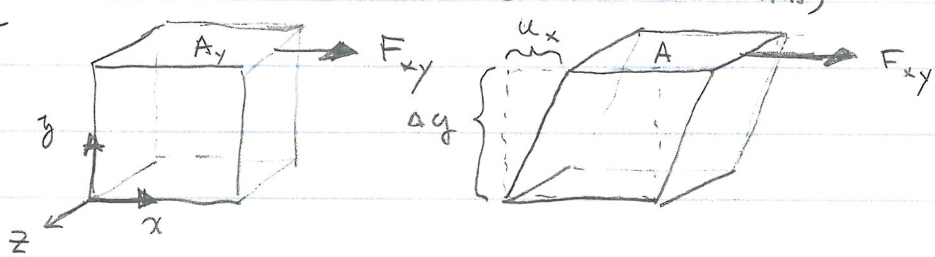
Introduction to Rheology (of complex fluids)

Rheology - the study of flow of materials

2 limiting cases

- Viscous flow of Newtonian fluids (water, simple liquids)
  → η → viscosity
- Elastic distortion of solids → springs
  → G → shear modulus (also a bulk modulus but we are less concerned with this)

Material element (liquid or solid)



Defining viscosity and shear modulus

- Force: F_x disturbs material element
- Strain: $\gamma = \dfrac{u_x}{\Delta y}$ measures distortion
- Stress: force / area [pressure is a normal stress]

$$\text{Shear stress} = \frac{F_{xy}}{A_y} = \sigma_{xy} \quad (\text{Pascal} = N/m^2)$$

- Constitutive eqns

Viscosity

- Liquid $\quad \sigma_{xy} = \eta \dfrac{\partial v_x}{\partial y}$ $\quad t^{-1}$

η -> Pa-s

water	1 mPa-s
honey	10 Pa-s

- Solid $\quad \sigma_{xy} = G \dfrac{\partial u_x}{\partial y}$

shear modulus

G → Pa

diamond	480 GPa
steel	80 GPa
glass	25 GPa
rubber	600 kPa

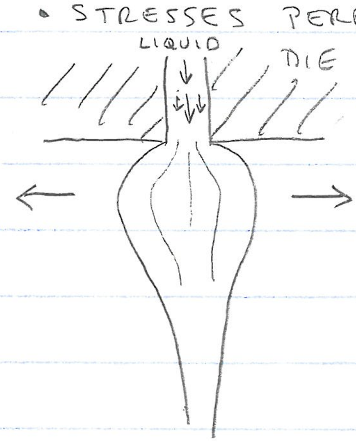
Notation: γ = strain $\quad \sigma_{xy} = G\gamma$

$\dot{\gamma}$ = strain rate or shear rate

$\sigma_{xy} = \eta \dot{\gamma}$

INTERESTING RHEOLOGY IS VISCOELASTIC

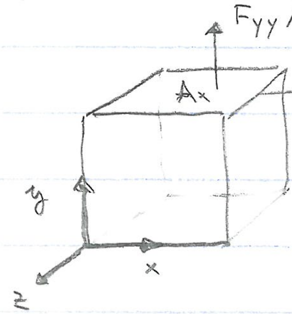
- EXAMPLES
  - ORBITZ DRINK – RECOIL WHEN STEADY FLOW STOPS
  - SILLY PUTTY – ELASTIC BOUNCE VS SLOW FLOW
  - SHAMPOO – DIE SWELL [NORMAL FORCES]
    - • STRESSES PERPENDICULAR TO FLOW



LIQUID MOVES $\perp$ TO FLOW DUE TO INTERNAL **NORMAL FORCES**

STRESS TENSOR STRESS = FORCE/AREA

$F_{yy}/A_{yy} = \sigma_{yy}$ (= -pressure for simple fluids)



$F_{xy} \rightarrow \sigma_{xy} = F_{xy}/A_y$

$\underset{\sim}{\sigma}$ is symmetric

$\sigma_{ij} = \sigma_{ji}$

$$\underset{\sim}{\sigma} = \begin{pmatrix} \sigma_{xx} & \sigma_{xy} & \sigma_{xz} \\ \sigma_{yx} & \sigma_{yy} & \sigma_{yz} \\ \sigma_{zz} & \sigma_{zy} & \sigma_{zz} \end{pmatrix}$$

FOR PURPOSES OF RHEOLOGY, OUR CONVENTION IS THAT DEFORMATION & FLOW FORCE IS APPLIED ALONG THE x DIRECTION. WITH THIS IN MIND, THE IMPORTANT STRESSES ARE

σ_{xy} – SHEAR STRESS $\sigma_{xy} = \eta \dot{\gamma}$ (FOR SIMPLE FLUID)

$\sigma_{xy} = G\gamma$ (FOR ELASTIC SOLID)

FOR A FLUID AT EQUILIBRIUM, THE NORMAL STRESSES ARE MINUS THE PRESSURE $\sigma_{xx} = \sigma_{yy} = \sigma_{zz} = -p$

NORMAL STRESSES

FIRST NORMAL STRESS (DIFFERENCE)

$$N_1 \equiv \sigma_{xx} - \sigma_{yy} = \Psi_1 \dot{\gamma}^2$$

SECOND NORMAL STRESS (DIFFERENCE)

$$N_2 = \sigma_{yy} - \sigma_{zz} = \Psi_2 \dot{\gamma}^2$$

CAVEAT: N_1 & N_2 ARE GENERALLY FUNCTIONS OF $\dot{\gamma}$

(ALTHOUGH CONSTANT AT LOW $\dot{\gamma}$)

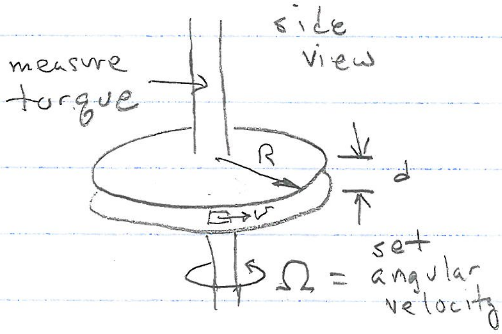
→ MANIFEST IN DIE SWELL

MEASURING RHEOLOGICAL PROPERTIES

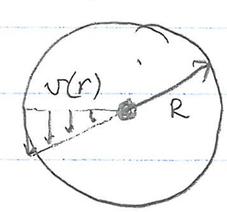
3 COMMON CONFIGURATIONS:

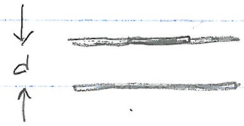
(1) PARALLEL PLATE

typical values
$d \simeq 1$ mm
$2R \approx 25$ mm



$v(r) = \Omega r$

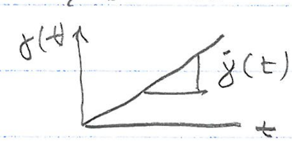




$\rightarrow v(r) = \Omega r \qquad \dot{\gamma} = \dfrac{v(r)}{d} \Rightarrow \dot{\gamma} = \dot{\gamma}(r)$

$\dot{\gamma}$ { is NOT CONSTANT; is a function of r

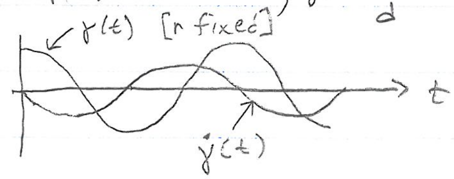
(a) steady shear mode: $\dot{\gamma} = v(r)/d \qquad \Omega = $ constant



(b) oscillatory shear mode:

$$\Omega = \Omega_0 \cos \omega t$$

- strain $\longrightarrow \gamma(r,t) = \gamma_0(r) \cos \omega t, \quad \gamma_0 = \dfrac{\Omega_0 r}{d}$

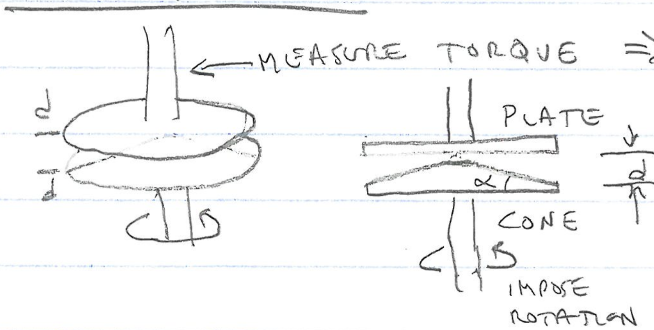


(1) PARALLEL PLATE continued

PARALLEL PLATE IS USED MOST COMMONLY FOR OSCILLATORY EXPERIMENTS. r dependence of γ & $\dot{\gamma}$ do not matter if $\gamma_0 << 1$ for all r, i.e. when $\frac{\Omega_0 R}{d} << 1$ SMALL STRAIN

→ virtue is that gap d can be made very small so that very little fluid is needed

(2) CONE AND PLATE



$\alpha \simeq$ few degrees

$d \simeq 1$ mm (fixed)

$2R = 25$ mm

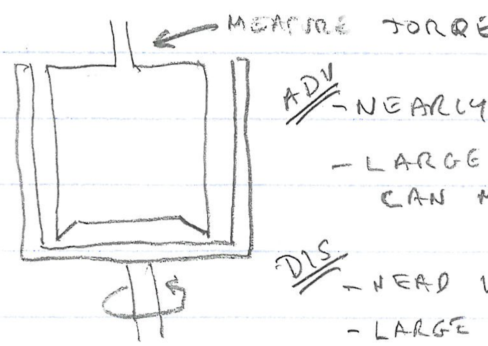
$$\dot{\gamma}(r) = \frac{v(r)}{gap} = \frac{\Omega r}{\alpha r} = \frac{\Omega}{\alpha} = \text{constant}$$

ADVANTAGE - CONSTANT SHEAR RATE

DISADVANTAGE - d is fixed by α

⇒ may need more sample than parallel plate

(3) COUETTE



ADV
- NEARLY CONSTANT SHEAR RATE
- LARGE SURFACE AREA ⇒ CAN MEASURE SMALL STRESSES

DIS
- NEED LARGE QUANTITY OF SAMPLE
- LARGE MOMENT OF INERTIA LIMITS OSCILLATION FREQUENCY

VISCOUS AND ELASTIC STRESSES IN COMPLEX FLUIDS

→ EXAMPLE – COLLOIDAL SUSPENSION

- MONODISPERSE SPHERES ~ 100 nm in diameter
- ϕ = volume fraction of spheres

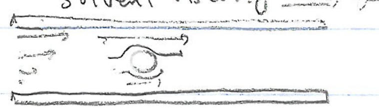
DILUTE SUSPENSION: $\phi \sim 0.01$

$$\eta = \eta_0 \left(1 + \frac{5}{2}\phi\right)$$

EINSTEIN CALCULATION

solution viscosity

solvent viscosity



EXTRA STRESS ASSOCIATED WITH FLOW OF SOLVENT AROUND PARTICLE

LESS DILUTE SUSPENSION

$$\eta = \eta_0 \left(1 + 2.5\phi + 6.2\phi^2 + O(\phi^3)\right)$$

Einstein

Batchelor JFM (1977)

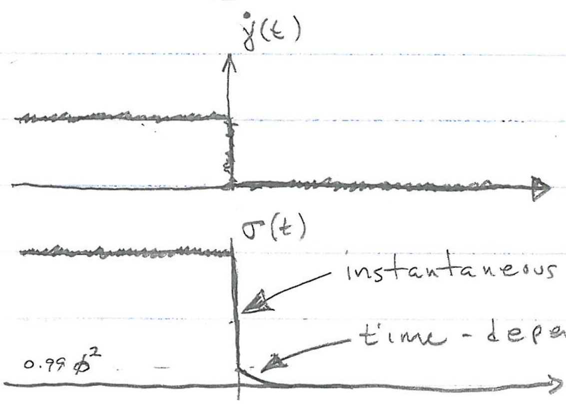
$5.2\phi^2$ — viscous stress

$0.99\phi^2$ — Brownian stress

what is this

STRESS RELAXATION AFTER STEP STRAIN

How does complex fluid respond?



instantaneous drop in stress → viscous stress

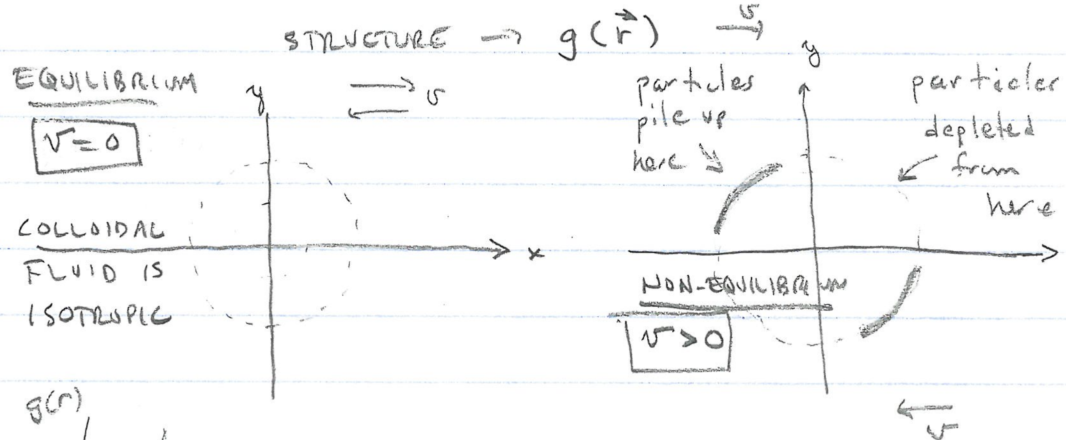
time-dependent drop in stress → Brownian stress

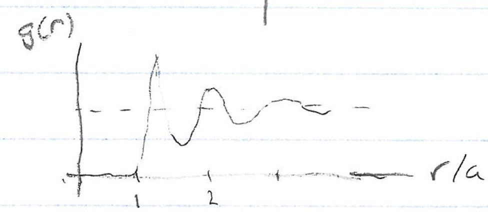
← low shear rate limit for $\phi \ll 1$

VISCOUS STRESS - PURELY HYDRODYNAMIC IN ORIGIN

- when $v = 0$, hydrodynamic force $\to 0$
- strongly affected by particle crowding and lubrication forces at high ϕ

BROWNIAN STRESS - COMES FROM DEFORMATION OF EQUILIBRIUM STRUCTURE $\to g(\vec{r}) \xrightarrow{v}$





- When flow ceases, fluid structure $g(\vec{r})$ returns to equilibrum structure
- Time scale for return to equilibrium is set by diffusion $\tau_R \equiv \frac{a^2}{D} \approx \frac{\eta a^3}{k_B T}$ $\qquad D \approx \frac{k_B T}{6\pi\eta a}$

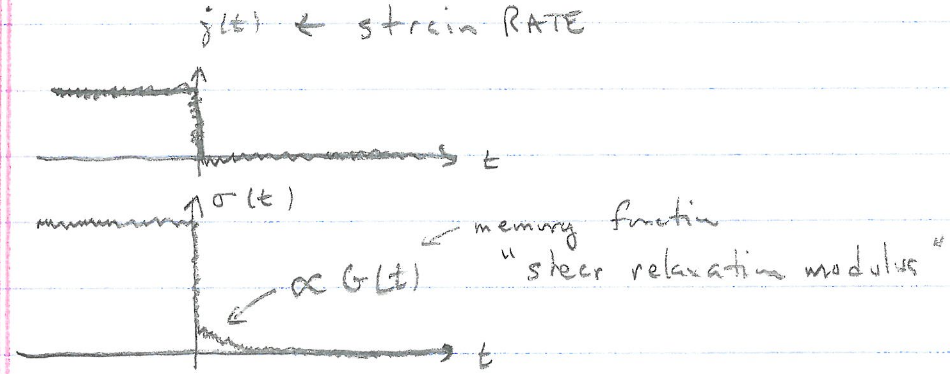
- RELATIVE IMPORTANCE OF VISCOUS (hydrodynamic) and Brownian stresses
  - Péclet number $Pe = \frac{\text{viscous stress}}{\text{thermal stress}} = \frac{\eta\dot{\gamma}}{k_B T/a^3} = \frac{\eta\dot{\gamma}a^3}{k_B T}$

$$Pe = \frac{\text{hydrodynamic rate}}{\text{diffusion rate}} = \frac{\dot{\gamma}}{D/a^2} = \frac{\eta\dot{\gamma}a^3}{k_B T}$$

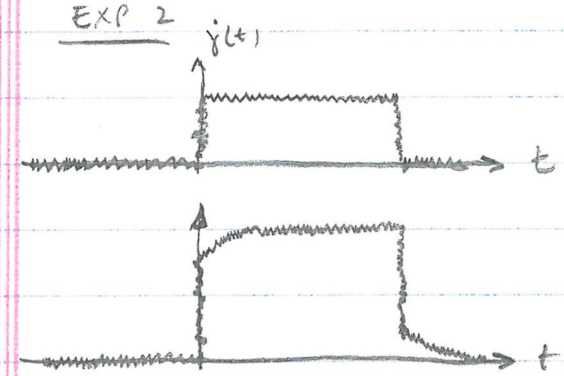
$Pe \gg 1$ viscous (hydrodynamic) stress dominates

$Pe \ll 1$ thermal (Brownian) stress dominates

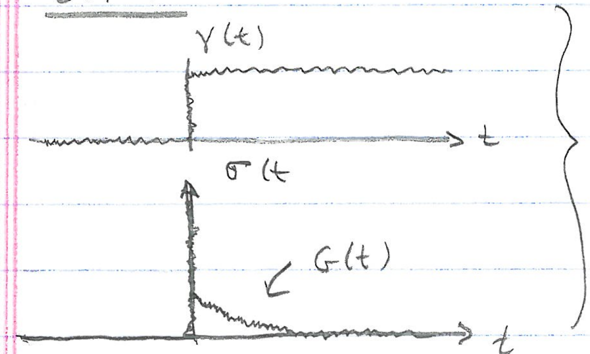
EXP 1



EXP 2



EXP 3



Use to define dynamic complex modulus $G^*(\omega)$

DYNAMIC MODULI: $G^*(\omega) = G'(\omega) + i\,G''(\omega)$

APPLY SINUSOIDAL STRAIN $\gamma(t) = \gamma_0 \cos \omega t = \gamma_0 \,\mathrm{Re}\left[e^{i\omega t}\right]$

Then $\sigma_{xy}(t) = \gamma_0 \left[G'(\omega) \cos \omega t - G''(\omega) \sin \omega t \right]$

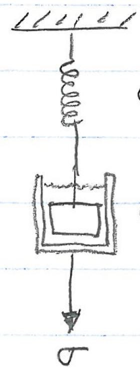
$= \gamma_0 \,\mathrm{Re}\left[G^*(\omega)\, e^{i\omega t} \right]$

$$\boxed{G^*(\omega) = i\omega \int_0^\infty G(t)\, e^{-i\omega t}\, dt}$$

Good only for small strains → "linear regime"

WE CAN MODEL THIS BEHAVIOR WITH A SIMPLE MECHANICAL SYSTEM OF A DASHPOT AND A SPRING.

MAXWELL MODEL



$\sigma_1 = G_M \gamma$

$\sigma_2 = \eta_M \dot{\gamma}$

$$\sigma = \sigma_1 = \sigma_2$$

$$\Rightarrow \dot{\gamma} = \frac{\sigma}{\eta} + \frac{\dot{\sigma}}{G}$$

$$\text{or} \quad \boxed{\sigma + \frac{\eta_M}{G_M}\dot{\sigma} = \eta_M \dot{\gamma}}$$

$$\frac{\eta_M}{G_M} = \tau_M$$

relaxation time

Case I: - constant stress & shear for $t < 0$

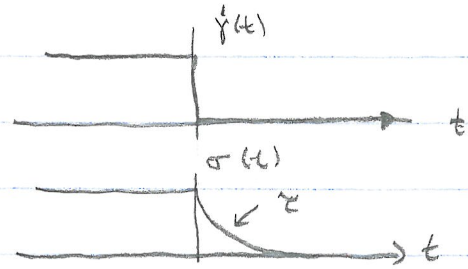
$$\Rightarrow \dot{\sigma} = 0$$

$$\Rightarrow \sigma = \eta_M \dot{\gamma}$$

- turn of shear at $t = 0$

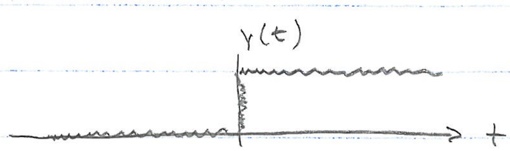
$$\Rightarrow \sigma + \tau_M \dot{\sigma} = 0 \qquad \text{where } \tau_M = \frac{\eta_M}{G_M}$$

$$\Rightarrow \sigma = \sigma_0 e^{-t/\tau}$$



Can add elements to mimic finite viscosity

Case II: STEP STRAIN



$$\sigma = \sigma_1 = \sigma_2$$

$$\Rightarrow G_M \gamma = \eta_M \dot{\gamma}$$

$$\Rightarrow \frac{d\gamma}{\gamma} = \frac{dt}{\tau} \qquad \tau_M = \frac{\eta_M}{G_M}$$

$$\Rightarrow \gamma(t) = \gamma_0 e^{-t/\tau_M}$$

#1 $\quad \sigma(t) = G_M \gamma(t) = G_M \gamma_0 e^{-t/\tau}$

Define relaxation modulus $G(t) = \dfrac{\sigma(t)}{\gamma_0} = G_M e^{-t/\tau}$

Boltzman superposition

All of these eqns are linear so we can generalize to find the stress from a sequence of step strains $\delta\gamma_i$ at times t_i

i.e. $$\sigma(t) = \sum_i G(t-t_i)\underbrace{\delta\gamma_i}_{\dot{\gamma}_i \delta t_i}$$

$$\Rightarrow \sigma(t) = \int_{-\infty}^{\infty} \underbrace{G(t-t_1)}\,\dot{\gamma}(t')\,dt'$$

in general need not be exponential

Oscillatory shear

Suppose we impose an oscillator strain of

$$\gamma(t) = \gamma_0 \cos \omega t = \gamma_0 e^{i\omega t}$$

Expect oscillatory response for stress

$$\sigma(t) = \sigma_0 e^{i\omega t}$$

Plug into Maxwell model

$$\sigma + \frac{\eta_M}{G_M}\dot{\sigma} = \eta_M \dot{\gamma}$$

$$\sigma_0 \cancel{e^{i\omega t}} + \frac{\eta_M}{G_M} i\omega \sigma_0 \cancel{e^{i\omega t}} = \eta_M \gamma_0 i\omega \cancel{e^{i\omega t}}$$

$$\sigma_0 \left(1 + i\omega \frac{\eta_M}{G_M}\right) = \gamma_0 i\omega \eta_M$$

$$\Rightarrow \frac{\sigma_0}{\gamma_0} = \frac{i\omega\eta_M}{1 + i\omega\frac{\eta_M}{G_M}} = \frac{\omega^2 \frac{\eta_M^2}{G_M} - i\omega\frac{\eta_M}{G_M}}{1 + \omega^2\left(\frac{\eta_M}{G_M}\right)}$$

$$= \frac{\omega^2\tau_M^2}{1+\omega^2\tau_M^2} G_M - i\frac{\omega}{1+\omega^2\tau_M^2}\eta_M$$

$$\boxed{\frac{\sigma_0}{\gamma_0} = G'(\omega) - i\,G''(\omega)}$$

$$G'(\omega) = \frac{\omega^2 \tau_M^2}{1+\omega^2\tau_M^2} G_M \sim \begin{cases} \omega^2 G_M & \text{for } \omega\tau_M \ll 1 \\ G_M & \text{for } \omega\tau_M \gg 1 \end{cases}$$

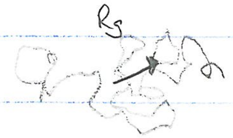
$$G''(\omega) = \frac{\omega}{1+\omega^2\tau_M^2}\eta_M \sim \begin{cases} \omega\,\eta_M & \text{for } \omega\tau_M \ll 1 \\ \dfrac{G_M}{\omega\tau_M} & \text{for } \omega\tau_M \gg 1 \end{cases}$$

$$= \frac{\omega\tau_M}{1+\omega^2\tau_M^2} G_M$$

POLYMER RHEOLOGY: SEE DOI & EDWARDS
The Theory of Polymer Dynamics
Oxford U.P. (1986)

→ DOMINATED BY BROWNIAN STRESS EXCEPT FOR DILUTE SOL'NS

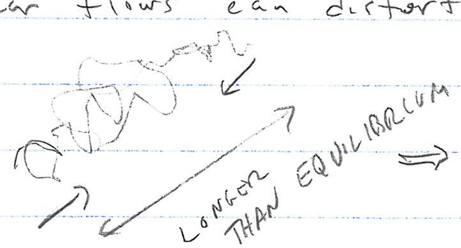
Shape of polymer – random walk



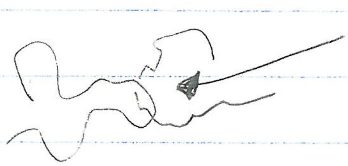
$R_g \sim N^\nu$ $\nu \sim 0.5-0.6$

$$\underbrace{A \sim k_B T \ln \Psi}_{\text{Entropic stress}}$$

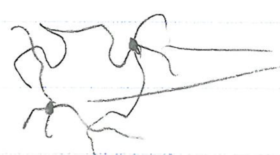
Shear flows can distort polymer



⇒ generates large stress



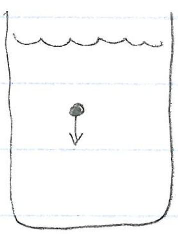
entanglements take long time to relax } τ_d [Reptation time]



permanent crosslinks never relax ⇒ $G(\omega=0) \neq 0$

MICRORHEOLOGY

Consider a particle diffusing by Brownian motion in a liquid. It's characterized by a diffusion coefficient D which characterizes its thermal motion. Einstein came up with a clever way of getting an equation for D by considering the particle's <u>response</u> to an external force $F = -\nabla U$. We can imagine that gravity is that force (although it need not be).



1) Sedimentation $\quad F = -\dfrac{dU}{dz} = \zeta v$

force imparts a velocity

drag of fluid on particle

$$\Rightarrow v = -\frac{1}{\zeta}\frac{\partial U}{\partial z} \qquad \zeta = 6\pi\eta_s a$$

depends on properties of the medium

Flux of particles $\quad J = \underbrace{-D\dfrac{\partial c}{\partial z}}_{\text{flux due to diffusion}} \underbrace{- \dfrac{c}{\zeta}\dfrac{\partial U}{\partial z}}_{\text{flux due to force } -\nabla U}$

In equilibrium $\quad J = 0 \quad$ and $\quad c = c_0\, e^{-U(z)/k_BT}$

$$\Rightarrow J = -D\left(-\frac{1}{k_BT}\frac{\partial U}{\partial z}\right)c - \frac{c}{\zeta}\frac{\partial U}{\partial z} = 0$$

$$\Rightarrow \frac{D}{k_BT} = \frac{1}{\zeta} \quad \text{or} \quad D = \frac{k_BT}{\zeta} = \frac{k_BT}{6\pi\eta a}$$

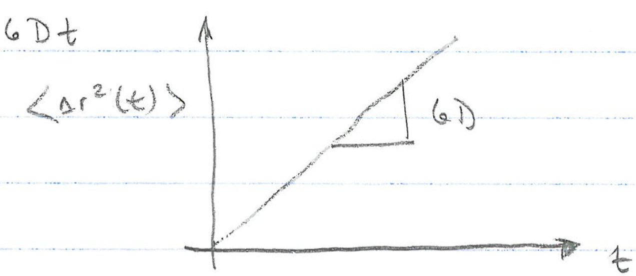
$$D = \frac{k_B T}{\zeta} = \frac{k_B T}{6\pi\eta a}$$

This Einstein relation relates D, which characterizes the thermal motion, to ζ, which specifies the response to an external force. Note that $\zeta = 6\pi\eta a$ depends on the rheology of the medium, i.e. on the viscosity η.

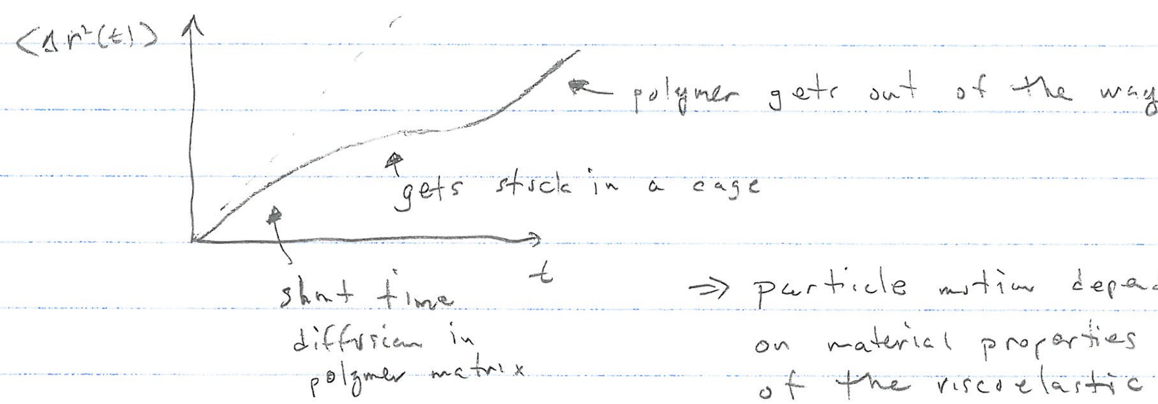
Suppose that the medium is viscoelastic, rather than simply viscous. How does that affect this result?

Consider the mean square displacement $\langle \Delta r^2(t) \rangle$. For a freely diffusing particle

$$\langle \Delta r^2(t) \rangle = 6Dt$$



What happens if particle is in a viscoelastic medium, say a polymer sol'n or gel



$\Rightarrow$ particle motion depends on material properties of the viscoelastic medium.

So let's look at the eqn of motion for the particle embedded in the viscoelastic medium → a Langevin eqn.

$$m\dot{v}(t) = \underbrace{f_R(t)}_{\text{random thermal forces}} - \underbrace{\int_{-\infty}^{t} \underbrace{\zeta(t-t')}_{\text{memory function that contains material properties}} \, \underbrace{v(t')}_{\text{velocity of particle}} \, dt'}_{\text{drag force}}$$

drag force [there is a bias in the "random" forces – a damping force – that slows particle]

$$\langle f_R(0)\, f_R(t)\rangle = k_B T\, 2\zeta\, \delta(t)$$

{normally assume forces are only correlated on a molecular collision Time

$$\rightarrow \underbrace{k_B T\, 2\zeta(t)}$$

Here we assume forces are correlated on a range of time scales determined by the visco-elastic properties of the fluid

Solve Langevin eqn by La Place transform to obtain

$$\tilde{G}(s) = s\tilde{\eta}(s) = \frac{s}{6\pi a}\left[\frac{6 k_B T}{s^2 \langle \Delta \tilde{r}^2(s)\rangle} - ms\right]$$

negligible except at high frequencies

For freely diffusing particle

$$\langle \Delta \tilde{r}^2(s)\rangle = \frac{6D}{s^2}$$

$G'(\omega)$ & $G''(\omega)$ are extracted from $\tilde{G}(s)$ using Kramers - Kronig