Bifurcating Transport of Glassy Matter
Within Annular Micropores

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Abstract
Glassy matter, as subjected to high shear rates, exhibit shear thinning: i.e., the viscosity diminishes with increasing shear rate. Meanwhile one prominent difference between the transport in micropores and that in macroscale is the (relatively) larger roughness observed inside micropores. As the pore size decreases, the surface-to-volume ratio increases and therefore, surface roughness will greatly affect the transport in micropores. By treating the glass as a shear-thinning matter and using the rate-dependent model together with the boundary perturbation method, we can analytically obtain the transport results up to the second order.

Keywords: Boundary perturbation; Tunneling; Shear-thinning; Wavy roughness;

1 Introduction

In recent years, considerable effort was geared towards understanding how glasses respond to shear [1-3]. Phenomena such as shear thinning (i.e., the higher the shear rate is, the smaller is the flow resistance) and ‘rejuvenation’ are common when shear flow is imposed. Unlike crystals, glasses age, meaning that their state depends on their history. When a glass falls out of equilibrium, it evolves over very long time scales [4-7].

Meanwhile most of the classical solutions of contact problems, starting from the Hertzian case, rely on the assumption of nominally smooth geometries, which is reasonable at large enough scales. However, real surfaces are rough at the micro- or even at the meso-scale [8-10]. The role of surface roughness has been extensively investigated, and opposite conclusions have been reached so far. For instance, friction can increase when two opposing surfaces are made smoother (this is the case of cold welding of highly polished metals). On the other hand, friction increases with roughness when interlocking effects among the asperities come into play. This apparent contradiction is due to the effects of length scales, which appear to be of crucial importance in this phenomenon.

In this paper we shall consider the transport of glassy matter in micropores which have radius-or transverse-corrugations along the cross-section. The glassy matter will be treated as a shear-thinning material. To consider the transport of this kind of glass (shear-thinning fluids) in microscopic domain, we adopt the verified transition-rate dependent model [4-5] which was used
to study the annealing of glass.

We noticed that Cagle and Eyring [5] tried a hyperbolic sine law between the shear (strain) rate $\dot{\xi}$ and (large) shear stress $\tau$ (because the relaxation at the beginning was steeper than could be explained by the bimolecular law) and obtained the close agreement with experimental data. They can obtain the law of annealing of glass for explaining the too rapid annealing at the earliest time. This model has sound physical foundation from the thermal activation process [4] (a kind of (quantum) tunneling which relates to the matter rearranging by surmounting a potential energy barrier was proposed therein; cf., Fig. 1). With this model we can associate the (glassy) fluid with the momentum transfer between neighboring atomic clusters on the microscopic scale and reveals the atomic interaction in the relaxation of flow with (viscous) dissipation.

The outline of this short paper is as follows. Section 2 describes the general mathematical and physical formulations of the framework. In this Section, explicit derivations for the glassy flow are introduced based on a microscopic model proposed before [4]. The boundary perturbation technique [8-9] will be implemented, too. In the 3rd. and 4th. Sections, relevant results and discussion are given therein.

2 Mathematical and physical formulations

By the beginning of this century the concept of activation entropy was included in the model, and it was considered that molecules go both in the forward direction (product state) and in the backward direction (reactant state). The development of statistical mechanics, and later quantum mechanics, led to the concept of the potential energy surface. This was a very important step in our modern understanding of atomic models of deformation. Eyring’s contribution to this subject was the formal development of the transition state theory which provided the basis for deformation kinetics, as well as all other thermally activated processes, such as crystallisation, diffusion, polymerisation, etc. [4-5]

The motion of atoms is represented in the configuration space; on the potential surface the stable molecules are in the valleys, which are connected by a pass that leads through the saddle point. An atom at the saddle point is in the transition (activated) state [4]. Under the action of an applied stress the forward velocity of a (plastic) flow unit is the net number of times it moves forward, multiplied by the distance it jumps. Eyring proposed a specific molecular model of the amorphous structure and a mechanism of flow. With reference to this idea, this mechanism results in a (shear) strain rate given by

$$\dot{\xi} = 2\frac{V_h k_B T}{h} \exp\left(-\frac{\delta G}{k_B T}\right) \sinh\left(\frac{V_h \tau}{2 k_B T}\right)$$

(1)
where \( V_h = \lambda_2 \lambda_3 \lambda_1 \), \( V_m = \lambda_2 \lambda_3 \lambda_1 \), \( \lambda_1 \) is the perpendicular distance between two neighboring layers of molecules sliding past each other, \( \lambda \) is the average distance between equilibrium positions in the direction of motion, \( \lambda_2 \) is the distance between neighboring molecules in this same direction (which may or may not equal \( \lambda \)), \( \lambda_3 \) is the molecule to molecule distance in the plane normal to the direction of motion, and \( \tau \) is the local applied stress, \( \delta G \) is the activation energy, \( h \) is the Planck constant, \( k_B \) is the Boltzmann constant, \( T \) is the temperature, \( V_h \) is the activation volume for the molecular event [4-5]. The flow of the glass is envisaged as the propagation of kinks in the molecules into available holes. In order for the motion of the kink to result in a plastic flow, it must be raised (energised) into the activated state and pass over the saddle point.

Solving Eqn. (1) for the force or \( \tau \), one obtains:

\[
\tau = \frac{2k_B T}{V_h} \sinh^{-1}\left(\frac{\dot{\xi}}{B}\right),
\]

which in the limit of small \( (\dot{\xi}/B) \) reduces to Newton’s law for viscous flow.

We start to consider a steady, fully developed flow of the glassy fluid in a wavy-rough microannulus of \( r_2 \) (in mean-averaged outer radius) with the outer wall being a fixed wavy-rough surface: \( r = r_2 + \epsilon \sin(k\theta) \) and \( r_1 \) (in mean-averaged inner radius) with the inner wall being a fixed wavy-rough surface: \( r = r_1 + \epsilon \sin(k\theta + \beta) \), where \( \epsilon \) is the amplitude of the (wavy) roughness, and the wave number: \( k = \frac{2\pi}{L} \) \((L \) is the wave length\), \( \beta \) is the phase shift. The schematic is illustrated in Fig. 2.

Firstly, this glassy fluid can be expressed as \( \dot{\xi} = \dot{\xi}_0 \sinh(\tau/\tau_0) \), \( \tau_0 \equiv 2k_B T/V_h \), where \( \dot{\xi} \) is the shear rate, \( \tau \) is the shear stress, and

\[
\dot{\xi}_0 \equiv B = \frac{2V_h k_B T}{V_m h} \exp\left(-\frac{\delta G}{k_B T}\right)
\]
is a function of temperature with the dimension of the shear rate (for small shear stress \( \tau \ll \tau_0 \), \( \tau_0/\dot{\xi}_0 \) represents the viscosity of the material). In fact, the force balance gives the shear stress at a radius \( r \) as \( \tau = -(r dp/dz)/2 \). \( dp/dz \) is the pressure gradient along the flow (or tube-axis: \( z \)-axis) direction.

Introducing the forcing parameter \( \Pi = -(r_2/2\tau_0)dp/dz \) then we have \( \dot{\xi} = \dot{\xi}_0 \sinh(\Pi r/r_2) \). As \( \dot{\gamma} = -du/dr \) \((u \) is the velocity of the fluid flow in the longitudinal \((z\)-direction of the microannulus), after integration, we obtain

\[
u = u_s + \frac{\dot{\xi}_0 r_2}{\Pi} \left[ \cosh \Pi - \cosh \left( \frac{\Pi r}{r_2} \right) \right],
\]

here, \( u_s \) is the velocity over the surfaces of the microannulus, which is determined by the boundary condition. We noticed that a general boundary condition for fluid flows over a solid surface was proposed (cf., e.g., [10-11]) as

\[
\delta u = L_\xi^0 \dot{\xi}(1 - \frac{\dot{\xi}}{\dot{\xi}_c})^{-1/2},
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\[
\delta u = L_\xi^0 \dot{\xi}(1 - \frac{\dot{\xi}}{\dot{\xi}_c})^{-1/2},
\]
where $\delta u$ is the velocity jump over the solid surface, $L_s^0$ is a constant slip length and $\dot{\xi}_c$ is the critical shear rate at which the slip length diverges. The value of $\dot{\xi}_c$ is a function of the corrugation of interfacial energy. We remind the readers that this expression is based on the assumption of the shear rate over the solid surface being much smaller than the critical shear rate of $\dot{\xi}_c$. $\dot{\xi}_c$ represents the maximum shear rate the fluid can sustain beyond which there is no additional momentum transfer between the wall and fluid molecules [10-11]. How generic this behavior is and whether there exists a comparable scaling for glassy fluids remain open questions.

With the boundary condition from [10-11], we shall derive the velocity field and volume flow rate along the wavy-rough microannuli below using the boundary perturbation technique (cf., e.g., [8-9]) and dimensionless analysis. We firstly select $L_a \equiv r_2 - r_1$ to be the characteristic length scale and set

$$r' = r/L_a, \quad R_o = r_2/L_a, \quad R_i = r_1/L_a, \quad \epsilon' = \epsilon/L_a.$$ 

After this, for simplicity, we drop all the primes. It means, now, $r$, $R_o$, $R_i$, and $\epsilon$ become dimensionless. The walls are prescribed as $r = R_o + \epsilon \sin(k\theta)$, $r = R_i + \epsilon \sin(k\theta + \beta)$ and the presumed fully-developed flow is along the $z$-direction (microannulus-axis direction). Along the boundary, we have

$$\dot{\xi} = (du/dn)|_{\text{on surface}},$$

where, $n$ means the normal. Let $u$ be expanded in $\epsilon : u = u_0 + \epsilon u_1 + \epsilon^2 u_2 + \cdots$, and on the boundary, we expand $u(r_0 + \epsilon dr, \theta(= \theta_0))$ into

$$u(r, \theta)|_{(r_0+\epsilon dr, \theta_0)} = u(r_0, \theta) + \epsilon [dr u_r(r_0, \theta)] + \epsilon^2 [\frac{dr^2}{2} u_{rr}(r_0, \theta)] + \cdots$$

$$= u_{\text{slip}} + \frac{\dot{\xi} R_o}{\Pi} \cosh(\frac{\Pi r}{R_o})|_{r_0+\epsilon \sin(k\theta)},$$

(5)

where the subscript means the partial differentiation (say, $u_r \equiv \partial u/\partial r$) and

$$u_{\text{slip}}|_{\text{on surface}} = L_s^0 \dot{\xi} [(1 - \frac{\dot{\xi}}{\dot{\xi}_c})^{-1/2}]|_{\text{on surface}},$$

(6)

$$u_{\text{slip}_0} = L_s^0 \dot{\xi}_0 [\sinh \Pi (1 - \frac{\dot{\xi}_0 \sinh \Pi}{\dot{\xi}_c})^{-1/2}].$$

(7)

Now, on the outer wall (cf., e.g., [8-9]),

$$\dot{\xi} = \frac{du}{dn} = \nabla u \cdot \frac{\nabla (r - R_o - \epsilon \sin(k\theta))}{|\nabla (r - R_o - \epsilon \sin(k\theta))|} = [1 + \frac{\epsilon^2 k^2}{r^2} \cos^2(k\theta)]^{-\frac{1}{2}} |u_r|_{(R_o+\epsilon dr, \theta)} - \frac{k}{r^2} \cos(k\theta) u_\theta|_{(R_o+\epsilon dr, \theta)} = u_0, |R_o + \epsilon |u_1, |R_o + u_{0rr}, |R_o, \sin(k\theta) -$$
\[
\frac{k}{r^2} u_{0\theta} |R_o | \cos(k\theta) + \epsilon^2 \left\{ - \frac{1}{2} \frac{k^2}{r^2} \cos^2(k\theta) u_{0\theta} \right\} |R_o | + u_{2r} |R_o | + u_{1rr} |R_o | \sin(k\theta) + \frac{1}{2} u_{0rrr} |R_o | \sin^2(k\theta) - \frac{k}{r^2} \cos(k\theta) (u_{1\theta} |R_o | + u_{0\theta} |R_o | \sin(k\theta)) + O(\epsilon^3).
\]

(8)

Considering \( L^0_s \sim R_o, R_i \gg \epsilon \) case, we presume sinh \( \Pi \ll \dot{\xi}_c \) so that we can approximately replace \([1 - (\dot{\xi}_0 \sinh \Pi) / \dot{\xi}_c]^{-1/2}\) by \([1 + \dot{\xi}_0 \sinh \Pi / (2\dot{\xi}_c)]\). With equations (5), (6) and (8), using the definition of \( \dot{\xi} \), we can derive the velocity field up to the second order. The key point is to firstly obtain the slip velocity along the boundary or surface.

After lengthy mathematical manipulations and using \((1 - \frac{\dot{\xi}}{\dot{\xi}_c})^{-1/2} \approx 1 + \frac{\dot{\xi}}{2\dot{\xi}_c}\),

\[
\begin{align*}
  u_0 &= -\frac{\dot{\xi}_0 R_o}{\Pi} [\cosh(\frac{\Pi r}{R_o}) - \cosh \Pi] + u_{slip_0}, \quad u_1 = \dot{\xi}_0 \sin(k\theta) \sinh \Pi + u_{slip_1}, \\
  u_{slip} &= L^0_s \{ -u_{0\theta} (1 - u_{0\theta}) \} |r = R_o | + \epsilon [-u_f (1 - u_{0\theta}) ] |r = R_o | + \epsilon^2 \left\{ \frac{u_f^2}{2\dot{\xi}_c} - u_{sc} (1 - u_{0\theta}) \right\} |r = R_o | = u_{slip_0} + \epsilon u_{slip_1} + \epsilon^2 u_{slip_2} + O(\epsilon^3)
\end{align*}
\]

(9)

where

\[
  u_f = u_{1r} + u_{0rr} \sin(k\theta) - \frac{k}{r^2} \cos(k\theta) u_{0\theta} = -\frac{\Pi}{R_o} \dot{\xi}_0 \cosh(\frac{\Pi}{R_o} r) \sin(k\theta),
\]

and

\[
  u_{sc} = -\frac{k^2}{2r^2} \cos^2(k\theta) u_{0r} + \frac{1}{2} u_{0rr} \sin^2(k\theta) = \frac{\dot{\xi}_0}{\epsilon} \frac{k^2}{2r^2} \cos^2(k\theta) - \frac{\Pi^2}{R_o^2} \sin^2(k\theta) | \sinh(\frac{\Pi}{R_o} r).
\]

Thus, at \( r = R_o \), up to the second order,

\[
  u_{slip} \equiv u_s = L^0_s \dot{\xi}_0 \sinh \Pi (1 + \frac{K_0}{2}) + \epsilon \dot{\xi}_0 \sin(k\theta) | \sinh \Pi + \frac{\Pi}{R_o} L^0_s \cosh \Pi (1 + K_0) + \epsilon^2 L^0_s \dot{\xi}_0 \frac{\Pi}{R_o} \sinh \Pi (1 + K_0 - \frac{\Pi^2}{R_o^2} \cosh^2 \Pi \sin^2(k\theta)),
\]

(10)

where \( K_0 = 1 + (\dot{\xi}_0 \sinh \Pi) / \dot{\xi}_c \). From the velocity fields (up to the second order), we can integrate them with respect to the cross-section to get the volume flow rate \( (Q, \text{ also up to the second order here}) \). \( Q = \int_0^\theta \int_{R_i\sin(k\theta)}^{R_o \sin(k\theta)} u(r, \theta) r dr d\theta = \int_0^\theta \int_{R_i\sin(k\theta)}^{R_o \sin(k\theta)} u_{slip} \).
\[
\frac{\dot{\xi}_0 R_o}{\Pi} \cosh \Pi + \dot{\xi}_0 R_o (- \sinh \Pi + \frac{\cosh \Pi}{\Pi}) + \dot{\xi}_0 (R_i \sinh(\frac{R_i}{R_o}) - \frac{R_o}{\Pi} \cosh(\frac{R_i}{R_o})) + \\
\pi \dot{\xi}_0 \left[ (\sinh \Pi + \frac{\Pi \cosh \Pi}{R_o}(1 + \frac{\sinh \Pi}{\xi_c/\xi_0})) [R_o - R_i (\cos \beta + \sin \beta)] \right] + \\
L_s \frac{\pi}{4} \Pi^2 \dot{\xi}_0 \frac{\cosh \Pi}{\xi_c/\xi_0} [1 - (\frac{R_i}{R_o})^2 \cosh \chi].
\]

Here, \[
u_{slip} = L_s \dot{\gamma}_0 [\sinh \Pi (1 - \frac{\sinh \Pi}{\xi_c/\xi_0})]^{-1/2}.
\]

### 3 Results and discussion

In the following, as our interest is about the transport of glassy matter at very low temperature environment ($\Pi \to 0$), thus we should take the asymptotic limit of $Q$. In fact, we have, for the smooth surface of the micropore,

\[
Q_{\text{smooth}}|_{\Pi \to 0} = \pi \dot{\xi}_0 \left\{ L_s^0 (R_o^2 - R_i^2) \sinh \Pi (1 - \frac{\sinh \Pi}{\xi_c/\xi_0})^{-1/2} + \frac{R_o}{\Pi} [(R_o^2 - R_i^2) \cosh \Pi - \\
2 \frac{R_i}{\Pi} (R_o^2 \sinh \Pi - R_i R_o \sinh(\frac{R_i}{R_o})) + \frac{2 R_i^2}{\Pi^2} (\cosh \Pi - \cosh(\frac{R_i}{R_o})) \right\}|_{\Pi \to 0} = 0,
\]

and for the wavy-rough surface (up to the second order) $Q_{p2} = 0$ as $\Pi \to 0$. Now, the (referenced) shear-rate

\[
\dot{\xi}_0 \equiv B = 2 \frac{V_h}{V_m} \frac{k_B T}{h} \exp(-\delta G/k_B T),
\]

is a function of temperature and the activation energy. From equation (11), we can observe that the transport of glassy matter in very-low temperature : $T \to 0$ is rather small ($Q_{p2} \propto \dot{\xi}_0 \propto T \exp(-1/T)$)! It is worth pointing out that the Eyring model requires the interaction between atoms in the direction perpendicular to the shearing direction for the momentum transfer [4-5]. This might explain why our result is orientation dependent (due to $\beta$).

Note that, based on the rate-state Eyring model [4] (of stress-biased thermal activation), structural rearrangement is associated with a single energy barrier (height) $E$ that is lowered or raised linearly by an applied stress $\sigma$ or $\tau$. If the transition rate is proportional to the shear strain rate (with a constant ratio : $C_0$), we have

\[
\sigma = E/V^* + (k_B T/V^*) \ln(\dot{\xi}/C_0 \nu_0),
\]

where $V^*$ is a constant called the activation volume, $k_B$ is the Boltzmann constant, $T$ is the temperature, and $\nu_0$ is an attempt frequency [4-5,12]. Normally, the value of $V^*$ is associated with a typical volume required for a molecular shear rearrangement. Thus, the nonzero flow rate
(of the glass) as forcing is absent could be related to a barrier-overcoming or tunneling for shear-thinning matter along the wavy-roughness (geometric valley and peak served as atomic potential surfaces) in annular micropores when the wavy-roughness is present. Once the geometry-tuned potentials (energy) overcome this barrier, then the tunneling (spontaneous transport) inside wavy-rough annular micropores occurs.

We also noticed that, as described in [4], mechanical loading lowers energy barriers, thus facilitating progress over the barrier by random thermal fluctuations. The simplified Eyring model approximates the loading dependence of the barrier height as linear. The linear dependence will always correctly describe small changes in the barrier height, since it is simply the first term in the Taylor expansion of the barrier height as a function of load. It is thus appropriate when the barrier height changes only slightly before the system escapes the local energy minimum. This situation occurs at higher temperatures; for example, Newtonian flow is obtained in the Eyring model in the limit where the system experiences only small changes in the barrier height before thermally escaping the energy minimum. As the temperature decreases, larger changes in the barrier height occur before the system escapes the energy minimum (giving rise to, for example, non-Newtonian flow). In this regime, the linear dependence is not necessarily appropriate, and can lead to inaccurate modelling. This explains why we should adopt the hyperbolic sine law [4-5] to treat the glassy matter.

Finally, we present the calculated maximum velocity (unit: m/s) with respect to the temperature in Fig. 3. Geometric parameters: \( r_2 = 100 \text{ nm} \), the activation volume: \( 0.2 \text{ nm}^3 \) and the roughness amplitude \( \epsilon = 0.05r_2 \). We consider the effect of the activation energy: \( 10^{22} \) and \( 2 \times 10^{22} \) Joule. Around \( T \sim 0.25^\circ \text{K} \), the maximum velocity (of the glassy matter) either keeps decreasing as the temperature increases for larger activation energy or instead increases as the temperature increases for smaller activation energy! The latter observation might be related to the argues raised in [13] for annealing process of solid helium at similar low temperature environment if we treat the solid helium to be glassy at low temperature regime.

4 Conclusion

To conclude in brief, we obtain the transport of glassy matter inside annular wavy-rough micropores under very low temperature environment. The flow rate is rather small (of the order of magnitude of the square of the small wavy-roughness amplitude) and is proportional to the (referenced) shear rate (which is strongly temperature as well as activation energy dependent), the slip length and phase shift of the wavy-roughness as illustrated above. Acknowledgement.

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References

[1] R.N. Haward and R.J. Young, The Physics of Glassy Polymers, Chapman and Hall, London, 1997.
[2] R. Larson, The Structure and Rheology of Complex Fluids, Oxford University Press, Oxford, 1998.
[3] A.J. Liu and S.R. Nagel, Jamming and Rheology, Taylor and Francis, London, 2003.
[4] H. Eyring, Viscosity, plasticity, and diffusion as examples of absolute reaction rates, J. Chem. Phys. 4 (1936) 283-291.
[5] F.W. Cagle, Jr. and H. Eyring, An application of the absolute reaction rate theory to some problems in annealing, J. Appl. Phys. 22 (1951) 771-775.
[6] D.J. Lacks, Energy landscapes and the non-newtonian viscosity of liquids and glasses, Phys. Rev. Lett. 87 (2001) 225502/1-4.
[7] L. Ramos and F. Molino, Shear melting of a hexagonal columnar crystal by proliferation of dislocations, Phys. Rev. Lett. 92 (2004) 018301/1-4.
[8] W. K.-H. Chu, Slip flow over rough wavy wall, Z. Angew. Math. Mech. 76 (1996) 363-364.
[9] W. K.-H. Chu, Stokes slip flow between corrugated walls. Z. Angew. Math. Phys. 47 (1996) 591-599.
[10] Z. K.-H. Chu, Rapid transport of glassy supersolid helium in wavy-rough nanpores, arXiv:0707.2828 (2007). Z.K.-H. Chu, (in Press, 2008).
[11] E.M. Kotsalis, J.H. Walther and P. Koumoutsakos, Multiphase water flow inside carbon nanotubes, Int. J. Multiphase Flow 30 (2004) 995-1010
[12] F.M. Capaldi, M.C. Boyce, G.C. Rutledge, Molecular response of a glassy polymer to active deformation, Polymer 45 (2004) 1391-1399.
[13] A. Penzev, Y. Yasuta, M. Kubota, Annealing Effect for Supersolid Fraction in $^4$He, J. Low Temp. Phys. 148 (2007) 677-681.
Fig. 1. The structural contribution to the shear stress is: Shear thinning. Increasing strain causes a local energy minimum to flatten until it disappears (removing of energy barrier or quantum-like tunneling).

Fig. 2. Schematic of an annular micropore. $\beta$ is the phase shift between the outer and inner wavy-roughness. $\epsilon$ is the amplitude of small wavy-roughness.
Fig. 3. Comparison of calculated (maximum) velocity (unit : m/s) using two activation energies $10^{-22}$ and $2 \times 10^{-22}$ Joule. Around $T \sim 0.25^\circ$K, the monotonic trend of velocity bifurcates as the temperature increases. $r_2 = 100$ nm and $\epsilon = 0.05r_2$ here.