Part III. The rheology of suspensions

May 12, 2014

Microstructural studies for rheology

- To calculate the flow of complex fluids, need governing equations,

Microstructural studies for rheology

- To calculate the flow of complex fluids, need governing equations,
- in particular, the constitutive equation relating stress to flow and its history.

Microstructural studies for rheology

- To calculate the flow of complex fluids, need governing equations,
- in particular, the constitutive equation relating stress to flow and its history.
- Either ‘ad hoc’, such as Oldroyd-B differential equation and BKZ integral equation,
- Or look at microstructure for highly idealised systems and derive their constitutive equations.

Microstructural studies for rheology

- To calculate the flow of complex fluids, need governing equations,
- in particular, the constitutive equation relating stress to flow and its history.
- Either ‘ad hoc’, such as Oldroyd-B differential equation and BKZ integral equation,
- Or look at microstructure for highly idealised systems and derive their constitutive equations.
- Most will be suspensions of small particles in Newtonian viscous solvent.

Outline

Separation of length scales

Essential

$$\text{Micro} \quad \ell \ll L \quad \text{Macro}$$

$$\text{Micro} = \text{particle } 1\mu m \qquad \text{Macro} = \text{flow, } 1cm$$

- Micro and Macro time scales similar
- Need ℓ small for small micro-Reynolds number
  $Re_\ell = \frac{\rho\gamma\ell^2}{\mu} \ll 1$,
  otherwise possible macro-flow boundary layers $\not\ll \ell$
  But macro-Reynolds number $Re_L = \frac{\rho\gamma L^2}{\mu}$ can be large
- If $\ell \not< L$, then non-local rheology

Two-scale problem $\ell \ll L$

- Solve microstructure – tough, must idealise
- Extract macro-observables – easy

Here: suspension of particles in Newtonian viscous solvent

1. Macro$\to$micro connection

- Particles passively move with macro-flow $\mathbf{u}$
- Particles actively rotate, deform & interact with macro-shear $\nabla\mathbf{u}$

both needing $Re_\ell \ll 1$.

2. Micro→macro connection

Macro = continuum = average/smear-out micro details

E.g. average over representative volume V with $\ell \ll V^{1/3} \ll L$

$$\overline{\sigma} = \frac{1}{V}\int_V \sigma \, dV$$

Also ensemble averaging and homogenisation

To be used in averaged = macro momentum equation

$$\overline{\rho}\left[\frac{\partial\overline{\mathbf{u}}}{\partial t} + \overline{\mathbf{u}}\cdot\nabla\overline{\mathbf{u}}\right] = \nabla\cdot\overline{\sigma} + \overline{F}$$

NB micro-Reynolds stresses $\overline{(\rho\mathbf{u})'\mathbf{u}'}$ small for $Re_\ell \ll 1$.

Reduction for suspension with Newtonian viscous solvent

$$\text{Write:} \quad \sigma = -pI + 2\mu e + \sigma^{+}$$

with pressure p, viscosity μ, strain-rate e,
and σ^{+} non-zero only inside particles.

$$\text{Average:} \quad \overline{\sigma} = -\overline{p}I + 2\mu\overline{e} + \overline{\sigma^{+}}$$

with

$$\overline{\sigma^{+}} = \frac{1}{V}\int_V \sigma^{+}\,dV = n\left\langle \int_{\text{particle}} \sigma^{+}\,dV \right\rangle_{\text{types of particle}}$$

with n number of particles per unit volume

Reduction for suspension with Newtonian viscous solvent 2

Inside rigid particles $e = 0$, so $\sigma^+ = \sigma$.

Also $\sigma_{ij} = \partial_k(\sigma_{ik}x_j) - x_j\partial_k\sigma_{ik}$, so ignoring gravity $\partial_k\sigma_{ik} = 0$,

$$\int_{\text{particle}} \sigma^+ \, dV = \int_{\text{particle}} \sigma \cdot n \, x \, dA$$

so only need σ on surface of particle. (Detailed cases soon.)

Hence

$$\overline{\sigma} = -\overline{p}I + 2\mu\overline{e} + n\int_{\text{particle}} \sigma \cdot n \, x \, dA$$

Homogenisation: asymptotics for $\ell \ll L$

Easier transport problem to exhibit method

$$\nabla \cdot k \cdot \nabla T = Q$$

with k & Q varying on macroscale x and microscale $\xi = x/\epsilon$,

Multiscale asymptotic expansion

$$T(x;\epsilon) \sim T_0(x,\xi) + \epsilon T_1(x,\xi) + \epsilon^2 T_2(x,\xi)$$

Homogenisation 2

ϵ^{-2}:

$$\partial_\xi k \partial_\xi T_0 = 0$$
$$\text{i.e.} \quad T_0 = T(x)$$

Thus T varies only slowly at leading order, with microscale making small perturbations.

Homogenisation 3

ϵ^{-1}:

$$\partial_\xi k \partial_\xi T_1 = -\partial_\xi k \partial_x T_0$$

Solution T_1 is linear in forcing $\partial_x T_0$, details depending on $k(\xi)$:

$$T_1(x, \xi) = A(\xi) \partial_x T_0$$

Homogenisation 4

ϵ^0:

$$\partial_\xi k \partial_\xi T_2 = Q - \partial_x k \partial_x T_0 - \partial_\xi k \partial_x T_1 - \partial_x k \partial_\xi T_1$$

Secularity: $\langle \mathrm{RHS} \rangle = 0$ else $T_2 = O(\xi^2)$ which contradicts asymptoticity. (Periodicity not necessary.) Hence

$$0 = \langle Q \rangle - \partial_x \langle k \rangle \partial_x T_0 - \partial_x \langle k \frac{\partial A}{\partial \xi} \rangle \partial_x T_0$$

Hence macro description

$$\nabla k^* \nabla T = Q^* \qquad \text{with} \quad k^* = \left\langle k + k \frac{\partial A}{\partial \xi} \right\rangle \quad \text{and} \quad Q^* = \langle Q \rangle$$

Homogenisation 5

NB: Leading order T_0 uniform at microlevel, with therefore no local heat transport

NB: Micro problem forced by ∇T_0. Need to solve

$$\nabla \cdot k \nabla \cdot T_{\mathrm{micro}} = 0$$
$$T_{\mathrm{micro}} \to x \cdot \nabla T_0$$

Solution

$$T_{\mathrm{micro}} = (x + \epsilon A) \nabla T_0$$

Hence heat flux

$$\langle q \rangle = \langle k \nabla T_{\mathrm{micro}} \rangle = \langle k + \epsilon k \nabla A \rangle \nabla T_0$$

Einstein viscosity

Simplest, so can show all details.

Highly idealised – many generalisations

- Spheres – no orientation problems
- Rigid – no deformation problems
- Dilute and Inert – no interactions problems

Micro problem

- Isolated rigid sphere
- force-free and couple-free
- in a general linear shearing flow $\nabla\overline{U}$
- Stokes flow

Stokes problem for Einstein viscosity

$$\nabla \cdot \mathbf{u} = 0 \quad \text{in} \quad r > a$$

$$0 = -\nabla p + \mu \nabla^2 \mathbf{u} \quad \text{in} \quad r > a$$

$$\mathbf{u} = \mathbf{V} + \omega \wedge \mathbf{x} \quad \text{on} \quad r = a \quad \text{with} \quad V, \omega \text{ consts}$$

$$\mathbf{u} \to \overline{U} + \mathbf{x} \cdot \nabla \overline{U} \quad \text{as} \quad r \to \infty$$

$$\mathbf{F} = \int_{r=a} \sigma \cdot n \, dA = 0, \qquad \mathbf{G} = \int_{r=a} \mathbf{x} \wedge \sigma \cdot n \, dA = 0$$

Split general linear shearing flow $\nabla \overline{U}$ into symmetric strain-rate $\mathbf{E}$ and antisymmetric vorticity Ω, i.e.

$$\mathbf{x} \cdot \nabla \overline{U} = \mathbf{E} \cdot \mathbf{x} + \Omega \wedge \mathbf{x}$$

NB: Stokes problem is linear and instantaneous

Solution of Stokes problem for Einstein viscosity

$$\mathbf{F} = 0 \quad \text{gives} \quad \mathbf{V} = \overline{U} \quad \text{i.e. translates with macro flow}$$

$$\mathbf{G} = 0 \quad \text{gives} \quad \omega = \Omega \quad \text{i.e. rotates with macro flow}$$

Then

$$\mathbf{u} = \overline{U} + \mathbf{E}\cdot\mathbf{x} + \Omega \wedge \mathbf{x} - \mathbf{E}\cdot\mathbf{x}\frac{a^5}{r^5} - \mathbf{x}\frac{5(\mathbf{x}\cdot\mathbf{E}\cdot\mathbf{x})}{2r^2}\left(\frac{a^3}{r^3} - \frac{a^5}{r^5}\right)$$

$$p = -5\mu\frac{(\mathbf{x}\cdot\mathbf{E}\cdot\mathbf{x})a^3}{r^5}$$

Evaluate viscous stress on particle

$$\sigma\cdot n\Big|_{r=a} = \frac{5\mu}{2a}\mathbf{E}\cdot\mathbf{x}$$

Evaluate particle contribution to macro/average stress

$$\int_{\text{particle}} \sigma\cdot n\,\mathbf{x}\,dA = 5\mu\mathbf{E}\frac{4\pi}{3}a^3$$

Result for Einstein viscosity (1905)

$$\overline{\sigma} = -\overline{p}I + 2\mu\mathbf{E} + 5\mu\mathbf{E}\phi \quad \text{with volume fraction} \quad \phi = n\frac{4\pi}{3}a^3$$

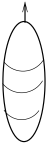
Hence effective viscosity

$$\mu^* = \mu\left(1 + \frac{5}{2}\phi\right)$$

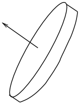
- Result independent of type of flow – shear, extensional
- Result independent of particle size – OK polydisperse
- Einstein used another averaging of dissipation which would not give normal stresses with $\sigma : E = 0$, which arbitrarily cancelled divergent integrals (hydrodynamics is long-ranged)

Rotation of particles – rigid and dilute

Spheroid: axes a, b, b, aspect ratio $r = \frac{a}{b}$.



rod $r > 1$



disk $r < 1$

Direction of axis $\mathbf{p}(t)$, unit vector.

Stokes flow by Oberbeck (1876)

Rotation of particles

Microstructural evolution equation

$$\frac{D\mathbf{p}}{Dt} = \Omega \wedge \mathbf{p} + \tfrac{r^2-1}{r^2+1}\left[\mathbf{E}\cdot\mathbf{p} - \mathbf{p}(\mathbf{p}\cdot\mathbf{E}\cdot\mathbf{p})\right]$$

(Last term to keep **p** unit, so can discard sometimes.)
Straining less efficient at rotation by $\frac{r^2-1}{r^2+1}$.

Long rods	$\frac{r^2-1}{r^2+1} \to +1$	i.e.	Upper Convective Derivative	$\overset{\nabla}{A}$
Flat disks	$\frac{r^2-1}{r^2+1} \to -1$	i.e.	Lower Convective Derivative	$\overset{\triangle}{A}$

Micro→macro link: stress

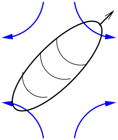
$$\overline{\sigma} = -\overline{p}I + 2\mu\mathbf{E} + 2\mu\phi\left[A(\mathbf{p}\cdot\mathbf{E}\cdot\mathbf{p})\mathbf{pp} + B(\mathbf{pp}\cdot\mathbf{E} + \mathbf{E}\cdot\mathbf{pp}) + C\mathbf{E}\right]$$

with A, B, C material constants depending on shape but not size

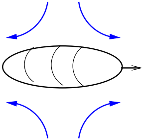
	A	B	C
$r\to\infty$	$\frac{r^2}{2(\ln 2r - \frac{3}{2})}$	$\frac{6\ln 2r - 11}{r^2}$	2
$r\to 0$	$\frac{10}{3\pi r}$	$-\frac{8}{3\pi r}$	$\frac{8}{3\pi r}$

Rotation in uni-axial straining

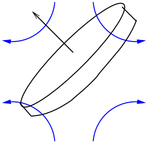
$$\mathbf{U} = E(x, -\tfrac{1}{2}y, -\tfrac{1}{2}z)$$



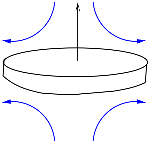
rotates to



Aligns with stretching direction → maximum dissipation



rotates to



Aligns with inflow direction → maximum dissipation

Effective extensional viscosity for rods

$$\mu^*_{\rm ext} = \mu \left(1 + \phi \frac{r^2}{3(\ln 2r - 1.5)}\right)$$

Large at $\phi \ll 1$ if $r \gg 1$. Now $\phi = \frac{4\pi}{3} ab^2$ and $r = \frac{a}{b}$, so

$$\mu^*_{\rm ext} = \mu \left(1 + \frac{4\pi n a^3}{9(\ln 2r - 1.5)}\right)$$

so same as sphere of radius a its largest dimension(except for factor $1.2(\ln 2r - 1.5)$).
Hence 5ppm of PEO can have a big effect in drag reduction.

Dilute requires $na^3 \ll 1$, but extension by Batchelor to semi-dilute $\phi \ll 1 \ll \phi r^2$

$$\mu^*_{\rm ext} = \mu \left(1 + \frac{4\pi n a^3}{9 \ln \phi^{-1/2}}\right)$$

Effective extensional viscosity for disks

$$\mu^*_{\mathrm{ext}} = \mu \left(1 + \phi \frac{10}{3\pi r}\right) = \mu \left(1 + \frac{10nb^3}{9}\right)$$

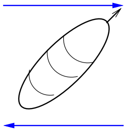
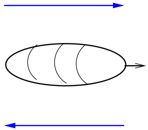
where for disks b is the largest dimension

(always the largest for Stokes flow).

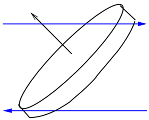
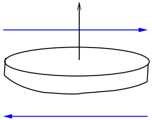
No semi-dilute theory, yet.

Behaviour in simple shear

$$\mathbf{U} = (\gamma y, 0, 0)$$

 rotates to 

Rotates to flow direction $\rightarrow$ minimum dissipation

 rotates to 

Rotates to lie in flow $\rightarrow$ minimum dissipation

Both Tumble: flip in $1/\gamma$, then align for r/γ $\quad(\delta\theta = 1/r$ with $\dot{\theta} = \gamma/r^2)$

Effective shear viscosity

Jeffery orbits (1922)

$$\begin{aligned} \dot{\phi} &= \tfrac{\gamma}{r^2+1}(r^2\cos^2\phi + \sin^2\phi) \\ \dot{\theta} &= \tfrac{\gamma(r^2-1)}{4(r^2+1)}\sin 2\theta \sin 2\phi \end{aligned}$$

Solution with orbit constant C.

$$\tan\phi = r\tan\omega t, \quad \omega = \tfrac{\gamma r}{r^2+1}, \quad \tan\theta = Cr(r^2\cos^2\phi + \sin^2\phi)^{-1/2}$$

Effective shear viscosity Leal & H (1971)

$$\mu^*_{\mathrm{shear}} = \mu\left(1 + \phi\begin{cases} 0.32r/\ln r & \text{rods} \\ 3.1 & \text{disks}\end{cases}\right)$$

numerical coefficients depend on distribution across orbits, C.

Remarks

Alignment gives $\mu^*_{\text{shear}} \ll \mu^*_{\text{ext}}$
and this material anisotropy will lead to anisotropy of macro flow.

Important to Turbulent Drag Reduction

Three measures of concentration of rods

$$\begin{cases} \phi r^2 \doteq na^3 & \text{for} \quad \mu^*_{\text{ext}} \\ \phi r \doteq na^2 b & \text{for} \quad \mu^*_{\text{shear}} \\ \phi \doteq nab^2 & \text{for permeability} \end{cases}$$

Brownian rotations – for stress relaxation

Rotary diffusivity $\quad D_{\mathrm{rot}} = \dfrac{kT}{8\pi\mu a^3}$ for spheres,

$$kT \Big/ \frac{8\pi\mu a^2}{3(\ln 2r - 1.5)} \quad \text{rods,} \qquad kT \big/ \tfrac{8}{3}\mu b^3 \quad \text{disks}$$

(NB largest dimension, again)

After flow is switched off, particles randomise orientation in time $1/6D \quad \sim 1$ second for $1\mu m$ in water.

State of alignment: probability density $P(\mathbf{p}, t)$ in orientation space $=$ unit sphere $|\mathbf{p}| = 1$. Fokker-Plank equation

$$\frac{\partial P}{\partial t} + \nabla\cdot(\dot{\mathbf{p}}P) = D_{\mathrm{rot}}\nabla^2 P$$

$\dot{\mathbf{p}}(\mathbf{p})$ earlier deterministic.

Average stress over distribution P

Averaged stress

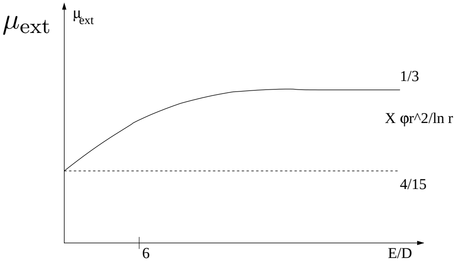
$$\sigma = -pI + 2\mu E + 2\mu\phi[AE : \langle \mathbf{pppp} \rangle + B(E \cdot \langle \mathbf{pp} \rangle + \langle \mathbf{pp} \rangle \cdot E) + CE + FD_{\mathrm{rot}} \langle \mathbf{pp} \rangle]$$

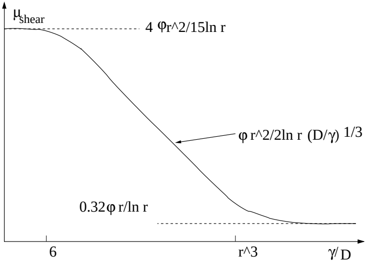
Last FD_{rot} term is entropic stress.
Extra material constant $F = 3r^2/(\ln 2r - 0.5)$ for rods and $12/\pi r$ for disks.

$$\text{with averaging:} \qquad \langle \mathbf{pp} \rangle = \int_{|\mathbf{p}|=1} \mathbf{pp} P \, dp$$

Solve Fokker-Plank: numerical, weak and strong Brownian rotations

Extensional and shear viscosities





Small
strain-hardening

$\updownarrow$ Orientation effects

Large
shear-thinning

Also $N_1 > 0$,
N_2 small < 0.

The closure problem

- Second moment of Fokker-Plank equation

$$\frac{D}{Dt}\langle \mathbf{pp}\rangle - \Omega\cdot\langle \mathbf{pp}\rangle\langle \mathbf{pp}\rangle\cdot\Omega$$
$$= \tfrac{r^2-1}{r^2+1}\left[E\cdot\langle \mathbf{pp}\rangle + \langle \mathbf{pp}\rangle\cdot E - 2\langle \mathbf{pppp}\rangle : E\right] - 6D_{\mathrm{rot}}\left[\langle \mathbf{pp}\rangle - \tfrac{1}{3}I\right]$$

  Hence this and stress need $\langle \mathbf{pppp}\rangle$, so an infinite hierarchy.

- Simple 'ad hoc' closure

$$\langle \mathbf{pppp}\rangle : E = \langle \mathbf{pp}\rangle\langle \mathbf{pp}\rangle : E$$

- Better: correct in weak and strong limits

$$\langle \mathbf{pppp}\rangle : E = \tfrac{1}{5}\left[6\langle \mathbf{pp}\rangle\cdot E\cdot\langle \mathbf{pp}\rangle - \langle \mathbf{pp}\rangle\langle \mathbf{pp}\rangle : E - 2I(\langle \mathbf{pp}\rangle^2 : E - \langle \mathbf{pp}\rangle :$$

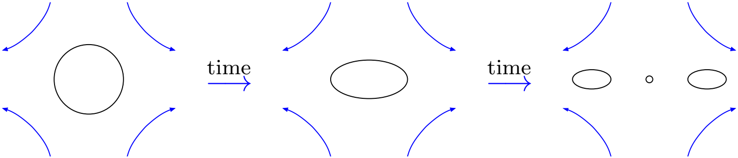
- New idea Brownian fields: simulate many random walks in orientation space for each point of the complex flow.

Emulsions - deformable microstructure

Reviews: Ann. Rev. Fluid Mech. Rallison (1984), Stone (1994)

- Dilute – single drop, volume $\frac{4\pi}{3}a^3$
- T = surface tension (in rheology σ and γ not possible)
- Newtonian viscous drop μ_{int}, solvent μ_{ext}

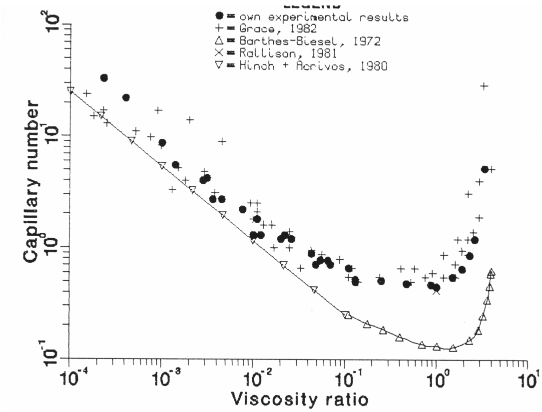
Rupture if $\mu_{\mathrm{ext}} > \frac{T}{Ea}$ (normally)



Irreversible reduction is size to $a_* = T/\mu_{\mathrm{ext}}E$, as coalescence very slow.

Rupture in shear flow

$$\frac{T}{\mu_{\text{ext}} Ea}$$



$$\frac{\mu_{\text{int}}}{\mu_{\text{ext}}}$$

Experiments: de Bruijn (1989) (=own), Grace (1982)

Theories: Barthes-Biesel (1972), Rallison (1981), Hinch & Acrivos (1980)

Rupture difficult if $\mu_{\rm int} \ll \mu_{\rm ext}$

Too slippery. Become long and thin. Rupture if

$$\mu_{\rm ext} E > \frac{T}{a} \begin{cases} 0.54\,(\mu_{\rm ext}/\mu_{\rm int})^{2/3} & \text{simple shear} \\ 0.14\,(\mu_{\rm ext}/\mu_{\rm int})^{1/6} & \text{extension} \end{cases}$$

but tip-streaming with mobile surfactants (makes rigid end-cap)

$$\mu_{\rm ext} E > \frac{T}{a} 0.56$$

Rupture difficult is simple shear if $\mu_{\mathrm{int}} > 3\mu_{\mathrm{ext}}$

- If internal very viscous ($\mu_{\mathrm{int}} \gg \mu_{\mathrm{ext}}$),
  - then rotates with vorticity,
  - rotating with vorticity, sees alternative stretching and compression,
  - hence deforms little.
- If internal fairly viscous ($\mu_{\mathrm{int}} \gtrsim 3\mu_{\mathrm{ext}}$),
  - then deforms more,
  - if deformed, rotates more slowly in stretching quadrant,
  - if more deformed, rotates more slowly, so deforms even more, etc etc
- until can rupture when $\mu_{\mathrm{int}} \leq 3\mu_{\mathrm{ext}}$

Theoretical studies: small deformations

Small ellipsoidal deformation

$$r = a\,(1 + \mathbf{x}\cdot\mathbf{A}(t)\cdot\mathbf{x} + \quad \text{higher orders})$$

Stokes flow with help of computerised algebra manipulator

$$\frac{D\mathbf{A}}{Dt} - \Omega\cdot\mathbf{A} + \mathbf{A}\cdot\Omega = 2k_1\mathbf{E} + k_5(\mathbf{A}\cdot\mathbf{E} + \mathbf{E}\cdot\mathbf{A}) + \dots \\ - \tfrac{T}{\mu_{\rm ext}a}\left(k_2\mathbf{A} + k_6(\mathbf{A}\cdot\mathbf{A}) + \dots\right)$$

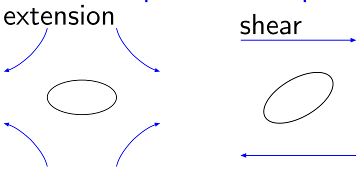
$$\sigma = -pI + 2\mu_{\rm ext}\mathbf{E} + 2\mu_{\rm ext}\phi\big[k_3\mathbf{E} + k_7(\mathbf{A}\cdot\mathbf{E} + \mathbf{E}\cdot\mathbf{A}) + \dots \\ - \tfrac{T}{\mu_{\rm ext}a}(k_4\mathbf{A} + k_8(\mathbf{A}\cdot\mathbf{A}) + \dots\big]$$

with k_n depending on viscosity ratio, k_1 inefficiency of rotating by straining $\lambda = \mu_{\rm int}/\mu_{\rm ext}$

$$k_1 = \tfrac{5}{2(2\lambda+3)}, \qquad k_2 = \tfrac{40(\lambda+1)}{(2\lambda+3)(19\lambda+16)}$$
$$k_3 = \tfrac{5(\lambda-1)}{3(2\lambda+3)}, \qquad k_4 = \tfrac{4}{2\lambda+3}$$

Theoretical studies: small deformations 2

Equilibrium shapes before rupture



internal circulation,
tank-treading

Rheology before rupture

Small strain-hardening, small shear-thinning, $N_1 > 0$, $N_2 < 0$.
Repeated rupture leaves $\mu^* \cong$ constant. Einstein: independent of size of particle, just depends on ϕ.

Form of constitutive equation

$$\frac{d}{dt}(\text{state}) \quad \& \quad \sigma \qquad \text{linear in} \quad \mathbf{E} \quad \& \quad \frac{T}{\mu_{\text{ext}} a}$$

Numerical studies: boundary integral method

deformation

angle

σ_{xy}

$N_1,\ N_2$

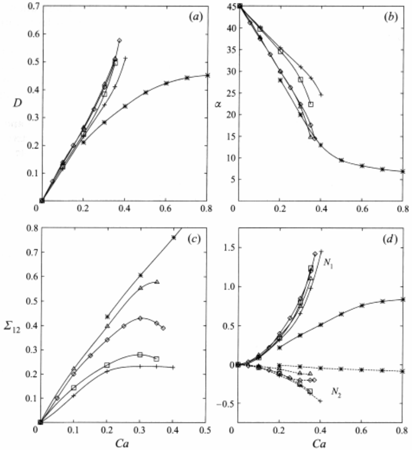


FIGURE 12. Steady-state results as a function of capillary number for $\phi = 10\%$; (*a*) average steady-state drop deformation, (*b*) drop orientation, (*c*) shear stress contribution of drops, and (*d*) contribution of drops to normal stresses: first normal stress difference (solid curves), second normal stress difference (dashed curves); $\lambda = 0$ (+), $\lambda = 0.2$ (□), $\lambda = 1$ (◇), $\lambda = 2$ (△), $\lambda = 5$ (∗).

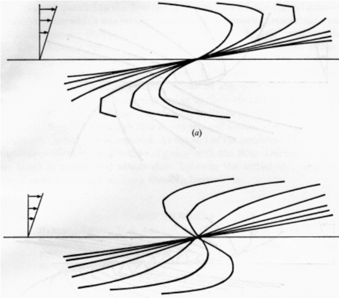
Different λ. No rupture for $\lambda = 5$ (*)

Flexible thread – deformable microstructure

Position $\mathbf{x}(s,t)$, arclength s, tension $T(s,t)$

$$\dot{\mathbf{x}} = \mathbf{x}\cdot\nabla\mathbf{U} + T'\mathbf{x}' + \tfrac{1}{2}T\mathbf{x}''$$

$$\text{with} \quad T'' - \tfrac{1}{2}(\mathbf{x}'')^2 T = -\mathbf{x}'\cdot\nabla\mathbf{U}\cdot\mathbf{x}' \quad \text{and } T = 0 \text{ at ends}$$



Snap straight

Electrical double layer on isolated sphere

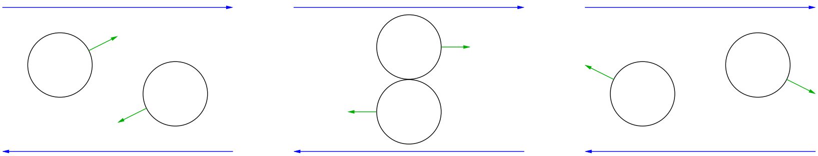
– another deformable microstructure

- Charged colloidal particle.
- Solvent ions dissociate,
- forming neutralising cloud around particle.
- Screening distance Debye κ^{-1}, with $\kappa^2 = \Sigma_i n_i z_i^2 e^2 / \epsilon k T$.
- In flow, cloud distorts a little
- $\longrightarrow$ very small change in Einstein $\frac{5}{2}$.

Hydrodynamic interactions for rigid spheres

Hydrodynamic: difficult long-ranged
Rigid spheres : two bad ideas

Dilute – between pairs (mostly)



Reversible (spheres + Stokes flow) $\rightarrow$ return to original streamlines

But minimum separation is $\frac{1}{2}\,10^{-4}$ radius $\rightarrow$ sensitive to roughness (typically 1%) when do not return to original streamlines.

Summing dilute interactions

Divergent integral from $\nabla \mathbf{u} \sim \dfrac{1}{r^3}$
Need renormalisation: Batchelor or mean-field hierarchy.

$$\mu^* = \mu \left[1 + 2.5\phi + 6.0\phi^2 \right]$$

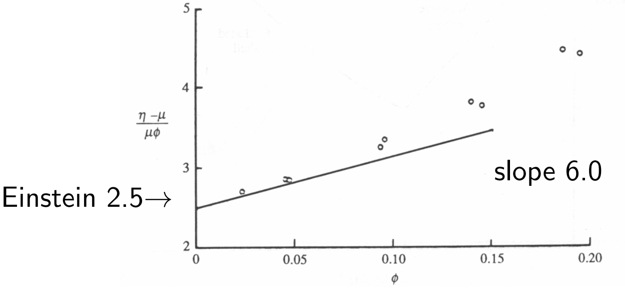
- 6.0 for strong Brownian motion
- 7.6 for strong extensional flow
- $\cong 5$ for strong shear flow, depends on distribution on closed orbits

Small strain-hardening, small shear-thinning

Test of Batchelor ϕ^2 result

$$\mu^* = \mu\left[1 + 2.5\phi + 6.0\phi^2\right]$$

Fig. 14.17. Low shear viscosity for dilute suspensions of hard spheres (Russel, 1980): ○, data for polystyrene latices (a=42, 87 nm) in water (Saunders, 1961); ——, theory of Batchelor (1977).

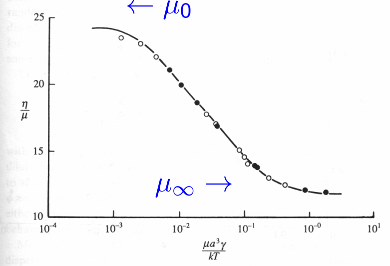


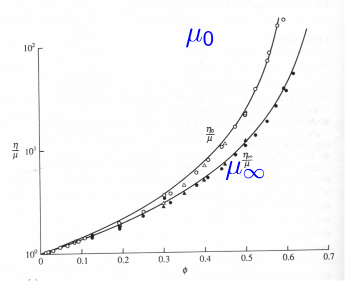
Russel, Saville, Schowalter 1989

Experiments – concentrated

Effective viscosities in shear flow

Fig. 14.3. Relative steady shear viscosity as function of Peclet number for polystyrene latices of radii listed in Table 14.3 dispersed in water (——) and benzyl alcohol or meta-cresol (○ ●) (Krieger, 1972).





$\mu a^3 \gamma / kT$

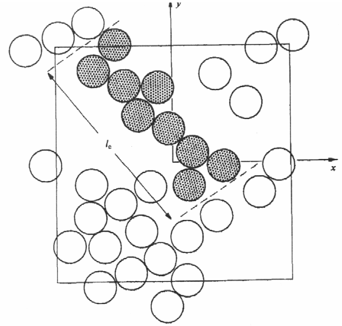
ϕ

Russel, Saville, Schowalter 1989

Stokesian Dynamics

– (mostly) pairwise additive hydrodynamics

Jamming/locking – clusters across the compressive quadrant

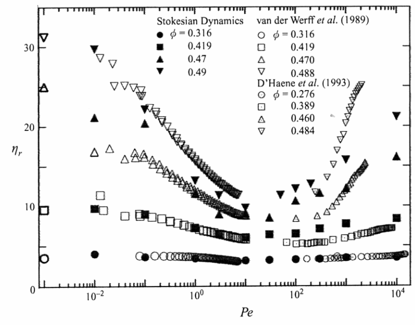


Brady & Bossis (1985)

Fragile clusters if include soft repulsion or Brownian motion

Stokesian Dynamics 2

Effective viscosity in shear flow



Foss & Brady (2000)

'Stokesian Dynamics' Brady & Bossis
Ann. Rev. Fluid Mech. (1988)

Electrical double-layer interactions

Interaction distance r_*:

$$6\mu\mu a\gamma r_* = \frac{\epsilon\zeta^2 a^2\kappa}{r_*} e^{-\kappa(r_* - 2a)}$$

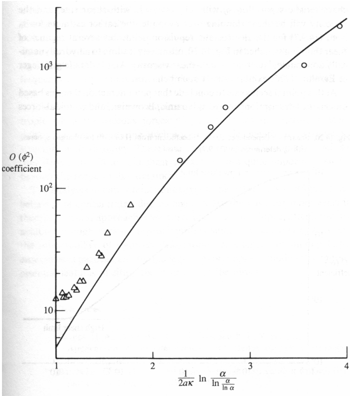
$$\mu_* = \mu\left(1 + 2.5\phi + 2.8\phi^2\left(\frac{r_*}{a}\right)^5\right)$$

$$\left(\frac{r_*}{a}\right)^5 = \text{velocity} \quad \gamma r_*$$

$$\times \text{ force distance} \quad r_*$$

$$\times \text{ volume} \quad \phi\left(\frac{r_*}{a}\right)^3$$

ϕ^2 coefficient as function of $\frac{r_*}{a}$



Experiments – concentrated

Stress as function of shear-rate at different pH.
Suspension of $0.33\mu m$ aluminium particles at $\phi = 0.3$

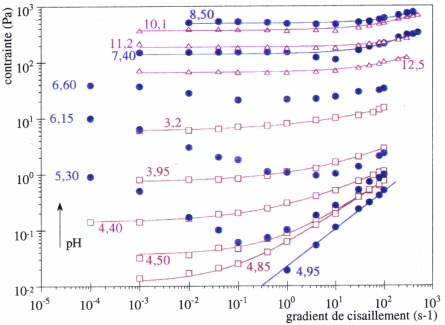


Fig.3 : Courbes d'écoulement de suspensions d'alumine P772SB, en fonction du pH, ϕ_v=0,30.

Ducerf (Grenoble PhD 1992)

Note yield stress very sensitive to pH

Interactions – van der Waals

Attraction $\rightarrow$ aggregation

$\rightarrow$ gel (conc) or suspension of flocs (dilute)

Possible model of size of flocs R

- Number of particles in floc $N = \left(\dfrac{R}{a}\right)^d$, d = 2.3?
- Volume fraction of flocs $\phi_{\mathrm{floc}} = \phi\left(\dfrac{R}{a}\right)^3$
- Collision between two flocs
- Hydro force $6\pi\mu R\gamma R =$ Bond force $F_b\times$ number of bonds $N\frac{a}{R}$
- Hence $\phi_{\mathrm{floc}} = \phi\dfrac{F_b}{6\pi\mu a^2\gamma}$
- So strong shear-thinning and yields stress $\phi F_b/a^2$.

Breakdown of structure in rheology $\mu(\gamma)$

Interactions – fibres

Cannot pack with random orientation if

$$\phi r > 1$$

leads to spontaneous alignment, nematic phase transition

Note extensional viscosity $\propto \phi r^2$ can be big while random, but shear viscosity $\propto \phi r$ is only big if aligned.

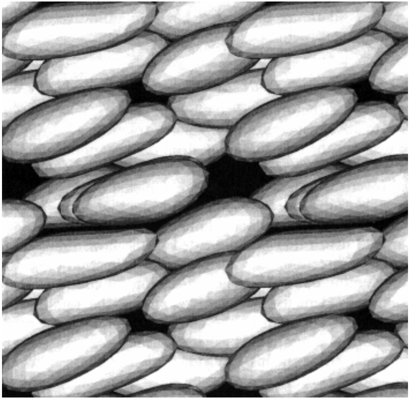
Disk not random if $\phi \frac{1}{r} > 1$.

Interactions – drops

- No jamming/locking of drops (cf rigid spheres)
  - small deformation avoid geometric frustration
  - slippery particle, no co-rotation problems
- Faster flow $\rightarrow$ more deformed $\rightarrow$ wider gaps in collisions
- Deformed shape has lower collision cross-section

  so 'dilute' at $\phi = 0.3$, blood works!

Numerical studies: boundary integral method



$\phi = 0.3$, $Ca = \mu_{\rm ext}\gamma a/T = 0.3$ $\lambda = 1$, $\gamma t = 10$,
12 drops, each 320 triangles.

Numerical studies: boundary integral method 3

deformation

angle

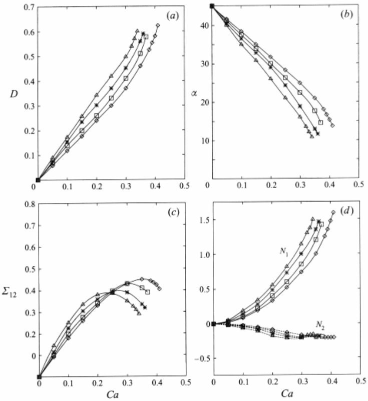


FIGURE 10. Steady-state results as a function of capillary number for $\lambda = 1$. (*a*) Average steady-state drop deformation, (*b*) drop orientation, (*c*) shear stress contribution of drops, and (*d*) contribution of drops to normal stresses: first normal stress difference (solid curves), second normal stress difference (dashed curves); $\phi = 0$ (◇), $\phi = 10\%$ (□), $\phi = 20\%$ (∗), $\phi = 30\%$ (△).

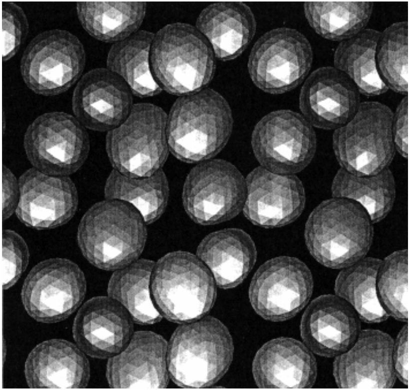
σ_{xy}

$N_1, \ N_2$

$\lambda = 1$, different $\phi = 0, 0.1, 0.2, 0.3$. Effectively dilute at $\phi = 0.3$.

Numerical studies: boundary integral method 4

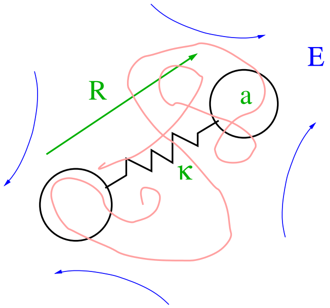
Reduced cross-section for collisions



into flow

Bead-and-Spring model of isolated polymer chain

– simplest, only gross distortion, Kuhn & Kuhn 1945, Kramers 1946



- Flow distortion = Stokes drag = $6\pi\mu a(R \cdot \nabla U - \dot{R})$
  $a = \frac{1}{6} b N^{0.5} \to N^{0.6}$
- Resisted by entropic spring force = κR, $\quad \kappa = \frac{3kT}{Nb^2}$

Hence

$$\dot{R} = R \cdot \nabla U - \frac{1}{2\tau} R \quad \text{with} \quad \tau = 0.8kT/\mu(N^{1/2}b)^3$$

Bead-and-Spring model of isolated polymer chain 2

- Adding Brownian motion of the beads: $A = \langle RR \rangle$

$$\overset{\nabla}{A} \equiv \frac{DA}{Dt} - A\cdot\nabla U - \nabla U^T\cdot A = -\frac{1}{\tau}\left(A - \frac{Nb^2}{3}I\right)$$
$$\sigma = -pI + 2\mu E + n\kappa A$$

with n number of chains per unit volume.

– Oldroyd-B constitutive equation with UCD time derivative $\overset{\nabla}{A}$

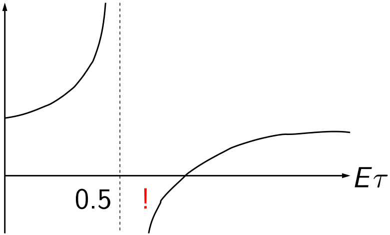
Rheological properties

Shear

- $\mu =$ constant, $N_1 \propto \gamma^2$, $N_2 = 0$.
- Distortion xy: $a\gamma\tau \times a$

Extension

- μ



- Distortion $\propto e^{(2E-\frac{1}{\tau})t}$
- For TDR: small shear and large extensional viscosities

Refinements

1. (boring) Spectrum of internal modes: Rouse 53, Zimm 56 with pre-averaged hydrodynamics
2. (boring) Polydisperse molecular weights
3. (important) Finite extensibility – to stop infinite growth $\propto e^{(2E-\frac{1}{\tau})t}$
   - Nonlinear spring force – inverse Langevin law

     $$F(R) = \frac{kT}{b}\mathcal{L}^{-1}\left(\frac{R}{Nb}\right) \quad \text{with} \quad \mathcal{L}(x) = \coth x - \tfrac{1}{x}$$

   - F.E.N.E approximation

     $$F(R) = \frac{kT}{Nb^2}\frac{R}{1 - R^2/L^2} \quad \text{with fully extended length} \quad L = Nb$$

   - FENE-P closure

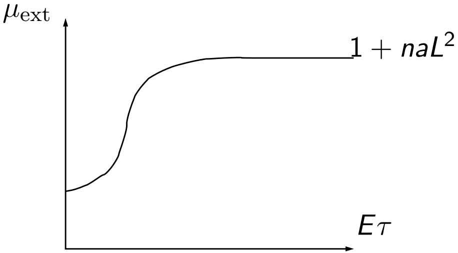
     $$\left\langle RR/(1 - R^2/L^2)\right\rangle = \langle RR\rangle/(1 - \langle R^2\rangle/L^2)$$

     but "molecular individualism"

FENE-P constitutive equation

$$\overset{\nabla}{A} = -\frac{1}{\tau}\frac{L^2}{L^2 - \operatorname{trace} A}\left(A - \frac{a^2}{3}I\right)$$

$$\sigma = -pI + 2\mu E + n\kappa\frac{L^2}{L^2 - \operatorname{trace} A}A$$

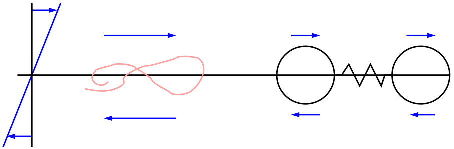


More refinements

4. Nonlinear bead friction
   Hydrodynamic drag increase with size $6\pi\mu(a \to R)$

$$\mu_{\text{ext}} = 1 + nL^3 \qquad \text{and hysteresis}$$

5. Rotation of the beads – simple shear not so simple



Couple balance

$$\text{Afine} \quad \overset{\nabla}{A} \longrightarrow \text{non-affine} \quad \overset{\circ}{A} - \frac{\operatorname{trace} A}{3 + \operatorname{trace} A}(A \cdot E + E \cdot A)$$

inefficiency of straining

One more refinement

6. Dissipative stress – nonlinear internal modes
   Simulations show growing stretched segments

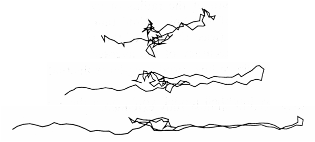
$$\text{segment length} \propto \frac{R^2}{L}, \quad \text{number} \propto \frac{L^2}{R^2}, \quad \text{dissipation} \propto \frac{R^4}{L}$$

$$\sigma = -pI + 2\mu\left(1 + n\frac{(\text{trace}\,A)^2}{L}\right)E + n\kappa\frac{L^2}{L^2 - \text{trace}\,A}A$$

   Good for contraction flows

Unravelling a polymer chain in an extensional flow

Simulation of chain with $N = 100$ in uni-axial straining motion at strains $Et = 0.8, 1.6, 2.4$.

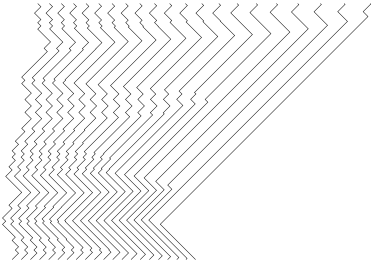


- Growing stretched segments
- Two ends not on opposite sides

Simplified 1D 'kinks' model

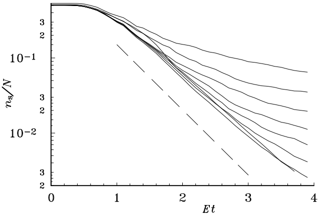
- $t = 0$: 1D random walk, N steps of ± 1
- $t > 0$: floppy inextensible string in $u = Ex$
- arclengths satisfy

$$\dot{s}_i = \frac{1}{4} E(-s_{i+1} + 2s_i - s_{i-1})$$



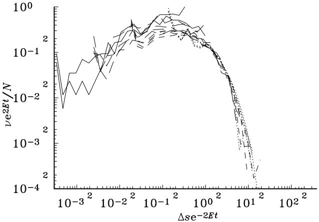
- Large gobble small

Kinks model 2



Number of segments $n(t)$

Scalings

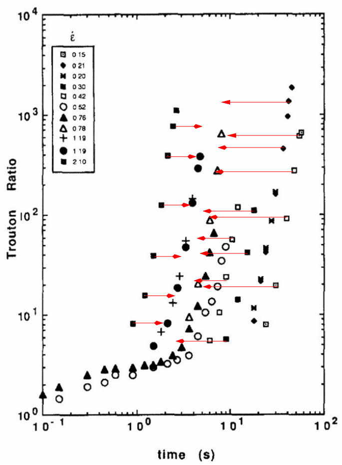


Distribution of lengths $\ell(t)$ scaled by e^{2Et}

$$\begin{cases} n\ell = N \\ \sqrt{n}\ell = R = \sqrt{N}e^{Et} \end{cases} \longrightarrow \begin{cases} n = Ne^{-2Et} \\ \ell = e^{2Et} \end{cases}$$

Evidence of a dissipative stress

Original data of Sridhar, Tirtaatmadja, Nguyen & Gupta 1991 plotted as viscosity as function of time



Replotted a function of strain = strain-rate×time

Improved algorithms for Brownian simulations

1. Mid-point time-stepping avoids evaluating $\nabla\cdot\mathbf{D}$
   Keep random force fixed in time-step, but vary friction
2. Replace very stiff (fast) bonds with rigid + correction potential

   $$-kT\nabla \ln\sqrt{\det M^{-1}} \quad \text{with} \quad M^{-1\,ab} = \sum_{i \text{ beads}} m_i^{-1}\frac{\partial g^a}{\partial \mathbf{x}_i}\cdot\frac{\partial g^b}{\partial \mathbf{x}_i}$$

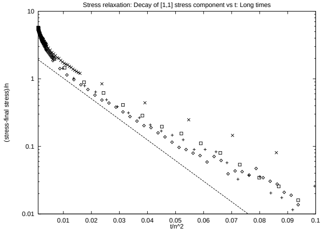
   where rigid constraints are $g^a(\mathbf{x}_1,\ldots,\mathbf{x}_N)=0$ and stiff spring energy $\frac{1}{2}|\nabla g^a|^2$
3. Stress by subtraction of large $\Delta t^{-1/2}$ term with zero average

   $$\tfrac{1}{2}(x^n + x^{n+1})f^n \longrightarrow \tfrac{1}{2}\Delta x^n f^n$$

Grassia, Nitsche & H 95

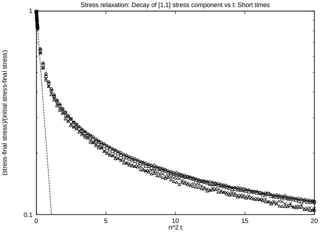
Relaxation of fully stretched chain

Long times - Rouse relaxation

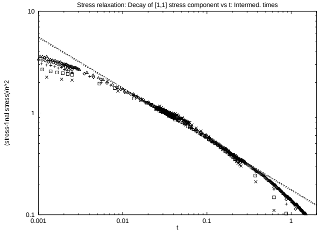


σ/N vs t/N^2 (Rouse)

Short times finite



$\sigma/\frac{1}{3}N^3$ vs $N^2 t$



Intermediate times

$\sigma \sim kTN^2 t^{-1/2}$

Constitutive equation – options

$$\overset{\nabla}{A} = -\frac{1}{h\tau} f\,(A - I)$$

$$\sigma = -pI + 2\mu E + G f A$$

- Oldroyd B $\quad f = 1$
- FENE-P $\quad f = L^2/(L^2 - \mathrm{trace}\, A)$
- Nonlinear bead friction $\quad h = \sqrt{traceA/3}$
- New form of stress

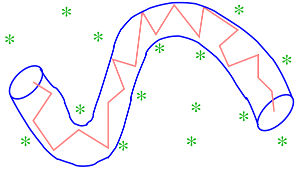
$$\sigma = -pI + 2\mu E + 2\mu_d (A : E)A + G\sqrt{\mathrm{trace}\, A}A$$

  - Last term for finite stress when fully stretched
  - μ_d term ($\propto N^{-1/2}$) for enhanced dissipation

Good for positive pressure drops and large upstream vortices in contraction flows.

Reptation model of De Gennes 1971 – often reformulated

Chain moves in tube defined by topological constraints from other chains.



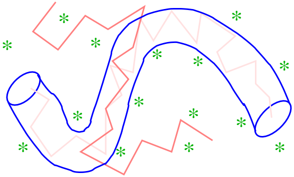
Chain disengages from tube by diffusing along its length

$$\tau_D = \frac{L^2}{D = kT/6\pi\mu L} \propto M^3$$

Modulus $G = nkT \longrightarrow \mu^* = G\tau_D \propto M^3$ (expts $M^{3.4}$)

Diffusion out of tube

At later time:



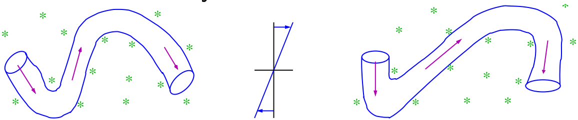
Fraction of original tube surviving

$$\sum_n \frac{1}{n^2} e^{-n^2 t/\tau_D}$$

Diffusion gives linear viscoelasticity $G' \propto \omega^{1/2}$

Doi-Edwards rheology 1978

Deformation of the tube by a shear flow.



Unit segments of the tube $\mathbf{u}$ aligned by flow:

$$\mathbf{u} \longrightarrow \mathbf{A}\mathbf{u} \quad \text{with Finger tensor} \quad \mathbf{A}$$

Stress

$$\sigma(t) = n \int_0^\infty \sum_p \frac{1}{p^2} e^{-p^2 s/\tau_D} \quad N_{\text{segements}} \frac{3kT}{a} a \left\langle \frac{\mathbf{A}^*\mathbf{u}\ \mathbf{A}^*\mathbf{u}}{|\mathbf{A}^*\mathbf{u}|^2} \right\rangle ds$$

surving tube segment tension

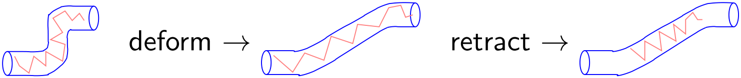
with relative deformation $\mathbf{A}^* = A(t)A^{-1}(t-s)$.

A BKZ integral constitutive equation

Problem maximum in shear stress

Refinements

1. Chain retraction

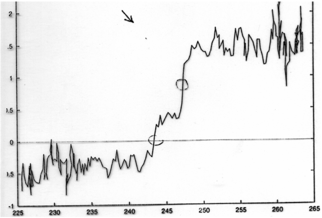
   Chain returns in Rouse time to natural length $\longrightarrow$ loss of segments
2. Chain fluctuations
3. Other chains reptate $\rightarrow$ release topological constraints
   "Double reptation" of Des Cloiseaux 1990. bimodal blends
   2 & 3 give $\mu \propto M^{3.4}$
4. Advected constraint release Marrucci 1996

$$\frac{1}{\tau_D} \longrightarrow \frac{1}{\tau_D} + \beta \nabla u : \langle uu \rangle$$

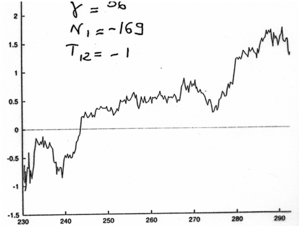
5. Flow changes tube volume or cross-section

Chain trapped in a fast shearing lattice

Lattice for other chains



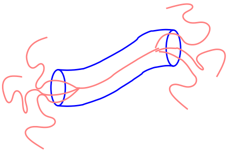
more shear $\rightarrow$



central section pulling chain out of arms $\rightarrow$ high dissipative stresses

Ianniruberto, Marrucci & H 98

Branched polymers – typical in industry



Very difficult to pull branches into central tube
$\mu \propto \exp(M_{\text{arm}}/M_{\text{entangle}})$
Pom-Pom model of Tom McLeish and Ron Larson 1999

$$\sigma = g\lambda^2 \mathbf{S}$$

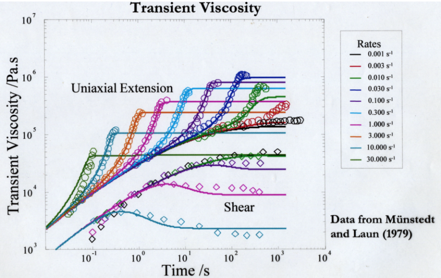
$$\text{Orientation:} \quad \mathbf{S} = \mathbf{B}/\text{trace}\mathbf{B} \qquad \overset{\nabla}{\mathbf{B}} = -\frac{1}{\tau_O}(\mathbf{B} - \mathbf{I})$$

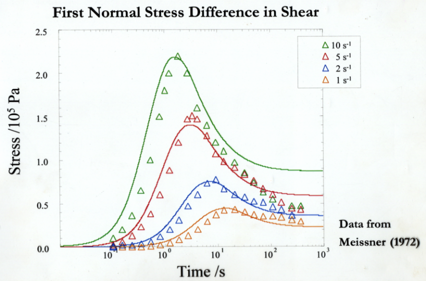
$$\text{Stretch:} \quad \dot{\lambda} = \nabla u : \mathbf{S} - \frac{1}{\tau_S}(\lambda - 1) \quad \text{while} \quad \lambda < \lambda_{\text{max}}$$

with $\tau_O = \tau_{\text{arm}}(M_C/M_E)^3$ and $\tau_S = \tau_{\text{arm}}(M_C/M_E)^2$ and
$\tau_{\text{arm}} \cong \exp(M_{\text{arm}}/M_E)$ where $M_C = M_{\text{crossbar}}$ and $M_E = M_{\text{entanglement}}$.

Test of Pom-Pom model – Blackwell 2002

Fit: Linear Viscoelastic data and Steady Uni-axial Extension.
Predict: Transient Shear and Transient Normal Stress





IUPAC-A data Müntedt & Laun (1979)

Other microstructural studies

- Electro- and Magneto- -rheological fluids
- Associating polymers
- Surfactants - micells
- Aging materials
- GENERIC
- Modelling ‘Molecular individualism’ and closure problems

Outline

Micro & macro views

Einstein viscosity

Rotations

Deformations

Interactions

Polymers

Others