"FRONTIERS OF METROLOGY"
Optimal Fourier Transform Rheometry for Probing Rheology of Gels & Time-Evolving Soft Matter Systems

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HATSOPOULOS MICROFLUIDS LABORATORY

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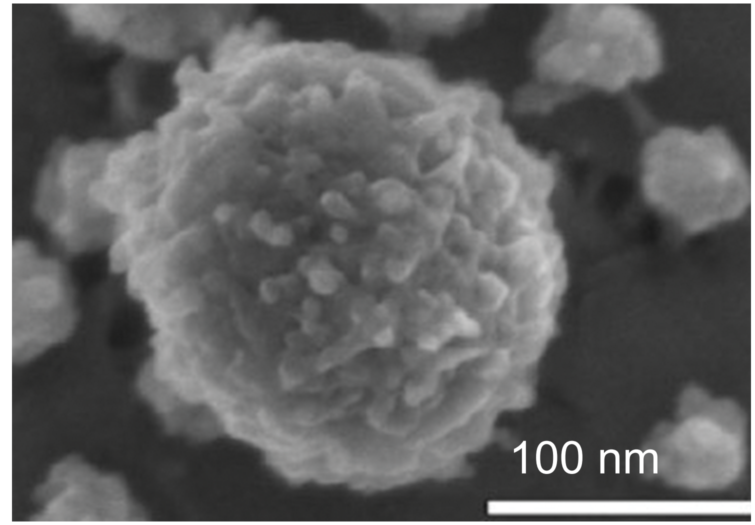
Outline

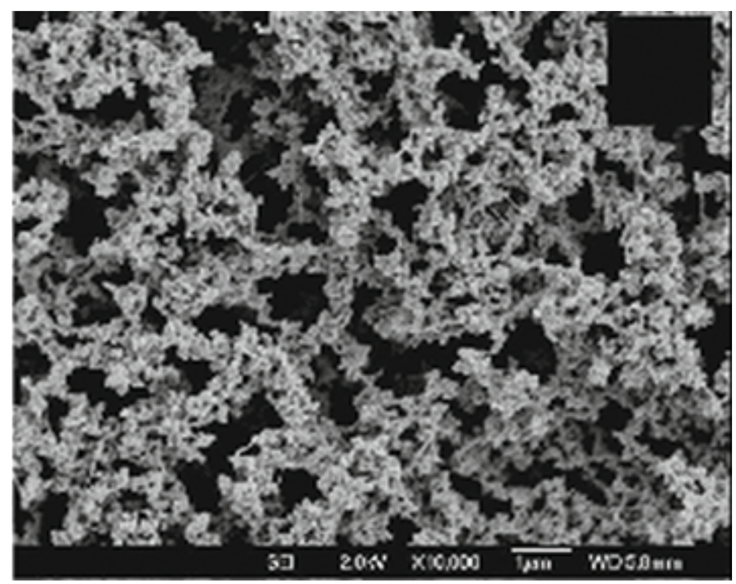
- And now for something completely different…*metrology*
- Focus on bulk rheology for time-evolving or *mutating* soft matter systems (thixotropy, gelation, drying…)
- Experimental protocols that can be used with existing rheometers (controlled strain & controlled stress) for rapidly extracting linear viscoelastic spectrum of a mutating material
  - ❑ Calibration and optimization using a simple viscoelastic liquid
  - ❑ Application to a time-evolving gelling protein gel
- Application of same technique to MD simulations of a particulate gel

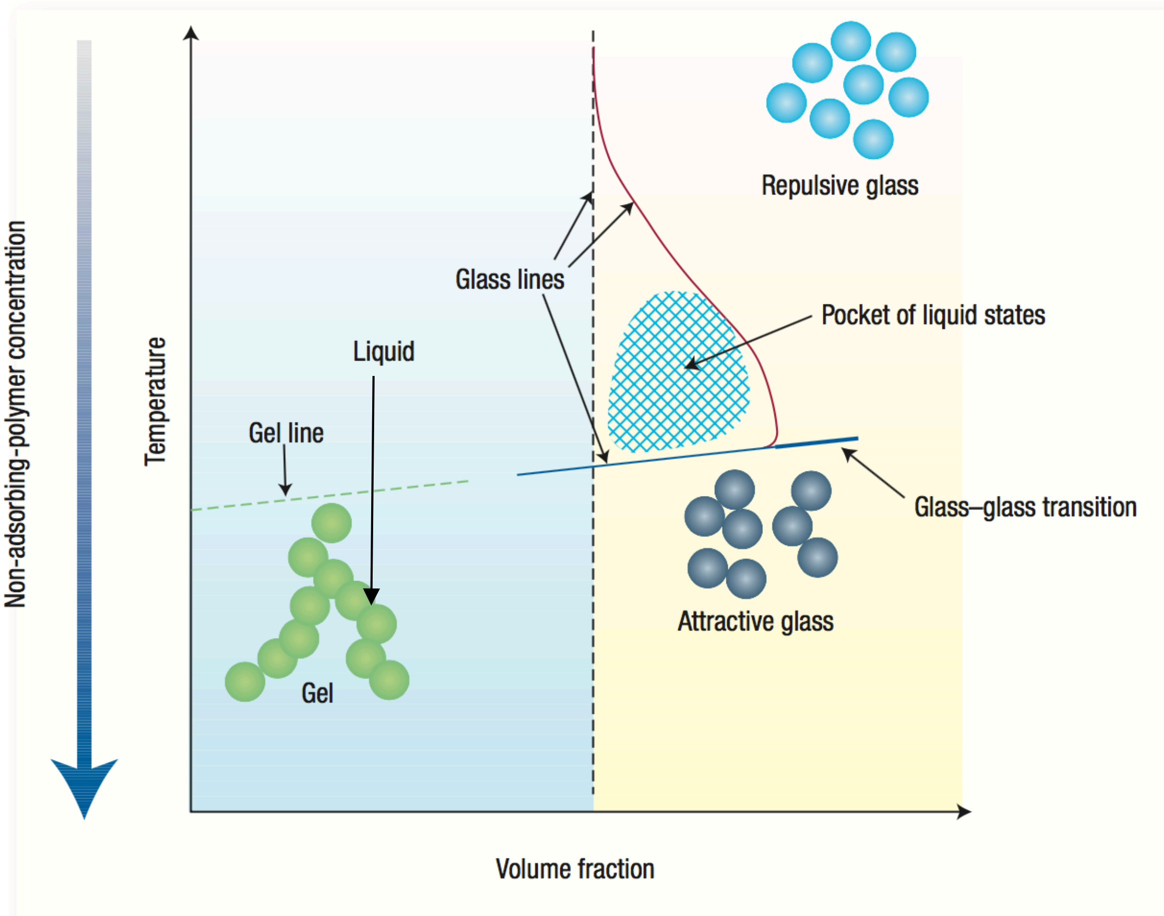
A connection to yesterday's session:

Martin et al., Food Hydrocolloids ***20(6)*** *(2006)*



pH, enzymes, …



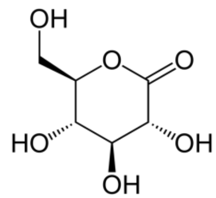


Sciortino, Nat. Mat. ***1*** *(2002)*

Acid-Induced Casein Protein Gel

Sample preparation (@ T=35°C)

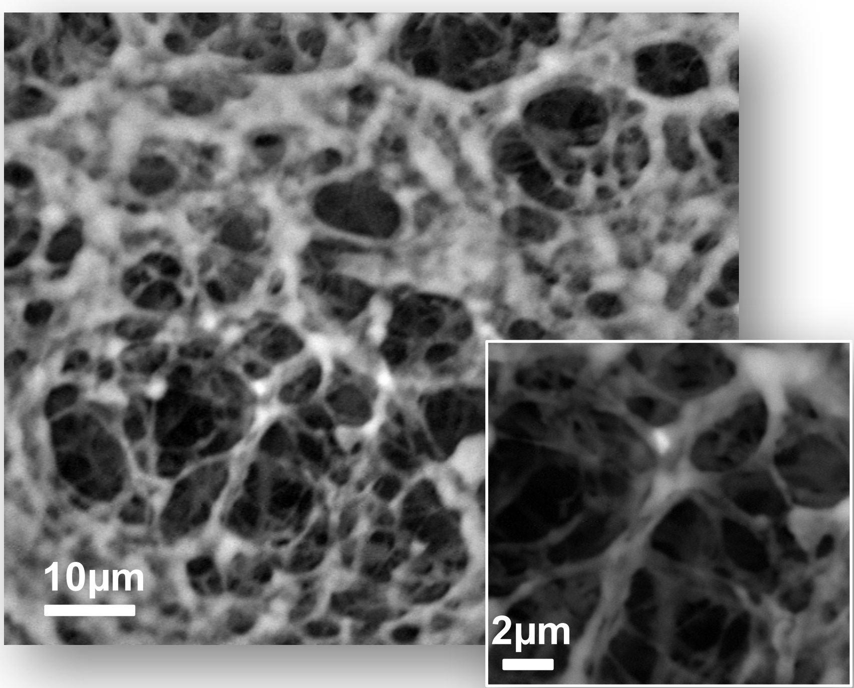
Sodium Caseinate [2 to 8 %] + Glucono-δ-lactone (**GDL**) [0.5 to 8 %]



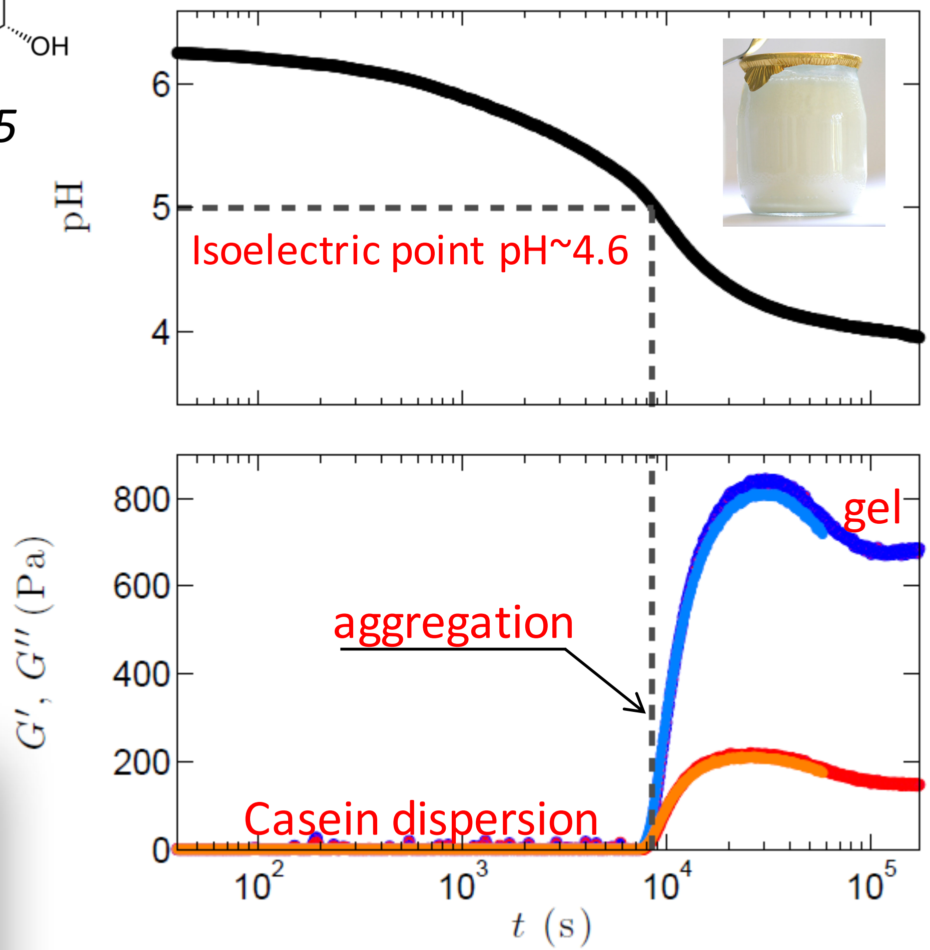
E575

Roefs & Van Vliet, Coll. Surf. 40, 161 (1990)
Roefs et al., Neth. Milk Dairy J. 44, 159 (1990)
Lucey & Singh, Food. Res. Int. 7, 529 (1998)
Arshad et al., J. Dairy Sci. 76, 3310 (1993)
Moschakis et al., J. Coll. Int. Sci. 345, 278 (2010)...

Environmental SEM images



Gelation kinetics (@ T=20°C)
Slow hydrolysis of GDL into gluconic acid

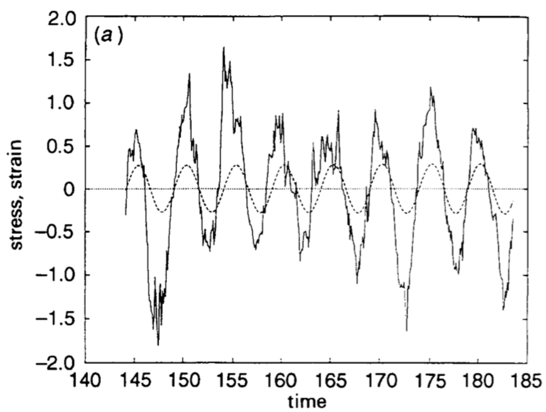


Gels show Power-Law Creep and Failure
Leocmach et al., PRL (2014)
*Keshavarz et al., ACS Macro Let **6** (2017)*

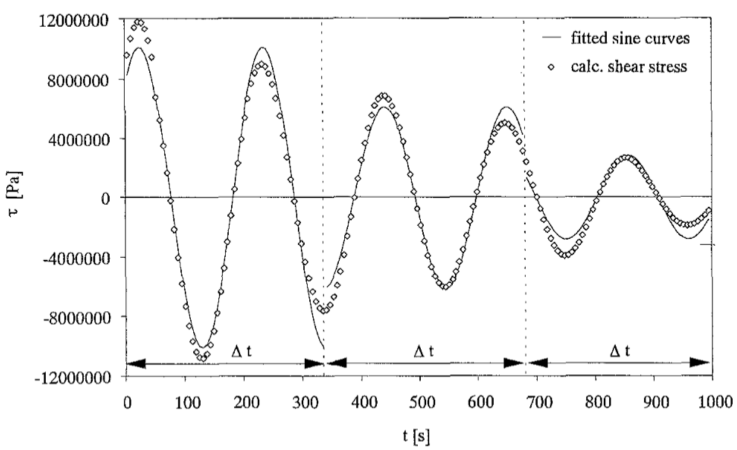
Time-Resolved Rheometry

- There have been numerous efforts to improve the speed of acquisition of linear viscoelastic spectra (esp. for gelling or *mutating* systems)

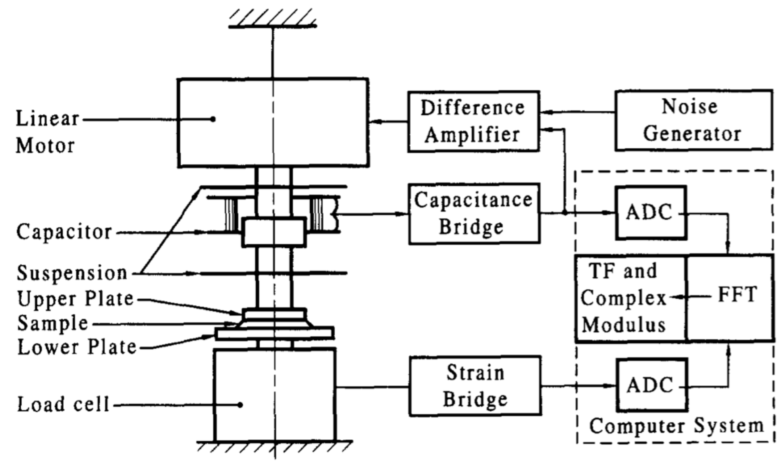
- Multi-Wave Analysis
  Heyes, Melrose *et al. Farad. Trans*. 1994



- Rapid Frequency Sweeps
  (Short Time Fourier Transform)
  Mours & Winter, *Rheol. Acta*, **33** 1994

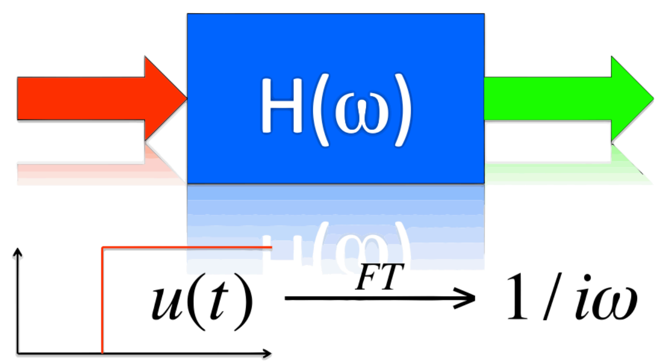


- Pseudo-White Noise (Micro-Fourier Rheometer)
  Field, Swain & Phan-Thien, *JNNFM* 1996



- Step Strain; iRheo

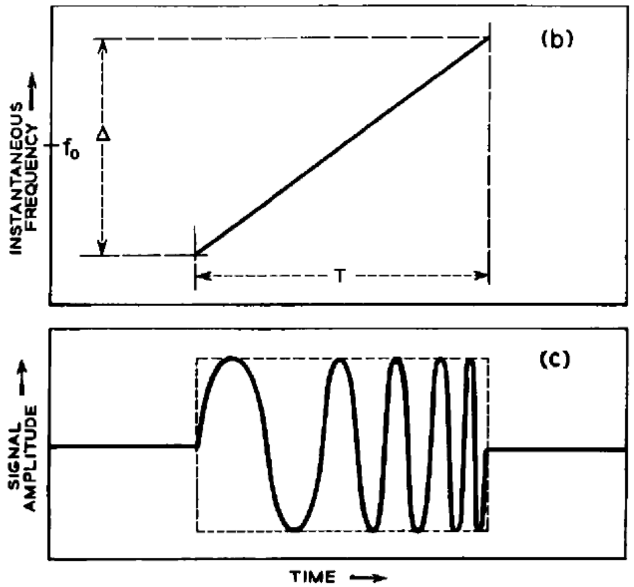
  Tassieri et al., *J.Rheol*. **60**(4), 2016



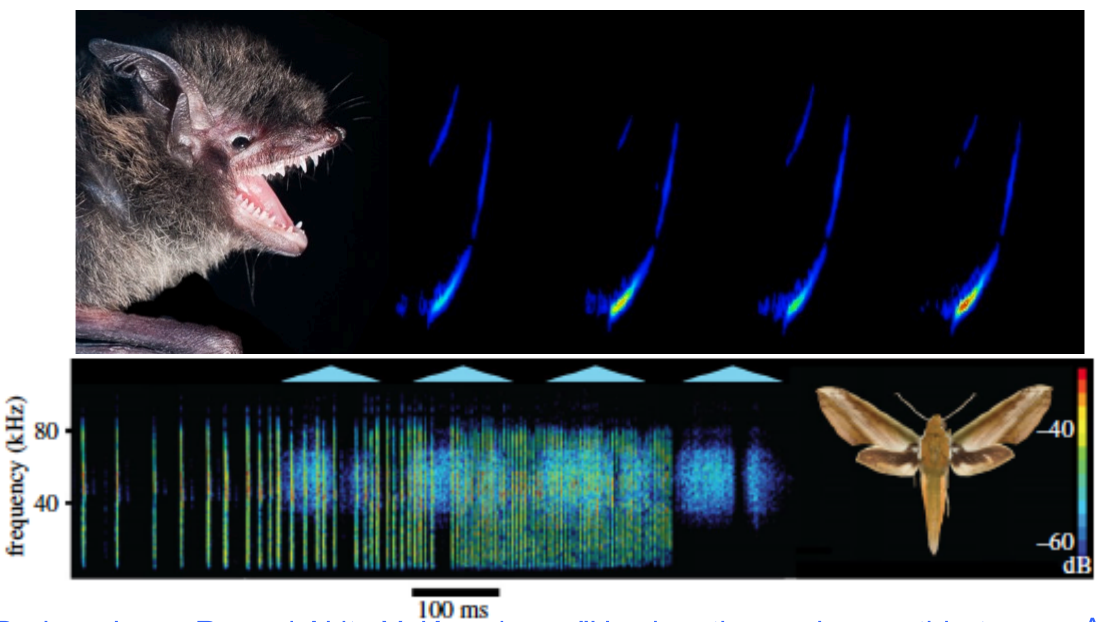
$$u(t) \xrightarrow{FT} 1/i\omega$$

The “Chirp”

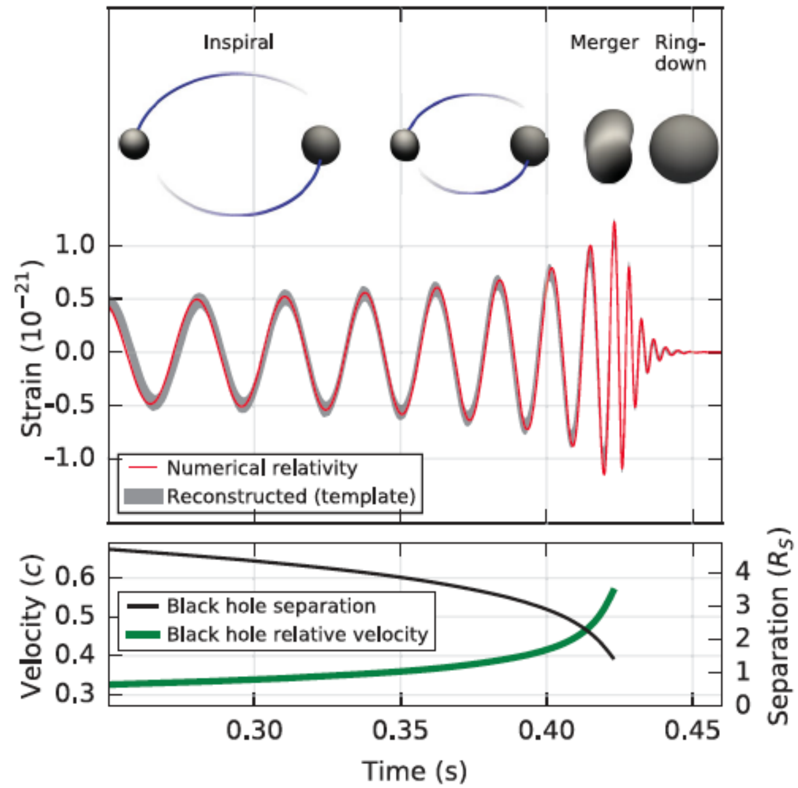
- **Radars**
- **Bats echolocation**
- **Gravitational Waves**

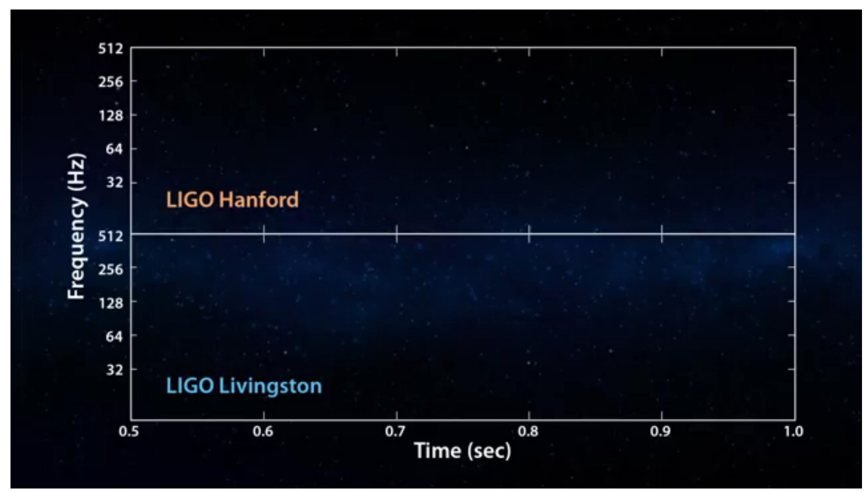


Klauder, John R., et al. "The theory and design of chirp radars." *Bell Labs Technical Journal* **39.4** (1960): 745-808.



Barber, Jesse R., and Akito Y. Kawahara. "Hawkmoths produce anti-bat ultrasound." *Biology Letters* **9**.4 (2013): 20130161.





Abbott, Benjamin P., et al. "Observation of gravitational waves from a binary black hole merger." *Phys. Review Lett.* **116.6** (2016): 061102.

The "Chirp" (or 'swept sine wave')

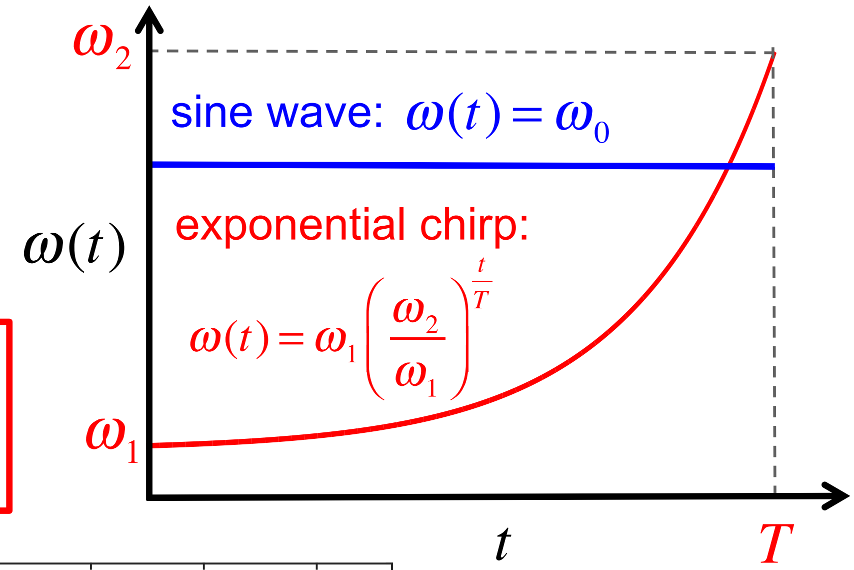
Frequency Modulated (FM) signal:

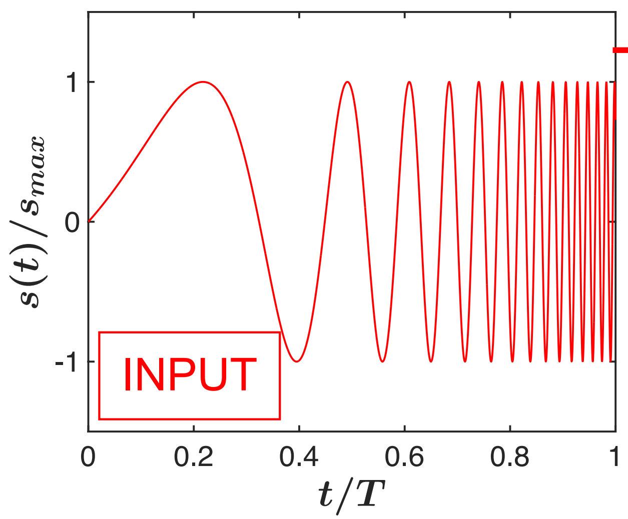
$$s(t) = s_0 \sin[\phi(t)], \qquad \frac{\mathrm{d}}{\mathrm{d}t}\phi(t) = \omega(t)$$

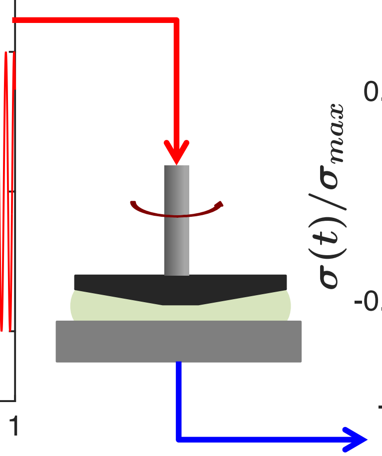
Instantaneous frequency

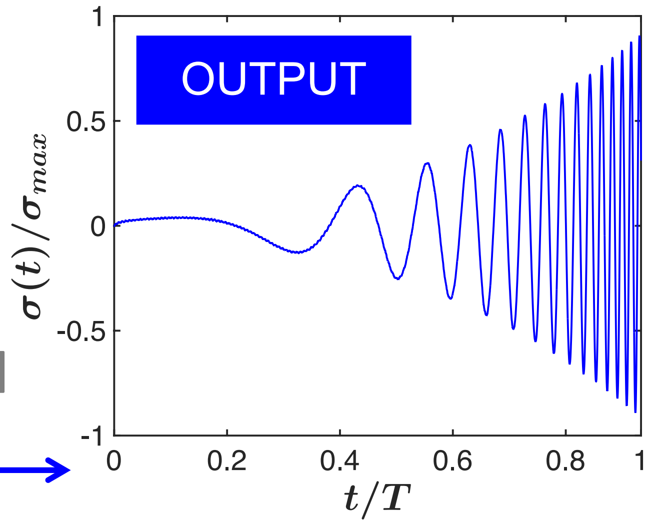
For an **exponential/logarithmic** chirp:

$$s(t) = s_0 \sin\left\{ \frac{\omega_1 T}{\log(\omega_2/\omega_1)} \left[\exp\left(\log(\omega_2/\omega_1)\frac{t}{T} \right) - 1 \right] \right\}$$









Post-Process:
DFT input & output

$$G^*(\omega) = \frac{\tilde{\sigma}(\omega)}{\tilde{\gamma}(\omega)}$$

Can we choose any combination of frequency range and length?

Time-Bandwidth Product

$$TB = \frac{(\omega_2 - \omega_1)}{2\pi} T$$

Larger TB (>100):

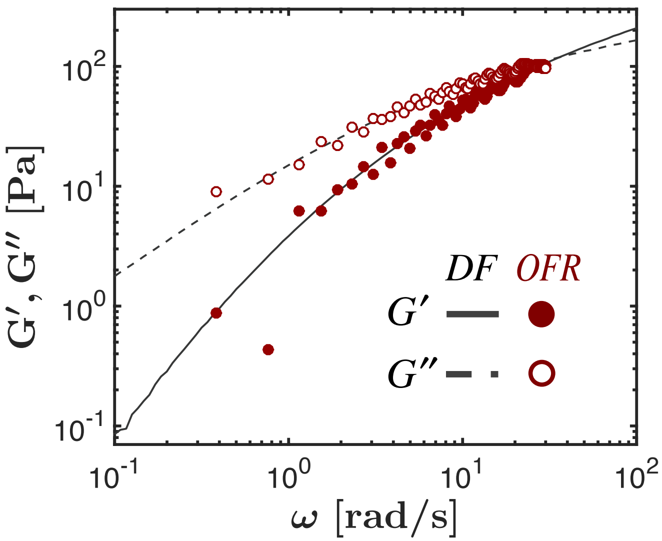
- *better signal spectrum*
- *worse temporal resolution for time-varying systems*

Ghiringhelli et al., *Rheol Acta* (2012) **51**:413–420
Curtis et al., *JNNFM* (2015), **222**:253-259

Noise Issues with Prior "Optimal Fourier Rheometry"

8.5% wt PIB solution in Hexadecane

(semidilute viscoelastic polymer solution)



$\gamma_0 = 6\%$

$f_s = 500\text{Hz}$

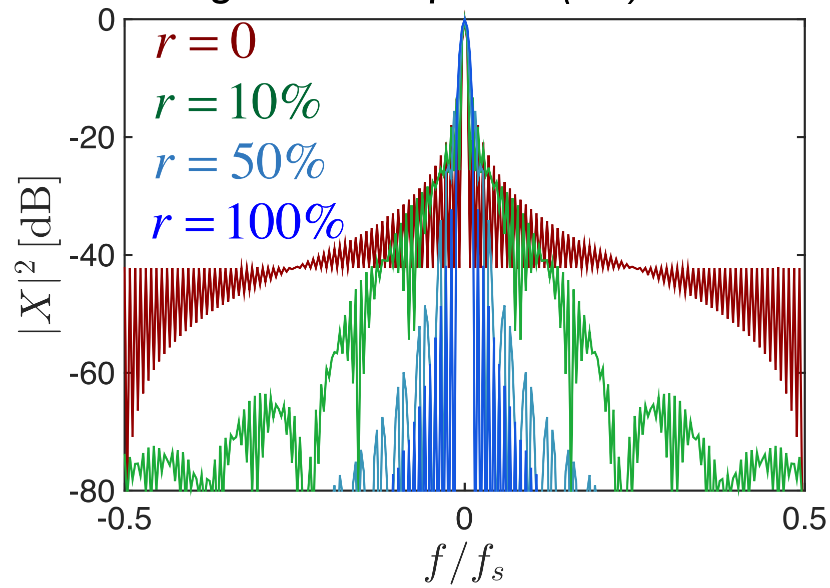
$\omega_1 = 0.3\text{rad/s}$

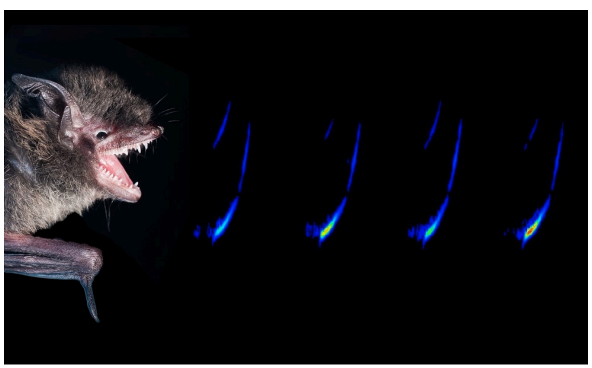
$\omega_2 = 30\text{rad/s}$

$\text{T} = 14\text{s} \; (+1\text{s})$

$TB \simeq 66$

Rectangular → Tapered (r%) → Full AM





Bats use **signals** which are both **frequency** and **amplitude modulated**:

FM & AM

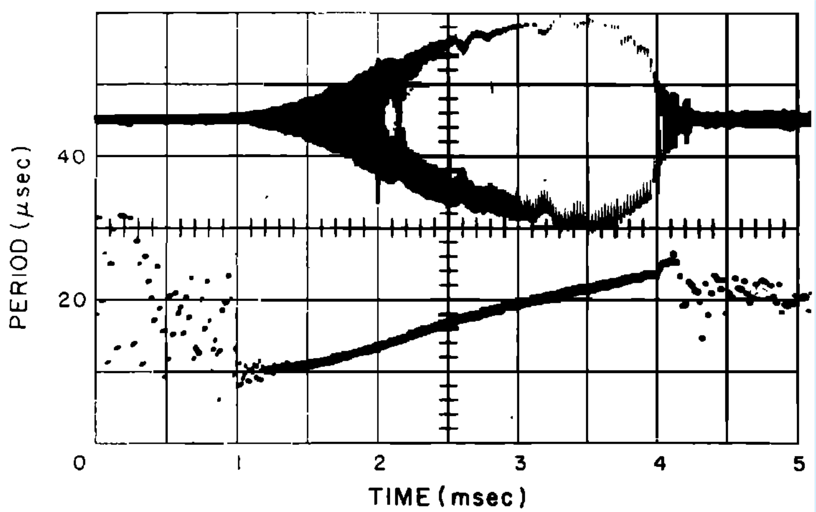
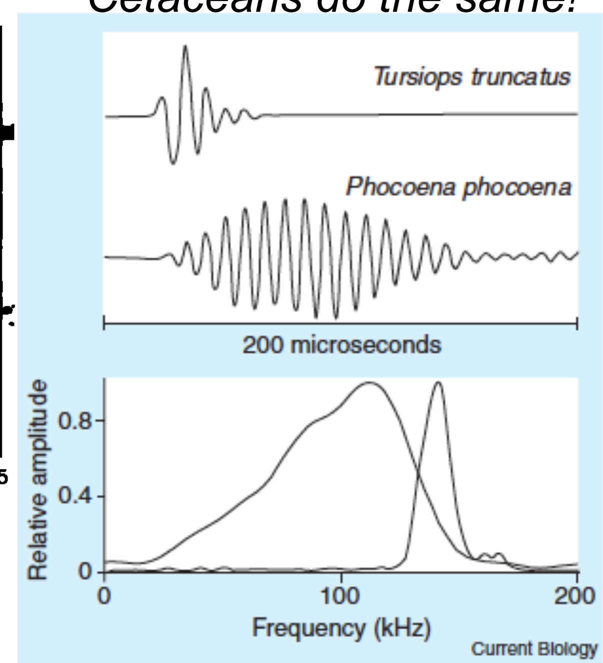


FIG. 1. Actual cruising pulse of *Myotis lucifugus*, showing amplitude and instantaneous frequency versus time. (From D. A. Cahlander,[7] courtesy of MIT Lincoln Lab.)

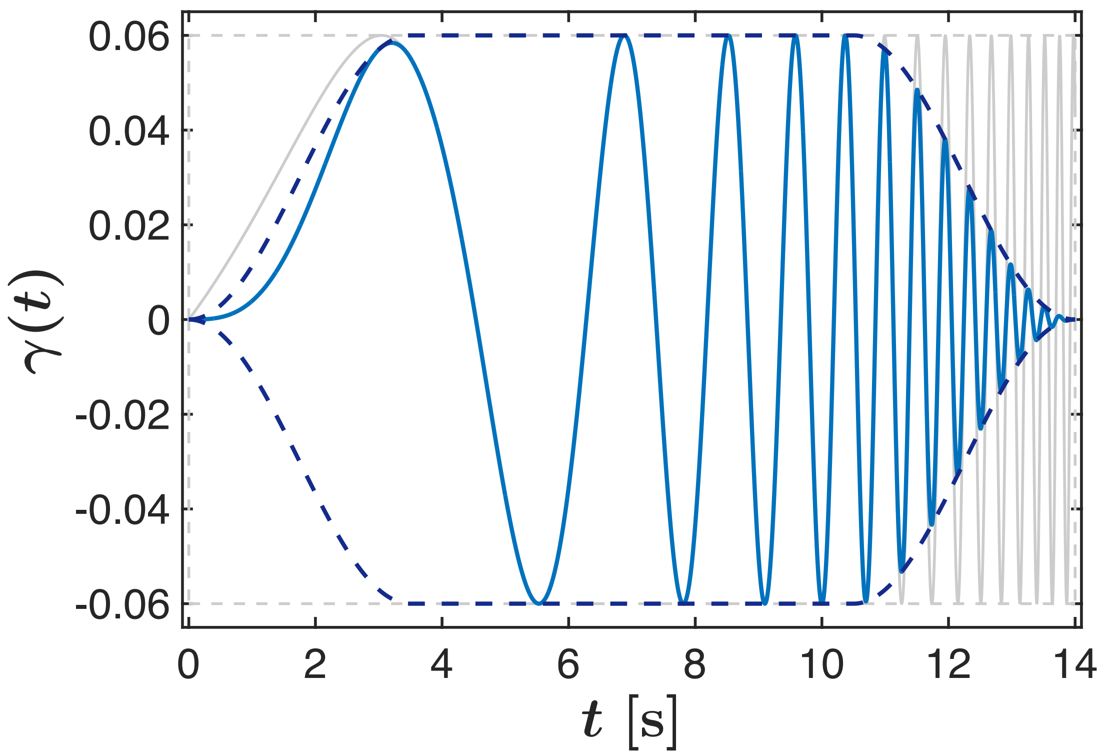
Altes and Titlebaum, *J Acoust. Soc. Am.*, **48**(4), 1014 (1970)

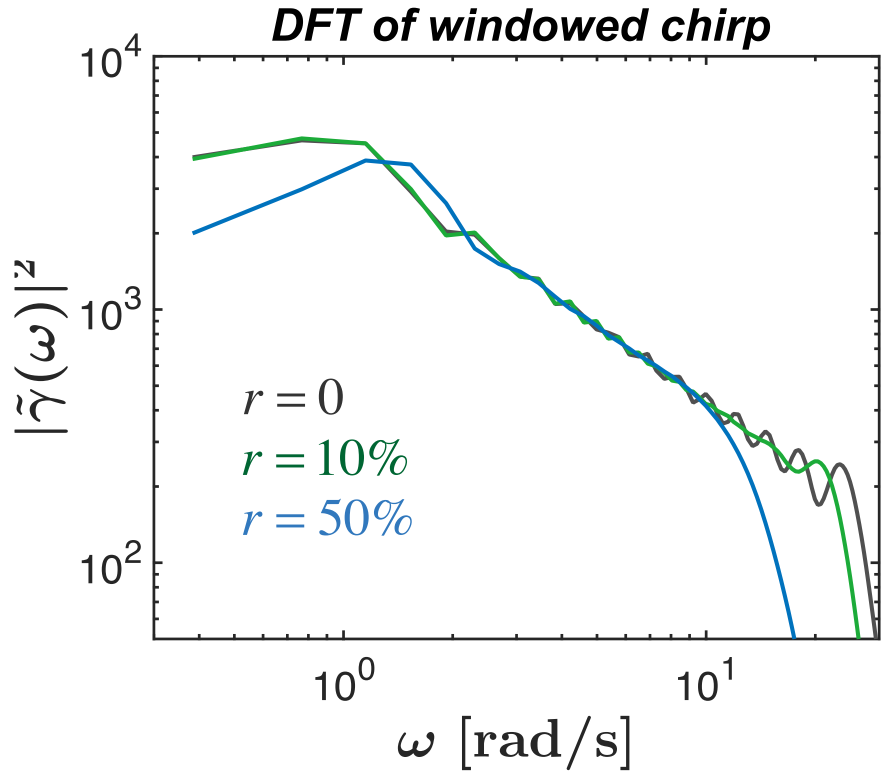
Cetaceans do the same!



Jones, *Curr Biology*, **15**(13), (2005)

Windowing





Tukey Window:

$$w(t;r) = \begin{cases} 0.5\left\{1+\cos\left[\frac{2\pi}{r}\left(\frac{t}{T}-\frac{r}{2}\right)\right]\right\}, & \text{if } \frac{t}{T} \le \frac{r}{2} \\ 1, & \text{if } \frac{r}{2} < \frac{t}{T} < 1-\frac{r}{2} \\ 0.5\left\{1+\cos\left[\frac{2\pi}{r}\left(\frac{t}{T}-1+\frac{r}{2}\right)\right]\right\}, & \text{if } \frac{t}{T} \ge 1-\frac{r}{2} \end{cases}$$

Limits of Tukey window:

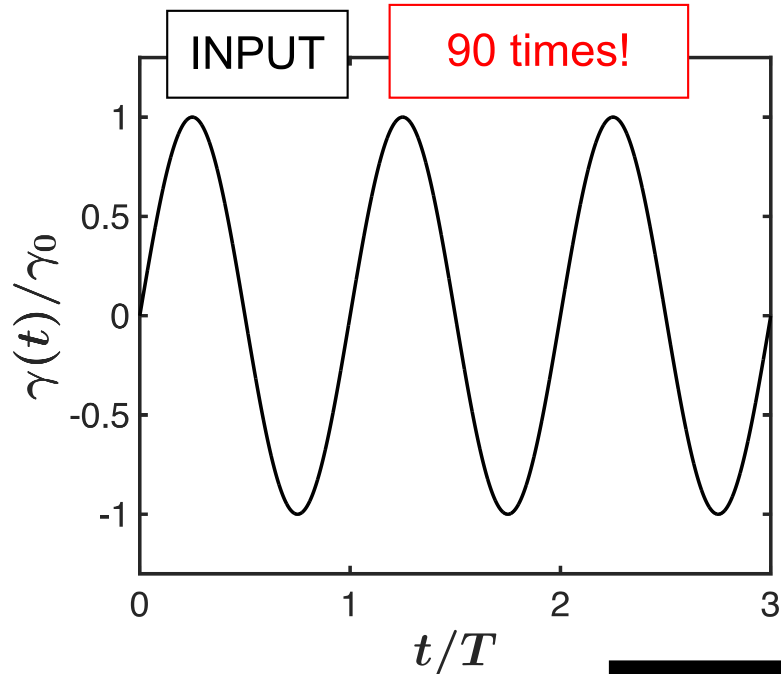
i. $r = 0$, *rectangular*

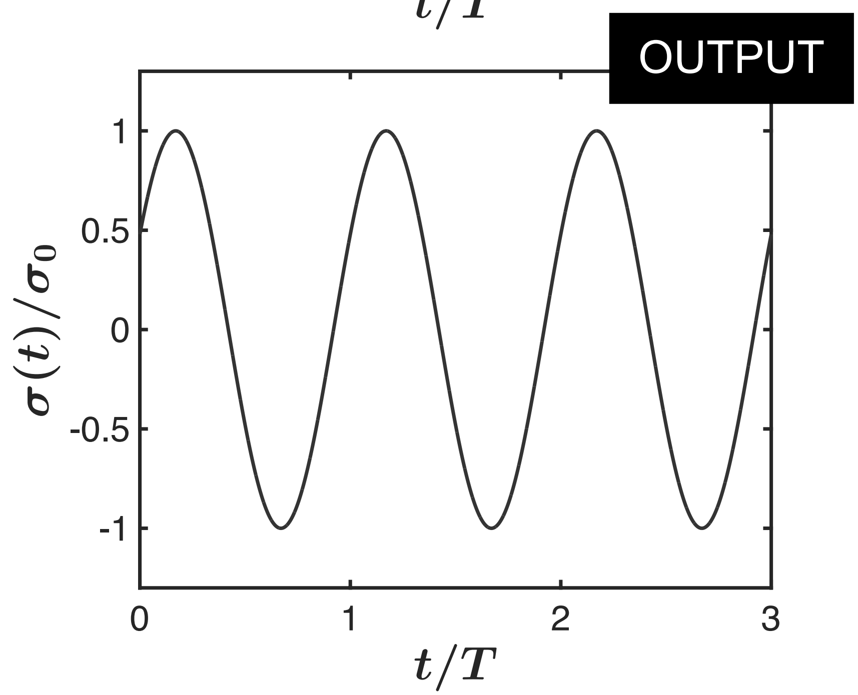
$$\lim_{r\to 0} w(t) = 1$$

ii. $r = 1$ (100%) , *Hann(ing)*

$$\lim_{r\to 1} w(t) = 0.5\left[1+\cos\left(\frac{2\pi t}{T}-\pi\right)\right]$$

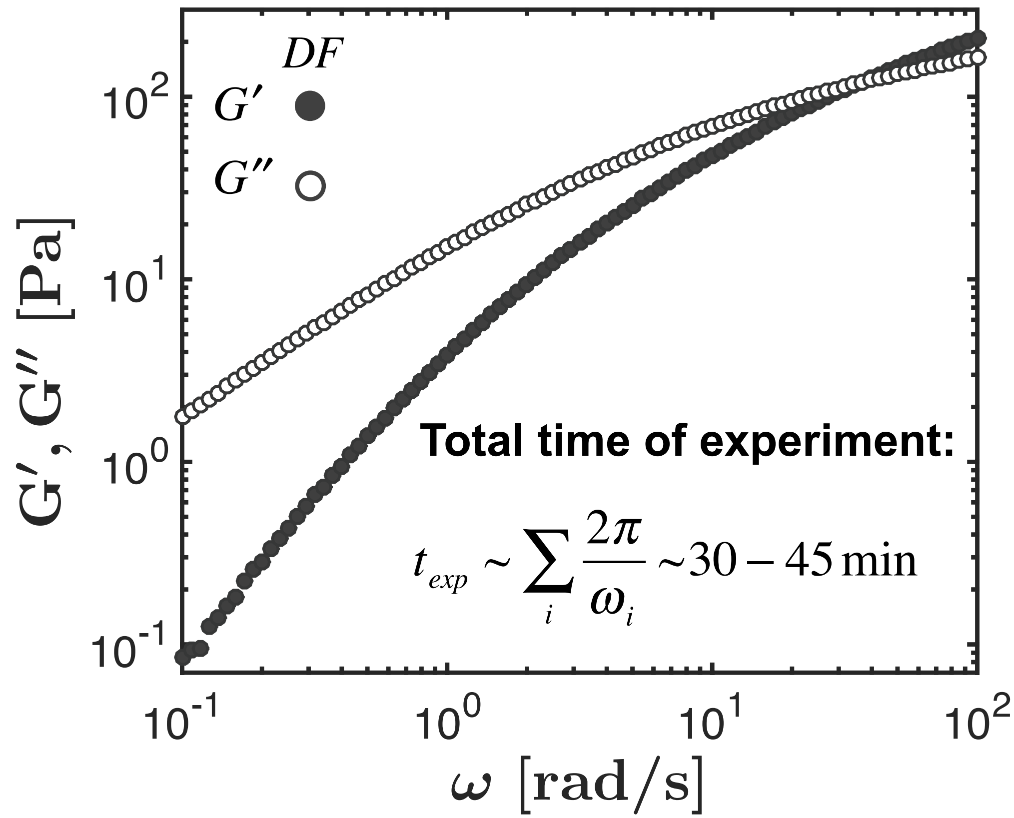
Demonstration: A Non-Gelling System





8.5% wt PIB solution in Hexadecane

(semidilute viscoelastic polymer solution)



Specs:

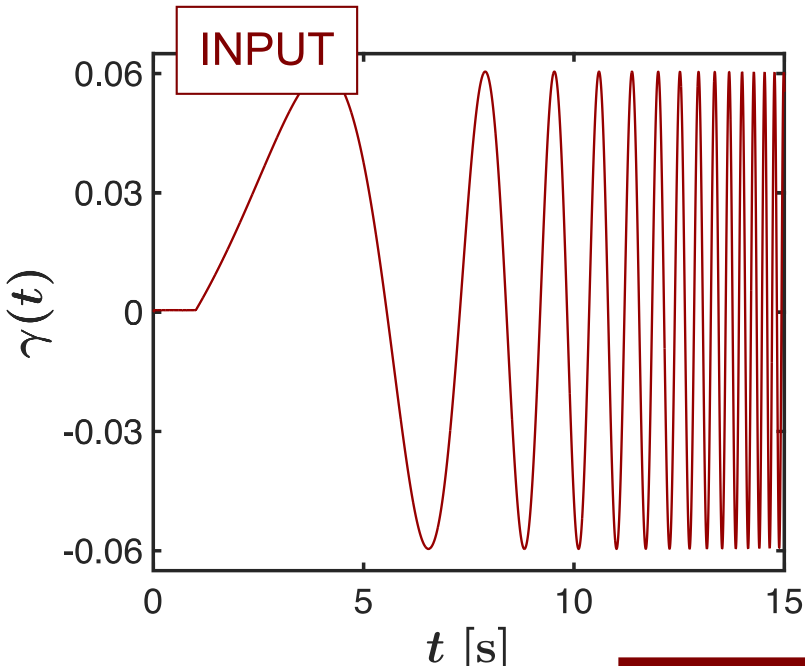
30 points/decade

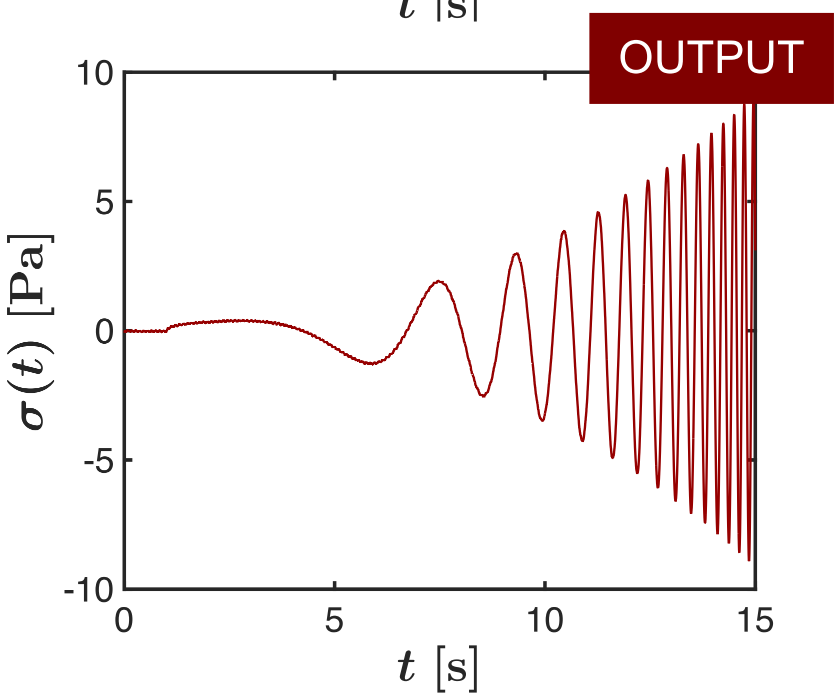
$\omega_1 = 0.1$ rad/s

$\omega_2 = 100$ rad/s

$\gamma_0 = 0.06$

Demonstration: A Non-Gelling System





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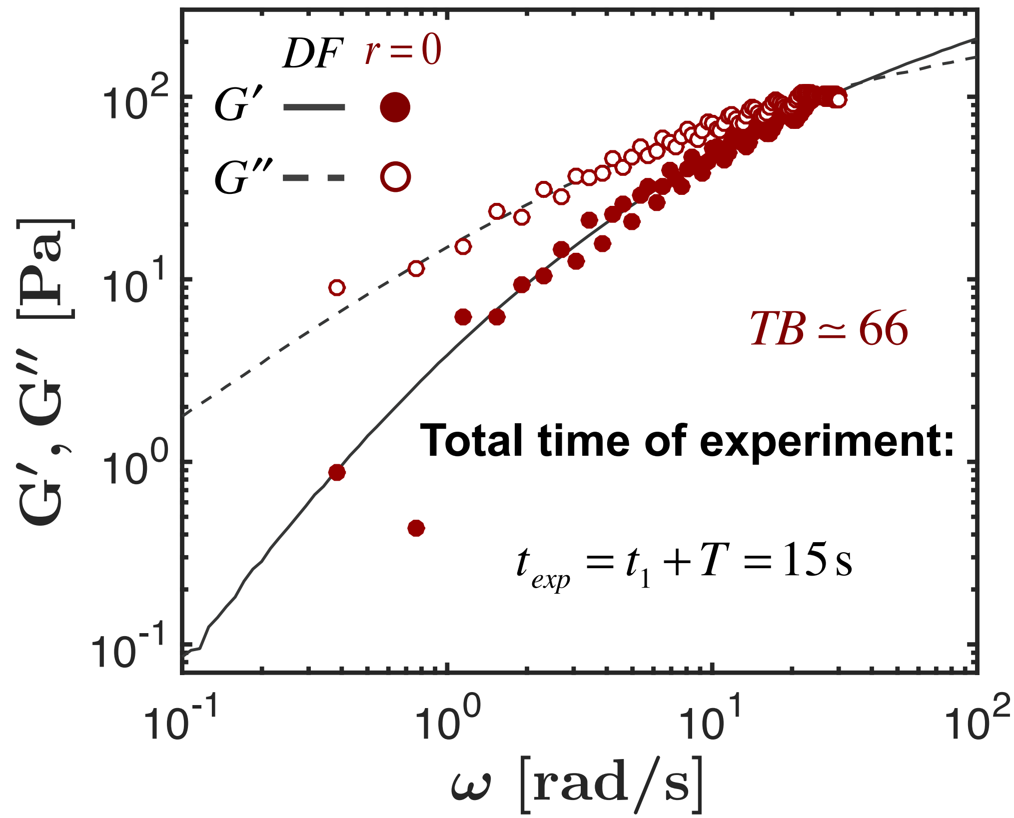
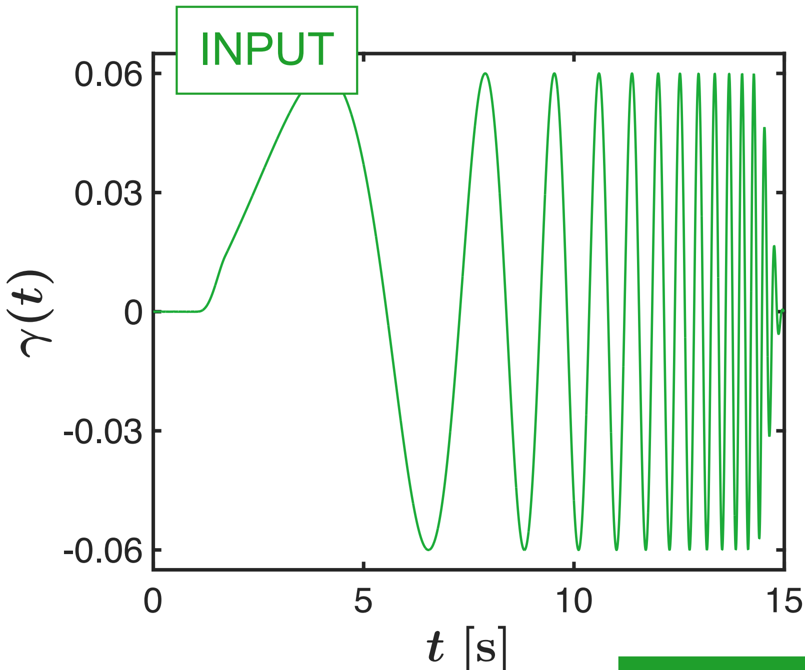
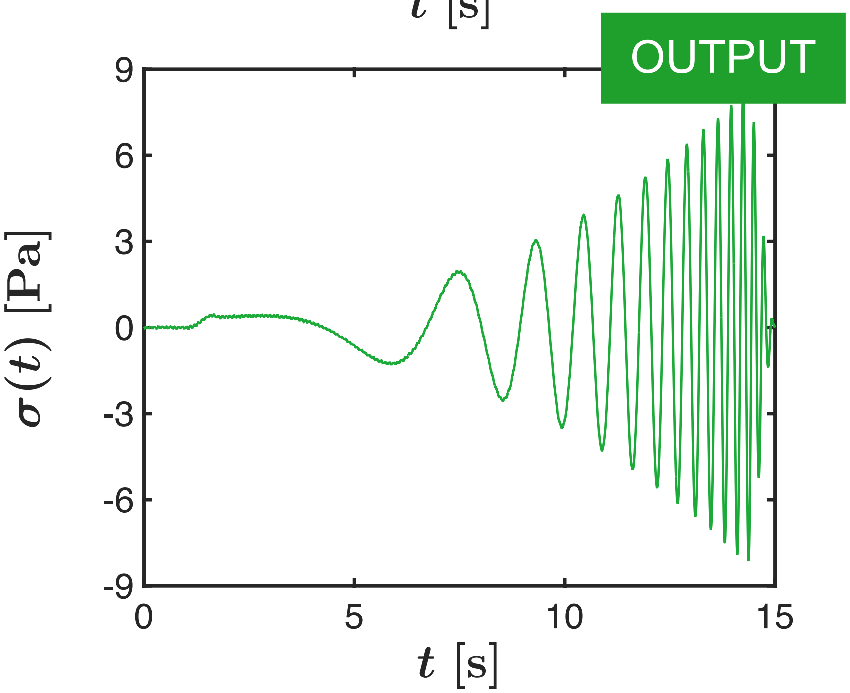


Specs:

$t_1 = 1\,\mathrm{s}$	$T = 14\ \mathrm{s}$	$\omega_1 = 0.3\ \mathrm{rad/s}$
	$f_s = 500\,\mathrm{Hz}$	$\omega_2 = 300\,\mathrm{rad/s}$
	$r = 0$	$\gamma_0 = 0.06$

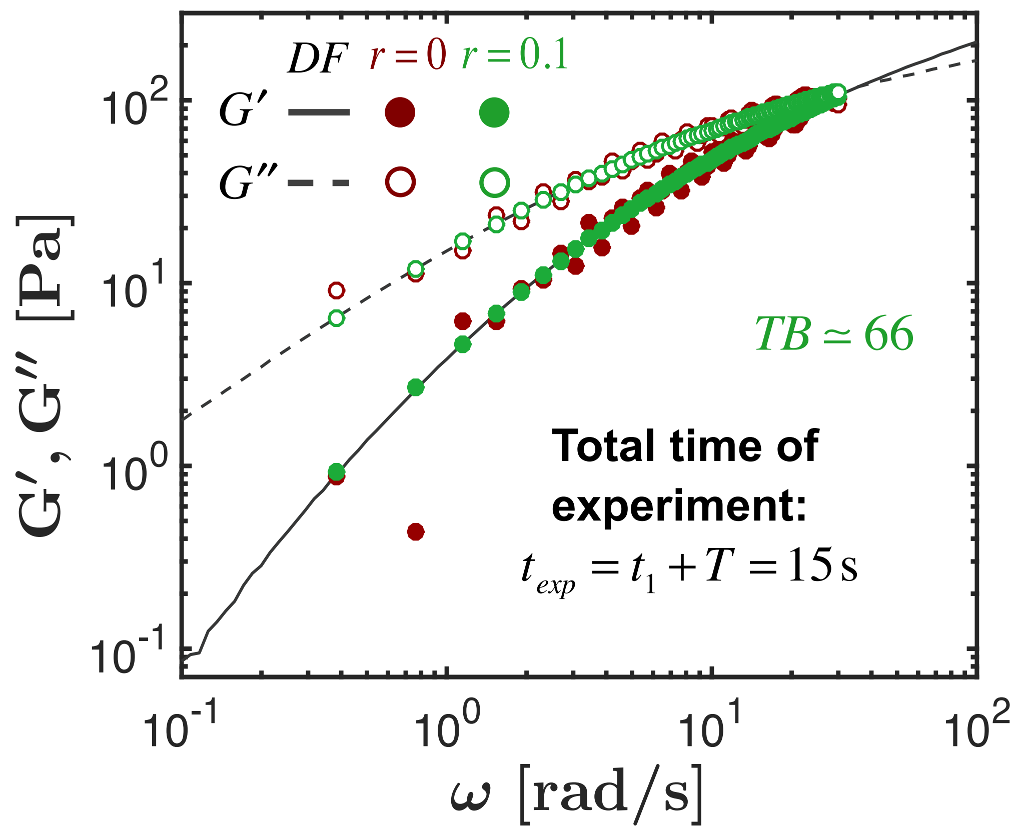
Demonstration: A Non-Gelling System





8.5% wt PIB solution in Hexadecane

(semidilute viscoelastic polymer solution)



Specs:	$T = 14$ s	$\omega_1 = 0.3$ rad/s
$t_1 = 1$s	$f_s = 500$ Hz	$\omega_2 = 300$ rad/s
	$r = 0.1$	$\gamma_0 = 0.06$

Minimizing Spectral Error using Optimal Windowing

Specs:

$T = 14$ s

$t_1 = 1$s

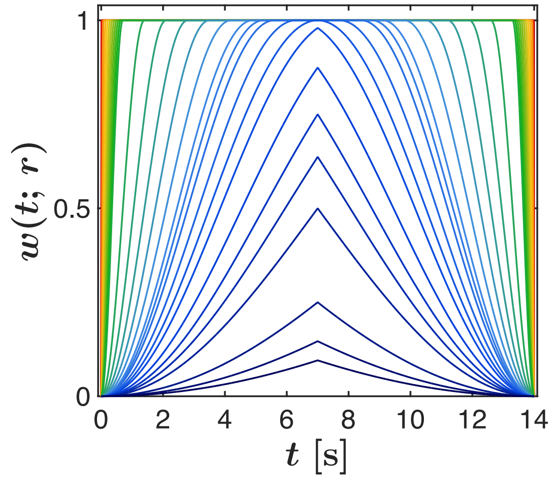
$f_s = 500$ Hz

$r \in [0,5]$

$\omega_1 = 0.3$ rad/s

$\omega_2 = 300$ rad/s

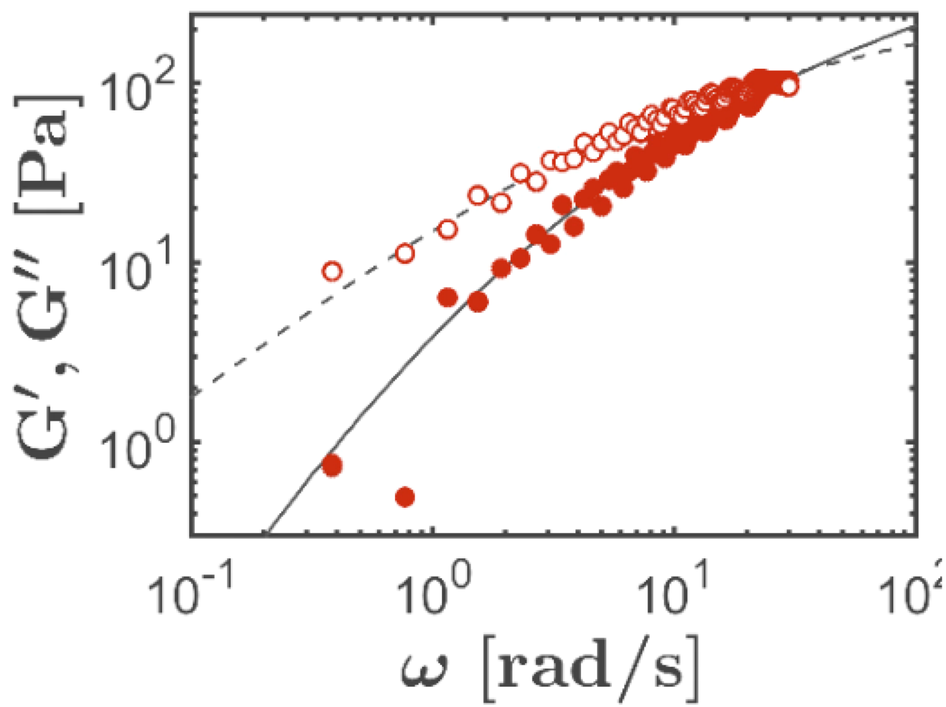
$\gamma_0 = 0.06$

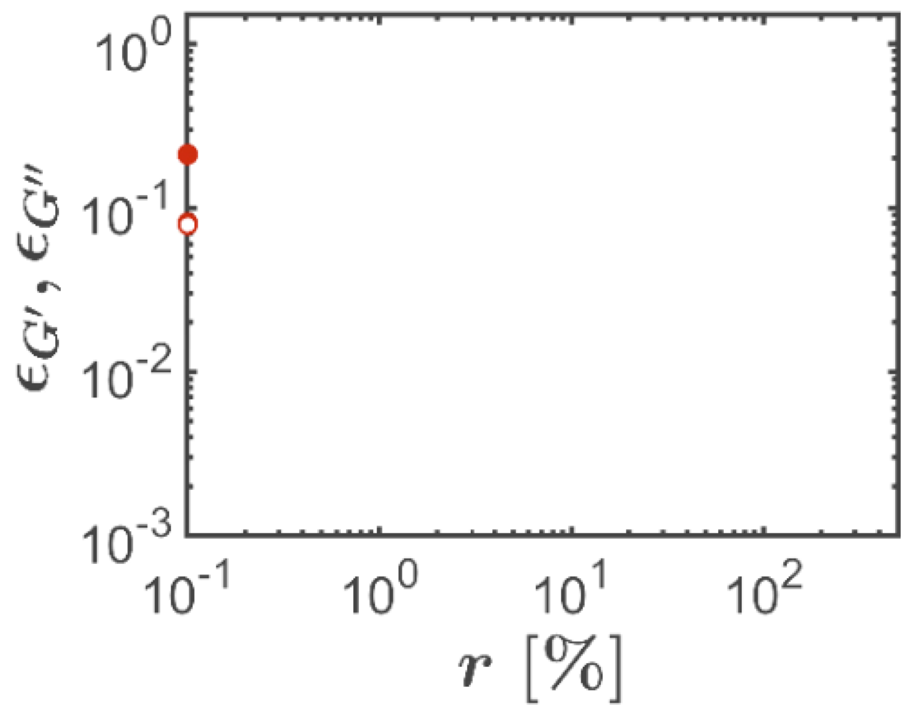


Error Definition:

$$\epsilon_{G'}(r) = \text{rms}\left[\log\left(\frac{G'_{chirp}(\omega_i, r)}{G'_{DF}(\omega_i)}\right)\right]$$

$$\epsilon_{G''}(r) = \text{rms}\left[\log\left(\frac{G''_{chirp}(\omega_i, r)}{G''_{DF}(\omega_i)}\right)\right]$$





Minimizing Spectral Error using Windowing

Specs:

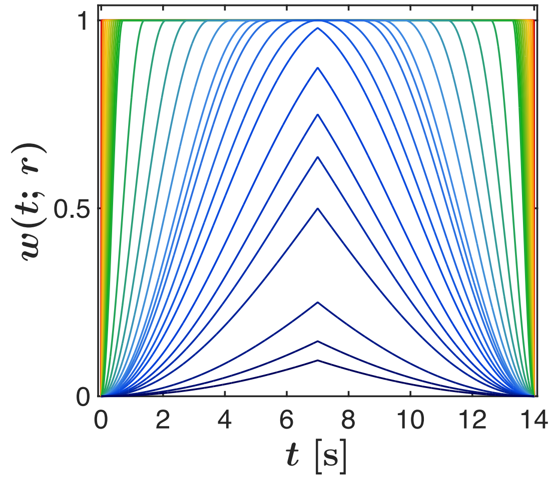
$T = 14\ \text{s}$

$t_1 = 1\,\text{s}$ $\quad f_s = 500\,\text{Hz}$

$r \in [0,5]$ $\quad \omega_1 = 0.3\ \text{rad/s}$

$\omega_2 = 300\,\text{rad/s}$

$\gamma_0 = 0.06$



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$$\epsilon_{G''}(r) = \text{rms}\left[\log\left(\frac{G''_{chirp}(\omega_i, r)}{G''_{DF}(\omega_i)}\right)\right]$$

Two limits:

i. $r \to 0$

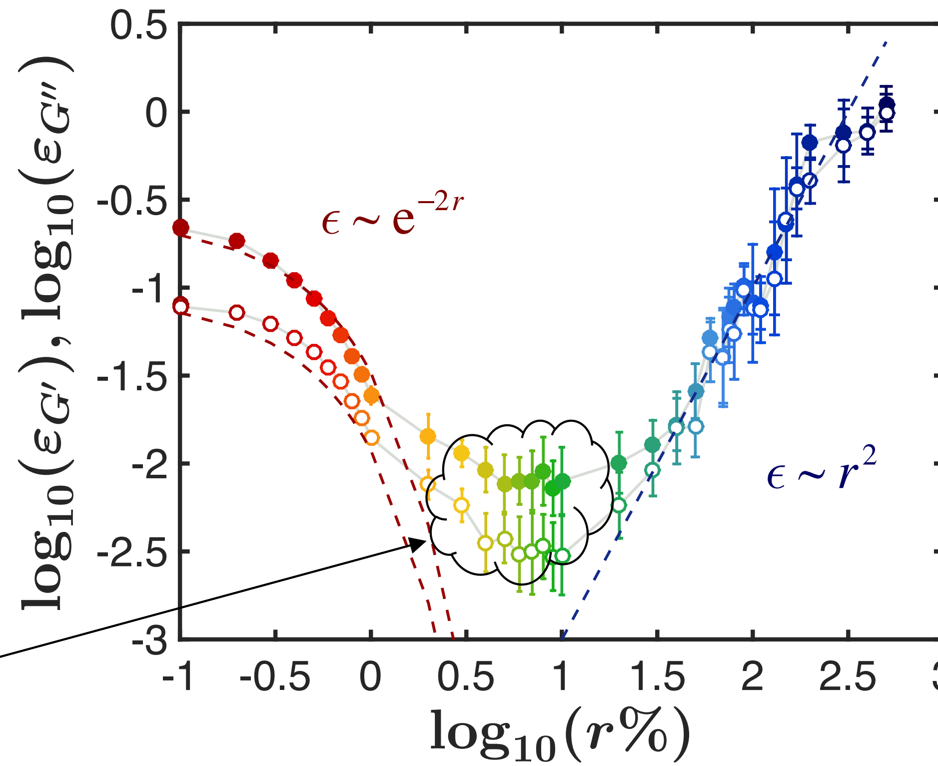
$$\epsilon(r) \sim \epsilon_0 \exp(-kr), \quad k \simeq 2$$

ii. $r > 1$

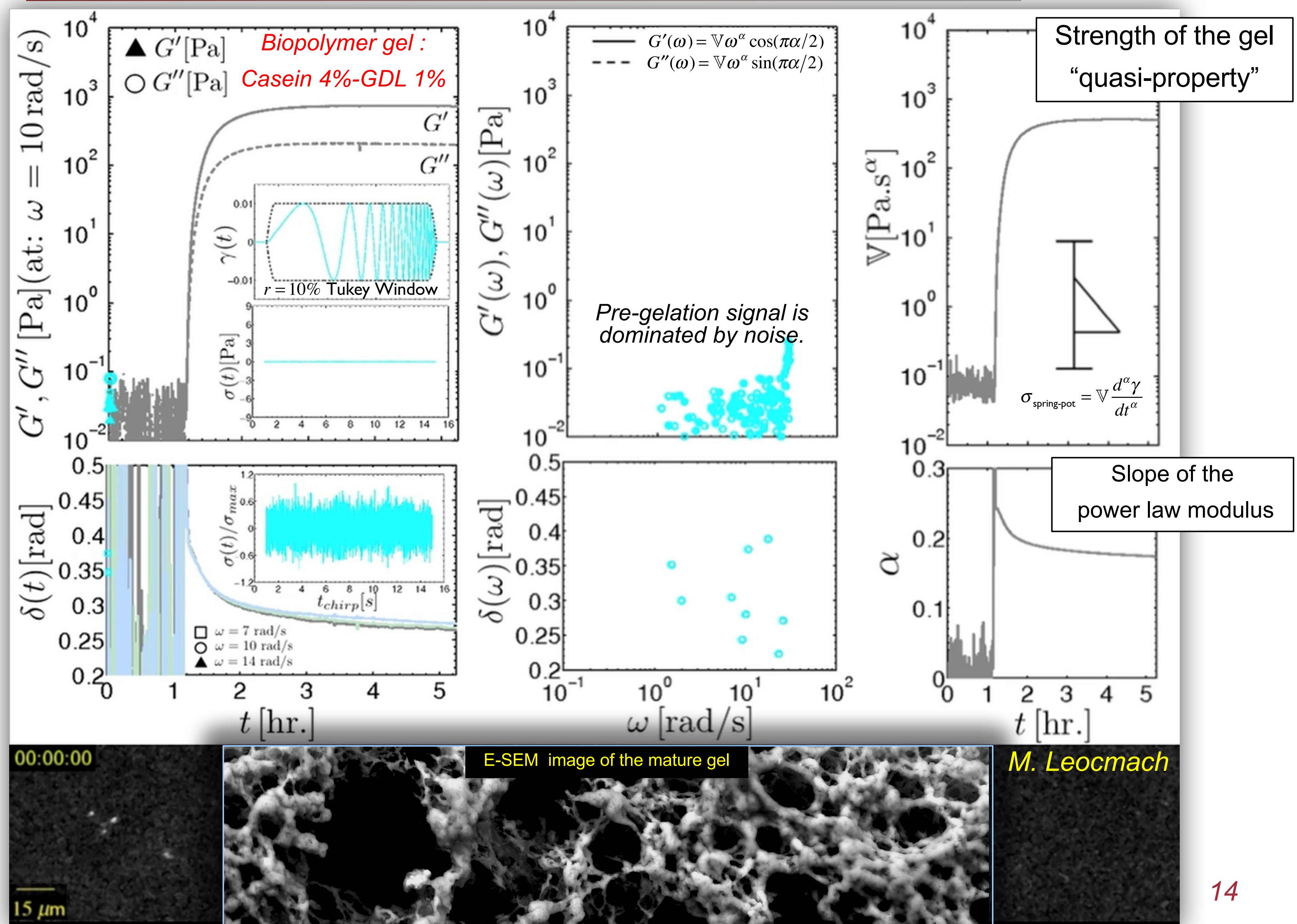
$$\epsilon(r) \sim \epsilon_0 r^2$$

For rheometric-type signals an Optimally Windowed Chirp (OWCh!) has a window ramp of 6% ≤ *r* ≤ 15%

Average over 6 experiments

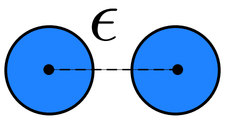


Gelation & Time-Resolved Rheometry $(TB \simeq 66; r = 10\%)$

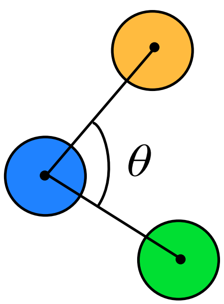


Chirps in Numerical Simulations Of A Model Soft Gel

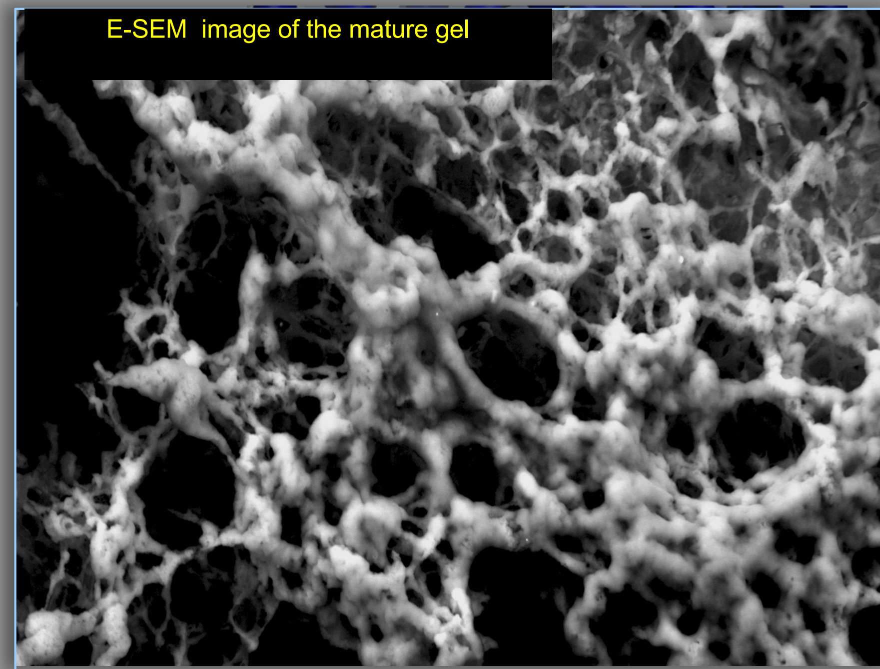
$\mathcal{U}(\mathbf{r}_i, \ldots, \mathbf{r}_N)$ *particle interactions*



short-range attraction



bending stiffness



- *Molecular Dynamics*
  - *~10^5, 10^6 particles*
    - *Φ ~ 0.05 - 0.2*
- *periodic boundaries*

Structural heterogeneities developed during solidification => mechanical inhomogeneities.

Internal stress distribution and coexistence of stiffer regions with softer domains.

Colombo et al., PRL 2013; Soft Matter 2014, JOR 2014.
Bouzid et al. Nat. Comm 2017, Langmuir 2017

Gel Preparation & Mechanical Tests

Colombo et al., PRL 2013; Soft Matter 2014, JOR 2014.
Bouzid et al. Nat. Comm 2017, Langmuir 2017

- Self-assembly by slow cooling ($k_B T/\varepsilon$ ~0.5 -> 0.05):

$$m\frac{d^2\mathbf{r}_i}{dt^2} = -\nabla_{\mathbf{r}_i}\mathcal{U} - \eta_f \frac{d\mathbf{r}_i}{dt} + \xi(t).$$

Particle mass (m) · Damping coefficient (η_f) · thermal fluctuations ($\xi(t)$)

- Draw down the kinetic energy to reach a local minimum:

$$m\frac{d^2\mathbf{r}_i}{dt^2} = -\nabla_{\mathbf{r}_i}\mathcal{U} - \eta_f \frac{d\mathbf{r}_i}{dt}$$

- Athermal oscillatory shear: $\gamma(t) = \gamma_0 \sin \omega t$

…or Optimized Windowed Chirp Function

$$m\frac{d^2\mathbf{r}_i}{dt^2} = -\nabla_{\mathbf{r}_i}\mathcal{U} - \eta_f \left(\frac{d\mathbf{r}_i}{dt} - \dot{\gamma}(t) y_i \mathbf{e_x}\right)$$

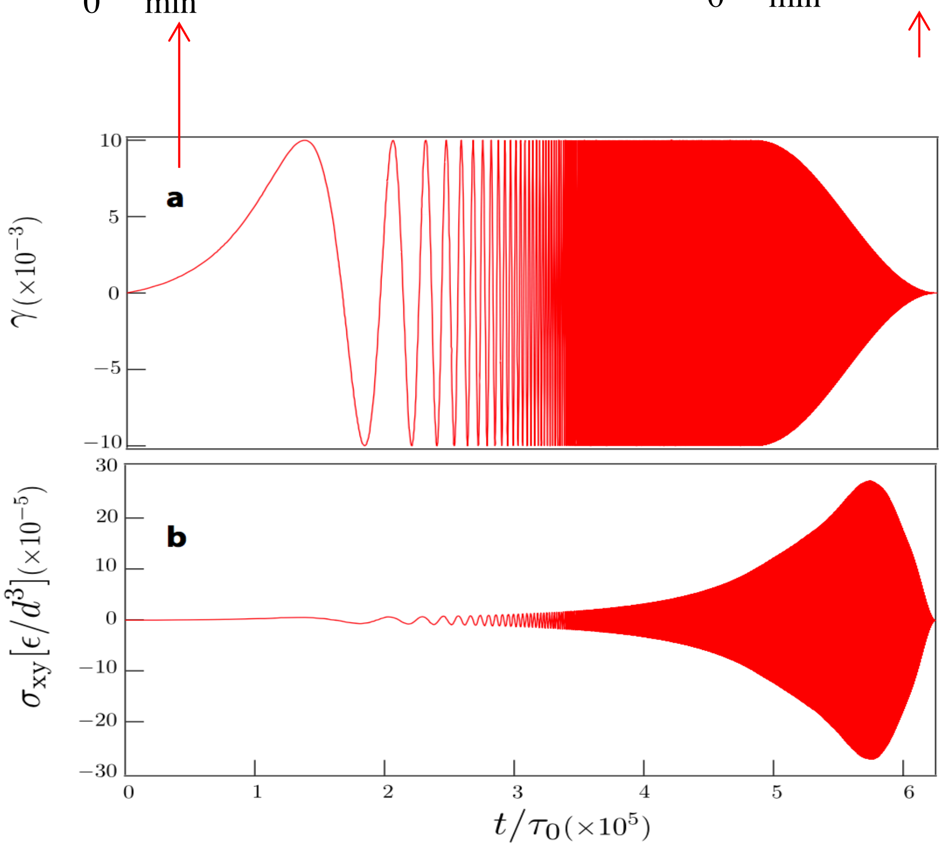
+ Lees-Edwards boundary conditions → virial stress $\sigma_{\alpha\beta} = \frac{1}{V}\sum_{i=1}^{N} \frac{\partial U}{\partial r_i^{\alpha}} r_i^{\beta}$

Optimized Windowed Chirp Simulations

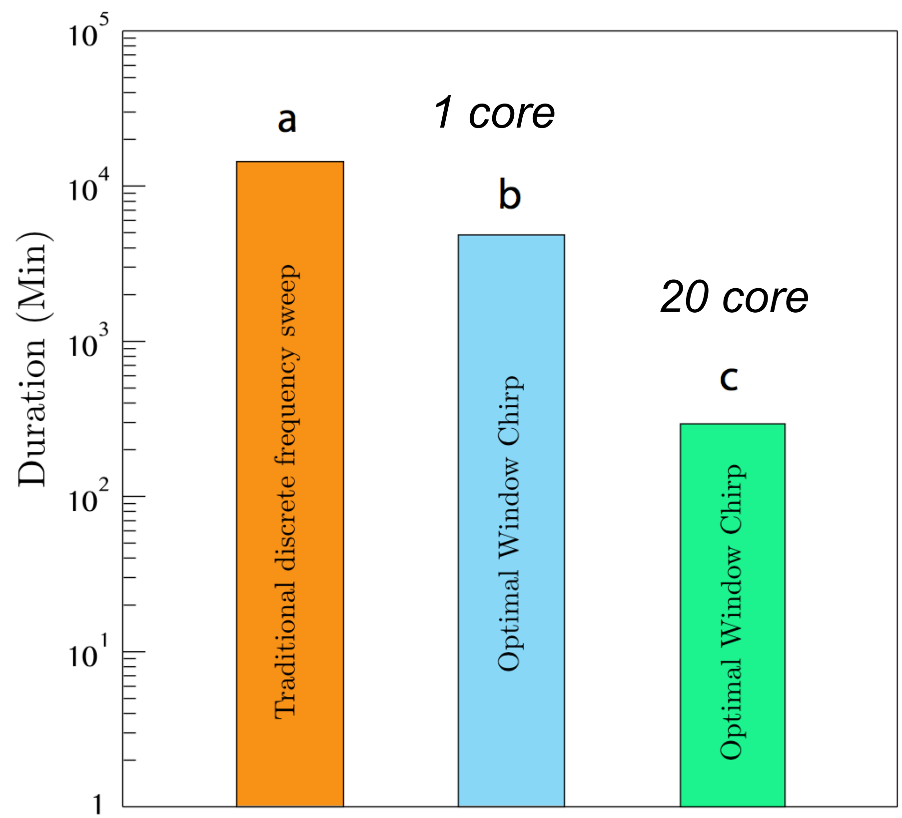
- Optimized Chirp (OWCh) response can also be exploited in numerical simulations
- Rapidly evaluate the full linear viscoelastic spectrum of attractive colloidal gel

$$TB \approx 1.8 \times 10^5$$

$$\tau_0 \omega_{\min} = 5 \times 10^{-4} \qquad \tau_0 \omega_{\min} = 18$$



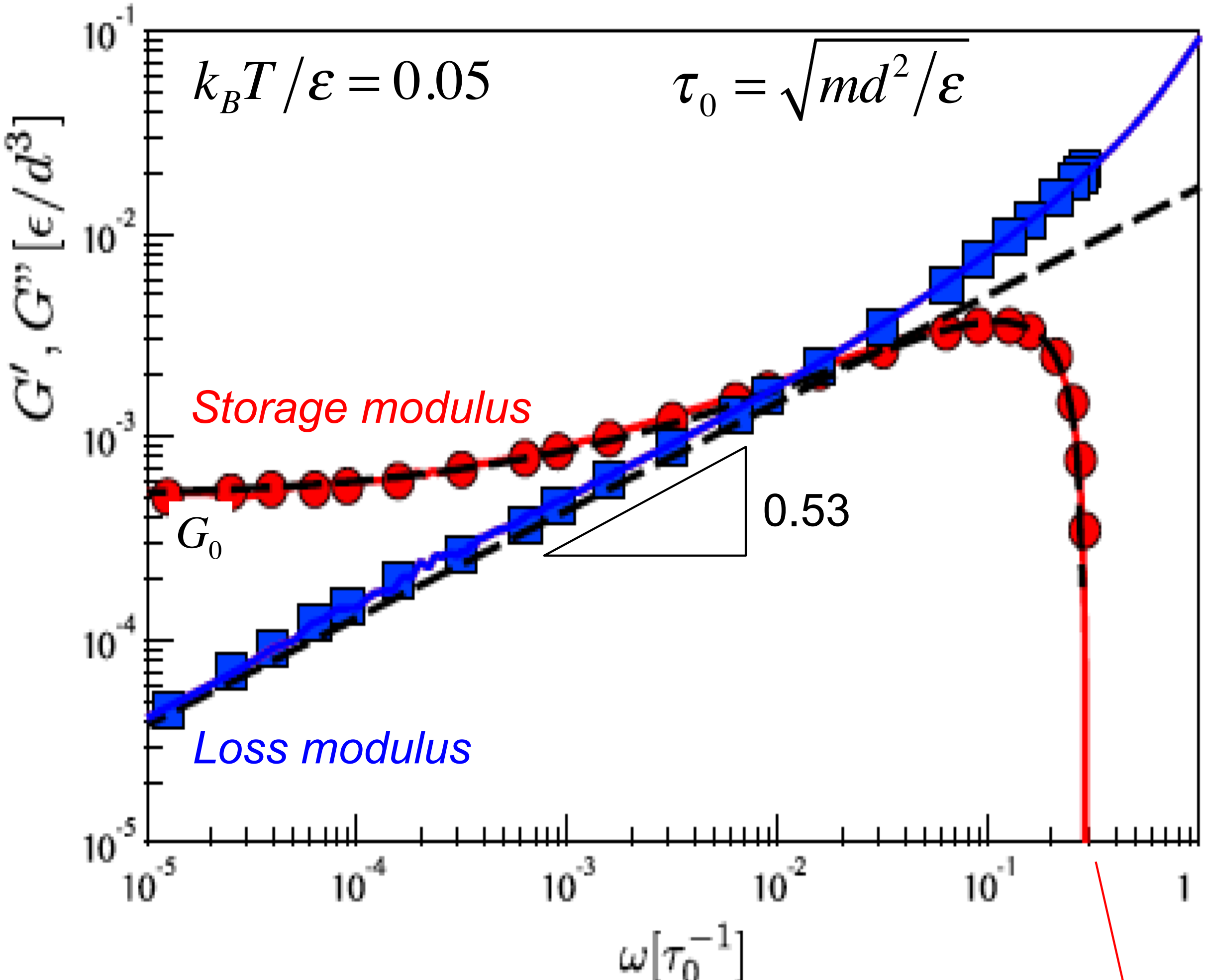
$$\tau_0 = \sqrt{md^2/\varepsilon} \qquad k_B T/\varepsilon = 0.05$$

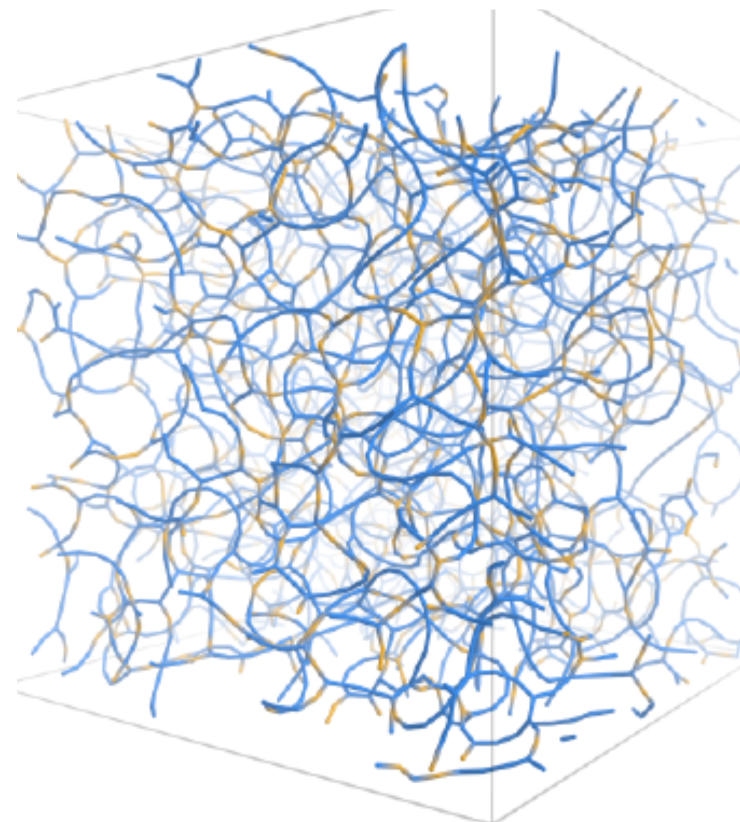


Factor of 50X speed up in computation time on a 20 core machine

Linear Viscoelastic Response

- Rapidly evaluate the full linear viscoelastic spectrum of attractive colloidal gel
- Power-law features over broad range of intermediate frequencies





N = 19652

L≈ 52d

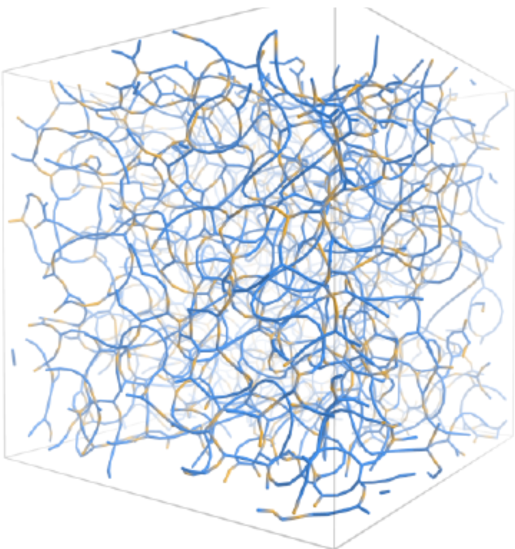
$\phi \approx 7.3\%$

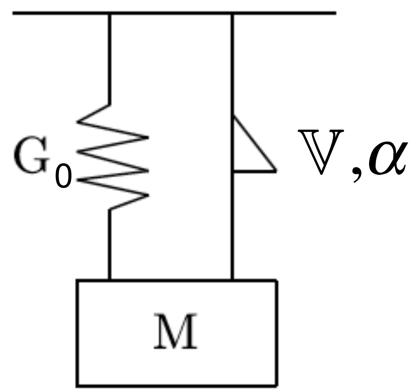
Broad power law frequency response in (both) dynamic moduli

Resonance from finite mass of system: results in "creep ringing" in constant stress (creep) simulations

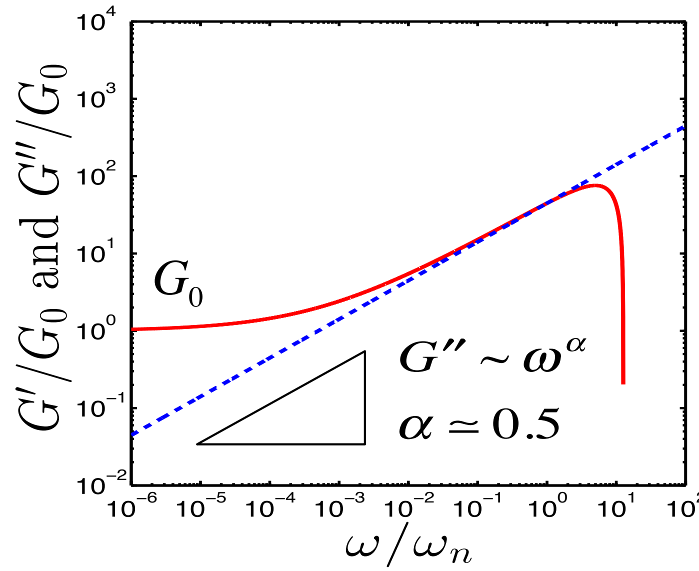
“Lumped Parameter” Model for Attractive Colloidal Gel

- Viscoelastic response of the gel can be compactly described by a fractionally-damped spring mass oscillator system:





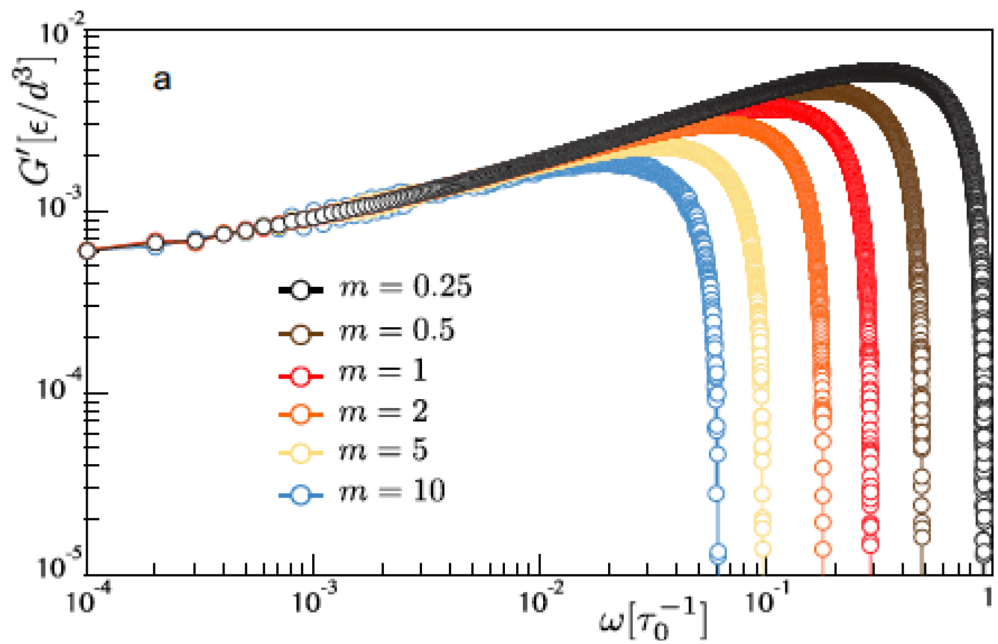
$$\omega_n = \sqrt{\frac{G_0}{M}}\ ;\ \xi = \frac{\mathbb{V}}{\sqrt{M^{\alpha} G_0^{\,2-\alpha}}}$$



Frequency Response of a Fractionally-Damped Spring-Mass Oscillator

$$\frac{G'(\omega)}{G_0} = 1 - (\omega/\omega_n)^2 + (\omega/\omega_n)^{\alpha}\,\xi\cos(\pi\alpha/2)$$

$$\frac{G''(\omega)}{G_0} = (\omega/\omega_n)^{\alpha}\,\xi\sin(\pi\alpha/2)$$

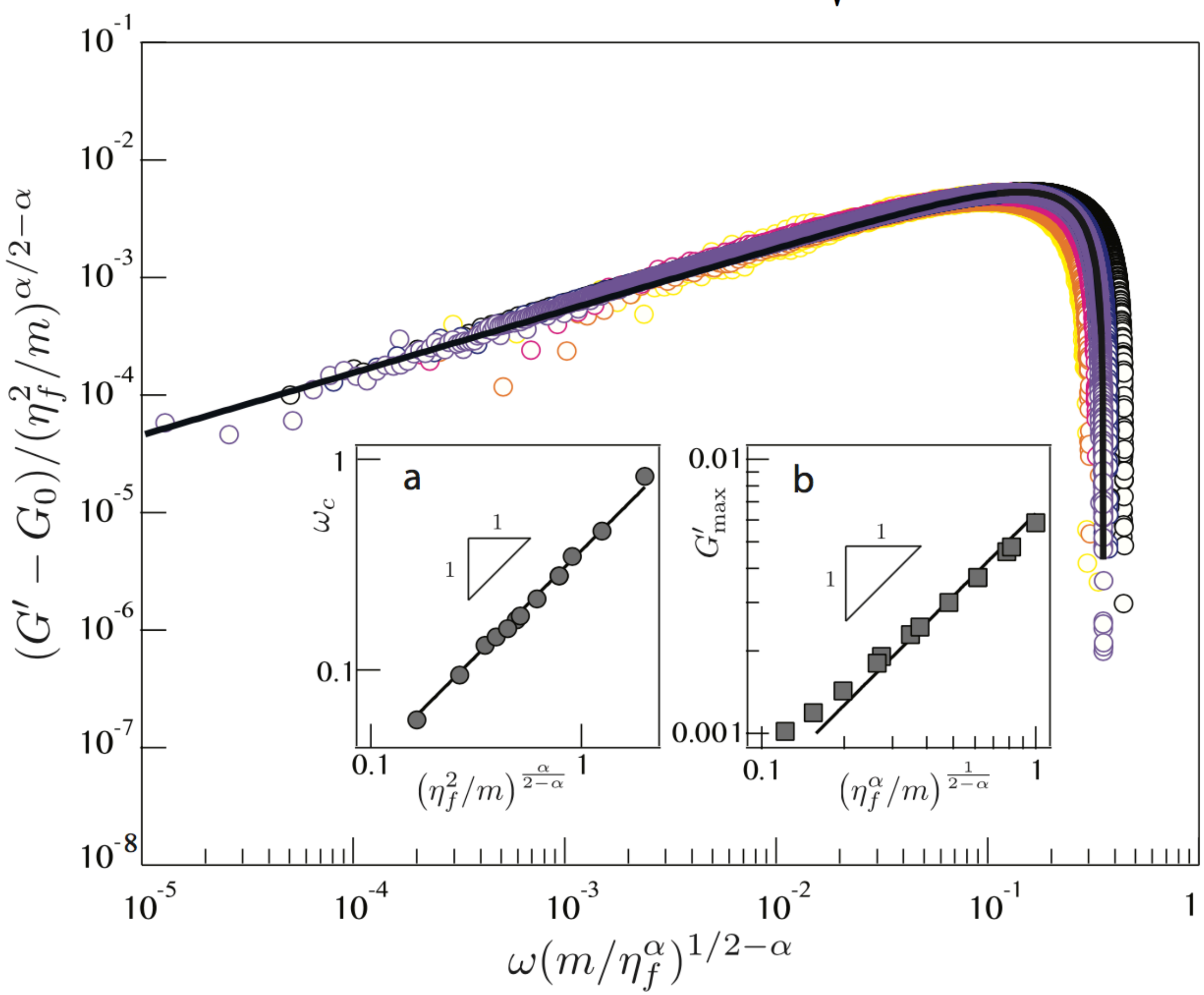


B. Keshavarz, M. Bouzid, M. Geri *et al.*,
J. Rheology (submitted), 2018

Rescaled Universal Response

- Simulations for different particle mass, viscosity coefficient can be rescaled onto single universal curve

$$\omega_c \sim \sqrt{\frac{G_0}{M}}\left(\frac{\alpha\cos(\alpha\pi/2)\eta_f^{\alpha}G_0^{1-\alpha}}{2\sqrt{M^{\alpha}G_0^{2-\alpha}}}\right)^{1/(2-\alpha)} \sim \left(\eta_f{}^{\alpha}/M\right)^{1/(2-\alpha)}$$

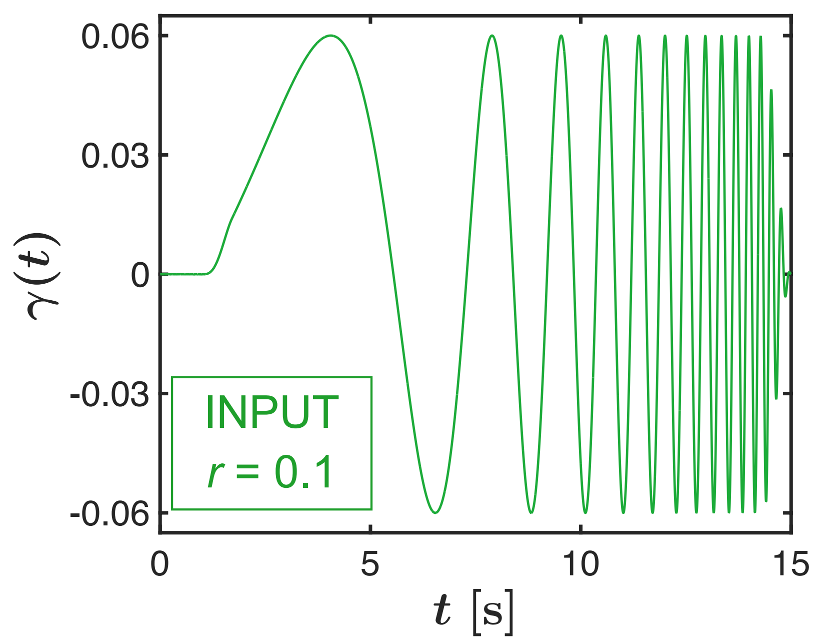


Use Chirp protocol to now ask:

- How does the plateau modulus scale with
  - ❑ the volume fraction of particles in the box?
  - ❑ the strength of the individual bond connector energies?
- How does the fractional relaxation exponent scale with:
  - ❑ fractal dimension of network?
  - ❑ Preparation history? (quench)

Conclusions & Outlook

- A truly "Optimized" Windowed Chirp function (OWCh)
  - Combine exponential swept sine function with a Tukey window ($r \approx 0.1$) to minimize spectral power leakage into side lobes of FFT.
  - Total signal length: $T_{\exp} \approx 2\pi/\omega_1$
  - Time Frequency bandwidth: $TB = T(f_2 - f_1) = T(\omega_2 - \omega_1)/2\pi \gg 1$
- Validated by experiments on
  - non-gelling viscoelastic fluid
  - Acid-catalyzed casein gel
  - MD simulations of colloidal attractive gel
  - *Suspensions*?
- Remaining experimental questions:
  - How do mechanical bandwidth issues of the motor constrain ω_2?
  - Limits of the time resolution?
  - How do the error measures grow with *mutation number* of the system?

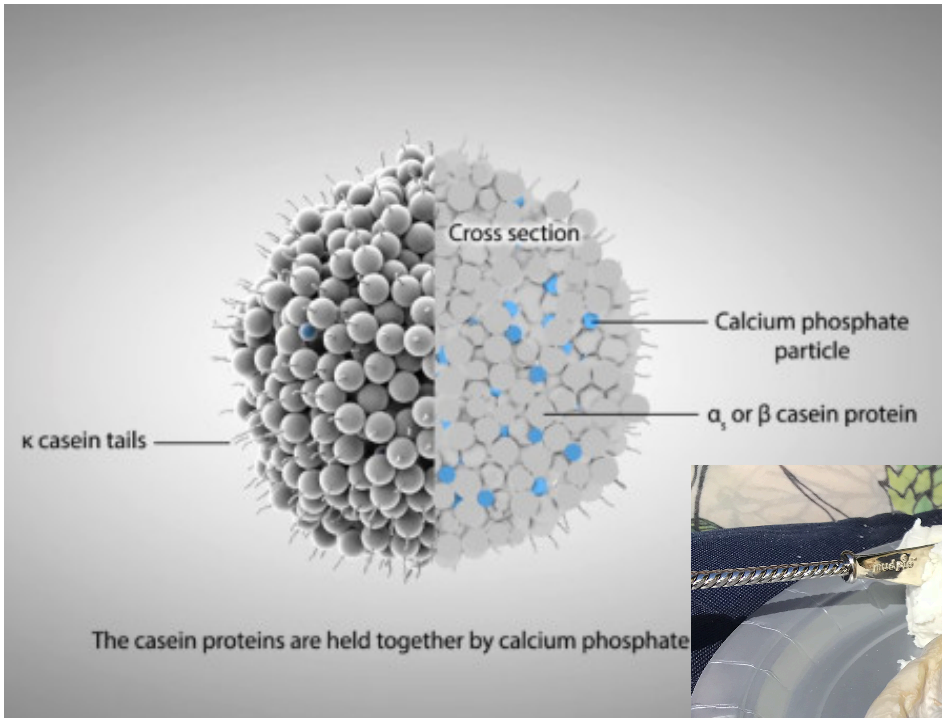


$$Mu^* = \frac{T_{\exp}}{\tau_{mu}} = \frac{f_1^{-1}}{(d\ln G^*/dt)^{-1}} = \frac{2\pi}{\omega_1}\frac{d\ln G^*}{dt} \leq ?$$

Geri *et al.*, to be submitted to *Phys. Rev. Applied*, 2017

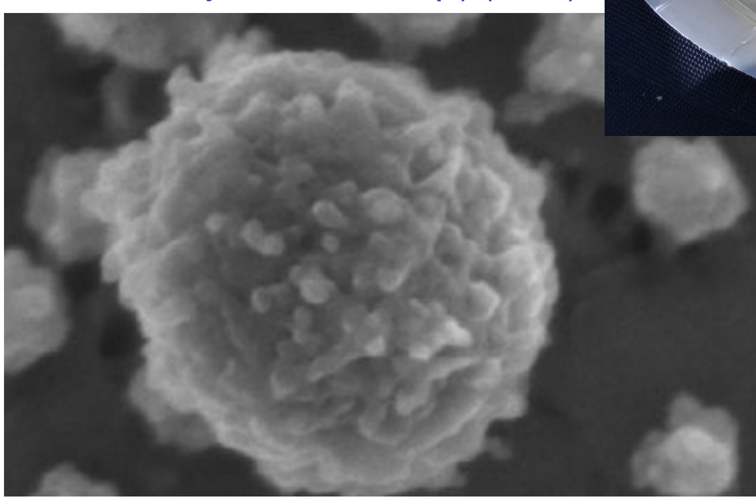
Subtleties in Cheese Science

Cheese Curds

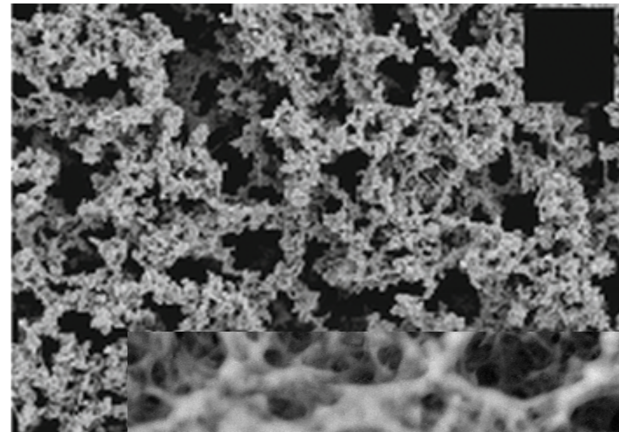


Van Vliet & Walstra (2003)

Martin et al., Food Hydrocolloids ***20(6)*** *(2006)*



Rennet



Sodium Caseinate

No Calcium Phosphate