

# Atomic scale friction in the function of modified Eyring activation energies

W.W.F. Chong<sup>1, 2, a</sup> and H. Rahnejat<sup>3, b</sup>

<sup>1</sup> National Centre for Advanced Tribology (nCATS), Faculty of Engineering and the Environment, University of Southampton, Southampton, UK

<sup>2</sup> Faculty of Engineering and the Environment, University of Southampton Malaysia Campus, Nusajaya, Malaysia

<sup>3</sup> Wolfson School of Mechanical & Manufacturing Engineering, Loughborough University, Loughborough, UK

<sup>a</sup> w.chong@soton.ac.uk, <sup>b</sup> h.rahnejat@lboro.ac.uk

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## Abstract

At microscale, friction is better understood fundamentally through hydrodynamic and elastohydrodynamic lubrication. However, the mechanisms governing friction at nanoscale remains a subject of interest. With the emergence of small-scale devices such as Microelectromechanical Systems (MEMS) and Nanoelectromechanical Systems (NEMS), there is a need to improve on the fundamental understanding of friction at diminishing gaps. Therefore, the paper investigates the friction of a simple fluid (n-hexadecane 99%) using an atomic force microscope. The measurements are interpreted using modified Eyring’s thermal activation energy approach in order to examine the effect of molecular solvation at the assumed smooth summit of asperities. It is found out that solvation for a sliding contact could be observed through the shear stress activation volume due to generated thermal energy, which indicates the movement of the fluid molecules into and out of the contact.

## Introduction

Engineering surfaces are rarely smooth, consisting of valleys and peaks (also known as asperities). These are ubiquitous and randomly distributed across surfaces. With the advancement of technologies, machine elements are designed to be more compact. However, compact design package introduces new challenges for engineers, especially related to the tribological characteristics of moving parts. These challenges include frictional losses, particularly in the form of adhesion of relatively smooth surfaces as a result of direct interactions of surfaces because of surface energy effect. Friction may be reduced through use of lubrication, which decreases the surface energy effect. In particular, boundary active elements are blended in formulated lubricants to adhere to summits of asperities and reduce the chance of asperity pair adhesion on the contacting counterfaces. The mechanism governing boundary lubrication involves adsorption of friction modifier molecules to the surfaces that eventually forms an ultra thin layer of film, preventing direct surface-to-surface interactions.

Formation of ultra thin adsorbed boundary films over surface asperities cannot be dealt with using the traditional continuum mechanics tribological approaches such as hydrodynamic and elastohydrodynamic lubrication. This is because, at nano-scale, competing kinetic laws involving intermolecular and surface energy effects govern the boundary interactions between opposing sliding surfaces rather than the dominant viscous forces in micro-scale lubricated contacts. For very smooth surfaces, solvation dominates in gaps of several molecular diameters of the intervening fluid. The phenomenon is as the result of density variation of liquids near solid boundaries [1]. Horn and Israelachvili [2] and Chan and Horn [3] have measured this oscillatory force between smooth

mica surfaces in liquids such as Octamethyltetracyclosiloxane (OMCTS), Hexadecane and Tetradecane, using surface force apparatus (SFA). On the other hand, Lim and O’Shea [4] used an atomic force microscope (AFM) to measure the solvation force for fluid mixtures under normal loading.

Based on the concept of molecular oscillation for confined fluids, various theoretical models have been developed, integrating a mix of kinetic laws ranging from hydrodynamics to surface energy effects and intermolecular interactions. They include the works reported by Matsuoka and Kato [5], Al-Samieh and Rahnejat [6, 7, 8], Chong *et al* [9] in the study of lightly loaded conjunctions with diminutively thin films, entrained through by hydrodynamic viscous action. To describe the solvation force, Chong *et al* [10, 11] also adopted the use of Ornstein-Zernike (OZ) equation as expounded by Mitchel *et al* [12], Henderson and Lozada-Cassou [13] and Attard and Parker [14].

However, solvation observed experimentally and also modelled theoretically most of the time involves normal loading of the contact, often neglecting near surface shearing of fluid molecules. Understanding shearing of fluid molecules at such diminishing gaps could prove to be critical in optimization of boundary lubrication. Therefore, through the application of activation energy approach, the study attempts to understand the solvation phenomenon during shearing of a simple fluid (e.g. n-hexadecane 99%) confined by the sliding AFM tip on a molecularly smooth mica sheet.

## Experimental Approach

To observe the effect of solvation along a sliding contact, the study measures the friction of a silicon nitride AFM tip (Bruker DNP-10), separated by n-hexadecane 99% (Acros Organics), sliding on a mica sheet. Figure 1 shows the schematic representation of the AFM tip under a fluid-imaging configuration. In order to capture shearing of the fluid molecules separating the AFM tip and the mica sheet, a fluid tip holder is used. During the experiment, it is necessary to maintain a meniscus forming along the edges of the tip holder (see figure 1), which also ensures that the relatively large negative meniscus pressures between the fluid and tip holder do not affect the friction measurements.

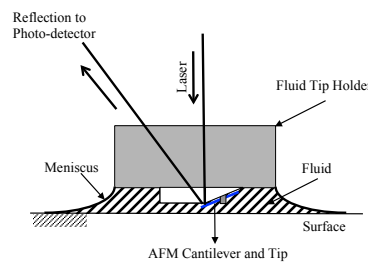


Fig. 1 Schematic diagram for Atomic Force Microscope – Fluid Imaging and Contact Mode

The current study uses the “blind calibration” approach proposed by Buenviaje *et al* [15] for calibration of the friction force microscopy (FFM) measurements. The calibration factor for the silicon nitride AFM tip on a silicon calibration sample [15, 16] is defined as:

$$\alpha = \frac{F_f(\text{volts})/\text{Load}(\text{nN})}{0.19} \quad (1)$$

## Mathematical Approach

Friction generated along the assumed opposing molecularly smooth asperity summits, separated by ultra-thin adsorbed films, follows the non-Newtonian shear as a result of chemical

reactions based on thermal activation. This can be explained using Eyring's thermal activation "cage" model" (see figure 2).

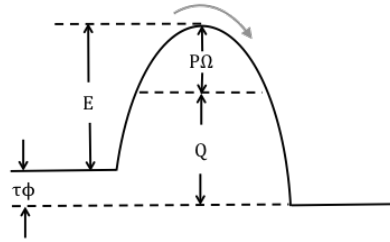


Fig. 2 Potential barrier in terms of thermal activation energy

The model describes the viscosity of fluids assuming that the motion of a volume of fluid molecules takes place in the presence of a potential barrier, known as the "cage". Eyring [17] assumed that in order to overcome the potential and to escape the "cage", confined fluid molecules would have to surmount the activation barrier. This forms the basis of the "cage" model, which can be simplified as:

$$E = Q + P\Omega - \tau\phi \quad (2)$$

where  $E$  refers to the barrier height,  $Q$  refers to the process activation energy,  $P$  refers to the pressure acting on an activation volume,  $\Omega$  and  $\tau$  refers to the shear stress acting on an activation volume,  $\phi$ . Briscoe and Evans [18] further modified Eyring's model to describe the shear stress of molecularly confined fluids in the function of applied pressure, sliding velocity and temperature. For isothermal conditions under a constant sliding speed, the shear stress is defined as:

$$\tau = \tau_0 + \xi P \quad (3)$$

where  $\tau_0 = \frac{1}{\phi} \left[ k_B T \ln \left( \frac{v}{v_0} \right) + Q \right]$  and  $\xi = \frac{\Omega}{\phi}$

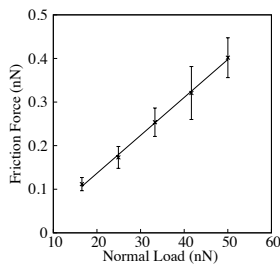
Using a similar approach of simplification assuming that the applied pressure is constant under an isothermal condition, Briscoe and Evans [18] described the shearing of confined fluid molecules in the function of sliding velocity as:

$$\tau = \tau_1 + \theta \ln v \quad (4)$$

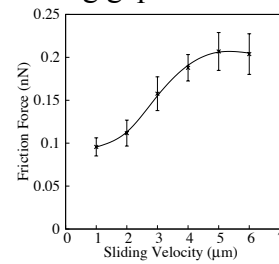
where  $\tau_1 = \frac{1}{\phi} [Q + P\Omega - k_B T \ln v]$  and  $\theta = \frac{k_B T}{\phi}$

## Results and Discussions

Figure 3 shows the friction force measured on the AFM for n-hexadecane. It has been observed using surface force apparatus (SFA) that n-hexadecane exhibits solvation when loaded normally. However, through the friction force measurements shown in figure 3(a) for increasing normal load and also figure 3(b) for increasing sliding velocity, no molecular solvation in the form of stepwise characteristics could be observed. The only interesting observation from figure 3(b) is that the friction force generated by shearing n-hexadecane shows a non-linear behaviour, which is in accord with the non-Newtonian behaviour of the fluid in diminishing gaps.



(a) Friction force vs Normal load at  $2\mu\text{m/s}$



(b) Friction force vs Sliding velocity at  $15\text{nN}$

Fig. 3 Frictional characteristics for AFM tip sliding on a mica sheet, separated by n-hexadecane

Figure 4(a) shows the barrier height,  $E$  and also the process activation energy,  $Q$  by translating the friction force measurements in figure 3 using the approach by Briscoe and Evans [19]. The barrier height,  $E$  reduces, presenting progressively a smaller barrier for the sliding process to overcome. The reducing barrier could be linked to the increasing numbers of n-hexadecane molecules adsorbing to the surface whilst in shear. This reduces boundary friction in the process. The process activation energy,  $Q$  shows a distinct oscillatory behaviour. Figure 4(b) shows an oscillatory activation volume. The shear stress activation volume,  $\phi$  can be interpreted as the size of the moving segment in the tangential direction for unit shearing process, which can either be attributed to a molecule or a dislocation line [19]. Based on this definition, the oscillatory characteristics observed in figure 4(b) indicate the existence of molecular restructuring during shearing of n-hexadecane molecules with an increasing sliding velocity. The negative activation volume,  $\phi$  exist because of the fluid molecules moving in the opposite sense to the shearing process, which would results in molecular ejection.

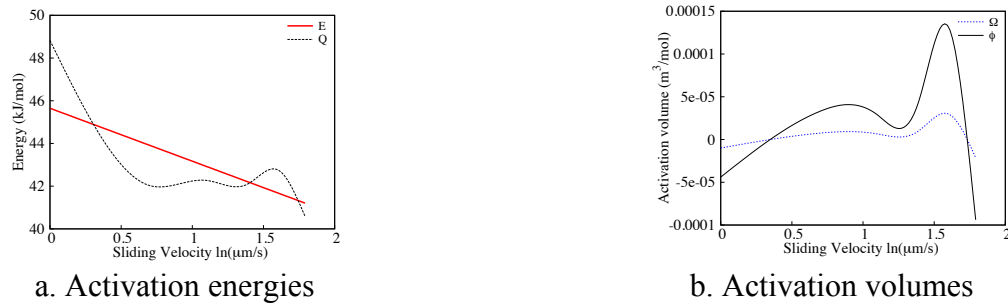


Fig. 4 Eyring Energy components for AFM tip sliding on a mica sheet, separated by n-hexadecane

## Conclusions

It has been observed that molecular solvation does occur even during shearing of fluid molecules. However, this could not be observed through friction measurements only. The study has shown that by using the modified Eyring thermal activation energy approach expounded by Briscoe and Evans, the molecular restructuring phenomenon known as solvation could be clearly explained by looking at the shear activation volume,  $\phi$ . As a next step forward, the authors would like to investigate further the possibilities of utilising the information that can be obtained through the energy approach to predict friction at a larger scale.

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## Nomenclature

$k_B$	Boltzmann constant (0.008314 kJ/mol/K)
$v$	Sliding velocity (m/s)
$v_0$	Characteristic velocity (m/s)
$E$	Barrier height (kJ/mol)
$P$	Contact pressure (Pa)
$Q$	Process activation energy (kJ/mol)
$T$	Contact temperature (K)
$\phi$	Shear stress activation volume (m <sup>3</sup> /mol)
$\tau$	Shear stress (Pa)
$\tau_0$	Pressure dependent Eyring shear stress (Pa)

$\tau_1$	Sliding velocity dependent Eyring shear stress (Pa)
$\theta$	Rate of change for friction at a given sliding velocity for constant applied load (-)
$\xi$	Rate of change for friction at an applied load for constant sliding velocity (-)
$\Omega$	Pressure activation volume ( $\text{m}^3/\text{mol}$ )

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