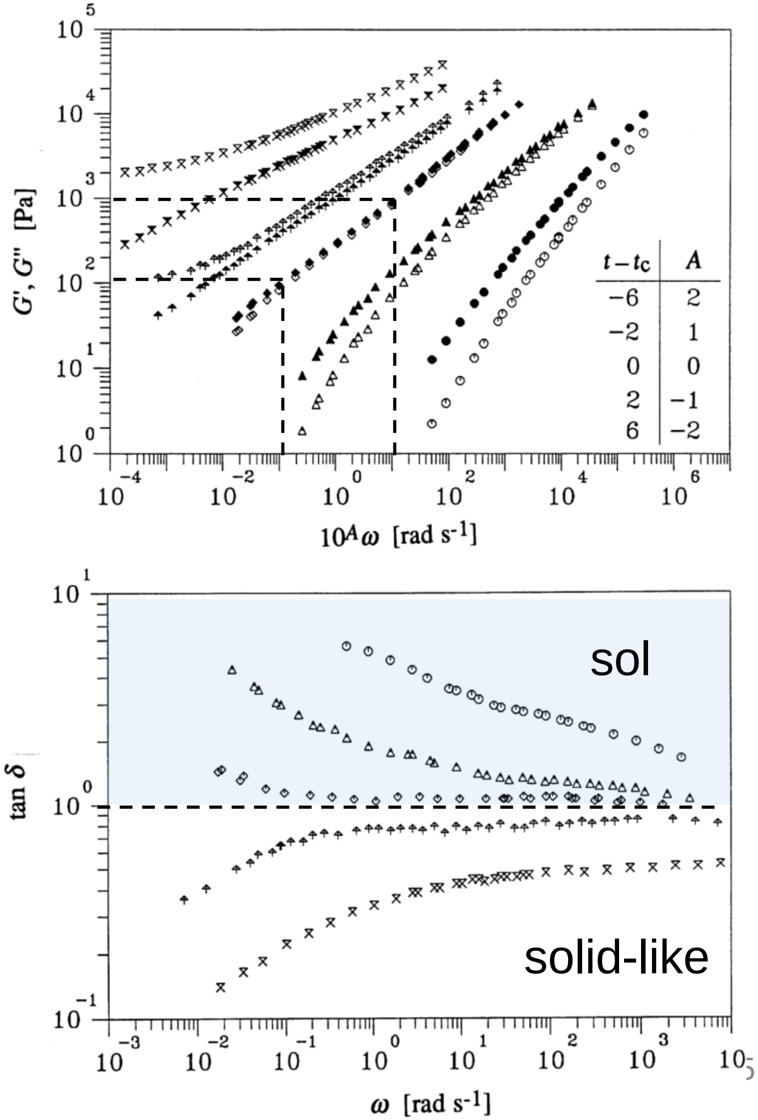
Background Knowledge (cont'd)

- **Gel point** from rheological perspective[1]
  - $G'(t)$ and $G''(t)$ crossover ($\tan \frac{G''}{G'} = 1$)
  - Power law at gel point with exponential of 0.5 for dynamic moduli

or

  - Relaxation modulus $G(t) = St^{-1/2}$

Winter, H et al. Advances in Polymer Science **134**, 165-234 (1997)



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1. Winter HH. Polymer Engineering and Science, **27**(22), 1698 (1987).
2. Winter HH et al. Advances in Polymer Science **134**, 165-234 (1997).

Relaxation Time Spectrum for Gel

- Typical gel spectrum (PDMS)[1]

$$H(\tau,\epsilon_i) = H_o\left(\frac{\tau}{\tau_0}\right)^n \quad (-1<n<0)$$

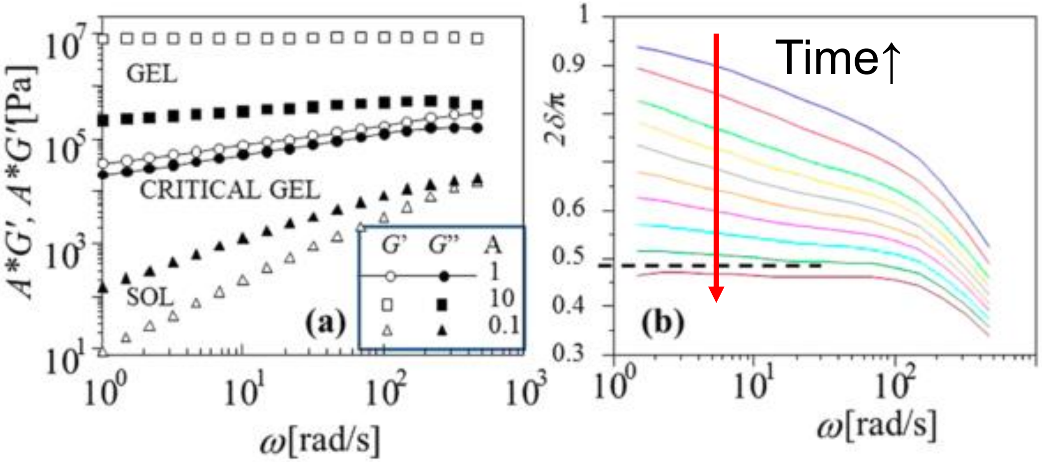
In SAOS from the previous slide:

$$G' = \frac{\pi H_0(\tau_0\omega)^{-n}}{2\sin(-\frac{n\pi}{2})}$$

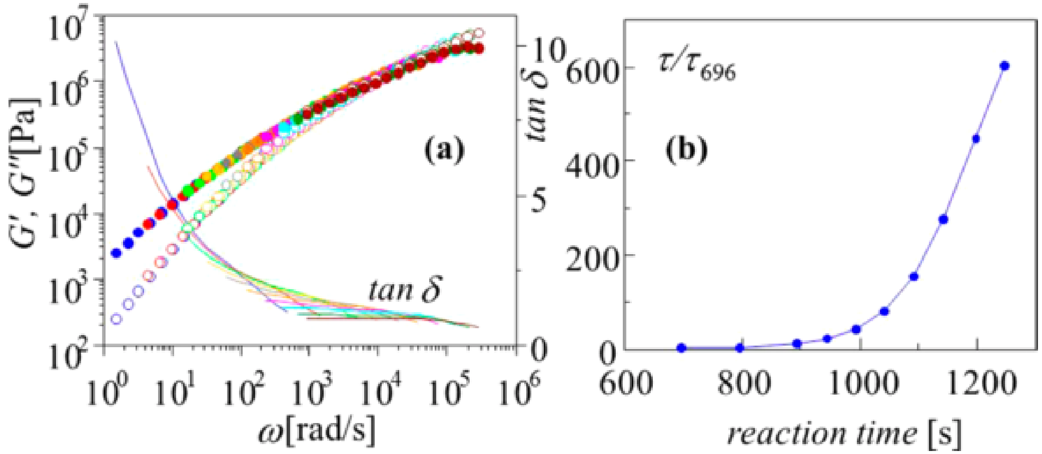
$$G'' = \frac{\pi H_0(\tau_0\omega)^{-n}}{2\cos(-\frac{n\pi}{2})}$$

Then $n = -\frac{2\delta}{\pi}$

Data from DeRosa et al.[2]
Material: Polybutadiene (Gel point 28°C)



- G' and G'' grow (orders of magnitudes) with time;
- $n \approx -0.5$ corresponds to gel point[3];
- Spectrum broadens close to gel point;
- Power law (constant n) only valid close to gel point.



Winter HH. ACS Macromolecules 46, 2425-2432 (2013). Same for followings unless specified.

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1. Chambon F et al. J. Rheol. **31**, 683 (1987).
2. De Rosa ME et al. Rheol. Acta. **33**, 220-237 (1994).
3. Winter, H, Polymer Engineering and Science **27**(22), 1698 (1987).

Relaxation Time Spectrum for GT

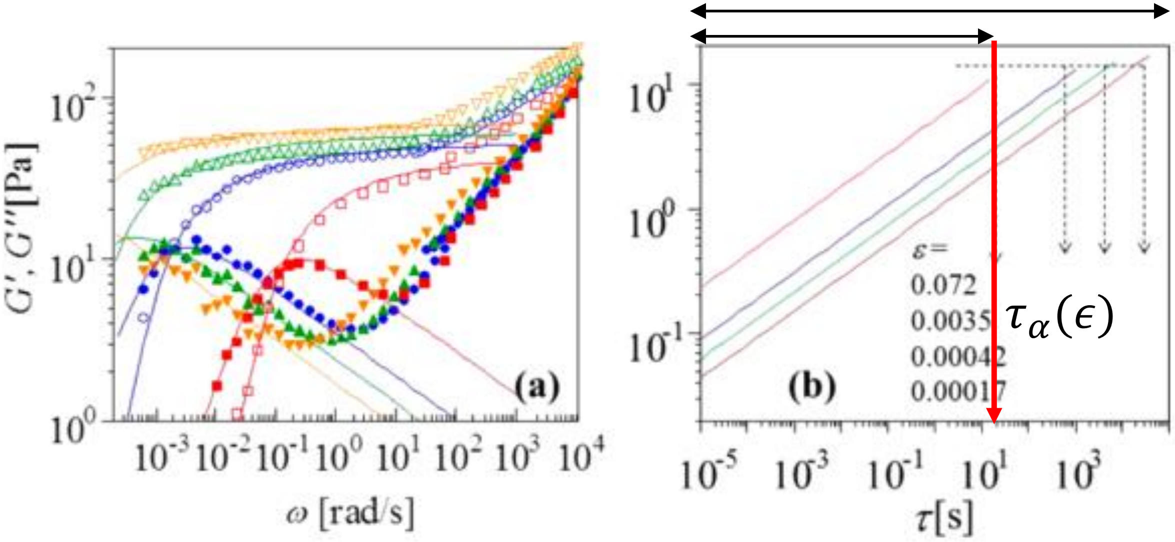
- **Colloid suspension:** Additive relaxation processes (α- and β-relaxation)

BSW spectrum[2]: $H(\tau,\epsilon) = n_\alpha G_c \left\{ \left(\frac{\tau}{\tau_\alpha(\epsilon)}\right)^{n_\alpha} + \left(\frac{\tau}{\tau_0}\right)^{n_\beta} \right\}$ for $\tau < \tau_\alpha(\epsilon)$

- Correspond to mode coupling theory
- As $\epsilon \to 0^+$, both $H(\tau,\epsilon) = n_\alpha G_c \left\{ \left(\frac{\tau}{\tau(\epsilon)}\right)^{n_\alpha} \right\}$

Closer to ϕ_c: broader distribution due to cage-forming (α)

Data from Siebenbürger et al.[1]
Material: Polystyrene particles (dia. 100nm) coated with PNINAM (poly-Nisopropylacrylamide)



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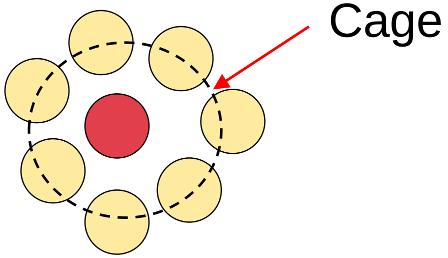
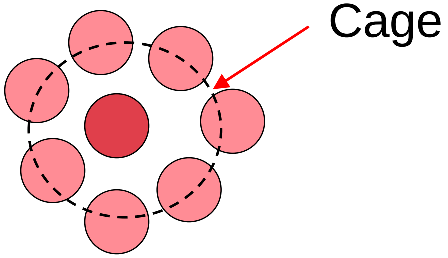
1. Siebenbürger M, Fuchs M, Winter HH, Ballauff M. J. Rheol. **53**, 707-720 (2009).
2. Baumgärtel M, Schausberger A, Winter HH. Rheol. Acta, **29**, 400-408 (1990).
3. Berry GC, Plazek DJ. Rheol. Acta, **36**, 320-329 (1997).

Relaxation Time Spectrum for GT

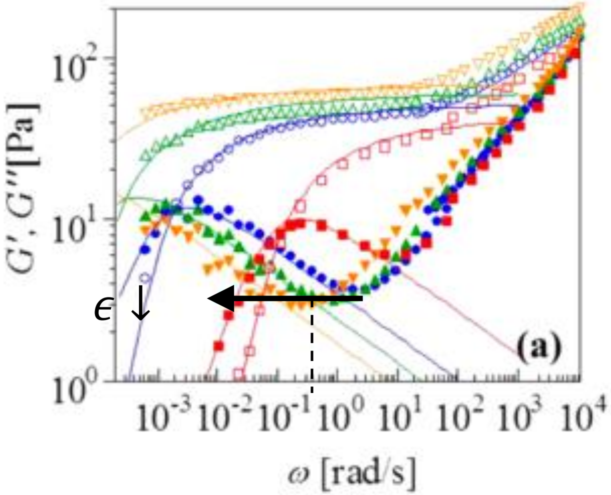
- α- and β-relaxation
  - β-relaxation: motion inside cages
    - Fast involving only single colloid motion, short-time dynamics



  - α-relaxation: motion with cages
    - Slow involving cooperative motion, long-time dynamics
    - Causing spatial heterogeneity[1]



- Crossover of α- and β-relaxation correspond to $\min G''$
  - Shifts to lower frequencies as ϵ decreases



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[1] Narumi T.,Franklin SV., Desmond KW., Tokuyama M., Weeks ER. Soft Matter, 7, 1472 (2011).

Relaxation Time Spectrum for GT

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- Correspond to mode coupling theory

- As $\epsilon \to 0^+$, both $H(\tau,\epsilon) = n_\alpha G_c \left\{ \left(\frac{\tau}{\tau(\epsilon)}\right)^{n_\alpha} \right\}$

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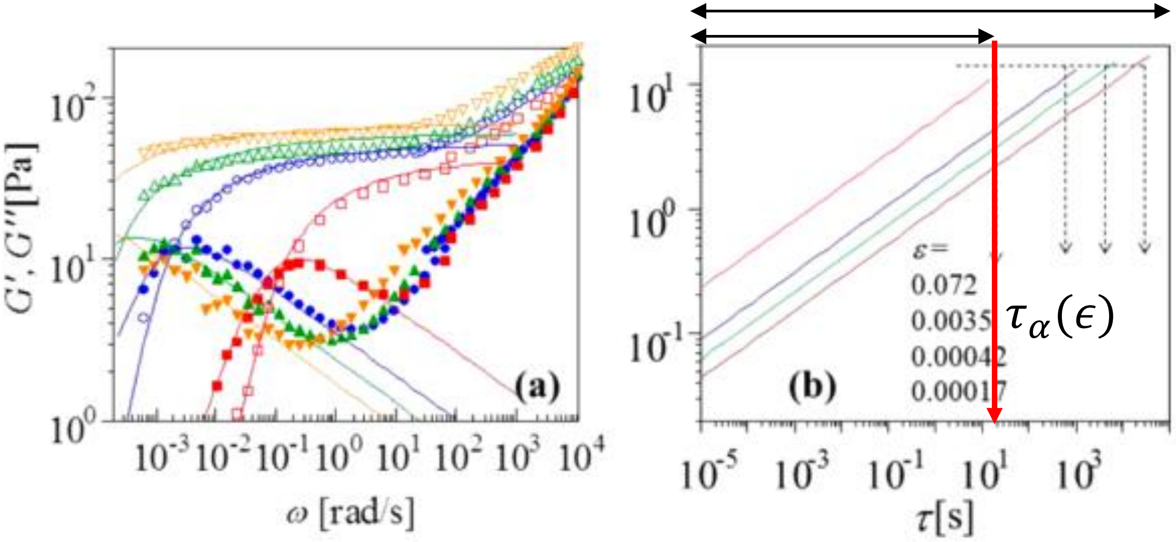

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1. Siebenbürger M, Fuchs M, Winter HH, Ballauff M. J. Rheol. **53**, 707-720 (2009).
2. Baumgärtel M, Schausberger A, Winter HH. Rheol. Acta, **29**, 400-408 (1990).
3. Berry GC, Plazek DJ. Rheol. Acta, **36**, 320-329 (1997).

Relaxation Time Spectrum for GT

- **Glass former**

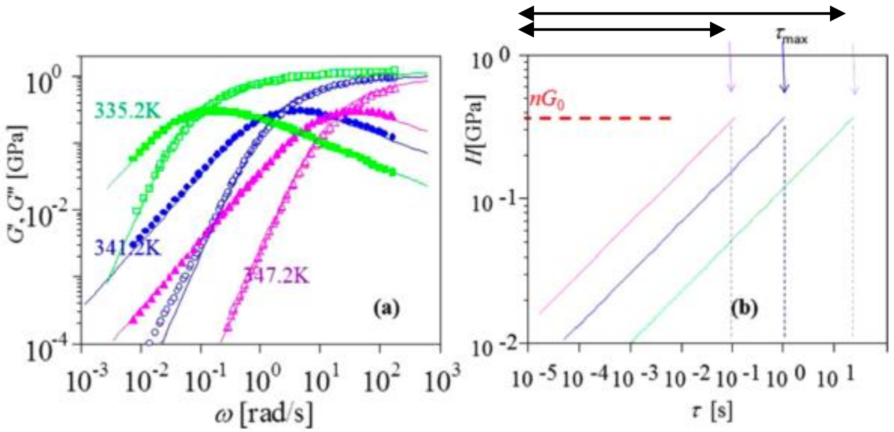
BSW as previously stated

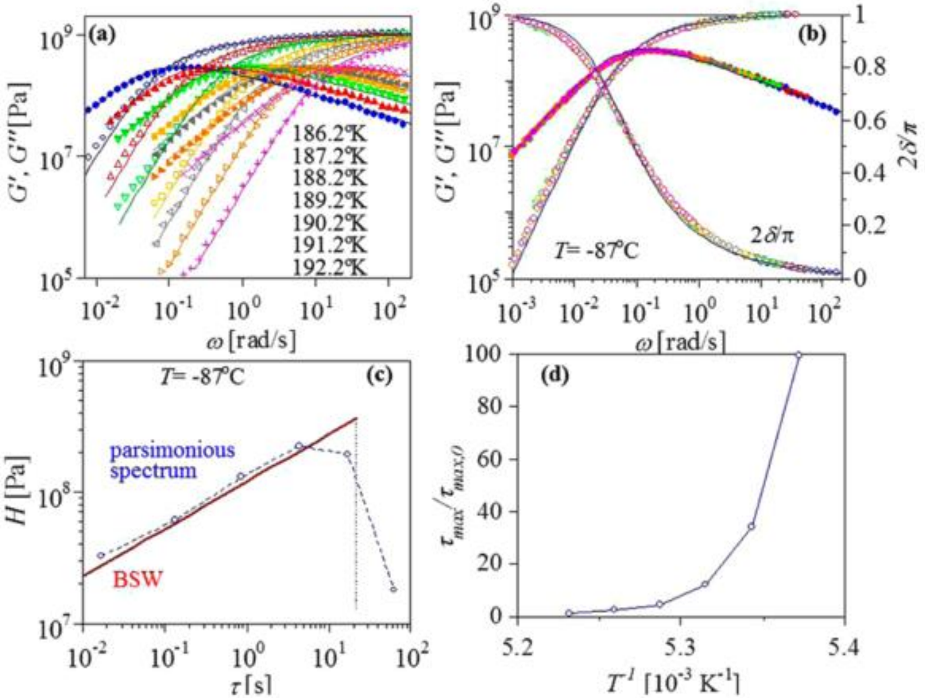
KWW relaxation modulus[3] $G(t) = g e^{-\left(\frac{t}{\tau}\right)^{n}}$

- Compared to **BSW**
  - $0.6 < n < 1$: similar
  - Broader spectrum at lower frequencies

Data from Xu and McKenna[1]
Material: Glass formers
m-toluidine and sucrose benzoate

Closer to T_g: broader distribution due to heterogeneity





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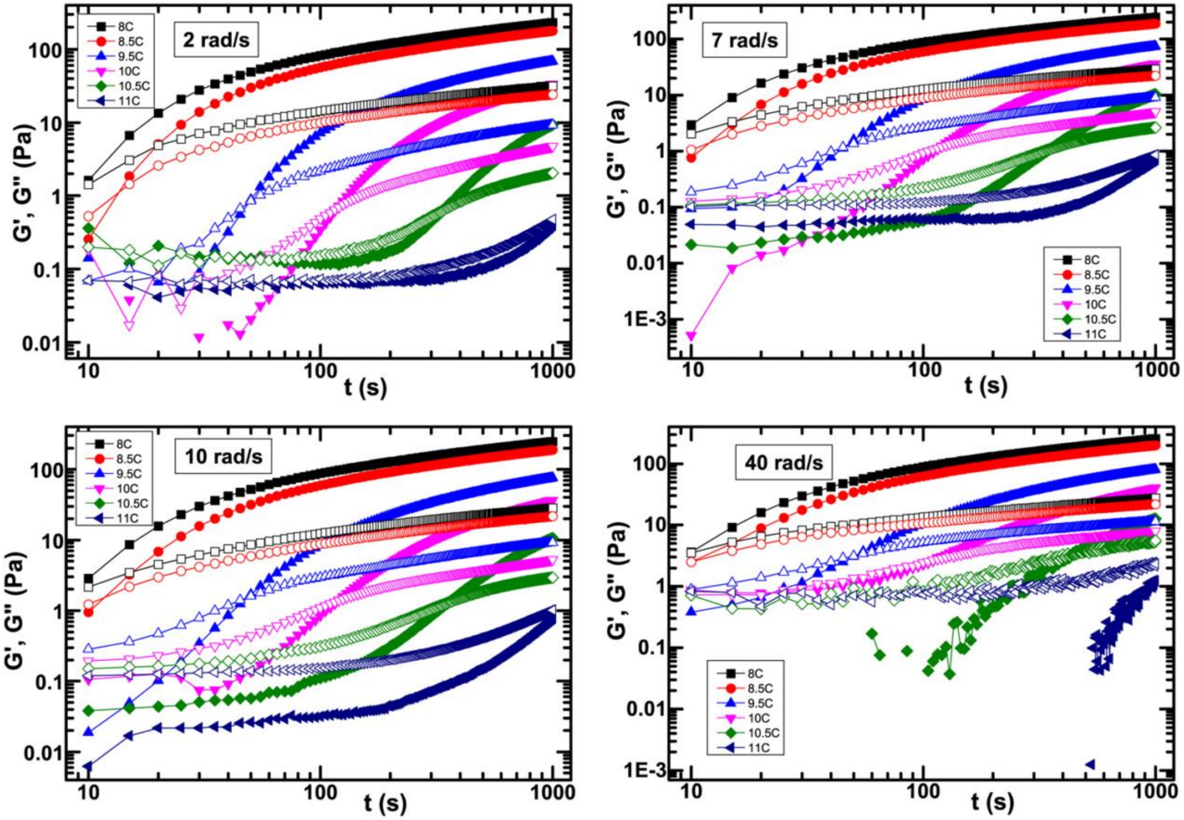
1. Xu B, McKenna GB. J. Chem. Phys. **134**, 124902-7 (2011).

Other Comparison

- Negi et al. performed another testing with colloidal gel and glass

Negi A et al. J. Rheol. **58**(5), 1557-1579 (2014)



Data from Negi et al.[1]
Material: Colloidal gel
silica particles coated with octadecyl chains

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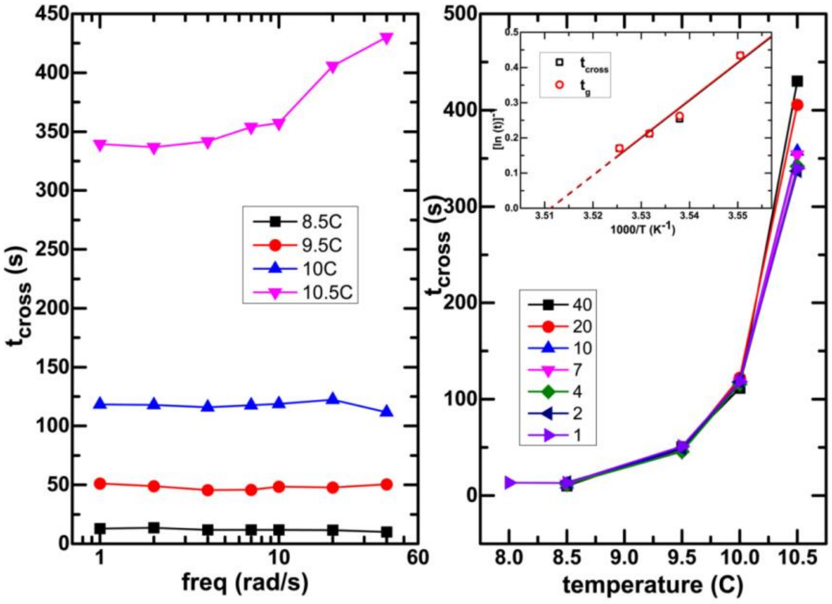
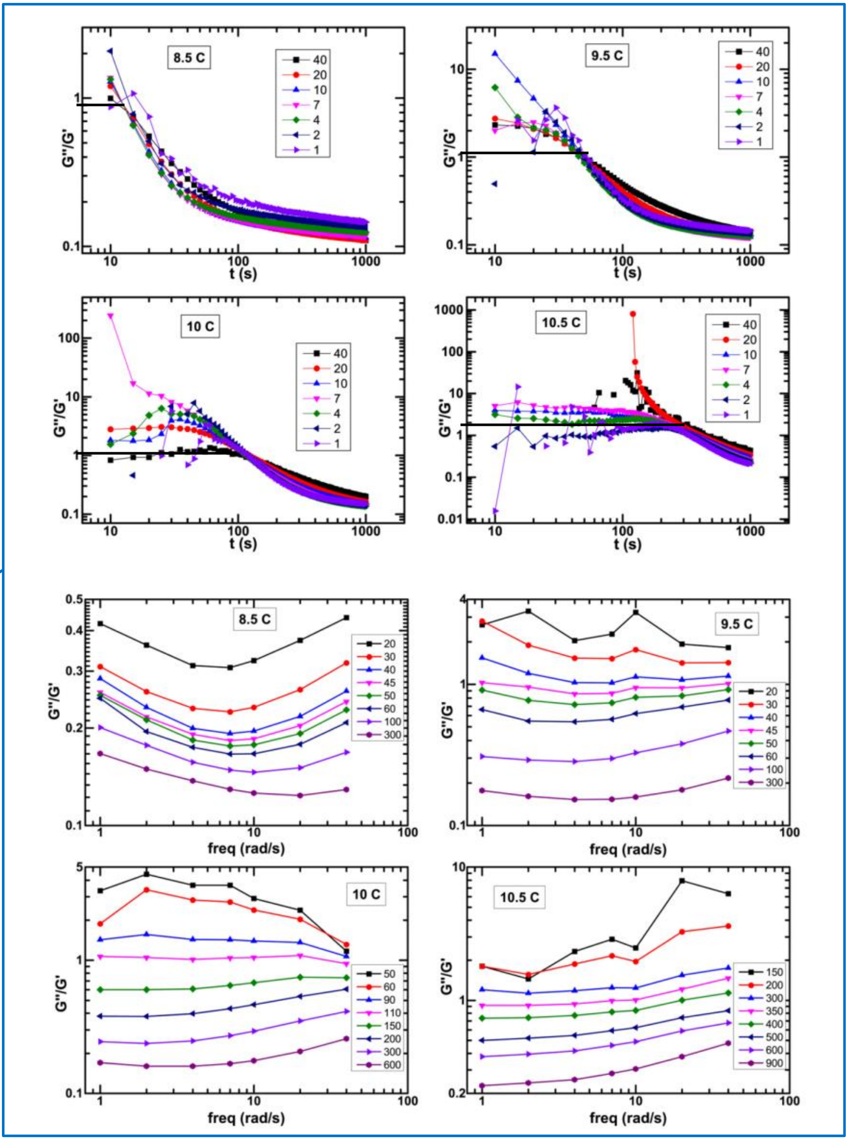
1. Negi A et al. J. Rheol. **58**(5), 1557-1579 (2014).

Other Comparison (cont'd)

- Determine T_g: $1/\ln(t_{cross})$ v. $1/T$
- Determine gel time: crossover time
- Infinite max relaxation time[2]

Negi A et al. J. Rheol. **58**(5), 1557-1579 (2014)





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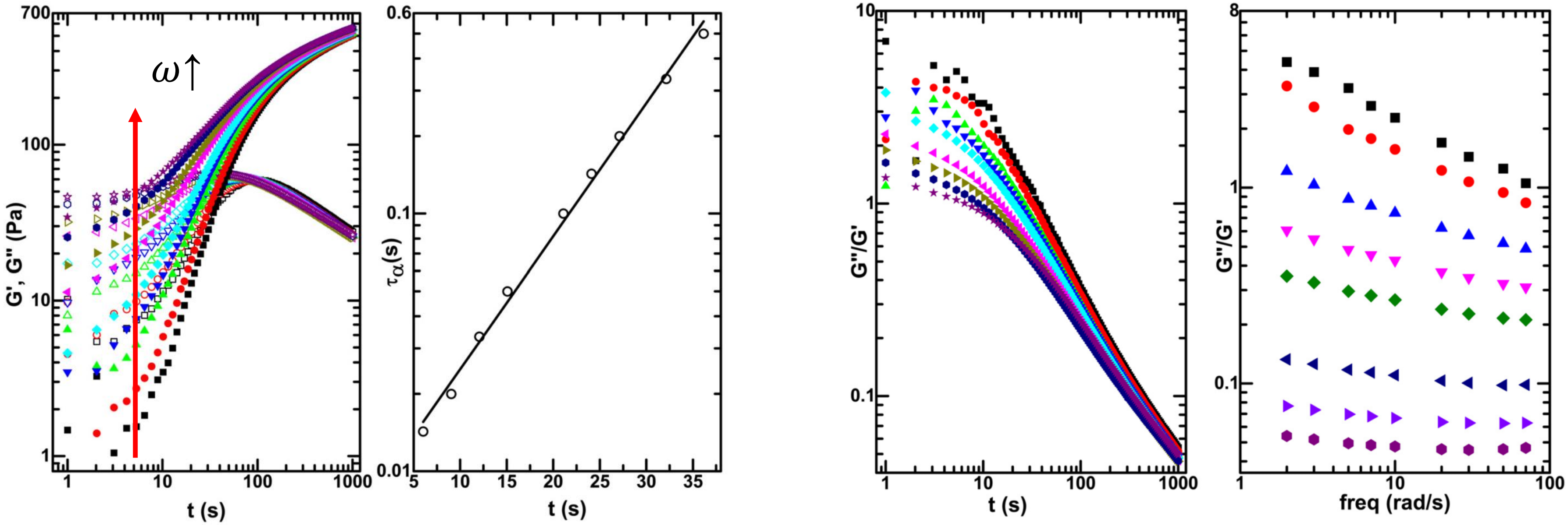
1. Negi A et al. J. Rheol. **58**(5), 1557-1579 (2014).
2. Rueb, CJ, Zukoski CF. J. Rheol. **41**, 197–218 (1997).

Other Comparison (cont'd)

- Linear correlation
  - Crossover time t
  - Relaxation time: $\tau_\alpha = \frac{1}{\omega}$

Data from Negi et al.[1]
Material: Colloidal glass
Laponite clay particles in low ionic strength aqueous suspension

Negi A et al. J. Rheol. **58**(5), 1557-1579 (2014)



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1. Negi A et al. J. Rheol. **58**(5), 1557-1579 (2014).

Relaxation Mode Interpretation

- Distinction of spectrum distribution
  - Gel

    MW distribution follows power law with negative exponent[1]
    - Stress dominated by small molecule rearrangement
    - Small relaxation mode dominates

    Branching[2]

Fast modes

  - GT (colloid suspension)

    Solid fraction is related to characteristic relaxation time and characteristic or correlation length
    - Cage-forming obstacles
    - Large relaxation mode dominates
  - GT (molecular glass formers)

    Less mobility of single molecule; relaxation process requires large-scale cooperative motion of molecule groups

Slow modes

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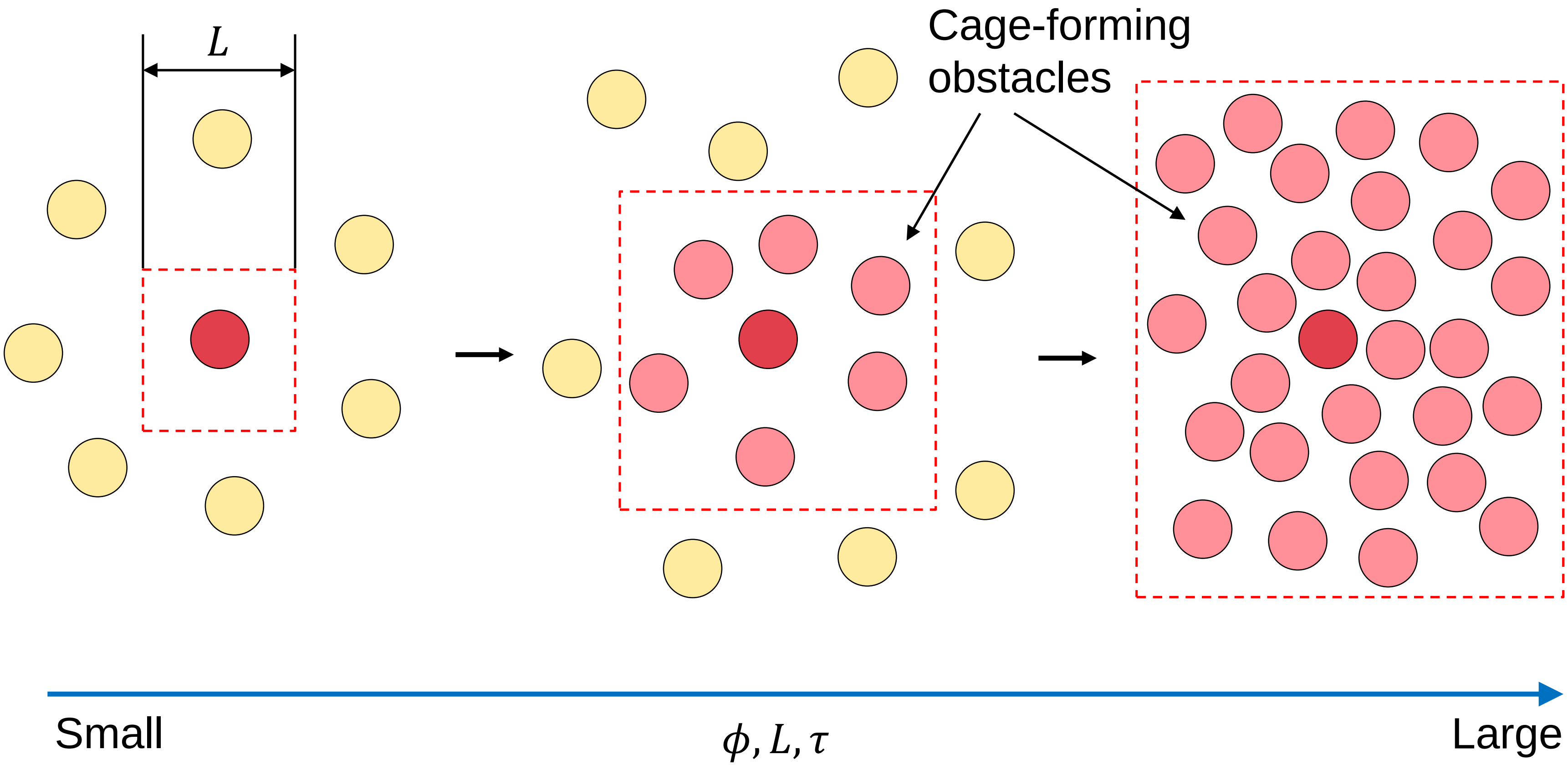
1. Martin JE, Adolf D, Wilcoxon JP. Phys. Rev. Lett. **61,** 2620-2623 (1988).
2. Cates ME. Phys. Rev. Lett. **53**, 926-929 (1984).

Relaxation Mode Interpretation



Cage-forming obstacles

Small

ϕ, L, τ

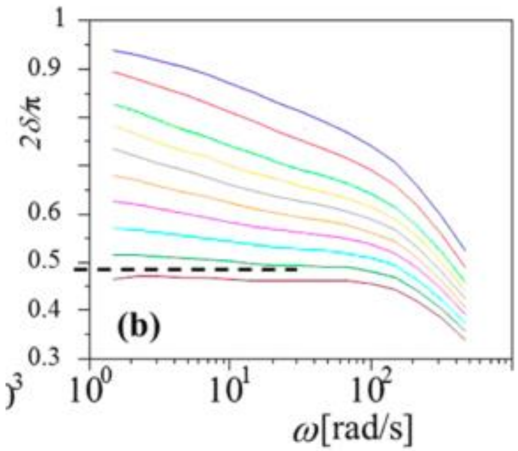
Large

Other discussions by Winter

- Zero shear rate viscosity

$$\frac{\eta_0}{\tau_{max}} = \frac{H_0}{n+1}$$

- ϵ range with power law spectrum
  - Wider range for glass transition near LSTLS
  - Narrower range for gelation dynamics, with exceptions[1,2]
- Other materials showing power law spectrum[3]



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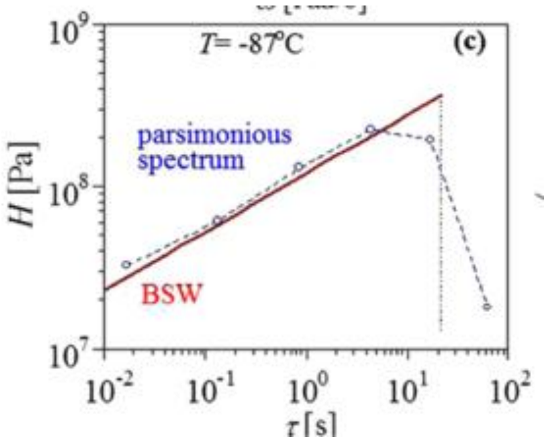
1. Adolf D, Martin JE. Macromol., **23**, 3700-3704 (1990).
2. Trappe V, Weitz DA. Phys. Rev. Lett. **85,** 449-452 (2000).
3. Abdel-Goad M, Pyckhout-Hintzen W, Kahle S, Allgaier J, Richter D, Fetters LJ. Macromolecules, **37**, 8135-8144 (2004).

Conclusions

- Conclusions
  - Different relaxation time spectrum for glass transition (positive power law) and gelation (negative power law)
  - Theoretical backing for colloidal glasses, but empirical for gel and molecule glasses
- Problems remained to be solved
  - Sharp cutoff of spectrum for glass transition
  - Steadiness of relaxation exponential passing through gel point
  - Theories behind glass/gel inverse property
  - Materials representative enough?



Thank you!

Questions?