Tutorial: Rheology of Soft Materials

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What Is Rheology?

The quantitative study of the manner in which materials *deform* and *flow.*

- Describe the mechanical constitutive relationship for a material (response to force):

Prescribe/measure

$$F = -kx, \quad \sigma = -G\gamma$$

(*Elastic solid*)

$$\sigma = -\eta\dot{\gamma}$$

(*Viscous liquid*)

- What kinds of materials do we study in our lab?

Soft materials - generally isotropic, disordered, both elastic and viscous components.

  - Allen, Lolo, Stefan: Biopolymer networks
  - Jim, Shmuel: Biofilms, polymers
  - Joris: Colloidal suspensions/gels, microgels, polymers
  - Sujit and Dustin: Colloidal suspensions, emulsions

Outline Of This Tutorial

- Basic definitions: stress/strain, affine/non-affine, flows, viscoelasticity, shear modulus

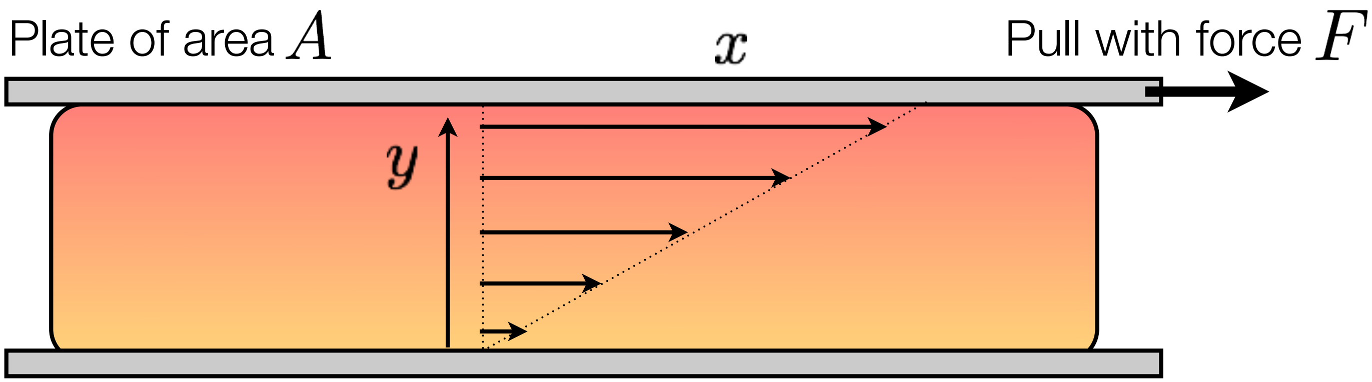
- Some different responses: Maxwell, Kelvin-Voigt, SGR

- How to actually measure things: controlled/stress strain, viscometry, geometries

- Two examples:
  - Soft glassy emulsions
  - Colloidal gels

- Other types of measurements/topics of interest:
  - SRFS
  - Non-linear (shear thinning/shear thickening)
  - Shear-banding
  - Yield stress
  - Pre-stress
  - LAOS

Basic Definitions: Stress/Strain



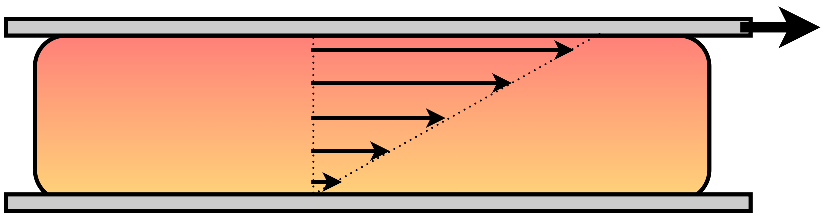
Strain: $\gamma \equiv x/y$

Stress: $\sigma \equiv F/A$

- Note: here, only consider shear flows/stresses; no extensional flows or normal stresses

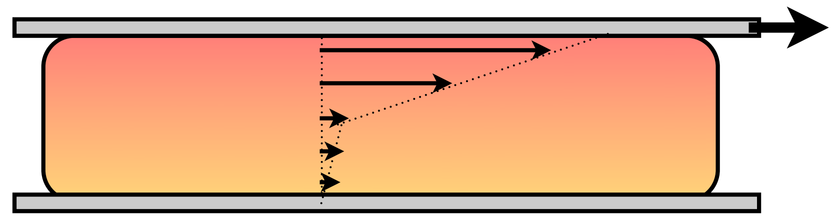
Basic Definitions: Affine/Non-Affine

Affine



- Uniform deformation
- Local strain = macroscopic strain

Non-Affine



Major subject of current research!

Significant influence on rheology of:

- Biopolymers (Lolo))
- Microgels (Joris)
- Emulsions (Simulations)
- Shear-banding of suspensions

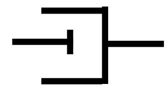
Basic Definitions: Viscoelasticity

- See video

- Materials have different mechanical responses depending on timescale of measurement

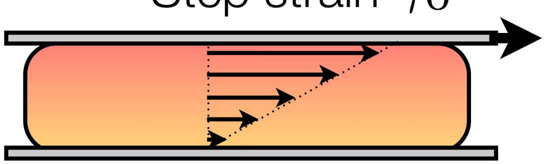
$$\sigma = -G\gamma \qquad\qquad \sigma = -\eta\dot{\gamma}$$

(*Elastic solid*) (*Viscous liquid*)



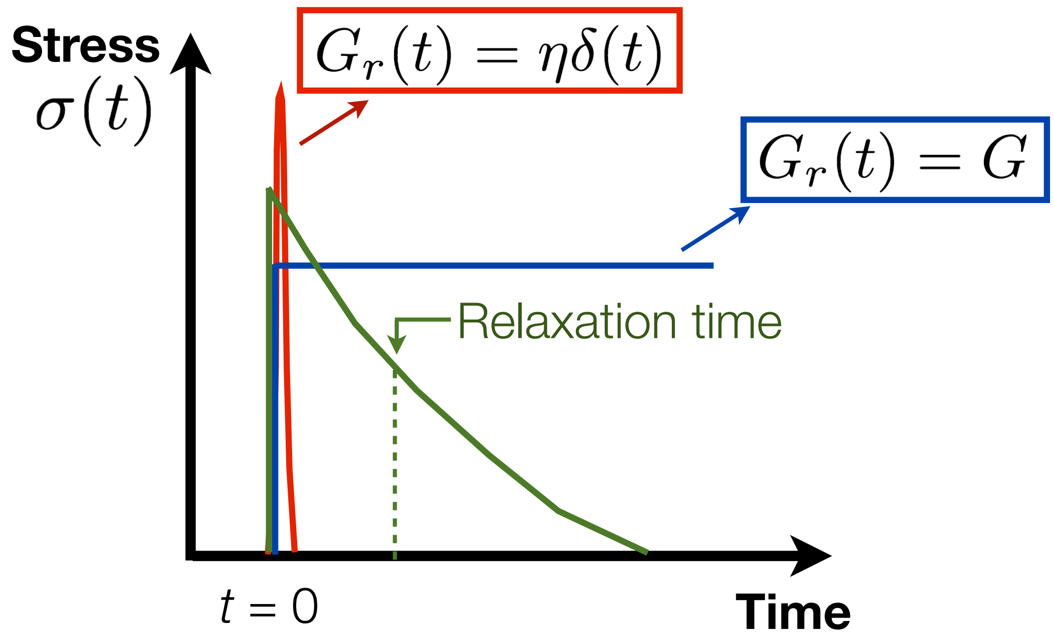
- How to quantify this? Stress relaxation modulus $G_r(t)$.
  - There are many equivalent ways to measure this! Different preferences based on experimental method, tradition, etc.

Step strain γ_0



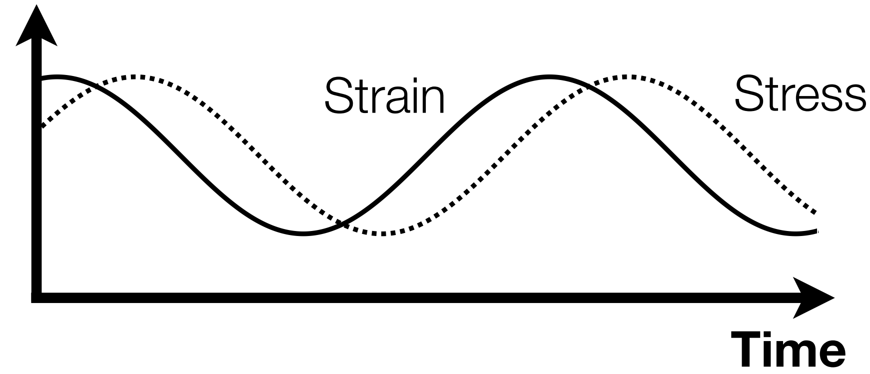
Measure $\sigma(t)$

$$G_r(t) \equiv \sigma(t)/\gamma_0$$



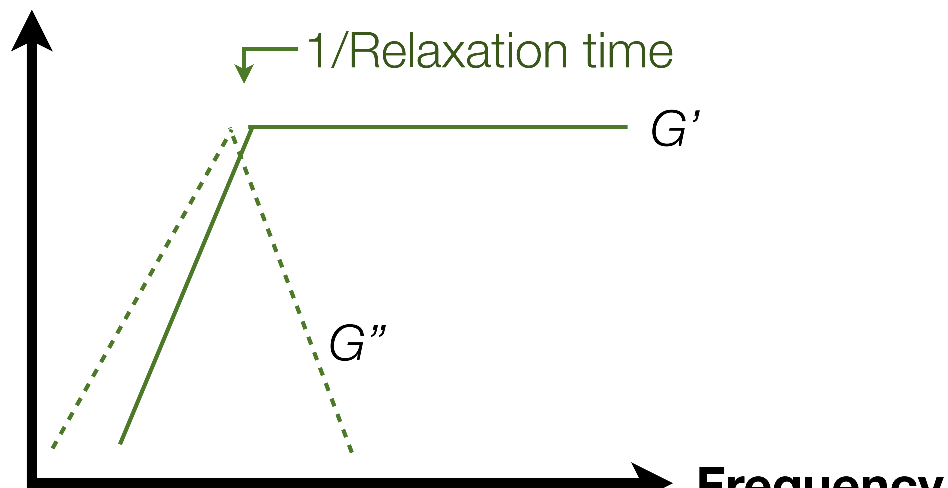
Basic Definitions: Complex Shear Modulus

- Another approach: frequency-domain



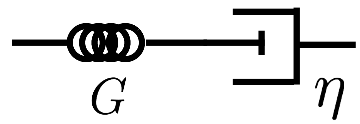
$$\gamma(t) = \gamma_0 \sin\omega t, \;\; \dot{\gamma}(t) = \gamma_0 \omega \cos\omega t$$

$$\sigma(t) = \sigma_0(\omega) \sin[\omega t + \delta(\omega)] = \gamma_0 \left[\underbrace{G'(\omega)}_{\text{Storage of elastic energy}} \sin(\omega t) + \underbrace{G''(\omega)}_{\text{Viscous dissipation}} \cos(\omega t) \right]$$



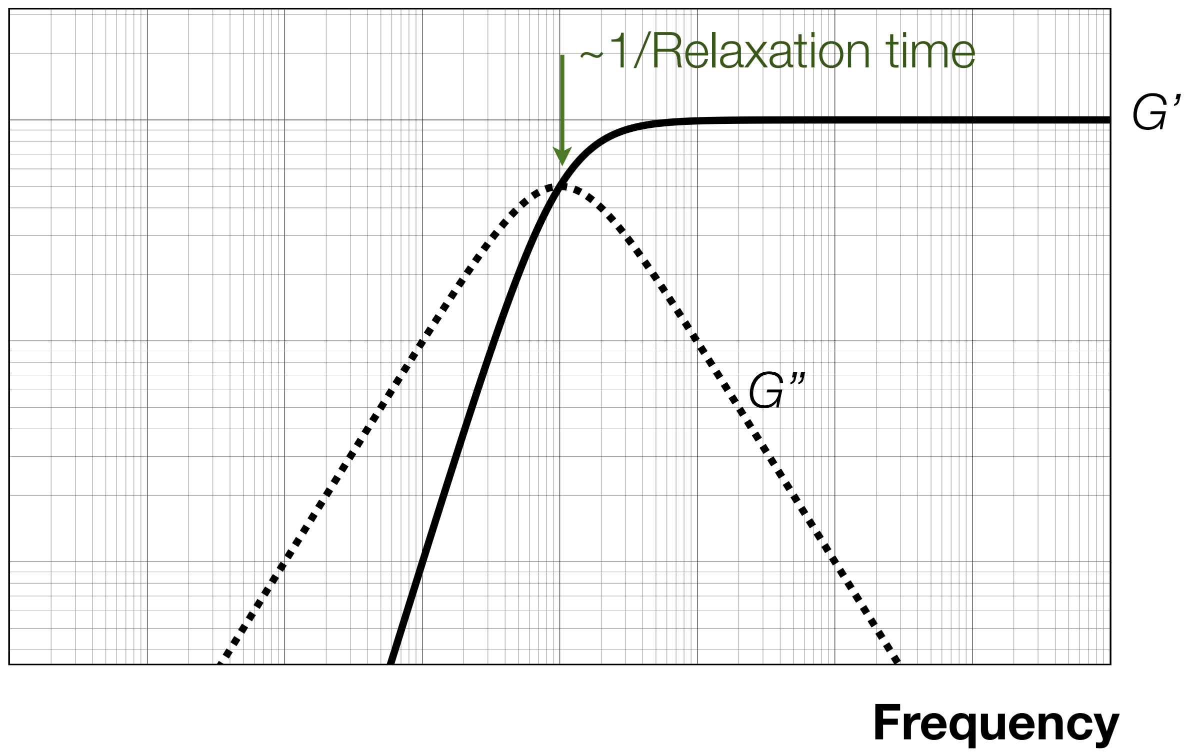
One Model: Maxwell (Low Frequency Relaxation)

- Elastic solid in series with viscous dashpot
  (e.g. entangled polymer solution)



- Timescale: η/G

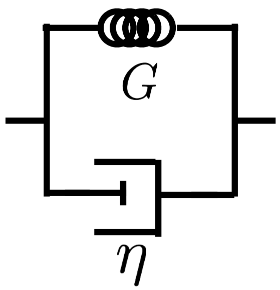
- Can derive functional form of *G'*, *G"* as a function of frequency



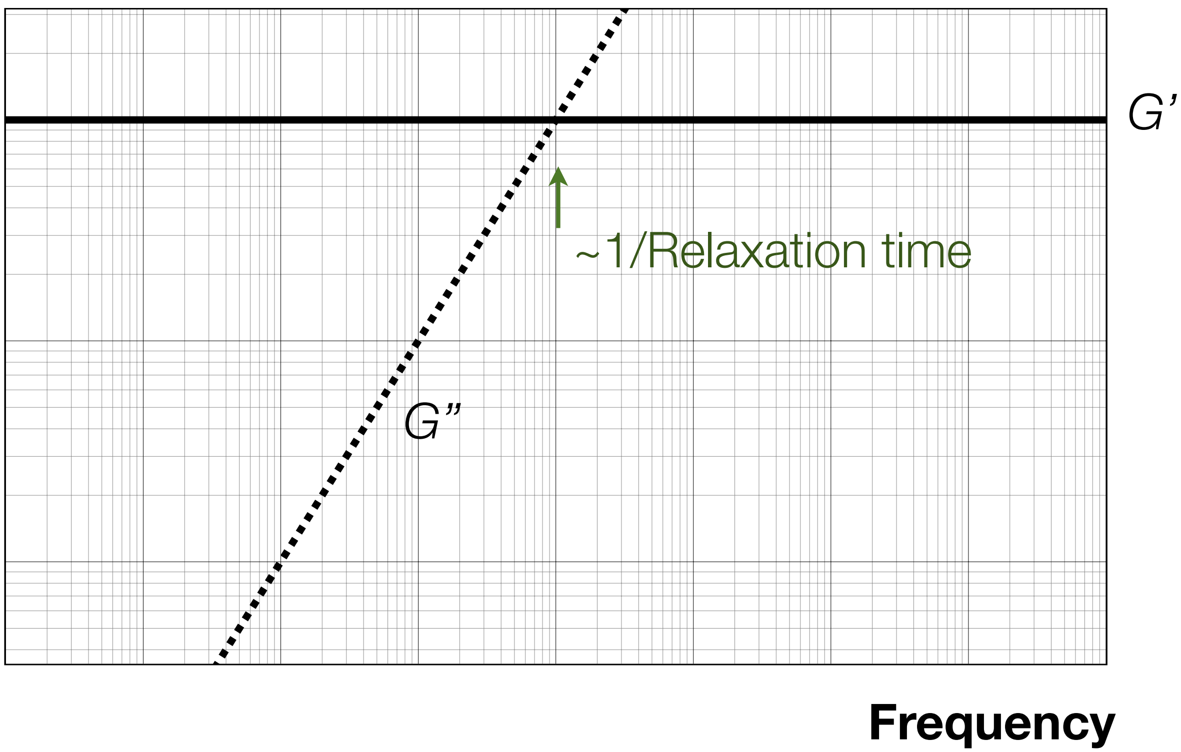
- This model captures stress relaxation behavior better

One Model: Kelvin-Voigt (Low Frequency Elasticity)

- Elastic solid in parallel with viscous dashpot



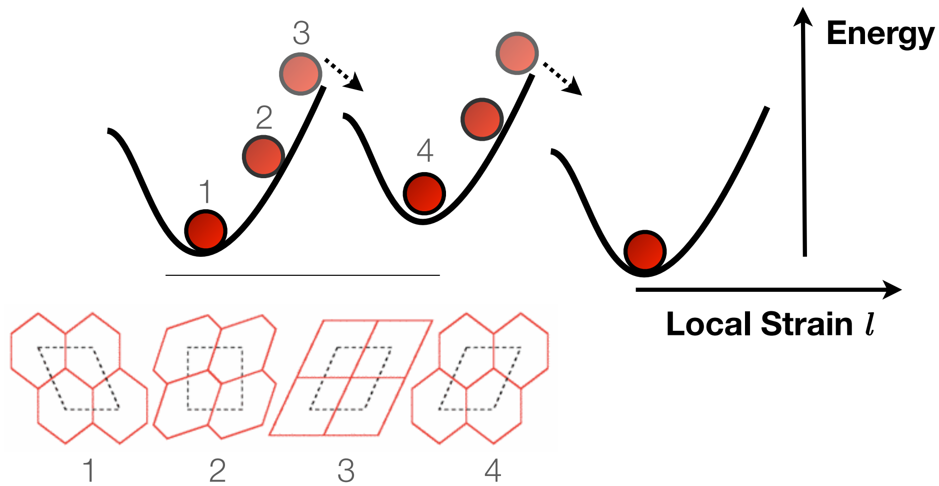
- Timescale: η/G
- *G', G"* as a function of frequency are very simple



- This model captures creep recovery behavior better

Phenomenological Model: Sollich's Soft Glassy Rheology

- Energy barriers >> thermal energy; these are due to microscopic structure of material



- Each mesoscopic region has own yield energy; distribution of yield energies
- Hopping activated by noise temperature x; this is related to how jammed
- Hopping time-scale is given by phenomenological attempt frequency

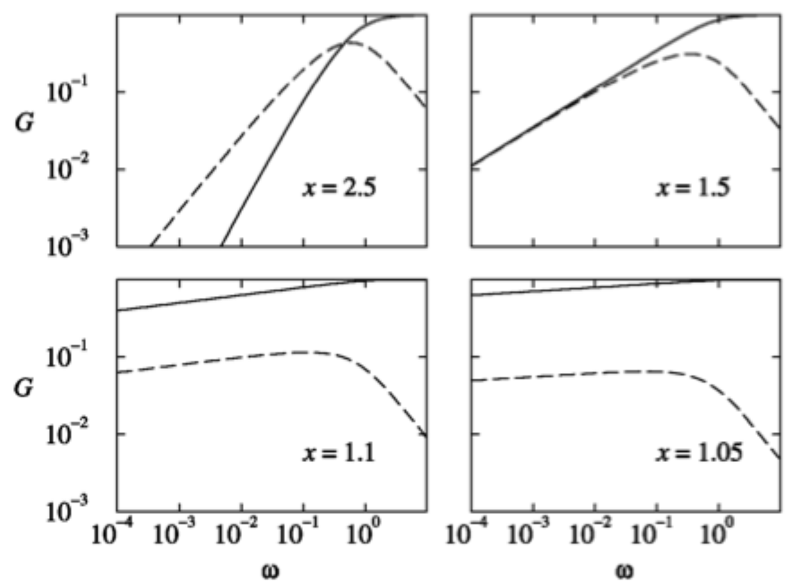


FIG. 1. Linear moduli G' (solid line) and G'' (dashed) vs frequency ω at various noise temperatures.

How To Actually Measure Things

TA AR-G2 (2 of them)

- Stress-controlled
- Most versatile set of geometries
- Standard solvent trap

...talk to Lolo.

Anton-Paar MCR 501

- Stress-controlled (claim also strain-controlled)
- Array of geometries
- High-performance solvent trap

...talk to Joris.

TA ARES G2

- True strain-control
- Array of geometries
- Standard solvent trap (high-performance maybe coming soon)

...talk to Sujit/Jim.

Strain versus Stress Controlled

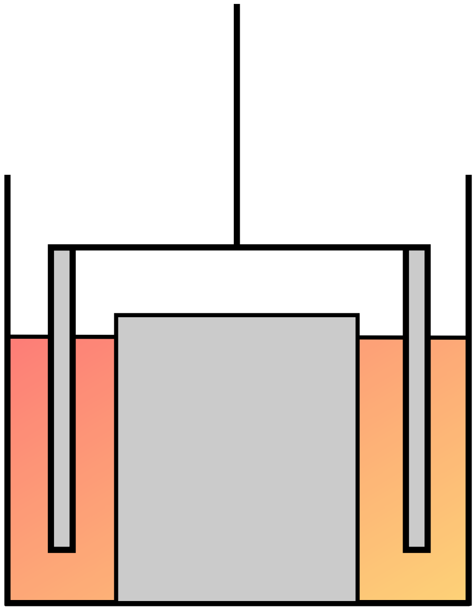
Strain Controlled

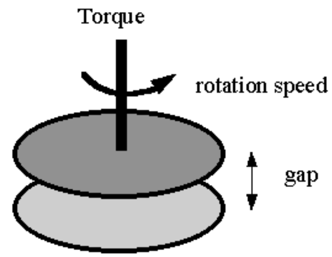
- Good for oscillatory measurements
- Good for fixed shear rate measurements
- Motors are really good - good for weak materials
- Very sensitive torque transducers
- Easier to damage

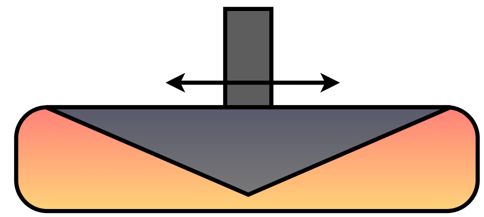
Stress Controlled

- OK for oscillatory measurements
- Good for fixed stress measurements
- Good for creep measurements
- Drag cup motors often cannot do low stresses well
- EC motors often have more inertial effects
- Often assumes certain type of material response

How To Actually Measure Things







Single/Double-Gap Couette

- Large volumes (~9 mL)
- Very sensitive
- Homogeneous strain field

Parallel Plates

- Small volumes (~0.1-3 mL)
- Inhomogeneous strain field

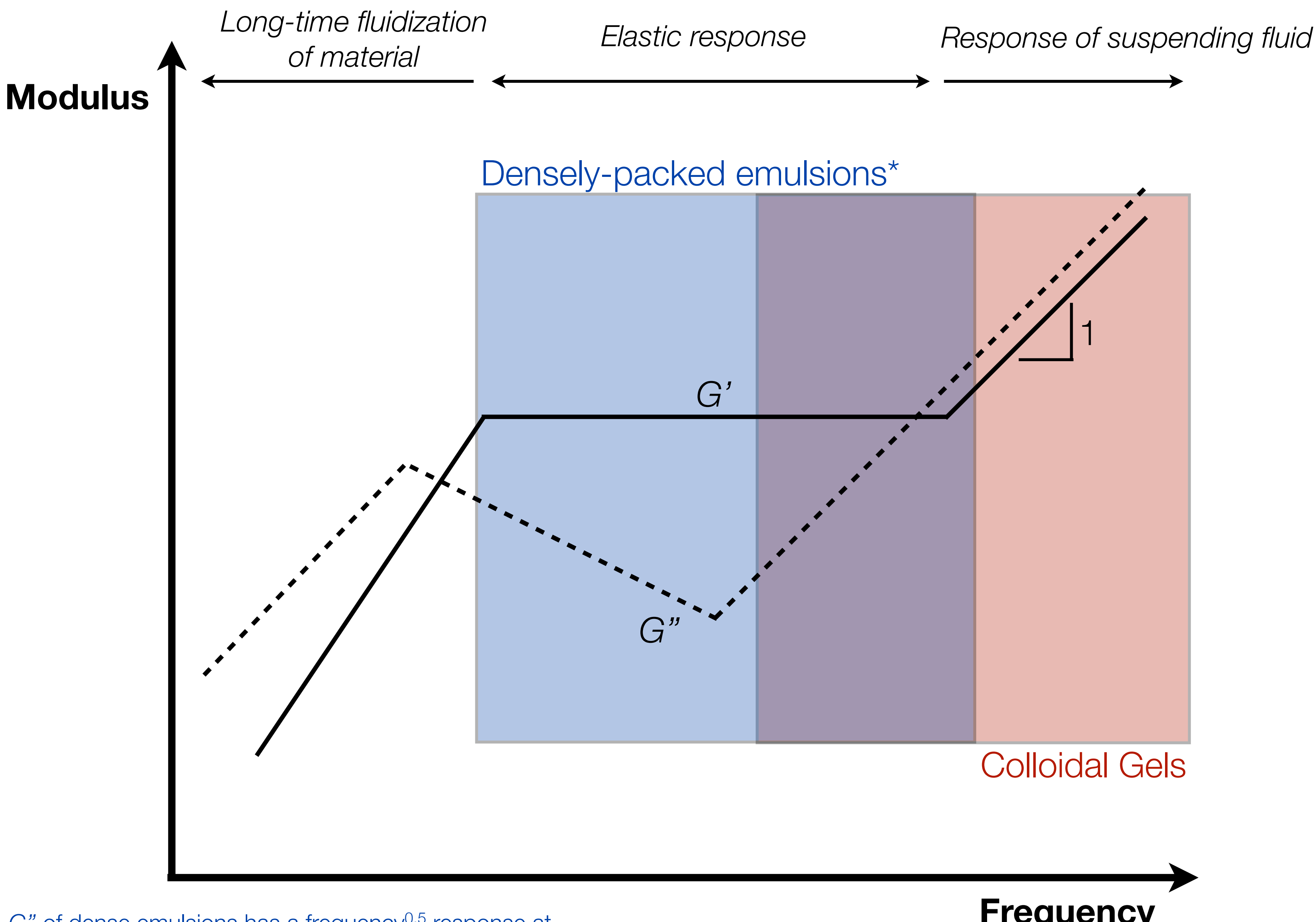
Cone-Plate

- Small volumes (~0.1's mL)
- Homogeneous strain field

How To Actually Measure Things

- Different types of measurement:
  - Frequency sweep (characteristic timescales, solid-like plateaus, gel scaling, ...)
  - Strain sweep (yielding behavior, linear regime, ...)
  - Flow curves (yield stress, viscosity, shear-banding, ...)
  - Stress-relaxation (characteristic timescales)
  - SRFS (relaxation spectrum)

Example: Colloidal Suspensions



*Note: *G"* of dense emulsions has a frequency$^{0.5}$ response at high frequencies, not discussed here

One Example: Densely-Packed Emulsions (Mason)

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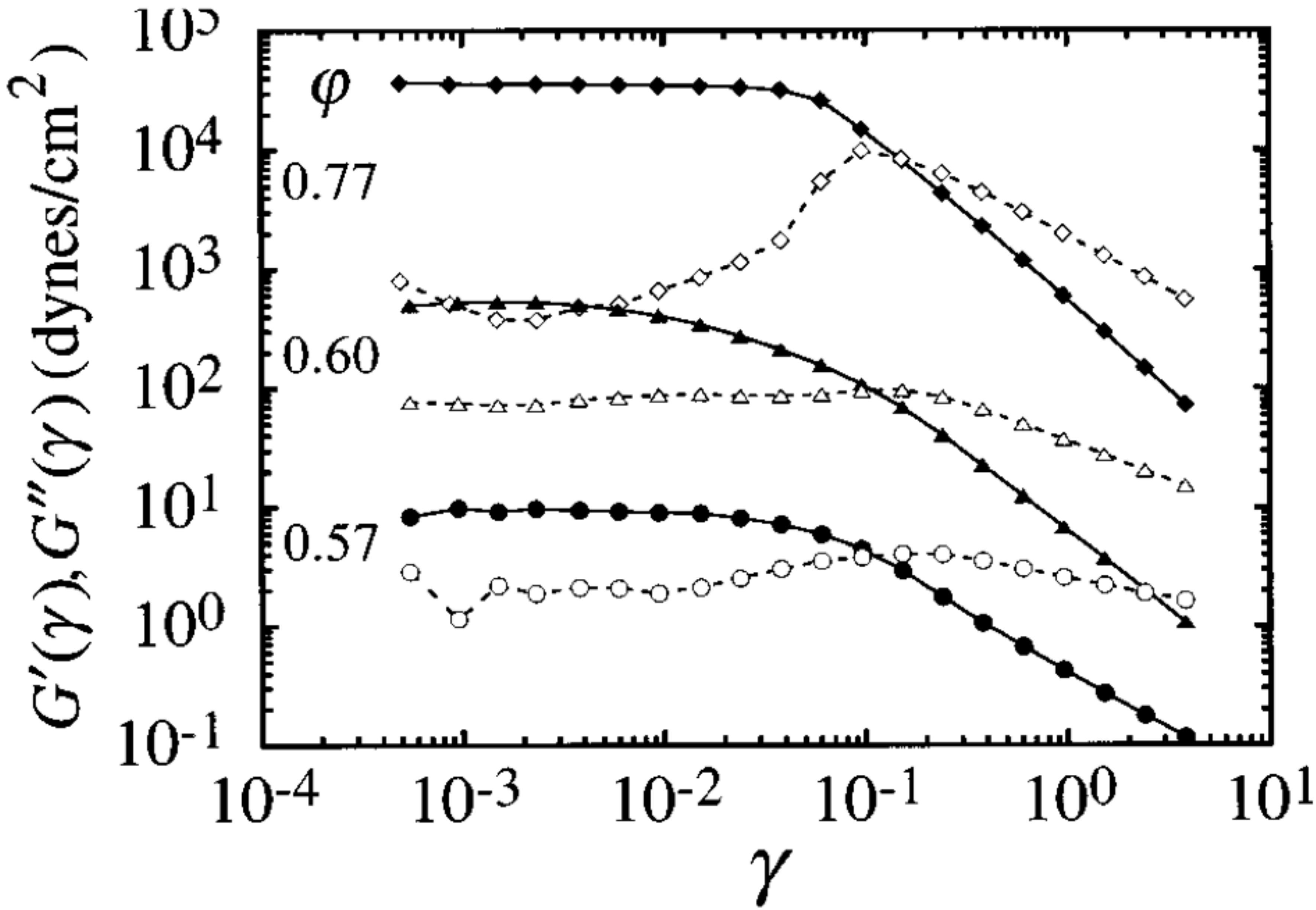

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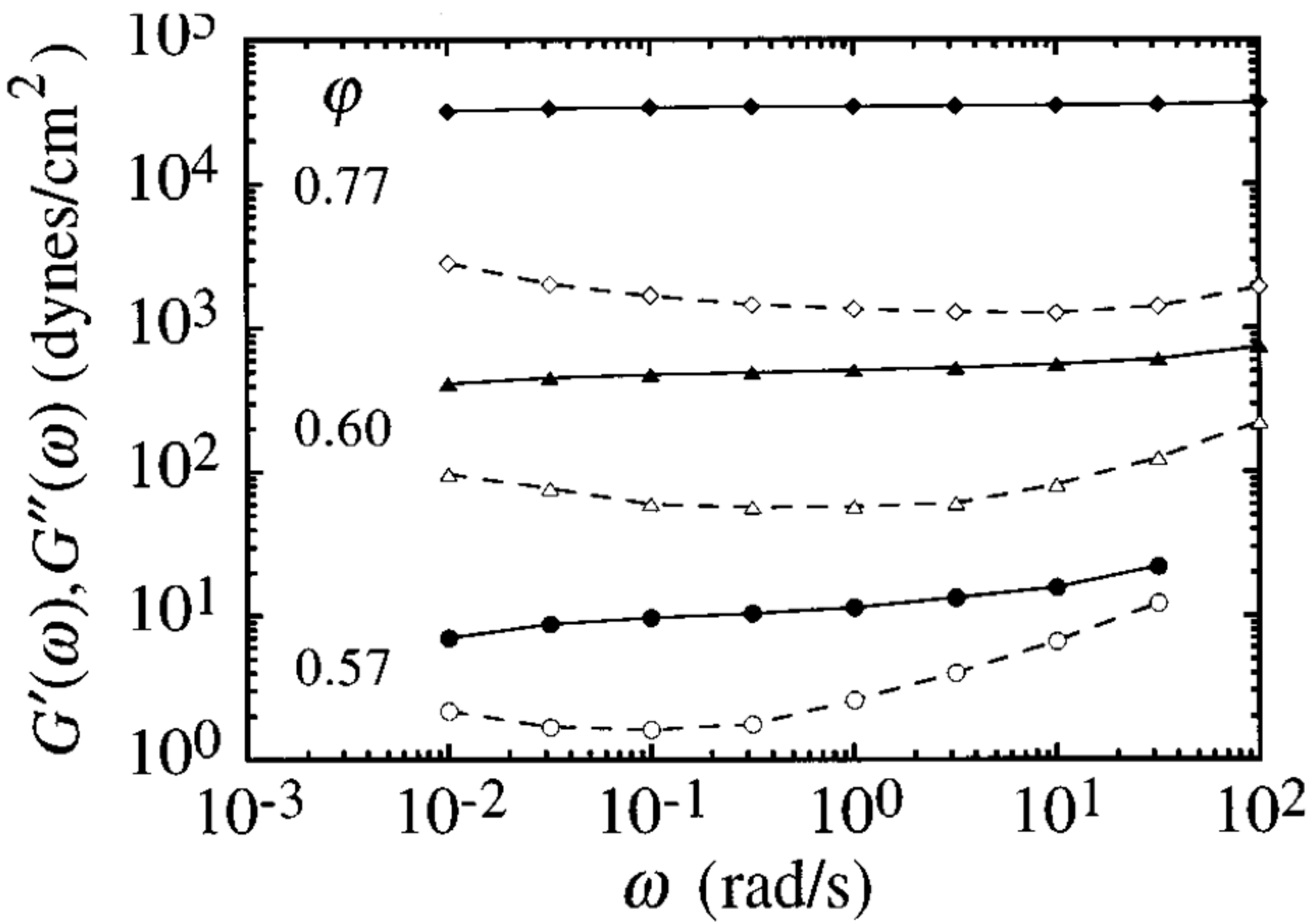

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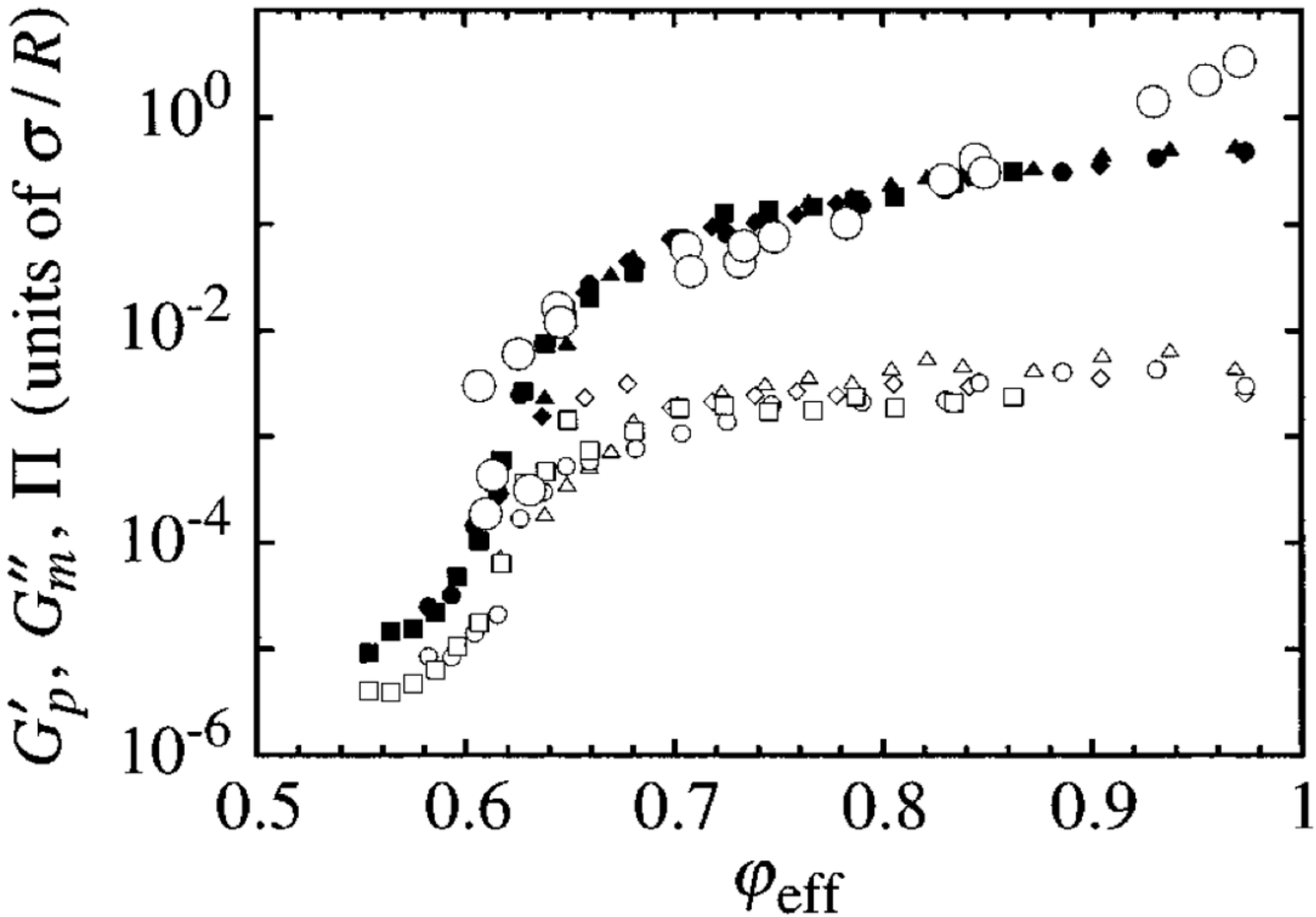
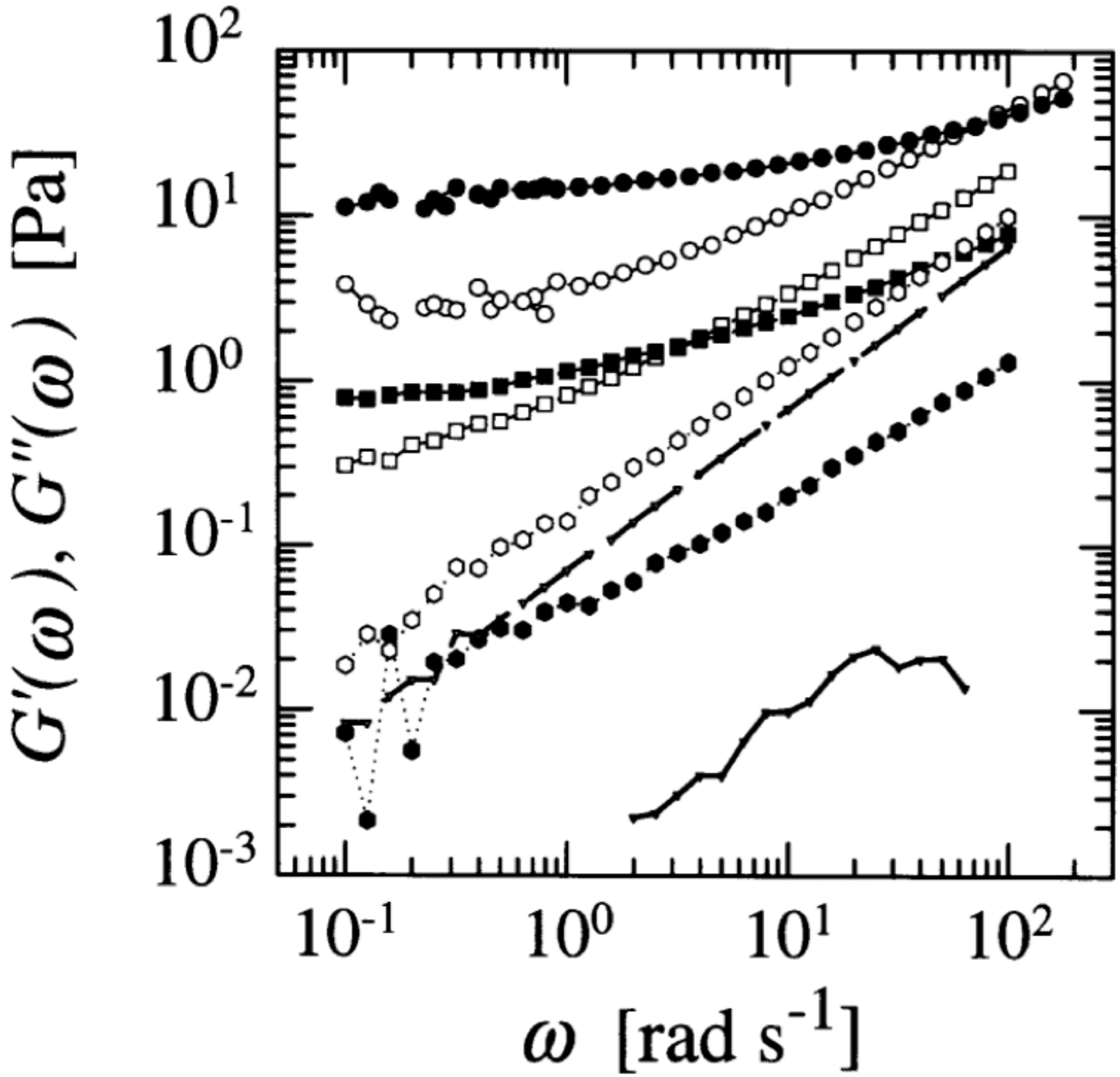


Another Example: Colloidal Gels (Trappe)



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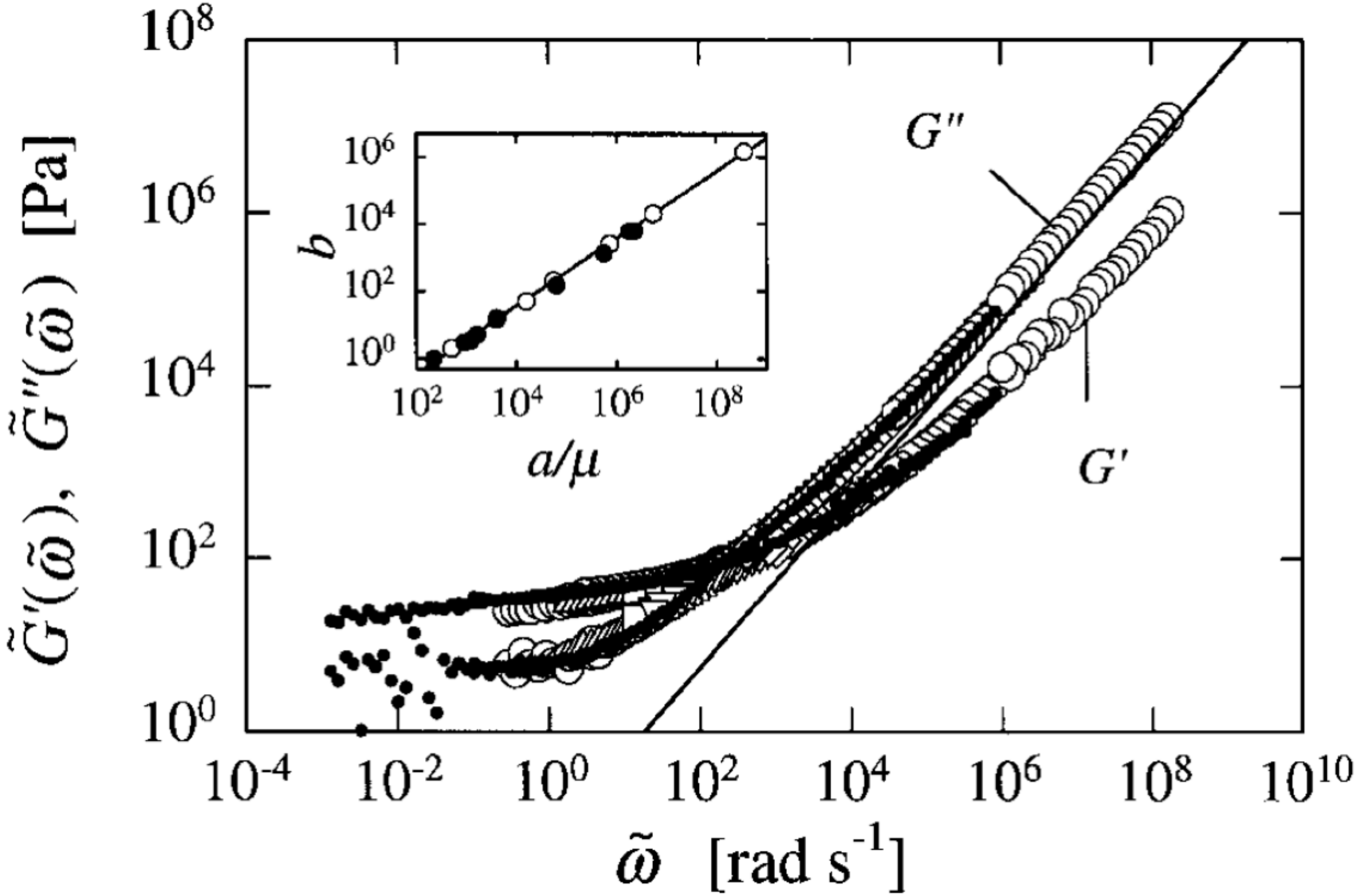

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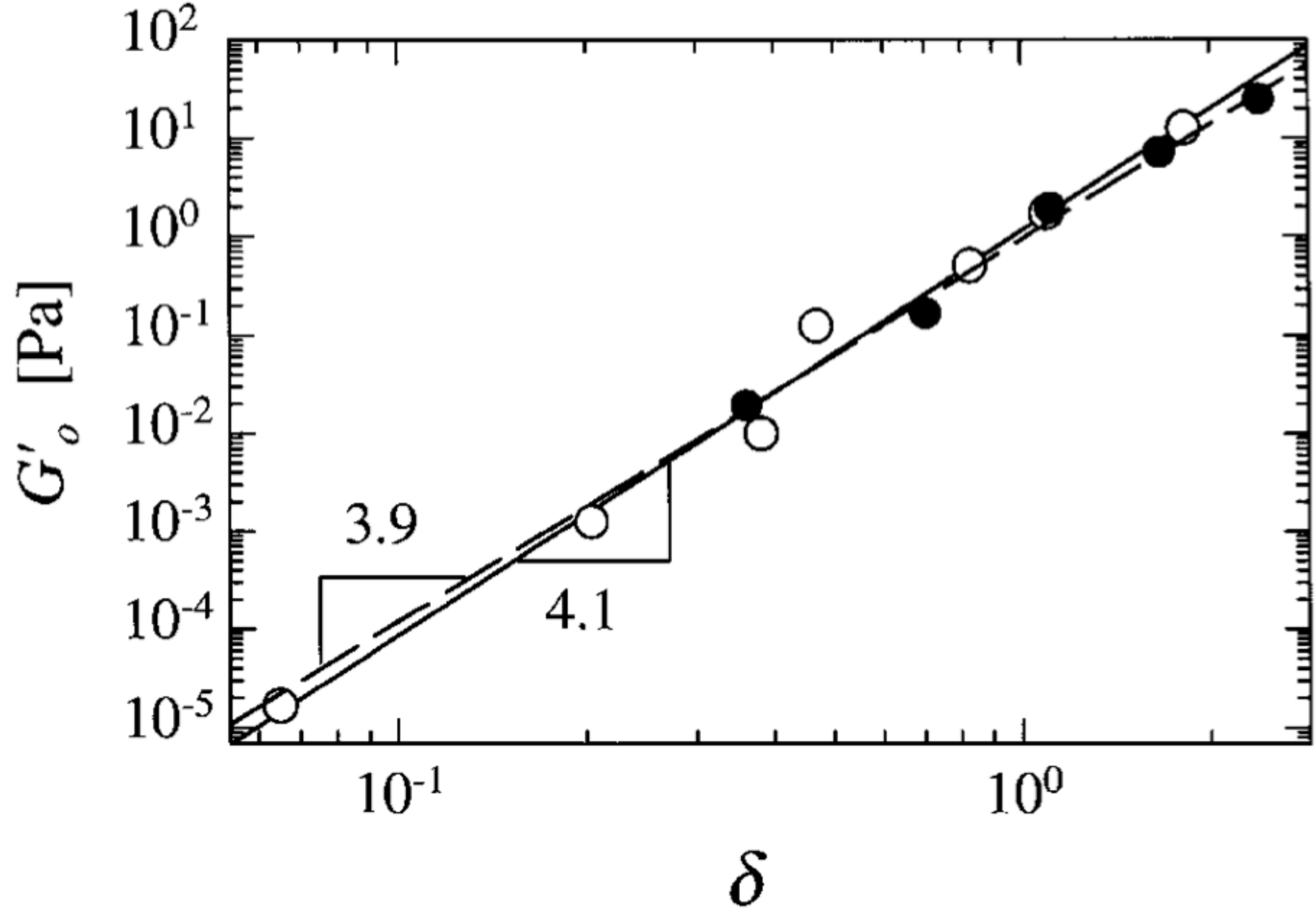


Strain Rate Frequency Superposition

- Structural relaxation of a material happens at a characteristic timescale τ_0 ; this is typically way longer than experimental timescales

- Shearing at high enough strain rate can make a material structurally relax; this is like speeding up the structural relaxation to a new timescale τ

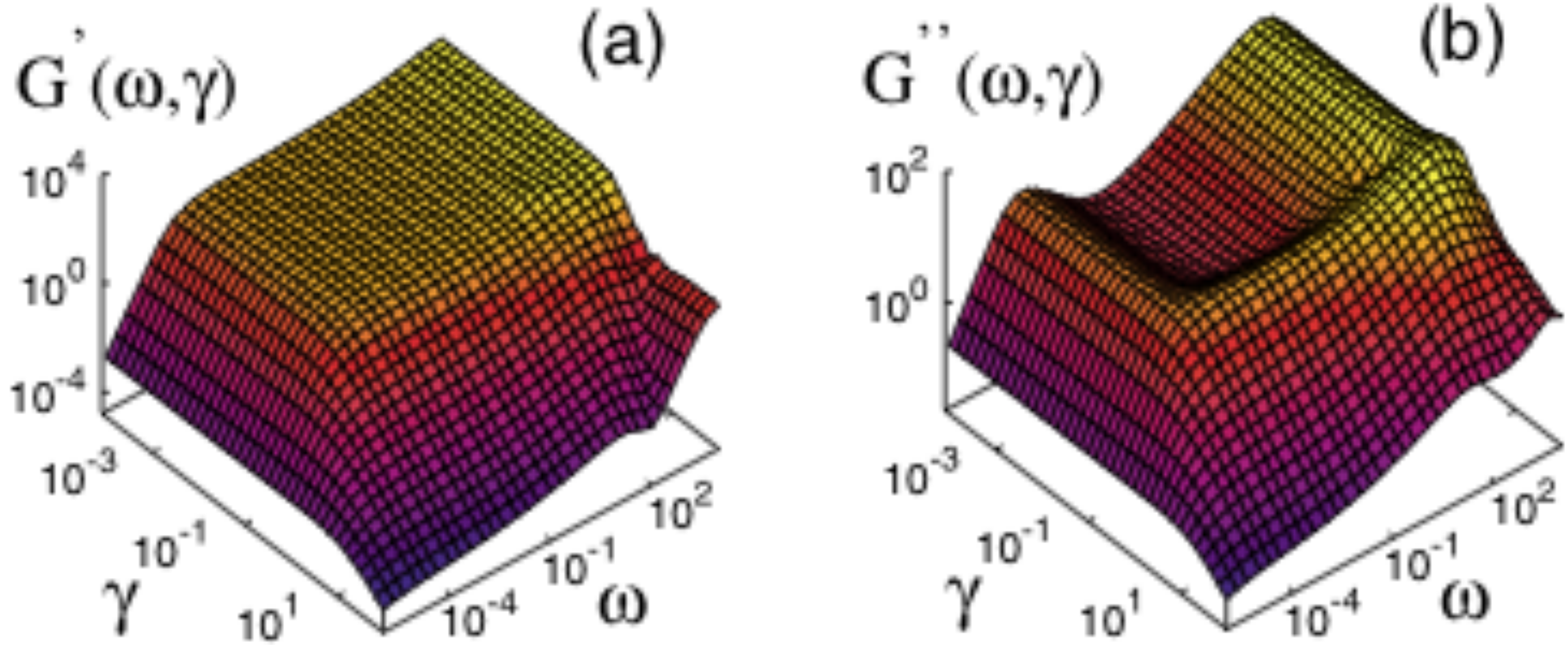
- Phenomenological expression: $1/\tau \approx 1/\tau_0 + K\dot{\gamma}_0^{\nu}$

- Instead of holding strain constant or frequency constant, hold strain rate constant

$$\gamma(t) = \gamma_0 \ \sin\omega t, \ \ \dot{\gamma}(t) = \boxed{\gamma_0\omega} \cos\omega t$$

$$\sigma(t) = \sigma_0(\omega) \ \sin[\omega t + \delta(\omega)]$$

Strain Rate Frequency Superposition



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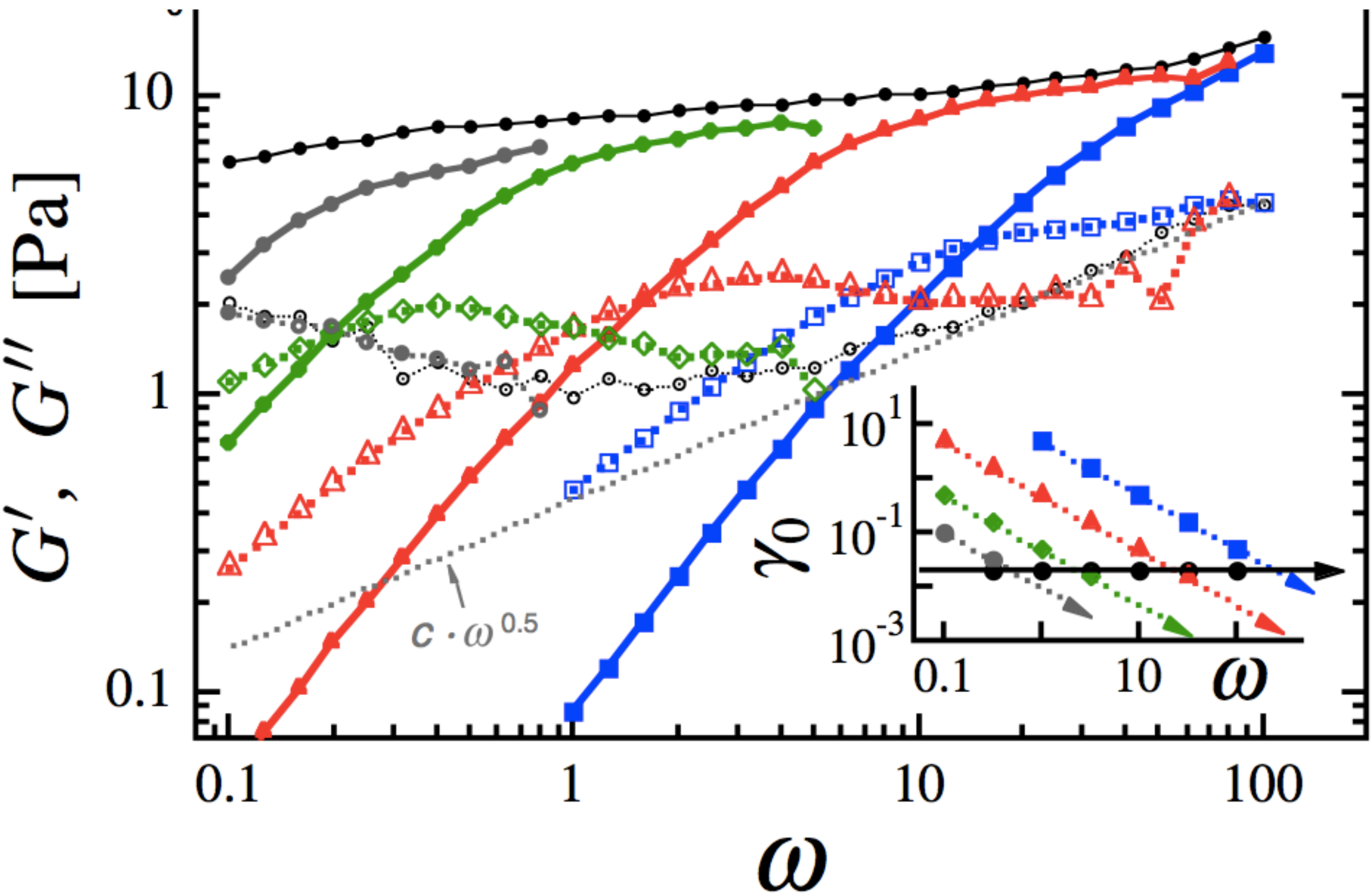

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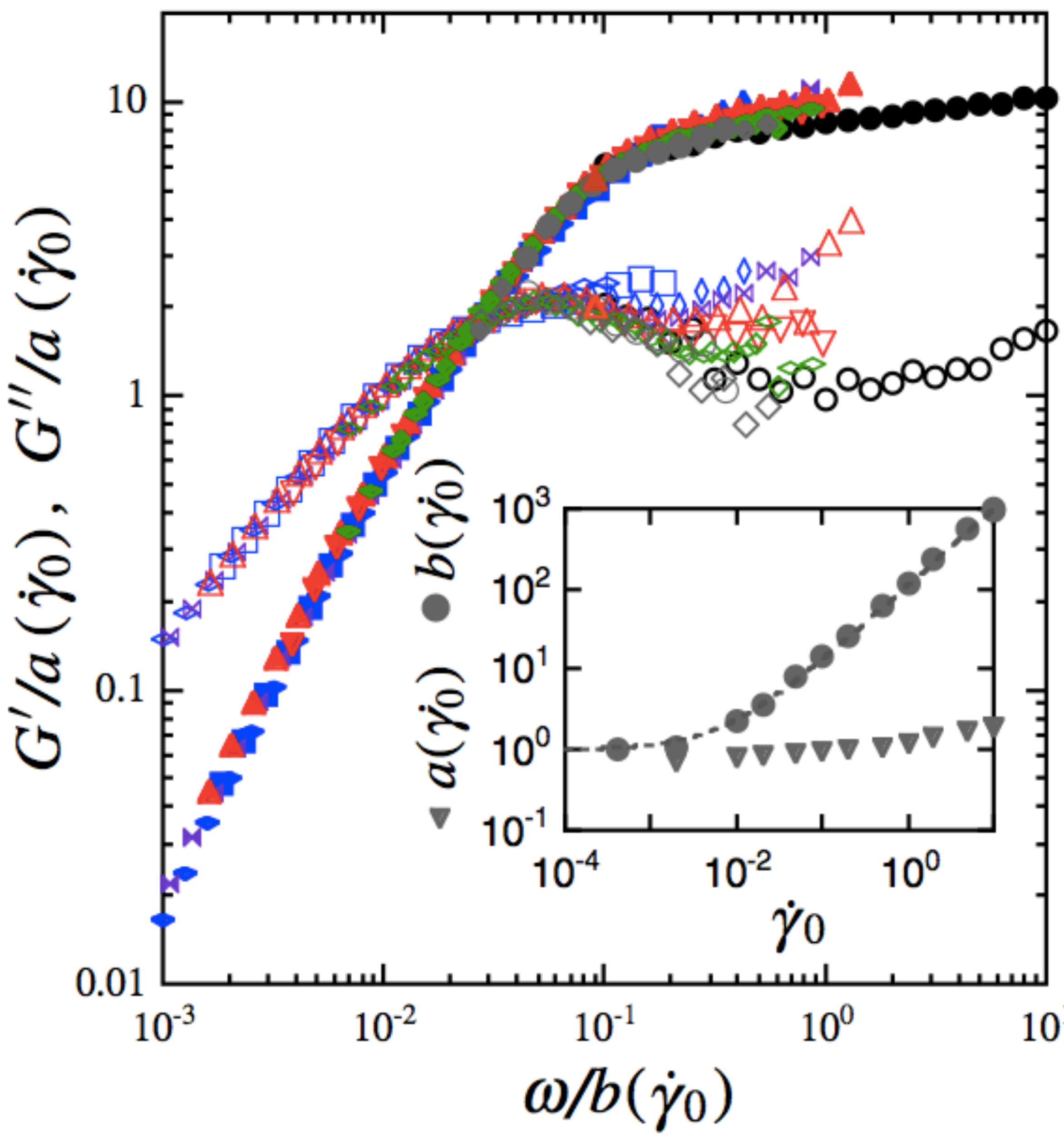

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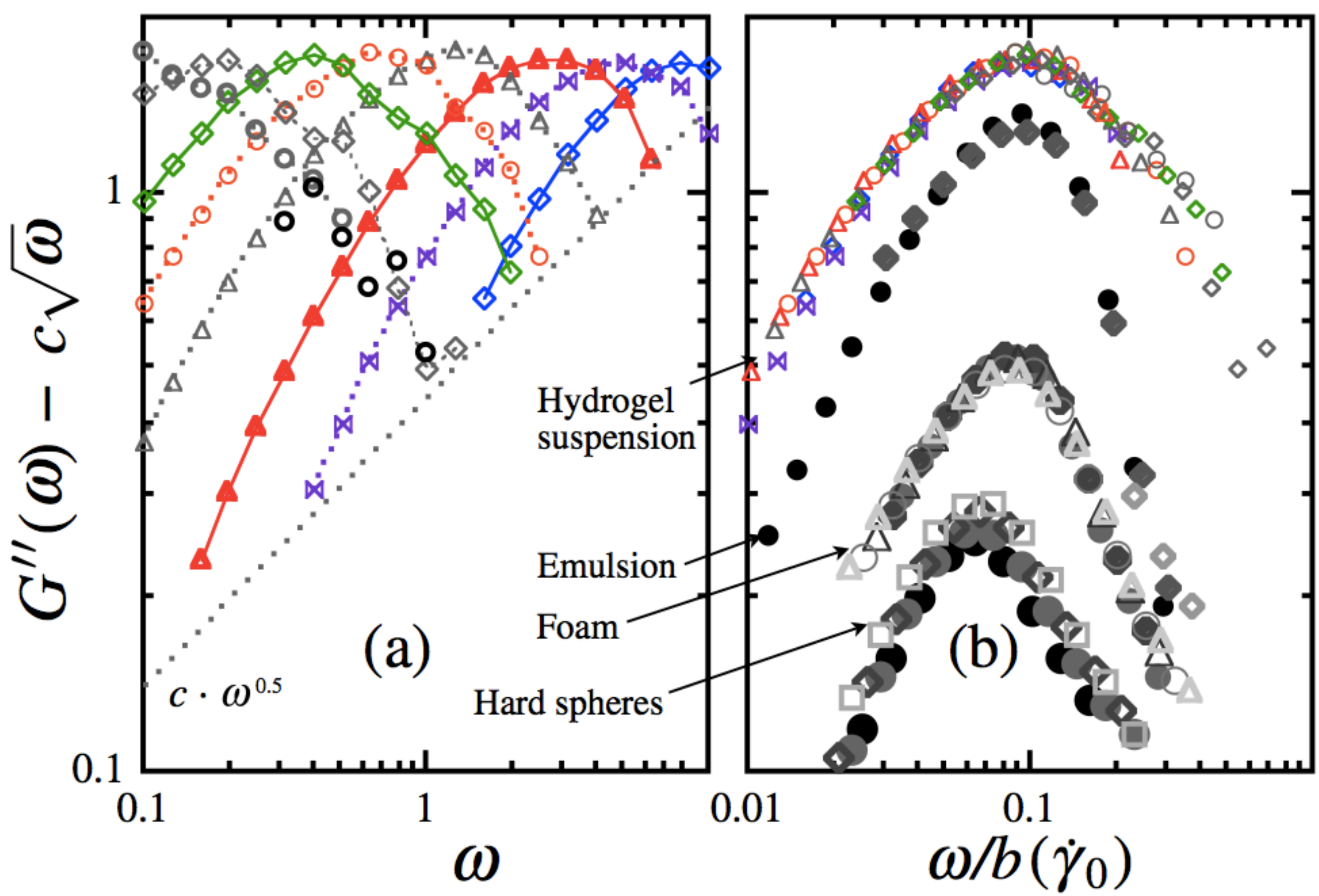

Other Stuff Of Current Interest

- Shear-thickening: role of hydrodynamics, etc.
- Shear-banding: why do some suspensions shear-band?
- Yield stress: do soft materials have a “true” yield stress, or does this just depend on measurement time?
- Pre-stress measurements: for biopolymer networks that stress stiffen, oscillating about large stress value gives valuable information
- LAOS: shapes of waveforms at large amplitudes can yield interesting information

Questions?