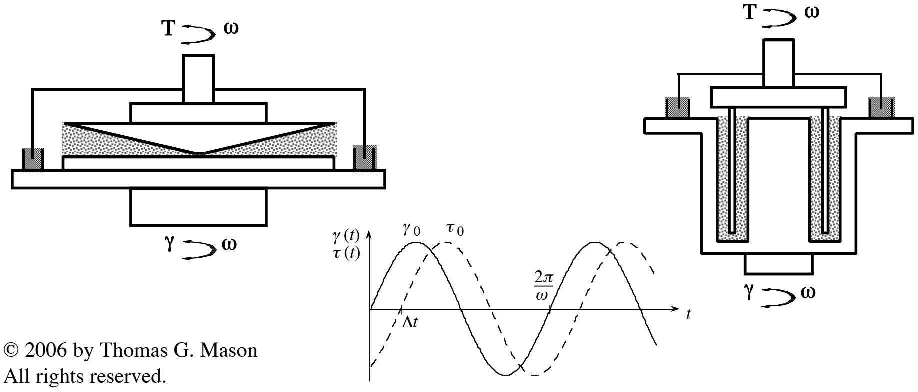
Rheology of Soft Materials

Thomas G. Mason

Department of Chemistry and Biochemistry
Department of Physics and Astronomy
California NanoSystems Institute



Rheology

Study of deformation and flow of materials

Elastic Solids   Viscous Liquids

And everything in between… “Soft Materials”

Emulsions, Polymers, Glassy Materials

Thermally agitated colloidal structures (1 nm - 1 μm)

Describe mechanical constitutive relationships: material response

Focus on isotropic disordered materials

(Math is more complicated for partially or fully ordered materials)

Rheology - Outline

Basic Definitions: Stress and Strain

Common Shear Flows and Simple Examples

Equations of Continuity and Momentum

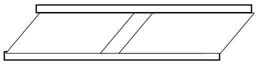
Linear Shear Viscoelastic Rheology

Introduction to Non-linear Rheology

Macroscopic Mechanical Shear Rheometry

Example of a Soft Glassy Material: Concentrated Emulsions

Affine and Non-Affine Shear Deformations



Affine	Non-Affine
All points in the material deform uniformly	Different points in the material deform differently
"Homogeneous flow"	Apparent macroscopic strain is not the local strain everywhere

Local non-affine motion of constituents in soft materials can have an important impact on their rheology

For simplicity, we focus on affine rheology

Incompressible Soft Materials

Isothermal Compressibility

$$\beta = -\frac{1}{V}\frac{\partial V}{\partial p}\bigg|_T$$

Important for gases, but much smaller for condensed matter

Mass Conservation of Fluid Flow: Equation of Continuity

$$\frac{\partial \rho}{\partial t} = -(\vec{\nabla} \cdot \rho \vec{v})$$

ρ is density
v is velocity

Constant density implies: $\boxed{(\vec{\nabla} \cdot \vec{v}) = 0 \quad \text{(Incompressible)}}$

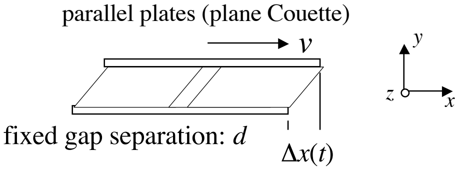
Good approximation for most complex fluids, but <u>not</u> for foams

---

Example of Shear Flow

Shear Deformations: Force is applied along surface, not normal to it

Unidirectional Simple Shear Flow

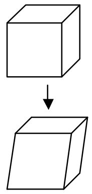


Shear Strain:
$\gamma = \Delta x / d$

Shear Strain Rate:
$\dot{\gamma} = v(t)/d = \Delta\dot{x}(t)/d$

Strain Tensor

$$\bar{\bar{\gamma}} = \begin{bmatrix} 0 & \gamma & 0 \\ \gamma & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$$



Rate of Strain Tensor

$$\dot{\bar{\bar{\gamma}}} = \begin{bmatrix} 0 & \dot{\gamma} & 0 \\ \dot{\gamma} & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} = [\vec{\nabla}\vec{v} + (\vec{\nabla}\vec{v})^{\dagger}]$$

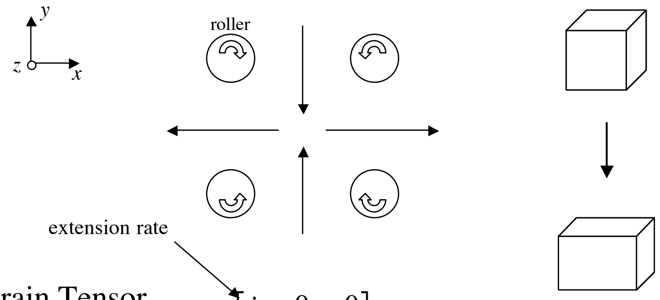
velocity gradient tensor

Convention: x is along shear direction (1-direction)
y is normal to shearing surface (2-direction)
z is tangential to shearing surface (3-direction)

Example of Extensional Flow

Planar Extensional (Elongational) Flow
"Pure Shear Flow"

4 roll mill

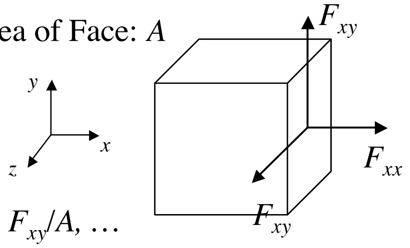


Rate of Strain Tensor

$$\dot{\bar{\bar{\gamma}}} = \begin{bmatrix} \dot{\varepsilon} & 0 & 0 \\ 0 & -\dot{\varepsilon} & 0 \\ 0 & 0 & 0 \end{bmatrix}$$

Applying Shear Stresses and Pressures

Area of Face: A



$\tau_{xy} = F_{xy}/A, \ldots$

Simple isotropic pressure:

$$\bar{\bar{p}} = \begin{bmatrix} -p & 0 & 0 \\ 0 & -p & 0 \\ 0 & 0 & -p \end{bmatrix} = -p\bar{\bar{\delta}}$$

Shear Stress Tensor

$$\bar{\bar{\tau}} = \begin{bmatrix} 0 & \tau_{xy} & \tau_{xz} \\ \tau_{yx} & 0 & \tau_{yz} \\ \tau_{zx} & \tau_{zy} & 0 \end{bmatrix}$$

Total Stress Tensor

$$\bar{\bar{\sigma}} = \bar{\bar{\tau}} - p\bar{\bar{\delta}} = \begin{bmatrix} -p & \tau_{xy} & \tau_{xz} \\ \tau_{yx} & -p & \tau_{yz} \\ \tau_{zx} & \tau_{zy} & -p \end{bmatrix}$$

Total description including shear-free flows is more complex

(we've neglected normal stresses τ_{xx}, τ_{yy}, τ_{zz} for now)

Momentum Conservation: Navier-Stokes Equation

Newton's Law for Fluid Elements

Form for Simple Shear Flow

$$\frac{\partial}{\partial t}\rho\vec{v} = -[\vec{\nabla}\cdot\rho\vec{v}\vec{v}] + [\vec{\nabla}\cdot\overline{\overline{\sigma}}] + \rho\vec{g}$$

Assume viscous dissipation: $\overline{\overline{\sigma}} = -p\overline{\overline{\delta}} + \eta\dot{\overline{\overline{\gamma}}}$ η is the viscosity

neglect dilational viscosity

A Very Simple Rheological Equation: Navier-Stokes Equation

$$\boxed{\rho\frac{D}{Dt}\vec{v} = -\vec{\nabla}p + \eta\vec{\nabla}^2\vec{v} + \rho\vec{g}}$$

where $\frac{D}{Dt} = \frac{\partial}{\partial t} + \vec{v}\cdot\vec{\nabla}$ is the convective or substantial derivative operator

(derivative operator in reference frame of moving liquid)

We'll simplify to scalar equations mostly from here on out

Simple Viscous Liquids and Elastic Solids

Viscous Liquid

Viscosity resists motion proportional to rate: $\tau_v = -\eta\dot{\gamma}$

"Newtonian Liquid"

Elastic Solid

Elasticity resists motion proportional to strain: $\tau_e = -G\gamma$

"Hookean Solid"

Both η and G are intensive thermodynamic properties

Thermodynamic Definition: Shear Modulus G

Helmholtz Free Energy

$$F = F_0 + VG\frac{\gamma^2}{2} + O[\gamma^4]$$

Intensive form of Hooke's Law: differentiate once w.r.t. strain

$$\tau = -\frac{1}{V}\frac{\partial F}{\partial \gamma}\bigg|_{\gamma=0} = -G\gamma$$

$\gamma = 0$ is used to eliminate any nonlinear dependence

Elastic Shear Modulus: differentiate again

$$G = \frac{1}{V}\frac{\partial^2 F}{\partial \gamma^2}\bigg|_{\gamma=0} = \frac{\phi}{V_\mathrm{d}}\frac{\partial^2 F}{\partial \gamma^2}\bigg|_{\gamma=0}$$

related to curvature
of energy well

Linear Viscoelastic Response of Soft Materials

Soft materials: colloidal components dispersed in a viscous liquid
Examples: polymer chains, clay platelets, emulsion droplets…

Strain response of material is dependent on strength of interactions between components (e.g. polymer chains, clay platelets, droplets) and relaxation time scales of microstructure

Response for small strains is neither perfectly viscous nor elastic

Mechanical response is called "viscoelastic"

Linear Shear Viscoelastic Rheology

Study of small (near-equilibrium) deformation response of materials

Key Idea
There is only one real function of one real variable (e.g. time t)
that describes the relaxation of shear stress

Stress Relaxation Modulus: $G_r(t)$

There are <u>many equivalent ways</u> of representing the information contained in this one real function $G_r(t)$

Preference for a particular representation is based on expt. method

This can be very confusing to people new to the field

Stress Response to a Step Strain

Step the strain: $\gamma(t) = \gamma_0\, u(t)$

Measure Shear Stress: $\tau(t)$

Strain:
$\gamma(t) = \gamma_0 << 1$

Define a function, the <u>Stress Relaxation Modulus</u> $G_r(t)$:

$$G_r(t) \equiv \frac{\tau(t)}{\gamma_0}$$

This one function contains all of the information about the equilibrium (linear) stress-strain response of the soft material

Simple viscous liquid: $G_r(t) = \eta\, \delta(t)$
Simple elastic solid: $G_r(t) = G\, u(t)$

Strain Response to a Step Stress

Step the stress: $\tau = \tau_0\, u(t)$

Measure Strain: $\gamma(t)$

Define an Equivalent Function, the Creep Compliance, $J(t)$:

$$J(t) = \gamma(t)/\tau_0$$

In principle, if measured over a large enough dynamic range in J and t, we can perform mathematical manipulations to determine $J(t)$ from $G_r(t)$.

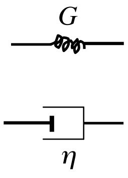
This is cumbersome and is usually done numerically

Simple viscous liquid:	$J(t) = t/\eta$
Simple elastic solid:	$J(t) = (1/G)\, u(t)$

Modeling Viscoelastic Materials

Spring and Dashpot Mechanical Models Are Useful
For Schematically Representing Relaxation Modes in Soft Materials

Hookean Spring	$\tau(t) = -G\,\gamma(t)$
Newtonian Dashpot	$\tau(t) = -\eta\ \dot{\gamma}(t)$



Maxwell combined the ideas behind these equations:

$$\tau + \frac{\eta}{G}\dot{\tau} = -\eta\dot{\gamma}$$

This is one of the first viscoelastic equations

General Linear Viscoelastic Model

Use as many springs and dashpots in series or in parallel
to model the response function of the material

A solution of the set of coupled differential equations
and crossover from discrete to continuum notation yields:

$$\tau(t) = -\int_{-\infty}^{t} G_r(t-t')\dot{\gamma}(t')dt'$$

Check: step strain ->
delta function strain rate

The shear stress is related to the convolution integral of the
stress relaxation modulus
with the strain rate history

You have to know the history of applied shear!

Equivalently:

$$\tau(t) = \int_{-\infty}^{t} M(t-t')\gamma(t')dt'$$

Memory function:

$$M(t-t') = \frac{\partial G_r(t-t')}{\partial t'}$$

Frequency Domain Representation: Complex Viscosity

What is the Unilateral Fourier Transform of $G_r(t)$?

Answer: the complex frequency-dependent viscosity

$$\eta^*(\omega) = \int_0^{\infty} G_r(t')\exp(-i\omega t')dt'$$

$$\eta^*(\omega) = \int_0^{\infty} G_r(t')[\cos(\omega t') - i\sin(\omega t')]dt'$$

$$\eta^*(\omega) = [\int_0^{\infty} G_r(t')\cos(\omega t')dt'] - i[\int_0^{\infty} G_r(t')\sin(\omega t')dt']$$

in-phase w.r.t. strain rate 90° out-of-phase w.r.t. strain rate

Complex Viscosity: $\eta^*(\omega) = \eta'(\omega) - i\eta''(\omega)$

$$\eta'(\omega) = \int_0^{\infty} G_r(t')\cos(\omega t')dt'$$

$$\eta''(\omega) = \int_0^{\infty} G_r(t')\sin(\omega t')dt'$$

Frequency Domain: Complex Shear Modulus

Another equivalent ω-domain representation of $G_r(t)$

Complex Modulus: $G^*(\omega) = \underset{\uparrow}{i\omega}\eta^*(\omega)$

pick up from time derivative

$$G^*(\omega) = G'(\omega) + iG''(\omega)$$

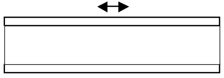
Real Part:	$G'(\omega)$	"Storage Modulus"
Imaginary Part:	$G''(\omega)$	"Loss Modulus"

Complex "phasor notation" is mathematically convenient
But in reality, we measure real functions of real variables

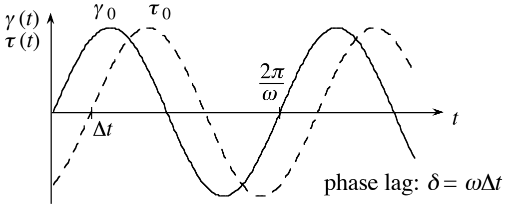
Forced Parallel Plate Oscillatory Viscometry

Controlled Strain Oscillations

$$\gamma(t) = \gamma_0 \sin(\omega t)$$
$$\dot{\gamma}(t) = \dot{\gamma}_0 \cos(\omega t)$$



Measure: Stress $\tau(t)$



phase lag: $\delta = \omega\Delta t$

Keep γ_0 small enough that the stress response is also sinusoidal

Measured Stress: $\tau(t) = \tau_0(\omega)\ \sin[\omega t + \ \delta(\omega)]$

$$\tau(t) = \left[\frac{\tau_0(\omega)}{\gamma_0}\cos\delta(\omega)\right]\gamma_0 \sin\omega t + \left[\frac{\tau_0(\omega)}{\gamma_0}\sin\delta(\omega)\right]\gamma_0 \cos\omega t$$

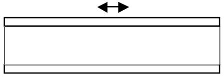
In-phase w.r.t. strain 90° out-of-phase w.r.t. strain

$$G'(\omega) = \frac{\tau_0(\omega)}{\gamma_0}\cos\delta(\omega) \qquad G''(\omega) = \frac{\tau_0(\omega)}{\gamma_0}\sin\delta(\omega)$$

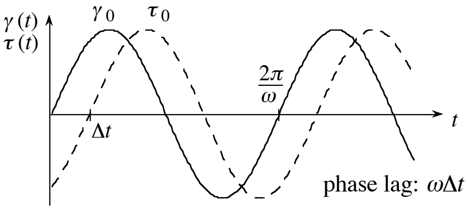
Forced Parallel Plate Oscillatory Viscometry

Controlled Strain Oscillations

$$\gamma(t) = \gamma_0 \sin(\omega t)$$
$$\dot{\gamma}(t) = \dot{\gamma}_0 \cos(\omega t)$$



Measure: Stress $\tau(t)$



$$\tau(t) = -\int_{-\infty}^{t} G_r(t-t')\dot{\gamma}(t')dt' = -\int_{-\infty}^{t} G_r(t-t')\dot{\gamma}_0 \cos(\omega t')dt'$$

$$\tau(t) = -\dot{\gamma}_0 \int_0^{\infty} G_r(s)\cos[\omega(t-s)]ds \qquad s = t - t'$$

$$\tau(t) = -[\int_0^{\infty} G_r(s)\cos(\omega s)ds]\dot{\gamma}_0 \cos(\omega t) - [\int_0^{\infty} G_r(s)\sin(\omega s)ds]\dot{\gamma}_0 \sin(\omega t)$$

In-phase w.r.t strain: $G'(\omega) = \omega\eta''(\omega)$

90° out-of-phase w.r.t strain: $G''(\omega) = \omega\eta'(\omega)$

Storage & Loss Moduli are Not Independent Functions

The complex function *G** consists of two real functions *G'* and *G''*

$$G^*(\omega) = G'(\omega) + iG''(\omega)$$

But both of these are derived from only one real function $G_r(t)$

$$G^*(\omega) = i\omega\int_0^{\infty} G_r(t')\exp(-i\omega t')dt'$$

So, *G'* and *G''* express the same information about stress relaxation

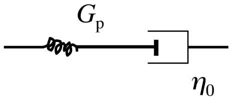
If either *G'* and *G''* are known over a large enough frequency range the other function can be determined by the Kramers-Kronig Relations

$$G'(\omega) = \frac{2\omega}{\pi}\int_0^{\infty} d\hat{\omega}\frac{\omega}{\hat{\omega}}\frac{G''(\hat{\omega})}{\omega^2 - \hat{\omega}^2}$$

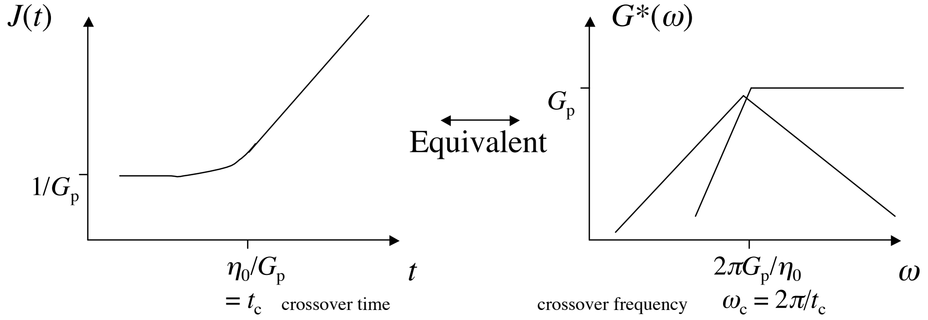
$$G''(\omega) - \eta'_{\infty}\omega = \frac{2\omega}{\pi}\int_0^{\infty} d\hat{\omega}\frac{G'(\hat{\omega})}{\hat{\omega}^2 - \omega^2}$$

Viscoelastic Soft Materials with Low Freq. Relaxation

Maxwell Model: combine high freq elasticity and low freq viscosity
Spring and dashpot in series (simple 1D model)



e.g. ideal polymer
entanglement solution



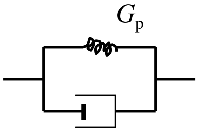
$J(t) = (1/G_p) + t/\eta_0$

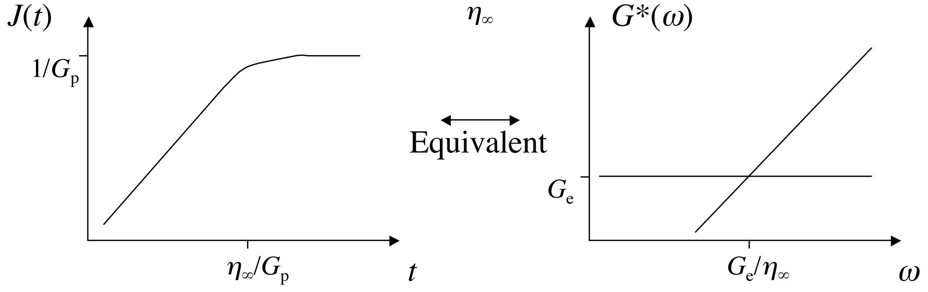
$G'(\omega)$ $\quad$ $G''(\omega)$

$$G^*(\omega) = G_p\{(\omega t_c)^2/[1+(\omega t_c)^2] + i\omega t_c/[1+(\omega t_c)^2]\}$$

Linear Viscoelastic Soft Material with Low Freq. Elasticity

Voigt Model: combine low freq elasticity and high freq viscosity
Spring and dashpot in parallel (simple 1D model)

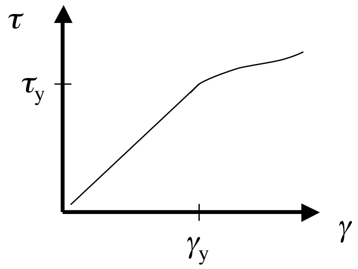




$J(t) = (1/G_p)\,[1-\exp(-G_p t/\eta_\infty)]$ $\qquad$ $G^*(\omega) = G_p + i\omega\eta_\infty$

Brief Introduction to Non-Linear Rheology

Sinusoid in does not give a sinusoid out: Harmonics are seen



Yield stress: τ_y

Yield strain: γ_y

Most Soft Glassy Materials:
$\gamma_y < 0.2$ typically

Shear Thinning: viscosity decreases as strain rate increases

Shear Thickening: viscosity increases as strain rate increases

Strain Hardening: stress increases greater than linear strain

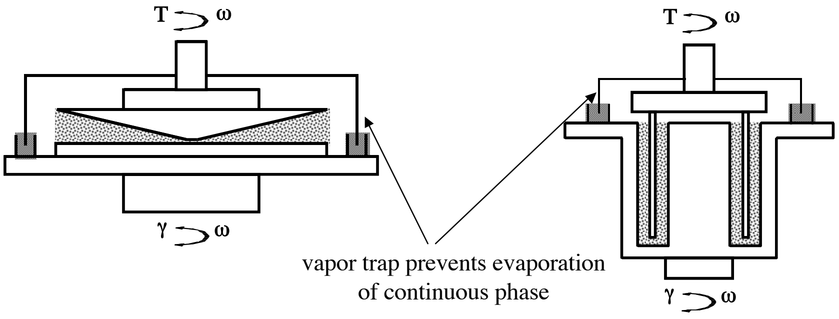
---

Measuring Viscoelastic Response: Mechanical Rheometry

- Controlled Strain Rheometry -
Apply a Strain (Motor) and Measure a Torque (Transducer)
Use Geometry to Convert Torque to Stress

Cone and Plate

Double Wall Couette



vapor trap prevents evaporation
of continuous phase

These are among preferred geometries:
the strain field is homogeneous throughout the gap

Controlled Stress vs Controlled Strain Rheometry

Controlled Strain:

- Good for $G^*(\omega)$ and $G_r(t)$, steady shear
- Best for very weak liquid-like materials
- Motors are excellent
- Torque transducers are very sensitive
- Can be damaged more easily

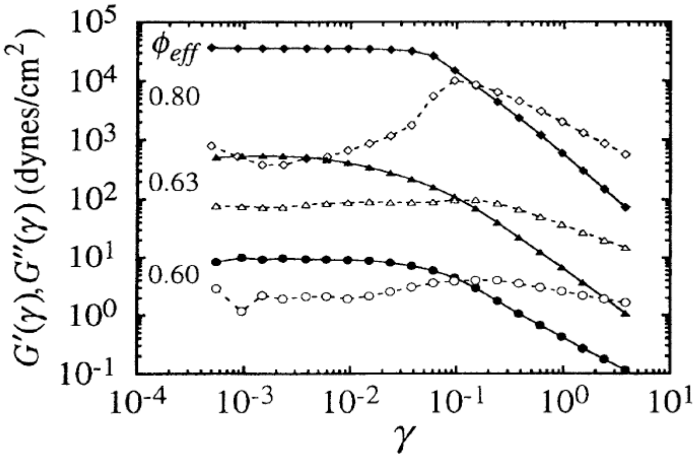
Controlled Stress:

- Good for $J(t)$, OK for $G^*(\omega)$, steady shear
- Bad for weak materials
- Drag cup motors can't produce low stresses
- Feedback strain control is problematic
- Assumes a certain type of material response

Some newer rheometers have both stress and strain control
Get the best of both worlds in principle

An Example: Viscoelasticity of Soft Glassy Emulsions

T.G. Mason & D.A. Weitz *PRL* **75** 2051 (1995)

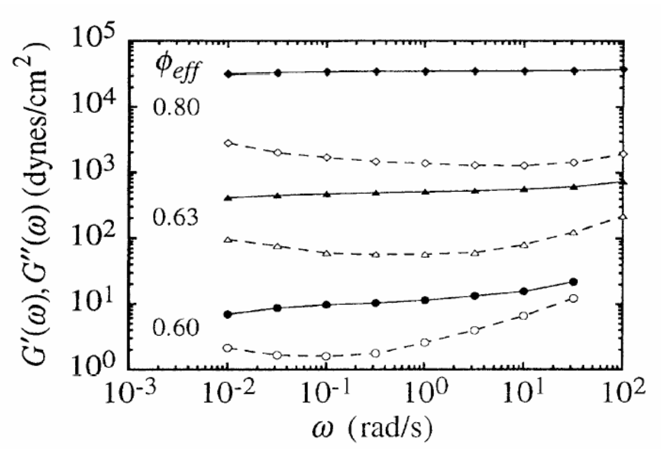


Linear regime at low strain: G' and G'' do not depend on γ

Yield strain is evident: $10^{-2} < \tau_y < 10^{-1}$

An Example: Viscoelasticity of Soft Glassy Emulsions

T.G. Mason & D.A. Weitz *PRL* **75** 2051 (1995)

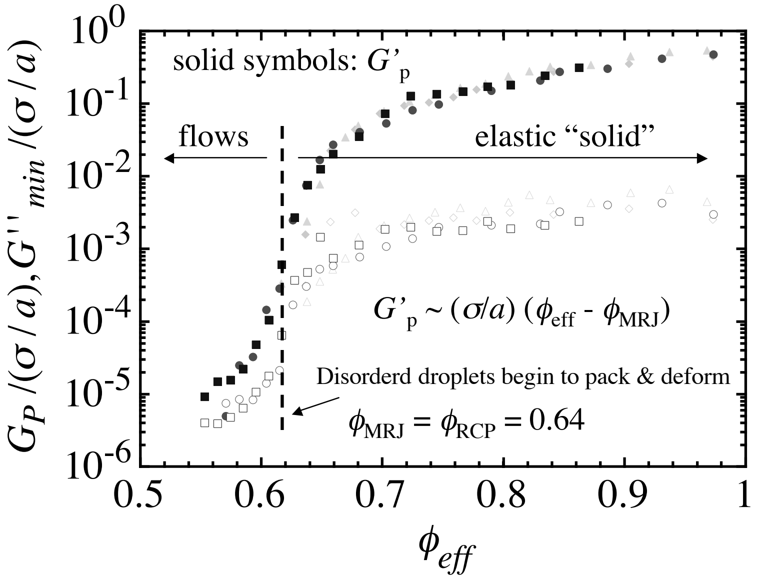


Plateau Storage Modulus over many decades in frequency: G'_p

Viscous Loss Modulus has a shallow minimum: G''_{min}

An Example: Viscoelasticity of Soft Glassy Emulsions

T.G. Mason & D.A. Weitz *PRL* **75** 2051 (1995)



solid symbols: G'_p

$G'_p \sim (\sigma/a)(\phi_{eff} - \phi_{MRJ})$

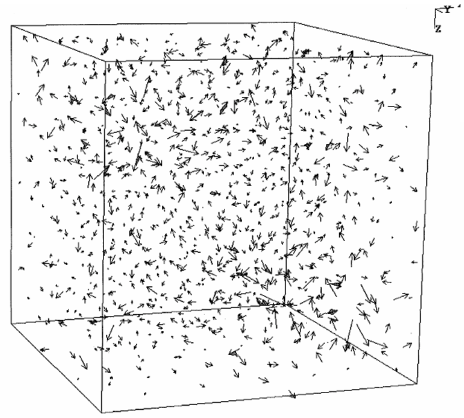
Disorderd droplets begin to pack & deform

$\phi_{MRJ} = \phi_{RCP} = 0.64$

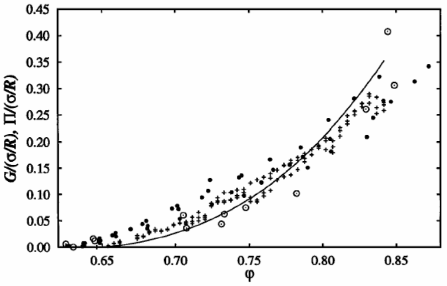
A Model and Simulation: Explains Emulsion Elasticity

M.-D. Lacasse, G. S. Grest, D. Levine, T. G. Mason, and D. A. Weitz, *PRL* **76**, 3448 (1996).

“Jamming” of disordered objects that interact with a repulsive potential



Surface Evolver:
-> Effective spring constant



Non-Affine Local Droplet Motion in Disordered Glassy Soft Materials
Response to Applied Shear is Complex!

Summary: Rheology of Soft Materials

Rheology is a convenient macroscopic measurement of stress-strain response of a micro or nano structured soft material

Stress-strain relationships are related to the structure and interactions of constituents in the soft material: a thermodynamic property

Many equivalent representations exist for linear viscoelasticity

We have only begun to scratch the surface of a very deep field

Describing non-Newtonian fluid dynamics mathematically is still an area of very active research

See reading list for references: Bird, Ferry, Russel, Tabor, Larson, …