

Few notes on rheology in soft materials

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Acknowledgments :

- **To my friend Grisha Volovik for being born 75 years ago.**
- **To all of you for coming to my talk.**

Basics of linear viscoelasticity

- Response of a material (shear stress $\sigma(t)$) is proportional to the the applied shear strain $\gamma(t)$

$$\left(1 + \alpha_1 \frac{\partial}{\partial t} + \dots + \alpha_n \frac{\partial^n}{\partial t^n}\right) \sigma(t) = \left(\beta_0 + \beta_1 \frac{\partial}{\partial t} + \dots + \beta_m \frac{\partial^m}{\partial t^m}\right) \gamma(t)$$

where n, m are integer numbers, and α_i, β_j are material constants.

- Hook's law ($\sigma = G\gamma$) when only $\beta_0 = G \neq 0$. Newton's viscosity law $\sigma = \eta\dot{\gamma}$ if only $\beta_1 = \eta \neq 0$.
- Kelvin - Voigt model and Maxwell model if $\beta_0 = G \neq 0$ and $\beta_1 = \eta \neq 0$.
Then

$$\sigma(t) = G\gamma + \eta\dot{\gamma}$$

If a constant stress $\bar{\sigma}$ is applied for $t \geq 0$, then the solution is

$$\gamma(t) = \frac{\bar{\sigma}}{G} [1 - \exp(-Gt/\eta)]$$

- Maxwell liquid is a series of one spring (Hook elasticity) and one damper (viscosity). Kelvin-Voigt model is represented by the parallel combination of the spring and of the damper. Any rheology can be modeled by more complex arrangements of springs and dampers.

Kelvin-Voigt liquids

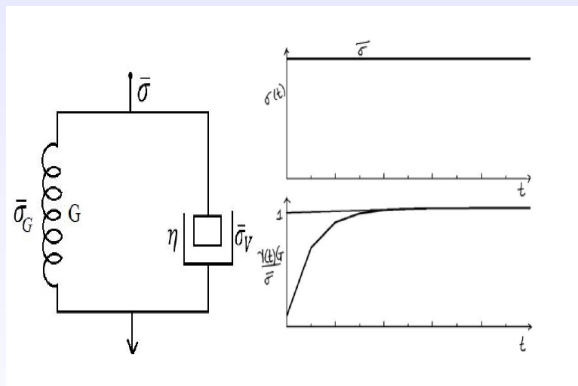


Figure – When a constant shear stress $\bar{\sigma}$ is applied, the strain $\gamma(t)$ builds up exponentially (whereas in a Hook case the strain builds up instantaneously).

Maxwell liquids

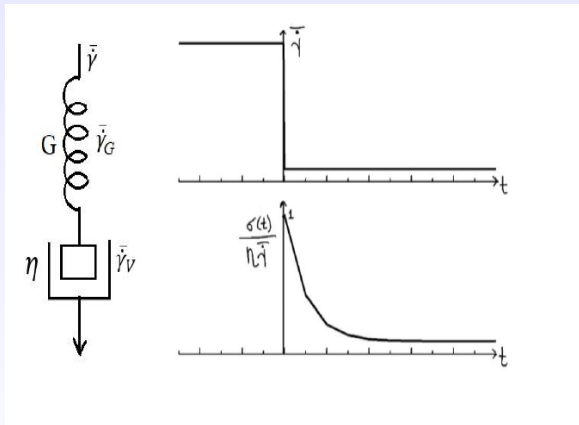


Figure – When shear strain $\bar{\gamma}$ is suddenly withdrawn, the stress decays exponentially with a relaxation time η/G in a contrast to the instantaneous dissipation in a Newtonian liquid.

Nomenclature of types of viscoelastic flows (non-linear viscoelasticity)

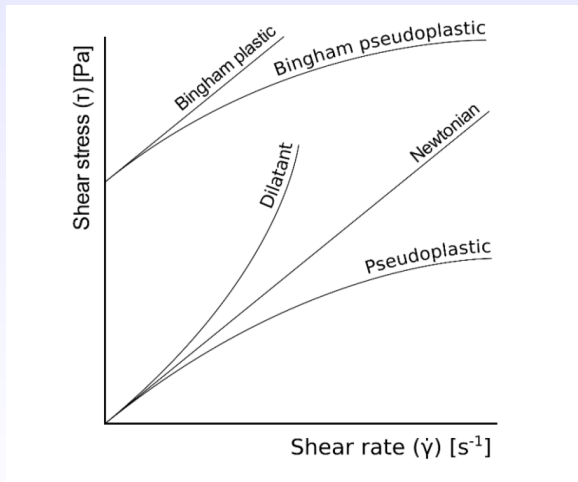


Figure – dilatants = shear thickening (starch), and pseudo-elastic = shear thinning (blood, paint), Bingham (toothpaste, ketchup).

Qualitative interpretation

- Shear thinning : In polymer melts and solutions, shear thinning is caused by the disentanglement of polymer chains during flow. This leads to less molecular/particle interaction and a larger amount of free space, decreasing the viscosity.
- Dilatancy (shear thickening, often due to aggregation into flock) : Material jams when it is stirred vigorously, and flows when stirred gently. It can be characterized by the Deborah number $De = \tau / \tau_{flow}$ (τ -material relaxation time, τ_{flow} is the time scale of the external flow ($De \ll 1$ -liquid-like behavior, $De \gg 1$ - solid-like).
- Thixotropy - viscosity depends on the time duration, and not on the rate of the applied shear. All thixotropic materials are shear-thinning (the converse is not necessary true)

Weissenberg effect

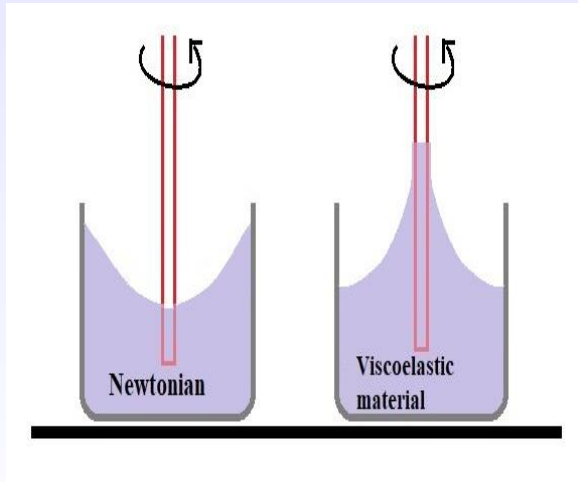
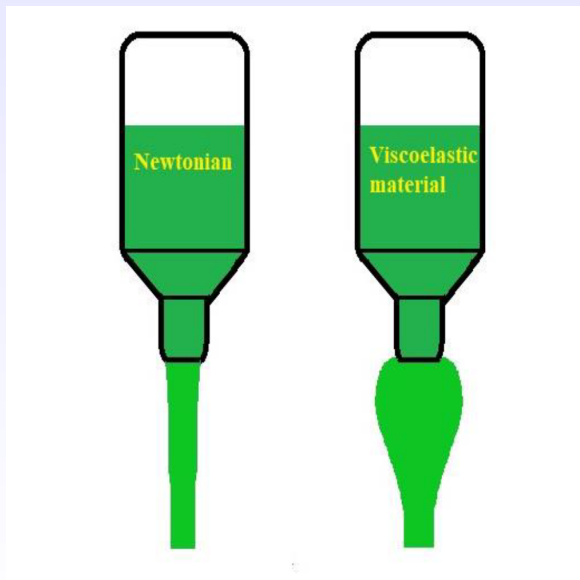


Figure – Normal stresses : $N_1 = \sigma_{xx} - \sigma_{yy} = -c_1(\dot{\gamma})^2$; $N_2 = \sigma_{yy} - \sigma_{zz} = -c_2(\dot{\gamma})^2$.

Qualitative interpretation of the Weissenberg effect

When a spinning rod is inserted in a viscoelastic liquid (polymer solution), the sample, instead of being thrown outward as it is the case for a Newtonian fluid, moves towards and climbs the rod. The effect arises due to positive normal stresses. The polymer chains twist around the rod as it rotates, and the free ends in the bulk of the solution remain entangled. During the rotation of the rod, the end of the chain is wrapped around the rod and is under tension (a pulling force acts on each end). When trying to decrease the distance between the two ends, the polymer tries to move up or down the rod to the area where the rod is less wrapped in the polymer chain. In contrast, a Newtonian liquid will move towards the edge due to inertial forces.

Barus effect



Qualitative interpretation of the Barus effect.

The viscoelastic liquid swells immediately upon exiting out of a small orifice. The matter is that the polymer material (in a poor solvent) prefer to exist as globules, such liquids experience high shear rates during their passage through the orifice and stretched out in the direction of flow. Immediately after exiting the orifice, the material coils up into globules (i.e., swells).

Fano effect

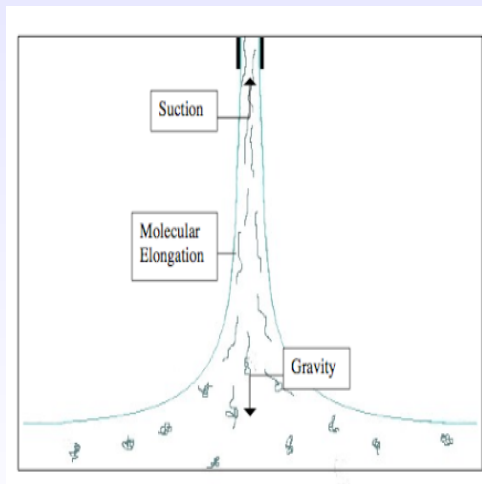


Figure – Normal stresses : $N_1 = \sigma_{xx} - \sigma_{yy} = -c_1(\dot{\gamma})^2$; $N_2 = \sigma_{yy} - \sigma_{zz} = -c_2(\dot{\gamma})^2$.

Qualitative interpretation of the Fano effect.

- Tubeless siphon - a syringe can draw out a viscoelastic liquid even without touching the surface. It arises from extensional viscosity, i.e., increase of a viscosity under extension. To create a tubeless siphon, a siphon is first started by inserting a nozzle (connected to a tube and vacuum source) into a dish of non-Newtonian fluid. The siphon nozzle is then raised above the free surface of the fluid, but the siphoning action continues.
- In Newtonian liquids, the liquid column breaks immediately. Non-Newtonian liquids can be pulled up to a considerable height due to large normal stresses that balance the weight of the fluid.
- Many other Fano contributions into atomic and nuclear physics, molecular physics, and radiological biophysics (Fano resonance, Fano factor, Fano mechanism, Fano effect, Fano theorem).

Kaye effect I.

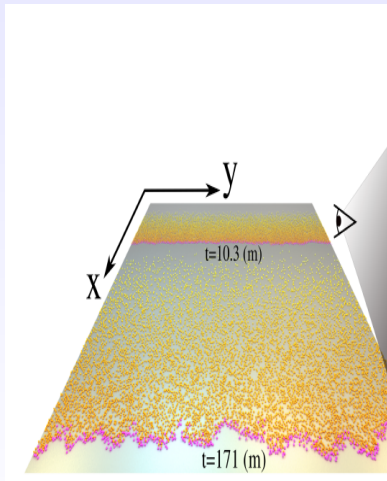


Figure – Intermittent jet formation

Kaye effect II.



Figure – Intermittent jet formation

Qualitative interpretation of the Kaye effect.

A viscoelastic liquid that is poured down an inclined plane shear thins as it slides down the plane. It produces intermittent jets of such a liquid.

Open questions

Twist-bend nematic rheology.

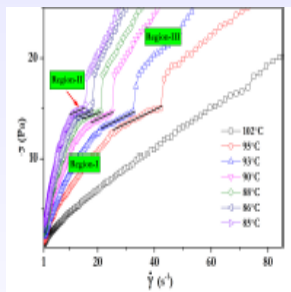


Figure – Not yet explained experimental data for a twist-bend nematic liquid crystal

Pending experimental data to explain

- N_{TB} nematics shows three shear stress responses. In region-I

$$\sigma \simeq C_1(T) \sqrt{\dot{\gamma}}$$

where $C_1(T)$ decays to zero, at about T^* below N to N_{TB} phase transition. Thus $\eta_{eff} \propto \dot{\gamma}^{1/2}$, i.e., shear thinning.

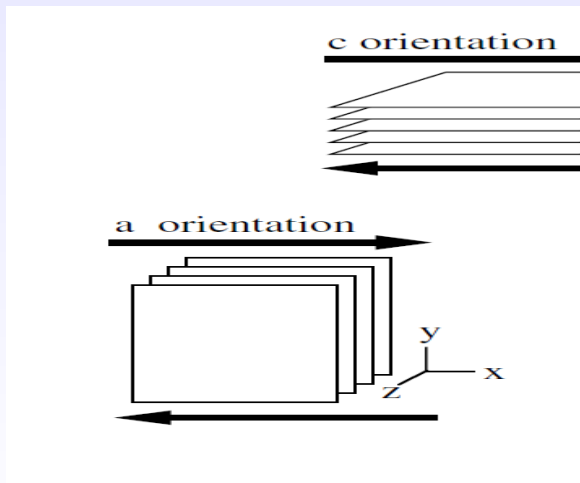
- In region-II,

$$\sigma \propto (\dot{\gamma})^\alpha$$

with α linearly increasing with T from $\simeq 0.1$ to $\simeq 0.4$. Stress plateau = shear banding (liquid crystal breaks up into coexisting bands of high and low viscosity). It could be shear-induced "phase" coexistence.

- In region-III, $\sigma \simeq C_3(T) \dot{\gamma}$.
- Transition I to II is continuous, whereas II to III transition is discontinuous with a hysteresis.
- Similar behavior is known for smectics. I to III transition can be related to shear induced reorientation of the pseudo-layers ($B \simeq K/P^2$).

Smectic-like configurations under shear.



Sedimentation of colloidal monolayers sliding on inclined plane I.

- For small ϕ the sedimentation velocity

$$v(\phi) \simeq v_0 + \frac{a}{2}\phi$$

where v_0 is the sedimentation velocity of an isolated particle (particles interact hydrodynamically and advect other particles via flow they create).

- The local conservation law

$$\frac{\partial \phi}{\partial t} + \frac{\partial}{\partial x} (v(\phi)\phi) = 0$$

Note of caution : the local mean-field approximation is not appropriate for the non-local in its nature hydrodynamic interaction.

- Then we got the Burgers equation

$$\frac{\partial \phi}{\partial t} + v_0 \frac{\partial \phi}{\partial x} + a\phi \left(\frac{\partial \phi}{\partial x} \right) = 0$$

We set $v_0 = 0$ for convenience (non-zero v_0 simply translates the solution by $v_0 t$).

Sedimentation of colloidal monolayers sliding on inclined plane II.

- We assume the initial density : $\phi(x, t = 0) = \phi_0$ for $0 < x < l$. Then there is a propagating shock wave with its front at $x_f(t)$ ($x_f(0) = l$), and a rarefaction wave at $x_b(t) = 0$.
- There is characteristic time in the problem

$$t^* = 2 \frac{l}{a\phi_0} ; x_f(t^*) = 2l$$

- Mass conservation law

$$M = \int_0^{x_f} \phi(x, t) dx = l\phi_0$$

- Solution to the Burgers equation

$$\phi(x, t > t^*) = \begin{cases} x/at & 0 \leq x \leq x_f(t) \\ 0 & x > x_f(t) \end{cases}$$

- Thus $x_f(t) = (2aMt)^{1/2}$, and presumably independent of the initial conditions.

Particle density profile

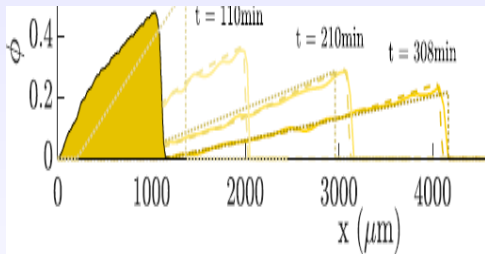


Figure – Triangle of area M . Accounting $v_0 \neq 0$, the back of the front position $x_b(t) = v_0 t$, and $x_f(t) - x_b(t) = [2aMt]^{1/2}$.

Conclusions

- A complete understanding of soft matter rheology (including also elastic turbulence, or drag reduction) is still lacking.
- I wish to Grisha Volovik, many Happy Returns to this Day!