NEARLY FRICTIONLESS TRANSPORT OF AMORPHOUS MATTER IN NANOPORES

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Summary Amorphous matter subjected to high shear rates exhibits shear thinning : Viscosity diminishes with increasing shear rate. One possible outcome is the nearly frictionless transport of amorphous matter in nanopores. Here we show that, by treating the amorphous matter as a shear-thinning matter and using the transition-state theory together with the specific activation energy, we can observe a series of sudden change of the shearing stresses (or resistance) at corresponding transition temperatures for different activation volumes.

INTRODUCTION

Transport of amorphous matter (polymer and glassy fluids of which the temperature effect is important) in micro- and nanodomains attracts many researchers' investigation recently (cf. [1-3]). One relevant issue is a possible solidification of liquids confined in a porous medium which has already attracted the attention of researchers over the years (cf. [2]). The elevation (of freezing pressure) and depression (of freezing temperature) are closely related to the mechanism for the nucleation of solid in the pores, and cannot be explained by the homogeneous nucleation theory using the bulk properties when the pore size becomes much smaller. Moreover the confinement changes the behavior of transition between liquid and solid [2].

Meanwhile real surfaces are rough at the micro- and nanoscale [4,5], and the effect of multi-point contact is important for a series of phenomena. Thus, the role of surface roughness in the microscopic transport should be investigated. In this presentation we shall consider the influence of activation energy and activation volume upon the nearly frictionless transport of amorphous matter at a wider temperature regime in nanopores which have radius- or transverse-corrugations along the cross-section. The amorphous matter will be treated as a shear-shinning material [3,4,6]. To consider the transport of this kind of amorphous matter in microscopic rough domain, we adopt the verified transition-state model [3-6] together with a general boundary condition [7] and the boundary perturbation approach [5,8]. We shall demonstrate the possible nearly frictionless states of amorphous matter in nanodomains which are temperature dependent. Interestingly these nearly frictionless states could have a wide range of viscosities from solid-like to liquid-like.

FORMULATIONS

The microscopic molecular theory of deformation kinetics came from a different stream of science than that of structure and motion of crystal defects (in particular dislocations). Its roots stretch to the developmental stages of theories of chemical reactions and thermodynamic description of their temperature dependence, culminating in the key formulation by Arrhenius of the equation for reaction rates [3]. By the beginning of 20th 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 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 possible pass that leads through the saddle point. An atom at the saddle point is in the transition (activated) state. 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 microscopic flow [3,6]. With reference to this idea, this mechanism results in a (shear) strain rate given by

$$\dot{\eta} = 2\frac{\Lambda}{\Lambda_1}\frac{k_B T}{h}\exp(\frac{-\delta G}{k_B T})\sinh(\frac{V_a \tau}{2k_B T}) \tag{1}$$

where Λ_1 is the perpendicular distance between two neighboring layers of molecules sliding past each other, Λ is the average distance between equilibrium positions in the direction of motion, τ is the local applied stress, δG is the activation energy, h is the Planck constant, k_B is the Boltzmann constant, T is the temperature and V_a is the activation volume for the molecular event [6].

We consider a steady, fully developed transport of the amorphous matter under a pressure gradient in a wavy-rough nanoannulus. Now, on the outer boundary or interface (cf., e.g., [3,5,8]), we have

$$|\dot{\eta}| = |\frac{du}{dn}| = |\nabla u \cdot \frac{\nabla(r - R_o - \epsilon\sin(k\theta))}{|\nabla(r - R_o - \epsilon\sin(k\theta))|}| \tag{2}$$

where the walls are prescribed as $r = R_o + \epsilon\sin(k\theta)$, $r = R_i + \epsilon\sin(k\theta + \beta)$, $R_o = r_2/(r_2 - r_1)$ (r_2 : mean-averaged outer radius, r_1 : mean-averaged inner radius); ϵ is the amplitude of the small (wavy) roughness, k is the wave number, β is the phase shift, n means the normal, and the presumed steady-state transport (u being the velocity) is along the z-direction (nanoannulus-axis direction).

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Based on the transition-state model of stress-biased thermal activation, structural rearrangement is associated with a single energy barrier (height) E ($\equiv \delta G$) that is lowered or raised linearly by a (shear) yield stress τ. If the transition rate is proportional to the shear strain rate (with a constant ratio : C_0), we have $\tau = E/V_a + (k_BT/V_a)\ln(\dot{\eta}/C_0\nu_0)$, where ν_0 is an attempt frequency [3]. Normally, the value of V_a is associated with a typical volume required for a molecular shear rearrangement. Note that to calculate $\dot{\eta}$ in above expression of τ we need to use equation (2) and $\dot{\eta}_0 = 2(\Lambda/\Lambda_1)(k_BT/h)\exp[-\delta G/(k_BT)]$ with a forcing parameter (cf. [4,5] for mathematical details).

NUMERICAL RESULTS AND DISCUSSION

To illustrate our novel approach and results we give a brief numerical example here. We fix the activation energy to be 10^{-19}J in Fig. 1 considering the room temperature regime. In fact, as shown in Fig. 1, the calculated shear stress (which is directly linked to the resistance of the amorphous matter, e.g., polymeric fluid under a pressure gradient) shows a sudden decrease around $T \sim 300$ K ($V_a \sim 3.1 \times 10^{-21}\text{m}^3$). Below around $T \sim 299$ K, the transport of amorphous matter (e.g., polymeric fluid) is almost frictionless. The mean outer radius (r_2) is fixed to be 0.1μm (100 nm) in Fig. 1. The contribution of small wavy-roughness (e.g., $\epsilon = 0.1$) to τ could be neglected here as it is of the first order perturbation and is comparatively small than the leading order term. The corresponding viscosities ($\tau/\dot{\eta}$) can also be calculated from solid-like to liquid-like by varying the activation energy. Note that recent direct numerical simulation has revealed that freezing of water inside carbon nanotubes occurs continuously; in contrast to the first order transition between bulk liquid and solid, there is no intrinsic distinction between the two phases confined in a one-dimensional nanometer-size channel [9]. The latter can be easily checked via our present approach.

CONCLUSIONS

To conclude in brief, using the verified transition-state theory [3-6] we can obtain possible very-low resistance transport of amorphous matter in nanodomains by tuning the activation energy and volume at a wide range of temperature regime. Our results could be applied to the flow control in material processing and nanofluidics as well as biofluidics. *Acknowledgements* The only author would like to thank the partial support of 2012-Inner Mongolia-University-of-Science-and-Technology Starting Funds for Scientific Researcher.

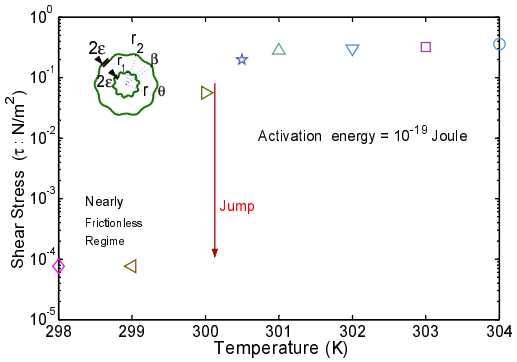

Fig. 1. Calculated shear stresses (or resistance) using an activation energy 10^{-19} Joule. There is a sharp decrease of shear stress around $T \sim 300$ K ($V_a \sim 3 \times 10^{-21}$ m^3). Below 299 K, the transport of amorphous matter (e.g., polymeric fluid) is nearly frictionless. Here (the mean outer diameter) $r_2 = 0.1\mu$m (100 nm).

References

[1] Lacks D.J. Energy landscapes and the non-newtonian viscosity of liquids and glasses. *Phys. Rev. Lett.* **87**:225502 , 2001.
[2] Geib L.D., Gubbins K.E., Radhakrishnan R., Sliwinska-Bartkowiak M. Phase separation in confined systems. *Rep. Prog. Phys.* **62**:1573, 1999.
[3] Krausz A.S., Eyring H.: Deformation Kinetics. Wiley-Interscience, New York 1975.
[4] Chu K.-H. W.: Effects of shear rate and small periodic corrugation on the slip velocity in microscopic domain. *Microfluid. Nanofluid.* **5**:273-279, 2008.
[5] Chu K.-H. W.: Sieving transport within wavy-rough nanoannuli. *J. Phys. Chem. B* **112**: 3019-3023, 2008.
[6] Powell R.E., Eyring H. Mechanisms for the relaxation theory of Viscosity. *Nature* **154**: 427-428 ,1944.
[7] Thompson P.A., Troian S.M. A general boundary condition for liquid flow at solid surfaces. *Nature* **389**: 360-362, 1997.
[8] Chu W. K.-H.: Stokes slip flows between corrugated walls. *ZAMP* **47**: 591-599, 1996.
[9] Koga K., Gao G.T., Tanaka H., Zeng X.C.: Formation of ordered ice nanotubes inside carbon nanotubes. *Nature* **412**: 802-805, 2001.