Shear Viscosity under Shock-Loading Conditions

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Although we rarely see a shock wave in everyday life, we experience them upon hearing the sound of an explosion, the bang of a gunshot, or the crack of a whip. In addition, objects that travel at supersonic speeds, such as bullets and missiles, also generate shock waves. During a typical shock-loading process, large pressures generated at the shock front can lead to an increase in the reactants’ reactivity via decomposition, as well as changes in mechanical and structural properties. Consequently, the initiation of shock waves often changes the nature of a reaction and, therefore, its final products.

In a fluid’s case, we can study the impact of a shock wave through variables that describe physical properties of the materials on both sides of the shock front, i.e. density, temperature, and particle velocity. As a result, shear viscosity, which measures a system’s resistance to flow as a function of the relative velocity of adjacent layers of particles, is changed drastically under shock-loading conditions.

More specifically, when a fluid is shocked, particles behind the shock front experience both a compressive force and a shear force, which together push particles away from their original equilibrium positions. In this process of deformation, shear viscosity largely depends on the speed of the relative movements between adjacent layers of particles. To describe this type of shock-activated process, we need to solve the momentum conservation equation, i.e. the Navier-Stokes equation,

$$\rho \frac{\partial \mathbf{v}}{\partial t} = -\nabla p + \eta \nabla^2 \mathbf{v}$$

and identify an accurate model of the fluid viscosity $\eta$. In Eq. (1), $\rho$ is the density of the fluid, $\mathbf{v}$ is the velocity of the fluid particles, $p$ is the momentum of the fluid particles, and $\eta$ is the shear stress of the fluid. By definition, $\eta$ is the ratio of the shear stress in the shear rate,

$$\eta = \frac{f}{\dot{\epsilon}}$$

where $f$ is the shear stress, and $\dot{\epsilon}$ is the shear rate and equals $\Delta V/\lambda$. In the expression of $\dot{\epsilon}$, $\Delta V$ is the velocity difference between two layers of particles that are a distance $\lambda$, apart. Based on the difference between forward and backward rate constants, Eyring proposed that

$$\Delta V = 2\lambda k_1 \sinh\left(\frac{\Delta E}{k_BT}\right)$$

where $\lambda$ is the distance between neighboring molecules in the direction of motion, $k_1$ is the molecule to molecule distance in the plane normal to the direction of motion, and $\lambda$ is the distance between equilibrium positions. $k_B$ is the Boltzmann constant and $T$ is the absolute temperature of the reactants. Based on this relation, our study aims to give a better estimate of shear viscosity, which in turn tells us the type of fluid motion, laminar or turbulent, that is occurring behind the shock front.

A brief review of the historical development of Eyring’s shear-rate dependent model for viscosity would be helpful. In 1935, Eyring proposed the formula

$$k_{Eyring} = \frac{k_BT}{h} Q^+ \frac{\epsilon^+}{\epsilon} e^{-\frac{\Delta E}{k_BT}}$$

for the activated rate processes based on Transition-State Theory (TST), where $Q^+$ is the partition function for the particles at the transition state, $Q_{RCT}$ is the partition function for reactants, $V^+$ is the barrier height, and $h$ is Planck’s constant. During the following year, he extended the result to calculate viscosity, which inherits the assumption of TST that particles in both the reactant well and the transition state are in thermal equilibrium. For many years, Eyring’s viscosity formula has been used for all chemical reactions, regardless whether they satisfy TST’s thermal equilibrium assumptions. As a result, many applications of the TST model to reactions under shock-loading conditions gave inaccurate predictions. Indeed, Valone showed in his 2003 paper that applying shock to a material drastically increases its reaction rate to several orders of magnitude higher than rates calculated under thermal equilibrium assumptions. Based on this model, our current study concentrates on adjusting Eyring’s shear-rate dependent model for viscosity to account for changes in reaction rate under shock-loading condition.

We will present arguments for using Valone’s model for shock-activated processes. First, we will analyze the conditions for thermal activated processes, and explain why TST are suitable for those processes. Then, we will discuss the differences between thermal and shock activated processes, and why the assumptions of TST are no longer applicable to reactions.
under shock-loading conditions. Finally, we propose two main modifications - reaction rates under shock-loading conditions and velocity dependence of shear rate - to the TST model for viscosity. We also include primary comparisons between the TST model and the new model for viscosity.

Transition-State Theory Kinetics

When a system of particles is in thermal equilibrium, each one of them is equally likely to go forward or backward on the reaction coordinate, as shown in Fig. 1. However, when there is an outside force, one direction is favored, as shown in Fig. 2. During this process, momentum is conserved. The dissipation of momentum depends on viscosity, which expresses the motion of the particle in terms of the rate constant $k_1$. This $k_1$ is in the same form as the reaction rate in TST.

The conventional TST was developed through a series of studies that started in 1889 by Arrhenius and fully developed by Eyring in 1935. To describe a system in reactions, the TST assumes that it is always possible to carry out coordinate transformation so that variables relevant to the current reaction are on one reaction coordinate, while all other coordinates are perpendicular to this reaction coordinate, as shown in Fig. 3.

Along the reaction coordinate, which is not necessarily a linear one, TST says that reaction rates are determined by the dynamics of the reactants as they pass through the potential barrier to the product well. Implicitly implied by this statement is the assumption that the system is at equilibrium at each point of the reaction coordinate. In particular, particles at the transition state and the reactant well need to be in equilibrium respectively. If these assumptions are satisfied, concentration at the transition state can be calculated by using a Boltzmann distribution. Specifically, the velocity distribution is Maxwellian.

In a thermal equilibrium, multi-dimensional system, the TST predicts that particles in the reactant well will always follow the lowest energy path to get to the product well. Fig. 4 shows sodium-fluorine and helium-fluorine reaction in a two-dimensional potential surface. Under thermal equilibrium conditions, particles go through the saddle point into the product well. However, under shock conditions, the amount of kinetic energy they acquire may dominate the thermal effect, so if the shock wave is in the same direction as the thermal reaction coordinate, the shock will facilitate particles going into the product well. However, if the shock points toward an unfavorable direction with respect to the thermal reaction coordinate, particles will be pushed onto reaction paths other than the thermal one and end up as different products. In this two dimensional picture, one can clearly see that in fact products in shock condition are different from those in thermal condition.

If we try to express this physical situation mathematically, we get the reaction rate constant from the following equation

![Figure 1](image1.png)

![Figure 2](image2.png)

![Figure 3](image3.png)

![Figure 4](image4.png)

with a weaker dependence on the shock speed.

The new reaction rate constant now can be expressed as

$$k_{\text{shock}} = \frac{\int \delta(q - q^*) u \theta(u) e^{-\frac{H(u, q)}{k_B T}} \, du \, dq}{\int \theta(q^* - q) e^{-\frac{H(u - u_q, q)}{k_B T}} \, du \, dq}$$

In this expression, $u_q$ is the projected particle velocity, while other variables are as defined above. When kinetic energy of the shocked particle is less than the barrier height, i.e. $\frac{1}{2} m u_q^2 < V^*$, Eq. (6) can be simplified as

$$k_{\text{shock}} = \frac{\omega}{2\pi} e^{-\frac{V^*}{k_B T}}$$

where $u^*_q = 0$, and $V^* = V^*$. However, when kinetic energy of the shocked particle is greater than barrier height, i.e.

$$k_{\text{shock}} = \frac{\omega}{2\pi} \left( e^{-\frac{m(u_q^*)^2}{2k_B T}} + u_q^* \sqrt{\frac{2m}{k_B T}} \text{erfc} \left( -\sqrt{\frac{m(u_q^*)^2}{2k_B T}} \right) \right)$$

where $u_q^* = \sqrt{u_q^2 - \frac{2V^*}{m}}$, and $V^*_q = 0$. Further examination of Fig. 6 also shows that, as expected, particle-velocity dependence is washed out at high temperature.

**Viscosity at shock front**

Assuming that Valone’s model of shock activation holds for shear processes, we now consider the shear process that takes place under shock-loading conditions in a fluid.

As the shock front passes through, particles are compressed in the same direction as the propagation of the shock wave. We also notice that right at the shock front, there is a force pushing particles away from the center of the compressive wave. This is the shear force that appears in shock-loading conditions. Apparently, the shear process depends on the strength of the
shock, which is manifested in the velocity of the particles behind the shock front. In 1988, Holian suggested

$$ \dot{\varepsilon} = -\frac{u_p}{\lambda_H} $$

to express the relation between particle-velocity and shear rate, where $\lambda_H$ is the shock-wave thickness and is equivalent to $\lambda_1$ in Eyring's expression. He also proposed the empirical relation between viscosity and the Reynolds number in shock-loading conditions to be:

$$ Re = \frac{\rho_0 u_s \lambda_H}{\eta} $$

where $\rho_0$ is the density of the unshocked material, $u_s$ is the shock-front speed. Eq. (10) suggests that viscosity is a main factor in determining the magnitude of $Re$, which tells us whether the flow inside a material is laminar or turbulent. This means that the particle-velocity dependence in viscosity can potentially change the character of the flow.

We put previous reasoning into mathematical expressions as follows. We first apply Valone's shock TST to the shear process in shock-loading condition to modify the rate constant in Eyring's viscosity model. In order to do this, we need to correctly interpret each variable in Eyring's definition of viscosity in terms of variables that appear under shock-loading conditions. This is accomplished by relating Eyring's viscosity to our normal understanding of Newton's law of viscosity in Eq. (2). With reference to Bird, Stewart and Lightfoot, who propose that

$$ f = A \arcsinh\left(\frac{1}{B \varepsilon}\right) $$

Newton's form of viscosity can be written as $\eta = \frac{4A \arcsinh\left(\frac{1}{B \varepsilon}\right)}{\varepsilon} \eta_0$.

To cast Eyring's formula into the same expression, we rewrite Eyring's $f$ in terms of $\eta$, so that

$$ f = \frac{\eta \Delta V}{\lambda_1} $$

Substitute Eq. (12) into Eq. (3), we get $\eta$ as a function of $\Delta V$ and $\lambda_1$'s, but not $f$. The result is

$$ \eta = \frac{2k_B T \lambda_1}{\Delta V \lambda_2 \lambda_3 \lambda} \arcsinh\left(\frac{\Delta V}{2k_1 \lambda}\right) $$

$$ \dot{\varepsilon} = \frac{\Delta V}{\lambda} \text{ in the same form as } \eta \text{ from Newton's theory. Since } \frac{\eta}{\lambda}, \text{ we can rewrite Eq. (13) as} $$

$$ \eta = \frac{2k_B T \lambda_1}{\lambda} \arcsinh\left(\frac{\varepsilon \lambda}{2k_1 \lambda}\right) $$

We further consider that in Eq. (14) the shear rate should depend on particle's shocked speed, instead of being a constant for all different shock strength. Therefore, based on Holian's argument, we substitute Eq. (9) into Eq. (14) and finally arrive at

$$ \eta = \frac{2k_B T \lambda_1}{\lambda} \arcsinh\left(\frac{u_p \lambda_1}{2k_1 \lambda^2}\right) $$

for the viscosity. To compare viscosity under shock and thermal conditions, we cancel the prefactors $u_s \lambda_1, \lambda_1^2$, and arrive at

$$ \eta_{\text{shock}} = \frac{\arcsinh\left(\frac{u_p \lambda_1}{2k_B \lambda_1}\right)}{\frac{2k_B T \lambda_1}{\lambda_1}} $$

$$ \eta_{\text{Eyring}} = \frac{\arcsinh\left(\frac{u_p \lambda_1}{2k_B \lambda_1}\right)}{\frac{2k_B T \lambda_1}{\lambda_1}} $$

**Result**

We first compare viscosity at different temperatures and different barrier heights. Since shear rate is now written as a function of particle velocity along the reaction coordinate, its effect on viscosity is determined by changes of particle velocity. Fig. 8 is our primary comparison between the new model and the thermal-equilibrium model of viscosity at the same barrier height but different temperatures. As expected the new shock-loading model of viscosity is several orders of magnitude smaller than the thermal model. We expect that this dramatic decrease in viscosity may bring the Reynolds number to the critical value by which different flow regimes are determined.

We also tested the new model at different barrier heights. Each one of the plots in Fig. 9 shows that the new model of viscosity is very sensitive to particle-velocity. At zero particle-velocity, the two models of viscosity give the same prediction. However, as velocity increases, viscosity decreases exponentially and then becomes linear. One may also observe that in each of
these plots, viscosity shows the same wash-out effect at high temperature as the chemical rate constant.

Conclusion

So far, we have analyzed some of the changes in the dynamics of a shock-loading material, in particular the effects of increasing particle-velocity in chemical reaction rates and their implications to the calculation of shear viscosity. As shocked particles acquire much greater kinetic energy compared to the system's original thermal energy, they follow a different reaction path than the thermal one. Indeed, the reaction rates under shock-loading conditions are orders of magnitudes greater than the thermal reaction rates.

The current standard model of viscosity is based on Eyring's thermal equilibrium TST model. To incorporate what we know from the above analysis, we propose to modify the TST model of viscosity under shock-loading conditions in order to account for higher reaction rate and particle-velocity dependence of shear rate. Initial computational tests of our model showed that the thermal equilibrium model of viscosity gives too high a prediction for viscosity in shock-loading conditions. In fact, our model of shock-activated viscosity gives values which are different enough from Eyring's model to change the flow regime. That is, a material originally expected to experience a laminar flow might in fact experience a turbulent flow. The difference will in turn lead to different predictions of the mechanical and structural properties of the material.

In order to obtain more conclusive information on the effects of shock waves on shear viscosity, we expect to test the new model with a computer simulation of viscosity under shock-loading conditions.

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