Part III. The rheology of suspensions

May 12, 2014

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

Micro & macro views

Einstein viscosity

Rotations

Deformations

Interactions

Polymers

Others

Separation of length scales

Essential

Micro $\ell \ll L$ Macro

Micro = particle $1\mu m$ Macro = 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 $\ell \not\ll L$, 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→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: $\langle \text{RHS} \rangle = 0$ 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

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

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

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

Solution

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

Hence heat flux

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

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

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

(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

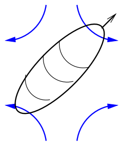
$$\overline{\sigma} = -\overline{p}I + 2\mu\mathbf{E} + 2\mu\phi\left[A(\mathbf{p}\cdot\mathbf{E}\cdot\mathbf{p})\mathbf{pp} + B(\mathbf{pp}\cdot\mathbf{E} + \mathbf{E}\cdot\mathbf{pp}) + C\mathbf{E}\right]$$

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

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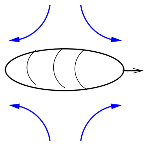
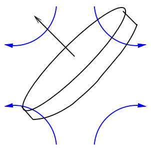


Aligns with stretching direction → maximum dissipation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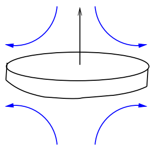


Aligns with inflow direction → maximum dissipation

Effective extensional viscosity for rods

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

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

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

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 $\phi \ll 1 \ll \phi r^2$

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

Effective extensional viscosity for disks

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

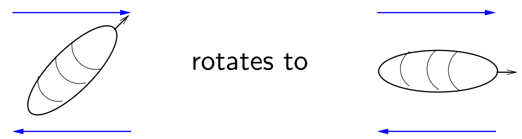
where for disks b is the largest dimension

(always the largest for Stokes flow).

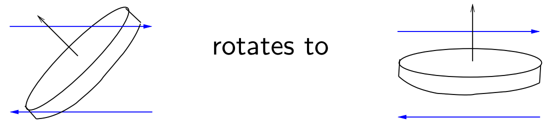
No semi-dilute theory, yet.

Behaviour in simple shear

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



Rotates to flow direction $\to$ minimum dissipation



Rotates to lie in flow $\to$ minimum dissipation

Both Tumble: flip in $1/\gamma$, then align for r/γ ($\delta\theta = 1/r$ 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)

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

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

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

(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

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

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

Average stress over distribution P

Averaged stress

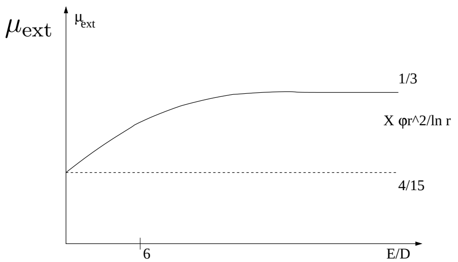
$$\sigma = -pI + 2\mu E + 2\mu\phi[AE : \langle\mathbf{pppp}\rangle + B(E\cdot\langle\mathbf{pp}\rangle + \langle\mathbf{pp}\rangle\cdot E) + CE + FD_{\rm rot}\langle\mathbf{pp}\rangle]$$

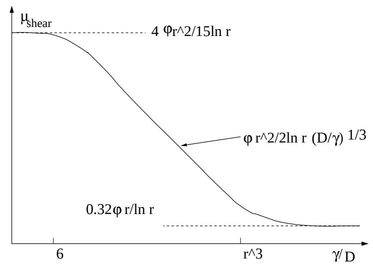
Last $FD_{\rm rot}$ term is entropic stress.
Extra material constant $F = 3r^2/(\ln 2r - 0.5)$ for rods and $12/\pi r$ for disks.

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

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

Extensional and shear viscosities





Small strain-hardening

↕ Orientation effects

Large shear-thinning

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

The closure problem

- Second moment of Fokker-Plank equation

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

  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

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

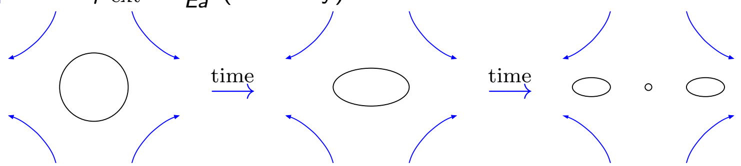
- New idea Brownian fields: simulate many random walks in orientation space for each point of the complex flow.

Emulsions - deformable microstructure

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

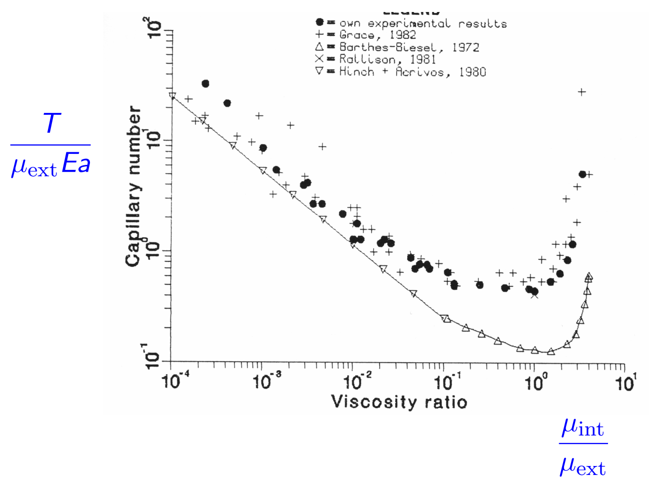
- Dilute – single drop, volume $\frac{4\pi}{3}a^3$
- T = surface tension (in rheology σ and γ not possible)
- Newtonian viscous drop μ_{int}, solvent μ_{ext}

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



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

Rupture in shear flow



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

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

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

Too slippery. Become long and thin. Rupture if

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

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

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

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

- If internal very viscous ($\mu_{\text{int}} \gg \mu_{\text{ext}}$),
  - then rotates with vorticity,
  - rotating with vorticity, sees alternative stretching and compression,
  - hence deforms little.
- If internal fairly viscous ($\mu_{\text{int}} \gtrsim 3\mu_{\text{ext}}$),
  - 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 $\mu_{\text{int}} \leq 3\mu_{\text{ext}}$

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

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

$$\sigma = -pI + 2\mu_{\text{ext}}\mathbf{E} + 2\mu_{\text{ext}}\phi\Big[k_3\mathbf{E} + k_7(\mathbf{A}\cdot\mathbf{E} + \mathbf{E}\cdot\mathbf{A}) + \ldots - \frac{T}{\mu_{\text{ext}} a}(k_4\mathbf{A} + k_8(\mathbf{A}\cdot\mathbf{A}) + \ldots\Big]$$

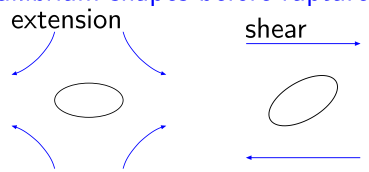
with k_n depending on viscosity ratio, k_1 inefficiency of rotating by straining $\lambda = \mu_{\text{int}}/\mu_{\text{ext}}$

$$k_1 = \frac{5}{2(2\lambda+3)}, \qquad k_2 = \frac{40(\lambda+1)}{(2\lambda+3)(19\lambda+16)}$$

$$k_3 = \frac{5(\lambda-1)}{3(2\lambda+3)}, \qquad k_4 = \frac{4}{2\lambda+3}$$

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

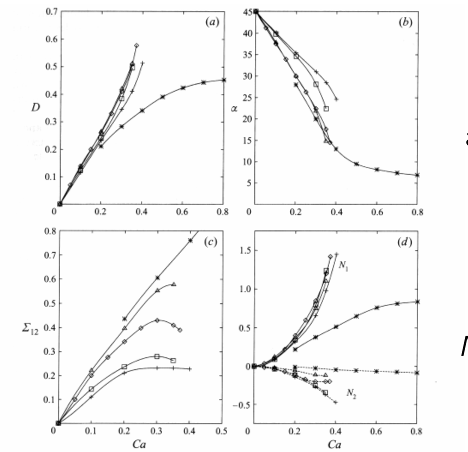


FIGURE 12. Steady-state results as a function of capillary number for $\phi = 10\%$: (a) average steady-state drop deformation, (b) drop orientation, (c) shear stress contribution of drops, and (d) contribution of drops to normal stresses: first normal stress difference (solid curves), second normal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

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

Electrical double layer on isolated sphere

– another deformable microstructure

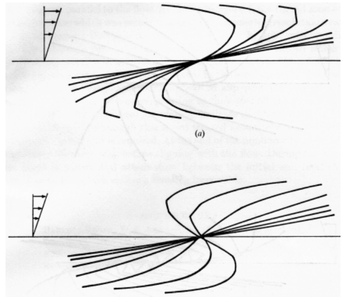
- Charged colloidal particle.
- Solvent ions dissociate,
- forming neutralising cloud around particle.
- Screening distance Debye κ^{-1}, with $\kappa^2 = \Sigma_i n_i z_i^2 e^2/\epsilon k T$.
- In flow, cloud distorts a little
- $\longrightarrow$ very small change in Einstein $\frac{5}{2}$.

Flexible thread – deformable microstructure

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

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

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

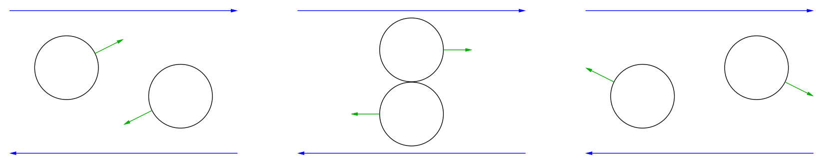


Snap straight

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.

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

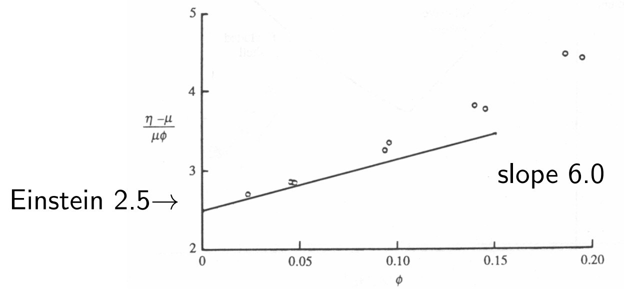
- 6.0 for strong Brownian motion
- 7.6 for strong extensional flow
- $\cong 5$ for strong shear flow, depends on distribution on closed orbits

Small strain-hardening, small shear-thinning

Test of Batchelor ϕ^2 result

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

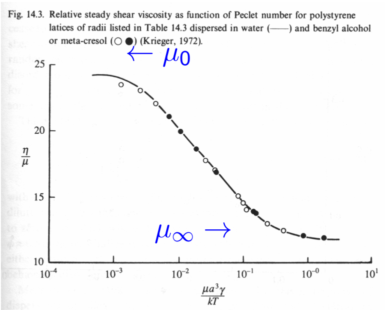
Fig. 14.17. Low shear viscosity for dilute suspensions of hard spheres (Russel, 1980): ○, data for polystyrene latices (a = 42, 87 nm) in water (Saunders, 1961); ——, theory of Batchelor (1977).

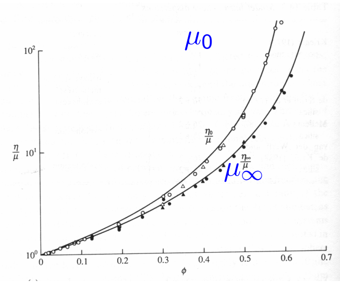


Russel, Saville, Schowalter 1989

Experiments – concentrated

Effective viscosities in shear flow





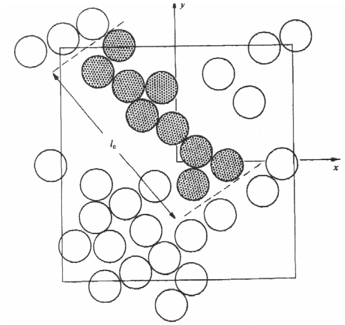
$\mu a^3\gamma/kT$ $\qquad$ ϕ

Russel, Saville, Schowalter 1989

Stokesian Dynamics

– (mostly) pairwise additive hydrodynamics

Jamming/locking – clusters across the compressive quadrant

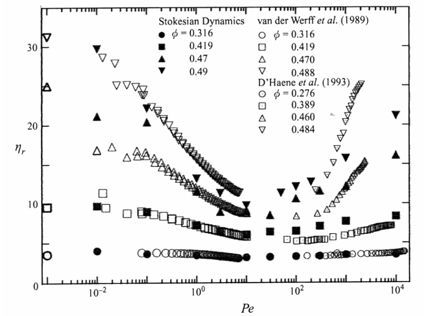


Brady & Bossis (1985)

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_*:

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

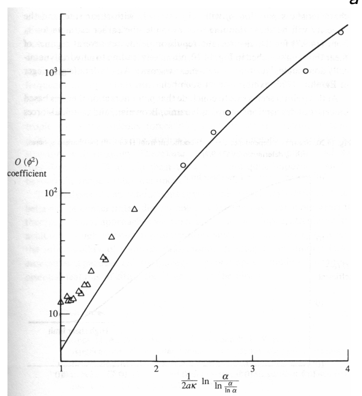
$$\mu_* = \mu\left(1 + 2.5\phi + 2.8\phi^2\left(\frac{r_*}{a}\right)^5\right)$$

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

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

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

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 $\phi = 0.3$

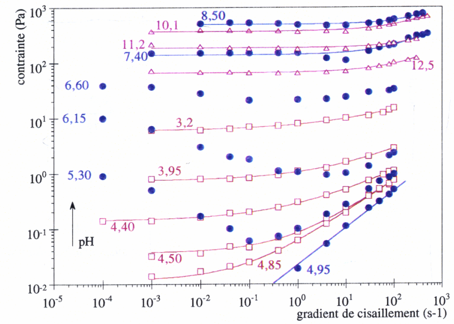


Fig.3 : Courbes d'écoulement de suspensions d'alumine P772SB, en fonction du pH, ϕ_v=0,30.

Ducerf (Grenoble PhD 1992)

Note yield stress very sensitive to pH

Interactions – van der Waals

Attraction → aggregation

→ gel (conc) or suspension of flocs (dilute)

Possible model of size of flocs R

- Number of particles in floc $N = \left(\frac{R}{a}\right)^d$, d = 2.3?
- Volume fraction of flocs $\phi_{\text{floc}} = \phi\left(\frac{R}{a}\right)^3$
- 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 $\phi_{\text{floc}} = \phi\frac{F_b}{6\pi\mu a^2\gamma}$
- 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.

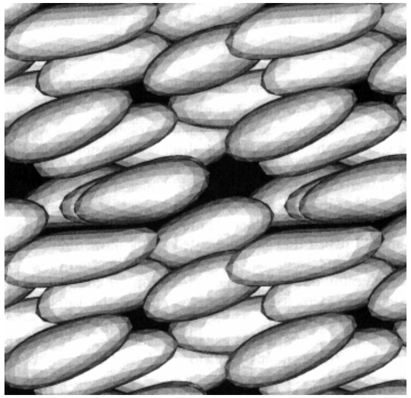
Disk not random if $\phi\frac{1}{r} > 1$.

Interactions – drops

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

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

Numerical studies: boundary integral method



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

Numerical studies: boundary integral method 3

deformation

angle

σ_{xy}

N_1, N_2

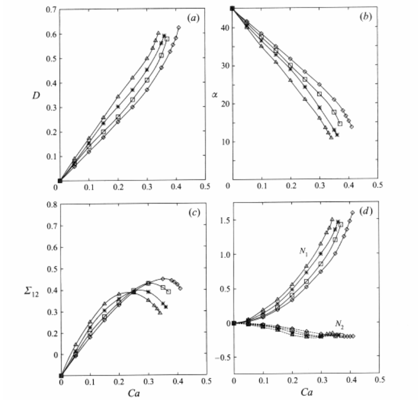
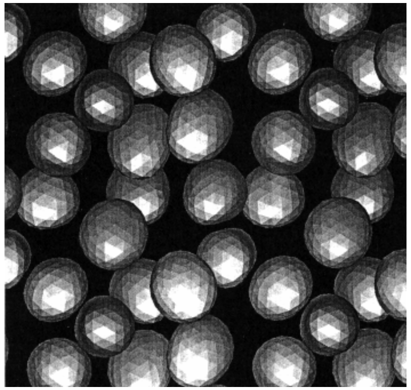


FIGURE 10. Steady-state results as a function of capillary number for $\lambda = 1$. (a) Average steady-state drop deformation, (b) drop orientation, (c) shear stress contribution of drops, and (d) contribution of drops to normal stresses: first normal stress difference (solid curves), second normal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

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

Numerical studies: boundary integral method 4

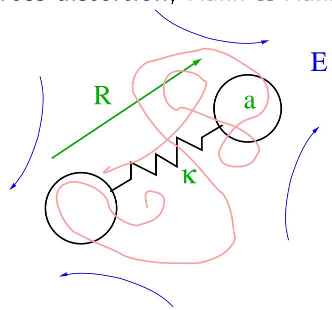
Reduced cross-section for collisions



into flow

Bead-and-Spring model of isolated polymer chain

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



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

Hence

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

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 $\overset{\nabla}{A}$

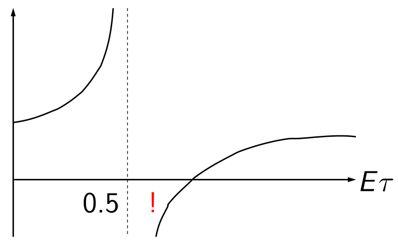
Rheological properties

Shear

- μ = 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

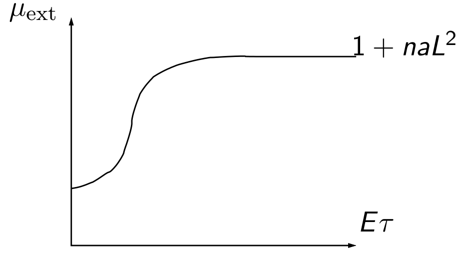
$$\langle RR/(1 - R^2/L^2)\rangle = \langle RR\rangle/(1 - \langle R^2\rangle/L^2)$$

but “molecular individualism”

FENE-P constitutive equation

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

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

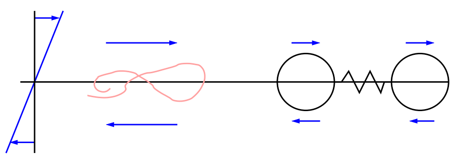


More refinements

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

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

inefficiency of straining

One more refinement

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

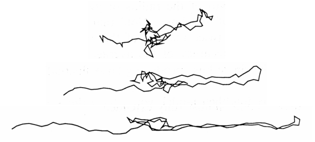
$$\text{segment length} \propto \frac{R^2}{L}, \quad \text{number} \propto \frac{L^2}{R^2}, \quad \text{dissipation} \propto \frac{R^4}{L}$$

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

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 $Et = 0.8,\ 1.6,\ 2.4$.

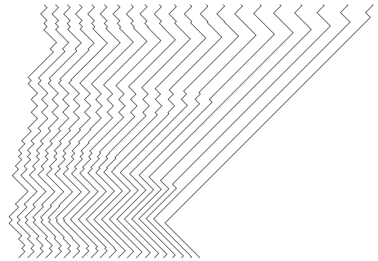


- Growing stretched segments
- Two ends not on opposite sides

Simplified 1D 'kinks' model

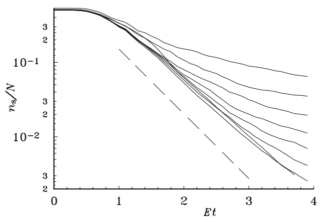
- $t = 0$: 1D random walk, N steps of ± 1
- $t > 0$: floppy inextensible string in $u = Ex$
- arclengths satisfy

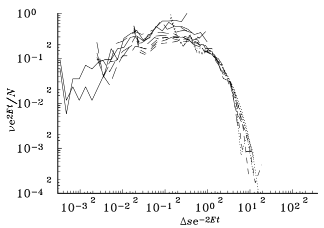
$$\dot{s}_i = \tfrac{1}{4}E(-s_{i+1} + 2s_i - s_{i-1})$$



- Large gobble small

Kinks model 2





Number of segments $n(t)$

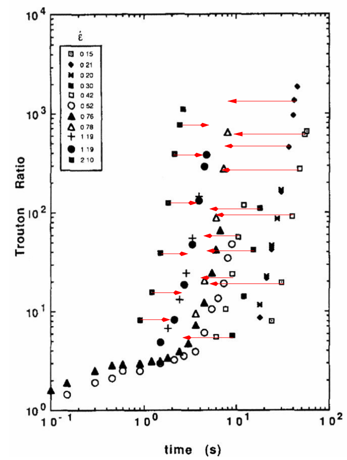
Distribution of lengths $\ell(t)$ scaled by e^{2Et}

Scalings

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

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

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

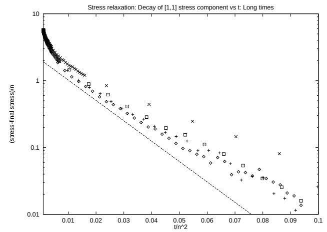
   where rigid constraints are $g^a(\mathbf{x}_1,\ldots,\mathbf{x}_N)=0$ and stiff spring energy $\frac{1}{2}|\nabla g^a|^2$
3. Stress by subtraction of large $\Delta t^{-1/2}$ term with zero average

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

Grassia, Nitsche & H 95

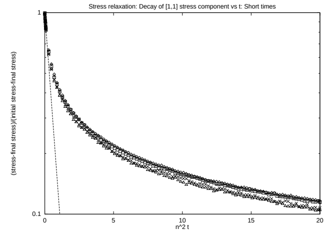
Relaxation of fully stretched chain

Long times - Rouse relaxation

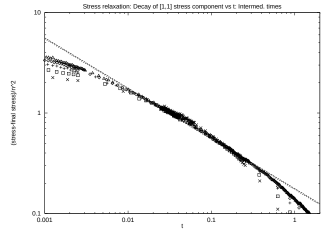


σ/N vs t/N^2 (Rouse)

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

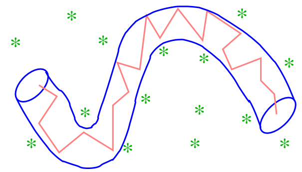
$$\sigma = -pI + 2\mu E + 2\mu_d(A:E)A + G\sqrt{\text{trace}\,AA}$$

  - 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.



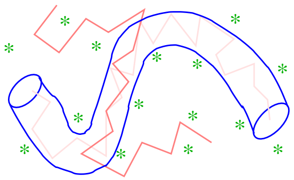
Chain disengages from tube by diffusing along its length

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

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

Diffusion out of tube

At later time:



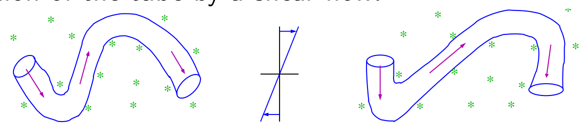
Fraction of original tube surviving

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

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:

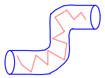
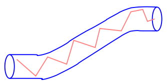
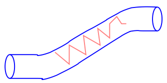
$$\mathbf{u} \longrightarrow \mathbf{A}\mathbf{u} \quad \text{with Finger tensor} \quad \mathbf{A}$$

Stress

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

with relative deformation $\mathbf{A}^* = A(t)A^{-1}(t-s)$.
A BKZ integral constitutive equation
Problem maximum in shear stress

Refinements

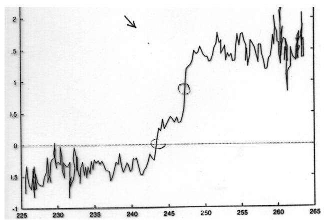
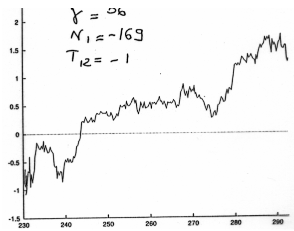
1. Chain retraction
    deform →  retract → 
   Chain returns in Rouse time to natural length $\longrightarrow$ loss of segments
2. Chain fluctuations
3. Other chains reptate → release topological constraints
   "Double reptation" of Des Cloiseaux 1990. bimodal blends
   2 & 3 give $\mu \propto M^{3.4}$
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

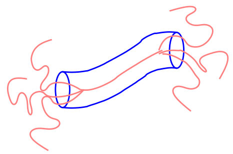
Lattice for other chains

 more shear → 

central section pulling chain out of arms → 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

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

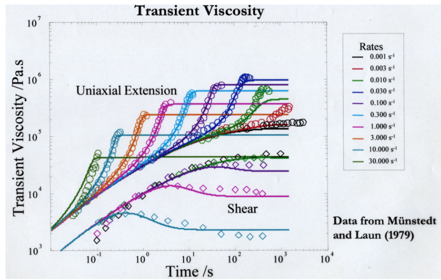
Orientation: $\mathbf{S} = \mathbf{B}/\text{trace}\mathbf{B} \qquad \overset{\nabla}{\mathbf{B}} = -\frac{1}{\tau_O}(\mathbf{B} - \mathbf{I})$

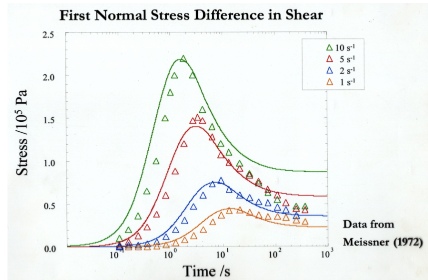
Stretch: $\dot{\lambda} = \nabla u : \mathbf{S} - \frac{1}{\tau_S}(\lambda - 1)$ while $\lambda < \lambda_{\text{max}}$

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