

Review

Understanding nanorheology and surface forces of confined thin films

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Understanding the nanorheology and associated intermolecular/surface forces of fluids in confined geometries or porous media is of both fundamental and practical importance, providing significant insights into various applications such as lubrication and micro/nanoelectromechanical systems. In this work, we briefly reviewed the fundamentals of nanorheology, advances in experimental techniques and theoretical simulation methods, as well as important progress in the nanorheology of confined thin films. The advent of advanced experimental techniques such as surface forces apparatus (SFA), X-ray surface forces apparatus (XSFA) and atomic force microscope (AFM) and computational methods such as molecular dynamics simulations provides powerful tools to study a wide range of rheological phenomena at molecular level and nano scale. One of the most challenging issues unresolved is to elucidate the relationship between the rheological properties and structural evolution of the confined fluid films and particles suspensions. Some of the emerging research areas in the nanorheology field include, but are not limited to, the development of more advanced characterization techniques, design of multifunctional rheological fluids, bio-related nanorheology, and polymer brushes.

Keywords: Nanorheology, surface forces, surface forces apparatus (SFA), atomic force microscope (AFM)

1. Introduction

1.1. How confinement influences forces?

Nanorheology is the study of rheological properties of materials in confined geometries and involves adhesion, friction and lubrication between particles and surfaces in nanometer scale or dimension of interacting molecules/particles. In general, the interactions between the molecules and particles in the confined fluids determine their rheological properties. Understanding the intermolecular and surface interaction mechanisms involved in confined thin liquid films is essential in many industrial and bioengineering applications such as stabilization or destabilization of colloidal suspensions, thin film lubrication, and lab-on-a-chip devices. Some of these important intermolecular and surface interactions include van der Waals forces, electrostatic double-layer force, steric force, solvation force, hydrogen bonding and hydrophobic interactions. The sum of the van der Waals and electrical double-layer forces between two surfaces can be described by the Derjaguin-Landau-Verwey-Overbeek (DLVO) theory. The DLVO theory predicts that the interaction energy per unit area between two flat surfaces can be given in Equation 1, where A_{121} is the Hamker constant of two surfaces 1 across confined liquid 2, D is the separation distance, ϵ_0 is the dielectric permittivity of free space, ϵ is the

dielectric constant of confined liquid, e_0 is the elementary charge of a single electron, l/κ is the so-called Debye length (viz. the characteristic decay length of the electrostatic double-layer interaction given in Equation 2: ψ_0 is the surface potential of flat surface, k_B is the Boltzmann constant, T is temperature), $\rho_{\infty i}$ is the number density of i th ion in the bulk solution and z_i is the valency of the i th ion. It is noted that van der Waals force is almost insensitive to solution conditions while double-layer force can be significantly affected (Israelachvili, 2011). As a result of these differences, DLVO forces can be repulsive or attractive depending on separation distance, solution conditions and surface properties, thus affecting the rheological properties of the confined liquid films

$$W_{DLVO} = -A_{121}/12\pi D^2 + 64\pi\epsilon_0\epsilon(k_B T/z e_0)^2 \times (\kappa/2\pi) \tanh^2(z e_0 \psi_0/4k_B T) e^{-\kappa D}, \quad (1)$$

$$1/\kappa = (\epsilon_0\epsilon k_B T / \sum_i \rho_{\infty i} e_0^2 z_i^2)^{1/2}. \quad (2)$$

In general, when a liquid is confined between two approaching surfaces and the separation distance is at molecular scale (e.g. less than 10 molecular diameters), the very thin liquid film between the two surfaces ceases to behave as structureless continuum in bulk state (Ruths *et al.*, 2011). Classic models of van der Waals and double-layer forces often fail to fully describe the interaction between confined surfaces, and both the properties of liq-

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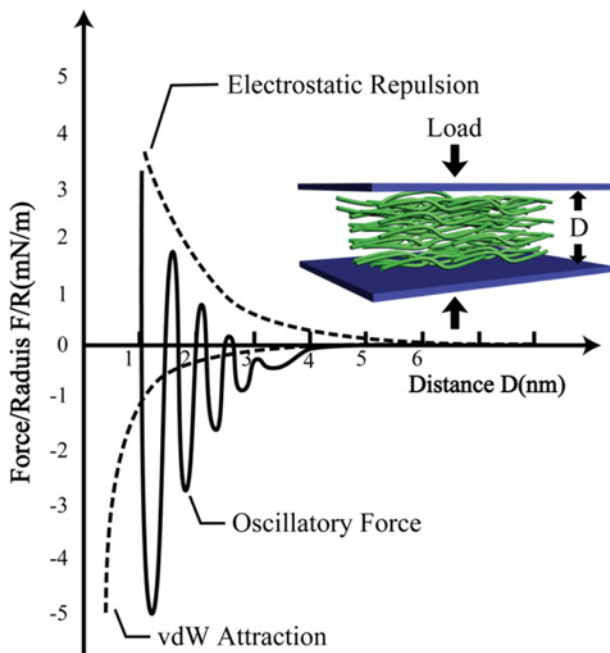


Fig. 1. (Color online) The solid curve shows oscillatory solvation force that acts on two smooth surfaces, the dashed curves illustrate the continuum van der Waals attraction and electrostatic repulsion, and the inset shows the schematic of liquids or polymers confined between two flat surfaces.

uid molecules and surfaces should be taken into consideration (Israelachvili, 2011). The confined liquids can form ordered layers and lead to an oscillatory force as shown in Fig. 1, which alternates between attraction and repulsion acting on the surfaces.

The oscillatory force is related to the density profiles and interaction pair-potential of the liquid molecules, which generally oscillate with distance with a periodicity close to the molecular diameter of the confined liquid within a range of a few molecular diameters (Israelachvili, 2011). Therefore the oscillatory force largely depends on the size and shape of confined liquid molecules. Rigid sphere molecules normally exhibit shorter range structural force than easily deformable molecules with higher configurational freedom such as hexane (Ruths *et al.*, 2011). The magnitude and range of molecular ordering in confined liquids can be normally enhanced by increasing the external pressure and lowering the temperature. The oscillatory force arises not only because liquid molecules tend to structure into semi-ordered layers on surfaces, but also due to the disruption or change of this ordering during the approaching of the two surfaces (Ruths *et al.*, 2011). Oscillatory forces have been directly measured by experimental techniques such as surface forces apparatus (SFA) for both simple liquids and polymers (Israelachvili *et al.*, 1972; Horn and Israelachvili, 1981; Christenson *et al.*, 1983; Horn and Israelachvili, 1988), and also confirmed

by theoretical simulations (Allen *et al.*, 1990; Aoyagi *et al.*, 2001; Jabbarzadeh *et al.* 2006). It has been proposed that the oscillatory force law may be described by Equation 3 in a first approximation (Israelachvili, 2011), where D is the separation distance, δ is the characteristic decay length and close to the mean dimension of the liquid molecules. For example, for simple hydrocarbon liquids, tetradecane $\delta \approx 0.4$ nm, cyclohexane $\delta \approx 0.5$ nm, octamethylcyclotetrasiloxan (OMCTS) $\delta \approx 0.9$ nm, while for water $\delta \approx 0.27$ nm (so-called hydration force)

$$W = W_0 \cos(2\pi D/\delta) e^{-D/\delta}. \quad (3)$$

1.2. Friction & lubrication forces: Stribeck curve

When two surfaces originally in contact are subjected to relative movement against each other a certain amount of force is required to initiate the movement which is known as the static friction force. The force which then resists the relative movement of the two surfaces is referred to as the kinetic friction force (Zeng, 2013). The molecular origin of friction forces is generally considered to be due to the energy dissipation as molecules of one surface past along the other surface (Israelachvili, 2011). The total friction force $F_{||}$ between two surfaces under normal load F_{\perp} can be given by Equation (4) (Israelachvili, 2011),

$$F_{||} = \mu F_{\perp} + \sigma A \quad (4)$$

where μ is the friction coefficient, σ is the shear stress and A is the contact area. The total friction force in Equation 4 is comprised of two terms which are load-controlled friction and adhesion-controlled friction, respectively. The load-controlled friction depends on the structure and topography of the surfaces and the adhesion-controlled friction depends on both the topography and intermolecular forces between the surfaces. Equation 4 shows that for adhesion-controlled friction, the friction force would not be directly proportional to the applied normal load as predicted by the empirical Amonton's laws.

Friction can cause severe wear and damage in many industrial machines where intimate contact between different parts and surfaces occurs. Lubricants are commonly used to decrease friction and prevent machinery failure. The pioneering scientific studies of lubrication started in the 19th century by Petrov, Tower and Reynolds in which two surfaces were separated by a relatively thick film (*e.g.* tens of micrometers) of lubricant. In this regime of lubrication also known as the fluid-film lubrication, the lubricant behaves like a bulk fluid and the pressure, velocity and stress profiles within the lubricant film can be obtained by applying general governing equations of fluid motion and the corresponding boundary conditions. Another lubrication regime is normally referred to as the boundary lubrication in which the thickness of the lubricant film is comparable with the size of the molecules.

The third lubrication regime is known as the intermediate or mixed regime, and the rheological properties of the lubricant film fall between the boundary lubrication and fluid-film lubrication regimes. The correlation between the friction or lubrication forces and the corresponding film properties is generally illustrated by an empirical curve known as the Stribeck curve. Fig. 2a shows the schematic of a typical Stribeck curve, viz. friction/lubrication forces or friction coefficients as a function of sliding velocity, bulk viscosity of the lubricating fluid, and the applied normal pressure. The Stribeck curve provides an overall view of friction variation in the entire range of lubrication which includes the three regimes described above (Rutts *et al.*, 2011).

For thick liquid lubricant films confined between two parallel planes, the friction or lubrication forces are simply hydrodynamic or viscous drag force (viz. in hydrodynamic lubrication regime) which can be described by the bulk properties of the fluids. The friction force $F_{||}$ is proportional to the bulk viscosity η of the fluid and the shear velocity $V_{||}$, $F_{||} = \eta V_{||} A/D$, where A is the surface area, D the confined film thickness (or surface separation distance). The shear rate is defined as $\dot{\gamma} = V_{||}/D$. It is noted that at high shear rates, the properties of certain fluids may become non-Newtonian, viz. the effective viscosity of the fluids may increase or decrease with the shear rates, referred to as shear-thickening fluids and shear-thinning fluids, respectively. Surface deformations can also occur for the sliding surfaces due to the large hydrodynamic forces, which may alter the hydrodynamic lubrication forces, generally referred to as elastohydrodynamic (EHD) lubrication.

As the liquid film thickness becomes only a few (*i.e.* 4-10) molecular diameters of the liquid, the properties of the confined film can be significantly different from its bulk properties. Generally, the confined fluid film becomes non-Newtonian and viscoelastic, and the effective viscosity of the fluid is usually higher than the bulk viscosity. Previous experimental studies have shown such an intermediate mixed lubrication regime and change of the fluid properties of the confined liquid films when D is about 2-5 nm for simple liquids (*e.g.* hexadecane) or less than 2-4 R_g of polymer fluids (Granick, 1991; Klein *et al.*, 1993; Klein *et al.*, 1994(a); Klein *et al.*, 1994(b); Luengo *et al.*, 1996). R_g is the radius of gyration of polymers. For freely jointed polymer chain, viz. the monomers of the polymer chain are able to rotate freely about each other in any direction and their movement is not affected by the monomer-monomer interaction, the polymer molecule has a random coil conformation and the radius of gyration (R_g) is given by $R_g = l\sqrt{N}/6$, where l is the monomer length and N is number of monomer units per polymer chain.

As the confined liquid film thickness is below 4-10 molecular diameters, the lubrication of such molecularly thin films is normally referred to as boundary lubrication. For these

confined molecularly thin liquids films, if the surface-fluid interactions and/or the confinement induce the liquid molecules to solidify, the molecular configuration during sliding can become quite complicated, and the film may alternately melt and freeze during the motion. So-called "stick-slip" friction has been reported to occur associated with the boundary lubrication of certain fluids (Rhykerd *et al.*, 1987; Thompson and Robbins, 1990; Israelachvili *et al.*, 1990), in which the frozen state gives rise to the static friction force and the molten state gives rise to the kinetic friction force (Bhushan *et al.*, 1995; Bhushan, 2005). Molecular dynamic simulation results also suggest that periodic solidification and subsequent melting of the confined films can lead stick-slip (Thompson *et al.*, 1990).

A general friction map of effective viscosity η_{eff} as a function of effect shear rates $\dot{\gamma}$ and a friction map of friction force $F_{||}$ as a function of sliding velocity $V_{||}$ were proposed by Luengo, *et al.* (Luengo *et al.*, 1996) and are shown in Fig. 2b and 2c. As mentioned above, generally, with increasing normal load and/or decreasing the confined film thickness, Newtonian flow in the elastohydrodynamic (EHD) lubrication regime crosses into the boundary lubrication regime where non-Newtonian flow typically occurs.

In addition to lateral forces, the adhesion force between confined surfaces is also important for understanding various rheological and interfacial phenomena (especially for highly deformable materials) such as surface adhesion, wear, and agglomeration of colloidal particles. The research on contact mechanics and adhesion mechanics has steadily progressed for over one century, beginning with the pioneering work by Hertz in 1882 (Israelachvili, 2011), followed by the Johnson-Kendal-Roberta (JKR) theory (Johnson *et al.*, 1971), Derhaguin-Muller-Toporov (DMT) theory (Derjaguin *et al.*, 1975), and Maugis model (Maugis *et al.*, 1992). These classic models well describe the adhesion and deformation of two curved purely elastic surfaces (Zeng *et al.*, 2007(a); Zeng *et al.*, 2007(b); Zeng *et al.*, 2007(c)). The JKR theory and DMT theory predict the adhesion force F_{ad} between two curved surfaces of radii R_1 and R_2 as given in Equation 5 and Equation 6 respectively, where $R = R_1 R_2 / (R_1 + R_2)$ is the equivalent radius and W_{ad} is the work of adhesion per unit area. The JKR theory is usually applicable to soft materials with large surface energies and radii, and the DMT theory applies to small, rigid spheres (or asperities) with low surface energies (Zeng *et al.*, 2007(c))

$$\text{JKR model: } F_{ad} = (3/2)\pi R W_{ad}, \quad (5)$$

$$\text{DMT model: } F_{ad} = 2\pi R W_{ad}. \quad (6)$$

For confined thin films of viscoelastic or pure viscous fluids, fingering instabilities and surface patterns have been commonly observed associated with the normal adhesion or tensile tests (Zeng *et al.*, 2007(a); Zeng *et al.*, 2007(b)).

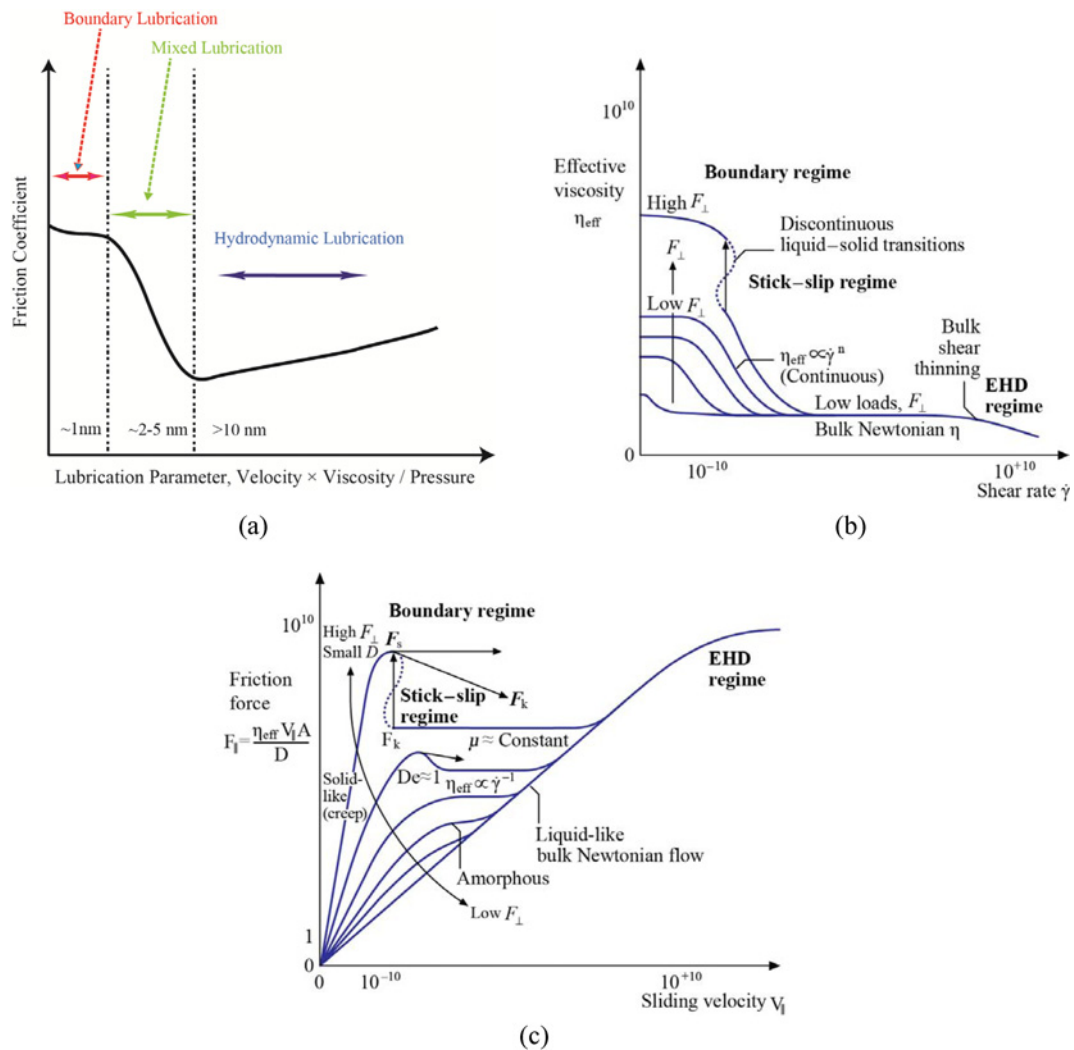


Fig. 2. (Color online) (a) Stribeck curve shows different rheology regimes of fluid films confined between two surfaces; (b) a general friction map of effective viscosity η_{eff} (arbitrary units) as a function of effect shear rates $\dot{\gamma}$ (arbitrary units) on logarithmic scales proposed by Luengo *et al.*; (c) a friction map of friction force $F_{||} = \eta V_{||} A / D$ as a function of sliding velocity $V_{||}$ in three different tribological regimes proposed by Luengo *et al.*, where De refers to so called Deborah number (viz. ratio of characteristic relaxation time of confined fluid to characteristic time of the experiment). In general, with increasing normal load and/or decreasing the confined film thickness, Newtonian flow in the elastohydrodynamic (EHD) lubrication regime crosses into the boundary lubrication regime where non-Newtonian flow typically occurs. (Panes (b-c) after reference (Luengo *et al.*, 1996), ©1996, with permission from Elsevier Science)

Nase *et al.* observed a transition between bulk deformation mechanism and interfacial crack propagation during the tensile tests of confined thin layers of poly(dimethylsiloxane) with different degrees of cross-linking (Nase *et al.*, 2008). Zeng *et al.* discovered that self-organized transient fingering pattern and instability generally exist during the adhesive contact and coalescence of two thin films such as polystyrene, poly(dimethylsiloxane), and polybutadiene, in the viscous or viscoelastic state (Zeng *et al.*, 2007(a); Zeng *et al.*, 2007(b); Zeng *et al.*, 2007(c)). Interesting transition from liquid-like viscous fingering to sharp solid-like cracking failure mechanism was also found during the tensile

adhesion tests of confined thin polymer films (Zeng *et al.*, 2010; Faghihnejad and Zeng, 2012).

2. Two Main Experimental Techniques for Nanorheology Study

Two major experimental techniques for studying the rheological behaviors of confined liquids include atomic force microscope (AFM) and surface forces apparatus (SFA). AFM and SFA have been widely used to measure normal and lateral forces between a tip (or a colloidal probe) and a flat surface (in AFM) or between two curved

surfaces (in SFA) with high force sensitivity (<10 pN and <10 nN for AFM and SFA, respectively). Force measurement principle in both AFM and SFA techniques is based on Hooke's Law: $F = k \cdot \Delta X$, where F is the measured force, ΔX is the spring deflection and k is the spring constant.

AFM is a very sensitive technique for both qualitative and quantitative analysis of various material surfaces with nanoscale spatial resolution. AFM has been widely applied for both topographical imaging and force measurements. The force measurements in AFM are usually conducted in two different modes: contact mode and dynamic mode. In contact mode, the AFM cantilever tip is moved toward the substrate in the normal direction at a desired approaching speed, and the deflection of the cantilever is recorded through a laser beam deflection technique. During the measurements, a laser beam is directed toward the top surface of the cantilever near the tip, and the reflected laser beam is detected by a photodetector. The differential signal detected by the four quadrants of the photodetector can provide a direct measurement of the cantilever deflection, which can be converted to force-distance profiles based on Hooke's Law. While in dynamic mode, the AFM tip vibrates in the vicinity of the substrate, the amplitude and phase change (also called amplitude modulation mode) or the frequency shift and the damping (also called frequency modulation mode) are recorded, respectively (Maali *et al.*, 2008). Colloidal AFM probes have also been widely employed in force spectroscopy for better control of the geometry between the probe and sample surface (Kappl *et al.*, 2002; Laurent *et al.*, 2013).

Using an AFM, the solvation force interactions in a liquid (*i.e.* octamethylcyclotetrasiloxane, dodecanol) near a solid wall (graphite, mica) were investigated by Oshea *et al.* (Oshea *et al.*, 1992; Oshea *et al.*, 1994). Their results showed evidence of the ordered layers of confined liquids at solid-liquid interfaces. The forces and structure of confined room-temperature ionic liquids were studied by Atkin *et al.* using AFM, which revealed the oscillatory behavior of three different room-temperature ionic liquids, ethylammonium nitrate (EAN), propylammonium nitrate (PAN), and 1-ethyl-3-methylimidazolium acetate (C2mimAc) confined between a Si_3N_4 tip and a flat solid substrate (*i.e.* mica, silica and graphite), with the size of the oscillations corresponding to the dimension of the ion pairs (Atkin *et al.*, 2011). Very recently the time-varying deformations and forces between a deformable surface and a solid substrate or between two deformable surfaces (*e.g.* bubbles, liquid droplets) and the drainage of the confined liquid films have been directly probed using an AFM and quantitatively analyzed (Dagastine *et al.*, 2006; Vakarelski *et al.*, 2010; Chan *et al.*, 2011; Tabor *et al.*, 2011). It is noted that the direct experimental determination of absolute surface separation, local geometry and contact area can be a

challenging issue in conventional AFM force measurements for soft materials and deformable surfaces.

The SFA has been widely used to study both static and dynamic properties of molecularly thin films sandwiched between two molecularly smooth surfaces, which was originally developed by Tabor, Winterton and Israelachvili (Tabor *et al.*, 1969; Israelachvili *et al.*, 1972; Israelachvili *et al.*, 2010; Israelachvili, 2011). SFA uses a multiple beam interferometry (MBI) technique to probe the absolute separation distance or confined film thickness in situ and in real time with a resolution of <0.1 nm, and fringes of equal chromatic order (FECO) is used to visualize local geometry, surface deformations, and properties of confined materials (*e.g.* refractive index) at the interaction region or shearing junction. The SFA technique has been significantly advanced over the past three decades, and various attachments have been developed for normal and lateral force measurements (Israelachvili *et al.*, 2010). In a typical SFA friction measurement, the surfaces can be sheared past each other by using a motor-driven micrometer to move the upper surface in the lateral direction, or by using a piezoelectric bimorph slider. The friction force is detected through the deflection of two vertical double-cantilever springs with four semiconductor or resistance strain gauges attached symmetrically to oppositely bending arms of the springs. The typical friction/lubrication force range and sliding speeds in SFA are about 10^{-7} to 10^{-1} N and 10^{-13} to 10^{-2} m/s, respectively (Israelachvili *et al.*, 2010).

SFA has been applied to probe the oscillatory solvation forces of confined simple liquids, such as octamethylcyclotetrasiloxane, benzene, tetrachloromethane, cyclohexane, isooctane, *n*-tetradecane and *n*-hexadecane (Horn and Israelachvili, 1981; Christenson *et al.*, 1983; Chan *et al.*, 1985; Israelachvili, 1988). SFA has also been widely applied to probe the rheological properties of confined thin liquid films (*e.g.* water, simple hydrocarbons) and polymer melts (Israelachvili, 1986(a); Israelachvili, 1986(b); Israelachvili, 1988; Israelachvili, 1989(a); Israelachvili, 1989(b); Israelachvili, 1990; Granick, 1991). Recently, SFA was used to probe the friction behaviors between immiscible polymer films confined between two mica surfaces, to study the characteristic relaxation times of interdigitation and disinterdigitation process at both the static and shearing interfaces of polybutadiene (PBD) and polydimethylsiloxane (PDMS) (Zeng *et al.*, 2009). Kristiansen *et al.* used an SFA to study the tribological behavior of confined carbon nanotubes (CNTs) suspended in aqueous humic acid (HA) solutions (Kristiansen *et al.*, 2011). It was found that adding CNTs to the HA solution changes the friction forces between two mica surfaces from "adhesion controlled" to "load controlled" (Kristiansen *et al.*, 2011). Very recently, the anisotropic (off-axis) friction-induced motion of confined liquids was studied using a modified 3D-SFA, and it was demonstrated that aniso-

tropic friction force between mica surfaces separated by a nanometer-thin film of hexadecane can induce complex transient and steady-state motions (Kristiansen *et al.*, 2012).

Although the basic principles of force measurements are similar, SFA and AFM are complementary techniques, which allow researchers to directly probe the rheological properties of confined thin films and the associated intermolecular and surface forces. SFA measures the interactions between two curved surfaces of relatively large radii (typically from ~ 1 mm to several cm). AFM usually probes the interaction between a sharp tip with radius of tens of nanometer and a sample surface. AFM normally provides relatively higher force sensitivity (<10 pN) than SFA (<10 nN) because of the softer spring (*i.e.* AFM cantilevers) commonly used. Based on the multiple beam interferometry technique, SFA is able to provide information such as absolute separation distance, confined film thickness (with a resolution of <0.1 nm) and surface deformation in situ and in real time, which is extremely useful for the investigation of surface forces, rheological properties and structure-property relation of confined complex fluids and deformable materials (Israelachvili *et al.*, 2010). Such information would usually be more difficult to extract from AFM measurements (especially for soft materials).

3. Molecular Dynamics Simulation of the Dynamics Of Confined Films

Rapid development of computer hardware and methodologies enables the study and modeling of tribological processes at the molecular scale. Molecular dynamics (MD) simulations have the advantage of obtaining high resolution structure and force information simultaneously of confined thin films between surfaces, which has been widely employed for studying rheology behaviors of various molecular systems (Allen *et al.*, 1990; Jabbarzadeh *et al.*, 2006).

For monomeric systems such as small spherical molecules, computer simulation studies are able to provide a clear picture for the dynamics of confined films. (Bitsanis *et al.*, 1987; Schoen *et al.*, 1994). For confined polymer system, simulation results indicate that the static structure of polymers under confined system can be understood by dividing the system into a surface layer region and a bulk region (Jabbarzadeh *et al.*, 2006; Aoyagi *et al.*, 2001). The bulk region is considered to have the same properties as the bulk polymeric liquids, while the surface layer is more solid-like (*i.e.* glass) rather than liquid-like. Coarse-grained molecular dynamics simulation of a bead-spring polymer model for polymer melt confined between two solid walls indicates that a surface layer exists near the walls, with the thickness about $R_g-1.5R_g$. Those adsorbed

polymer chains result in an attractive wall-polymer interaction, while the spatial confinement of polymer chains is independent of the wall-polymer interaction (Aoyagi *et al.*, 2001). Results from molecular dynamics simulations of polymer melts confined by weak attractive crystalline surfaces also show a distinct maximum exists in the velocity dependence of the friction coefficient (Priezjev *et al.*, 2012). The reason for this maximum is due to the shear-induced alignment of semiflexible chain segments in the first fluid layer near solid walls (Priezjev *et al.*, 2012).

Polyelectrolytes are important rheological fluids for the design and application of microfluidic devices, which normally behave differently from neutral polymer melts because of charged functional groups with long-range electrostatic interactions. The polyelectrolytes can be classified as flexible, semi-flexible or rigid depending on the intrinsic rigidity and ionic strength of solution medium. Chun *et al.* conducted Brownian Dynamics (BD) simulation study on the structure and dynamics of anionic polyelectrolyte xanthan in bulk solution and in confined spaces of slitlike channel by applying a coarse-grained model with nonlinear bead-spring discretization of a whole chain (Chun *et al.*, 2009). The impact of the electrolyte solution (*e.g.* screening effect) on confined polyelectrolyte chains was also faithfully characterized with BD simulations (Jeon and Chun 2007; Chun 2012). The simulation results were verified through single molecule visualization based on fluorescein-labeled xanthan using an inverted fluorescence microscope. The experimental results on the conformational changes in xanthan chain in electrolyte solution were found to agree well with the prediction by BD simulations (Chun *et al.*, 2009).

When the molecules are sheared between two highly confined surfaces, (*i.e.* molecularly thin films), the large number of molecules involved and the long adaptation and relaxation time is one of the major challenging issues for micro- and macro-scale molecular simulation (Gee *et al.*, 1990; Kristiansen *et al.*, 2012; Drummond *et al.*, 2000). More details about the molecular dynamics simulation of nanorheology can be found in a recent review (Jabbarzadeh *et al.*, 2006).

4. Perspectives

The rheological properties of liquids, polymers, and particle suspensions confined between two surfaces are of key importance in understanding lubrication and fluid flows in confined geometries or porous media or in microfluidic and nanofluidic devices (Klein *et al.*, 1995). Nanorheology has received increasing attention over the past two decades with the advances in nanomaterials, bioengineering, microfluidics and nanofluidics. Despite the significant process, there are still many remaining challenges in the field. For example, it is still experimentally

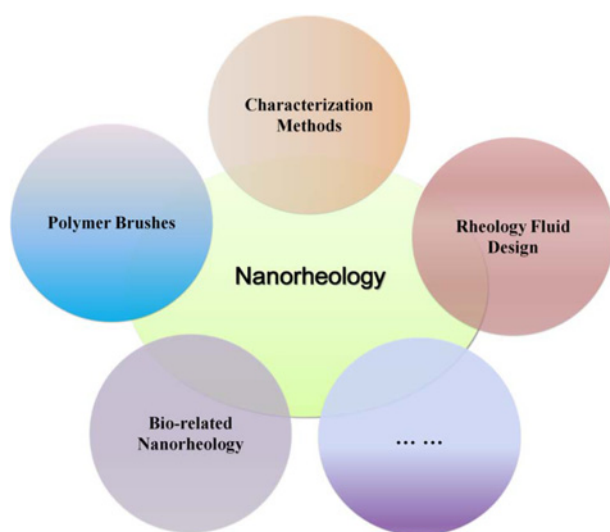


Fig. 3. (Color online) Several emerging research areas in nanorheology.

challenging to determine the detailed structure information of confined fluids in many systems. In this section, the perspectives of nanorheology research will be briefly discussed from several emerging areas including characterization methods, design of multifunctional rheological fluids, bio-related nanorheology, and polymer brushes on surfaces, as illustrated in Fig. 3.

4.1. Characterization Methods: modified SFA or AFM

One important emerging area in nanorheology is to combine conventional rheology characterization technique with other advanced techniques for structural characterizations of confined fluids or suspensions, such as optical spectroscopy, X-ray spectroscopy, and conductivity measurements. Therefore the composition and structure evolution of confined materials can be monitored simultaneously with rheology measurements to elucidate their structure-property relationship (Israelachvili, 2011).

(1) Nanorheology integrated with X-ray spectroscopy

The second generation x-ray surface forces apparatus (XSFA-II) developed by Israelachvili, Safinya and their co-workers allows for the simultaneous in situ small-angle x-ray scattering and surface force measurements (Golan *et al.*, 2001). Golan *et al.* (2001) used the XSFA-II to monitor shear-induced orientational transitions in a lyotropic model lubricant system composed of sodium dodecyl sulfate (SDS, surfactant), pentanol (cosurfactant), dodecane (oil), and water. The formation of an orientational boundary layer at the shearing surface was observed by XSFA-II, and time-resolved x-ray diffraction (XRD) revealed the gradual transition to shear-favored orientation by growth

of the boundary layer (Golan *et al.*, 2001). Integrating XRD technique to molecular and surface force measurement techniques allows researchers to simultaneously measure forces and probe structure and structural evolution in confined thin liquid films. Improving the spatial resolution and time resolution of XRD experiments in these integrated techniques will allow combined dynamic force and structural measurements of thin films of various thicknesses (ranging from boundary lubrication to hydrodynamic lubrication regimes), which is critical to elucidate the structure-property correlation and fully understand the interfacial and dynamic processes.

(2) Optical spectroscopy integrated with force measurements

The SFA technique has also been integrated with various optical visualization techniques to study the transition mechanisms of confined films between liquid-like snapping and solid-like failure at nano- and micro-scales (Zeng *et al.*, 2007(c); Zeng *et al.*, 2010). SFA technique integrated with non-linear optical spectroscopy also shows that the liquids confined between two surfaces are not uniform in density profile across the contact zone, displaying large variation in molecular diffusion from ordered solid-like to liquid-like behavior (Frantz *et al.*, 1997). Very recently Contreras-Naranjo and Ugaz reported a nanometre-scale resolution interference-based probe of interfacial phenomena between microscopic objects and surfaces based on reflection interference contrast microscopy (RICM) technique (Contreras-Naranjo *et al.*, 2013). This improved RICM technique provides almost instantaneous reconstruction of an arbitrary convex object's contour next to a bounding surface with nanometer resolution, which also allows direct observation of femtolitre-scale capillary condensation dynamics underneath micron-sized particles (Contreras-Naranjo *et al.*, 2013). Therefore, it is possible to integrate this improved RICM technique with force measurement techniques such as AFM to simultaneously probe the forces, surface deformations, separation distances and other properties of confined liquid films.

(3) Integration of force and conductivity measurements

Simultaneous force and conductivity measurements of hexadecane confined between a conducting AFM tip and a graphite surface have been reported (Gosvami *et al.*, 2007), which showed the discrete solvation layering of the hexadecane near the surface. Integrating force and conductivity measurements provide another new way to investigate the force-structure relationship of confined thin fluid films.

4.2. Design of multifunctional rheological fluids

Multifunctional rheological fluids (*e.g.* mostly colloidal suspensions) are of both fundamental and practical

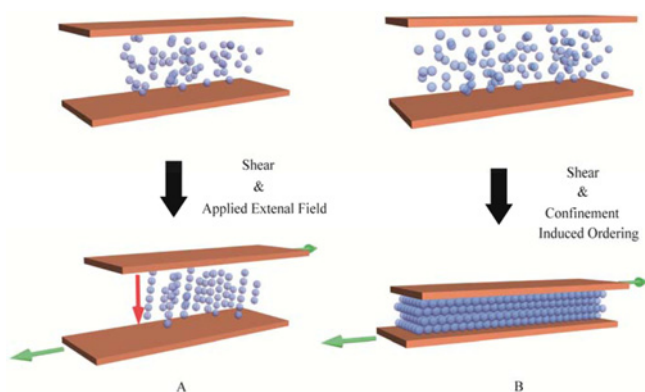


Fig. 4. (Color online) Schematic diagram of smart ER and MR rheology fluids (A), confinement and shearing can lead to the ordering of the particles in the confined thin films of suspensions (B).

importance in rheology research and various applications. Wen *et al.* reported the giant electrorheological effect (GEF) in suspensions of urea coated nanoparticles with a yield stress over 100 kPa (Wen *et al.*, 2003). Tian *et al.* reported a reversible shear thickening of electrorheological (ER) fluids above a low critical shear rate ($<1 \text{ s}^{-1}$) and a high critical electric field strength ($>100 \text{ V/mm}$), which could be characterized by a critical apparent viscosity by shearing ER fluids between two concentric cylinders (Tian *et al.*, 2011). The friction force between the electrorheological zeolite particles was considered to be responsible for the lateral shear resistance of the bulk ER fluids, and the applied electric field strengths could be used to modulate the extent of shear thickening (Tian *et al.*, 2011). Another type of smart materials of suspensions, whose rheological properties can be significantly modulated by an applied magnetic field, is called magnetorheological (MR) fluid (Zeng, 2013). The rheological properties of smart ER and MR fluids are responsive to an external field (*i.e.* E-field or magnetic field), and the particles can reversibly form particle chains to drastically modulate the rheological behavior of the suspensions as illustrated in Fig. 4, which have very promising applications such as dampers, clutches, brakes, and valves. It is also possible to introduce E-field and magnetic field into force measurement techniques such as SFA and AFM to simultaneously probe the field-sensitive forces and visualize the structural evolution of the confined thin films (Zeng *et al.*, 2008).

It is noted that confinement and shearing can lead to the ordering of the particles in the confined thin films of suspensions (Fig. 4), as confirmed experimentally and theoretically (Cohen *et al.*, 2004), thus contributing significantly to the evolution of the rheological properties. Micro-sized probe particle or fluorescent molecules have also been used to dope rheological fluids for rheology study. By

analyzing the Brownian motion of these tracer particles or molecules, mechanical properties of the fluid medium can be obtained. Techniques such as single-particle tracking combining optical tweezers and fluorescence-based single molecule probing may open new doors in rheology study of confined thin films (Mukhopadhyay *et al.*, 2011).

4.3. Bio-related nanorheology

Rheology in soft tissues and biological fluids play a critical role in numerous biological activities. Cartilage lubrication is one of the most interesting bio-related rheology problems. Articular joints show excellent lubrication and wear resistance, and typically cartilage surfaces show no signs of wear over a quite long time (~ 75 years). It is reported that cartilage surfaces in the synovial fluid support pressures up to $\sim 20 \text{ MPa}$ (Morrell *et al.*, 2005). The mechanical, structural, and fluid flow responses of cartilage under compression and shearing have been extensively studied for over 60 years, and the lubrication mechanism and lubrication-structure relationship of cartilage are still not fully understood (Raviv *et al.*, 2003; Klein, 2006; Benz *et al.*, 2004; Greene *et al.*, 2010; Greene *et al.*, 2011). SFA was applied to measure the normal and friction forces of the human glycoprotein lubricin, the major boundary lubricant in articular joints, adsorbed on various hydrophilic and hydrophobic substrates, which suggests that the presence of biological polyelectrolytes on the cartilage surfaces (Zappone *et al.*, 2007) plays an important role in the boundary lubrication and wear protection in articular joints. Recently, nuclear magnetic resonance (NMR) was applied to investigate the in situ mechanical response, structure change, diffusion and flow of interstitial water in a full-thickness cartilage sample under compressive load (Greene *et al.*, 2010). The force amplification response of actin filaments (a major component of the cell cytoskeleton) under confined compression between two mica surfaces was also probed using a SFA (Greene *et al.*, 2009). It was found that the actin filaments stiffen under compression, which increases the bending modulus, generating opposing forces even larger than the compressive force (Greene *et al.*, 2009). These nanomechanical characterization and analysis help to better understand the molecular-level mechanisms and dynamics of polymerizing actin during force generation. A better understanding of the nanorheology and microrheology involved in various biological systems is critical for the development of new biomaterials, biosensors and biochemical/biomedical processes, which is another emerging area in the research field.

4.4. Nanorheology of polymer brushes

Polymer brushes are long chain macromolecules end-attached to a surface via covalent bonds with desired grafting density. The chain length and terminal linking

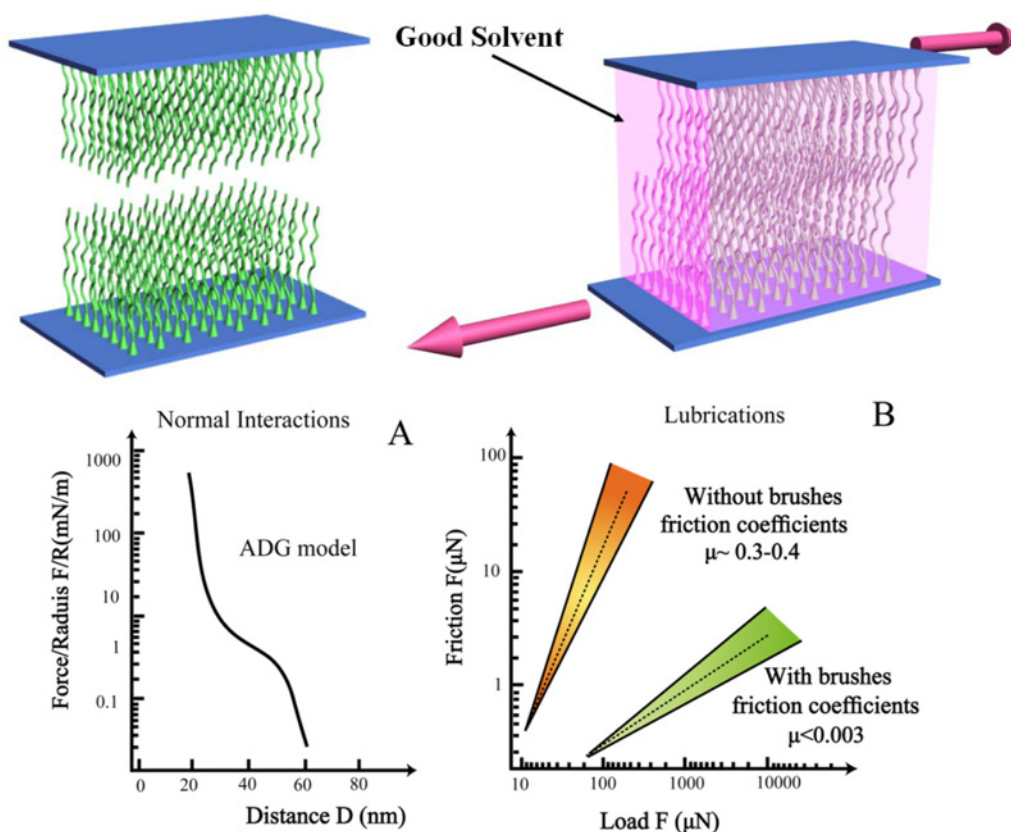


Fig. 5. (Color online) Alexander-de Gennes (ADG) scaling model for neutral polymer brushes in a good solvent (A), and polymer brushes can significantly reduce the friction/lubrication forces between surfaces in a good solvent (B).

groups can be modulated based on the types of substrates and applications, and grafted polymer brushes have great potential applications in boundary lubrication, especially in micro- and nano-electromechanical systems (MEMS and NEMS). Various polymer brushes have been developed to modulate the surface forces of confined thin liquid films, for example, to significantly reduce the friction forces in good solvents of the polymers (Klein, 1993; Klein, 1994 (a); Klein, 1995). The low friction forces and friction coefficients were proposed to be due to the long-ranged repulsion between brushes (*e.g.* steric repulsion for neutral brushes, electrostatic repulsion for charged brushes) which acts to keep the surface apart with a relatively fluid layer at the interface, as illustrated in Fig. 5 (Klein *et al.*, 1994 (a); Klein *et al.*, 1994 (b)). For neutral polymer brushes in good solvent, their normal interactions are generally interpreted in terms of the Alexander-de Gennes (ADG) scaling model (Equation 5, which gives the repulsive steric force per unit area between two flat surfaces), where L is the thickness of the brush layer, D is the separation distance, s is the mean distance between the attachment points of adsorbed polymer chains, k_B is the Boltzmann constant ($1.381 \times 10^{-23} \text{ J K}^{-1}$), T is temperature, as illustrated in Fig. 5

$$P(D) = \frac{k_B T}{s^3} [(2L/D)^{9/4} - (D/2L)^{3/4}] \text{ for } D < 2L. \quad (5)$$

Several methods have been employed for the preparation of polymer brush surfaces. One common approach is to selectively adsorb end-functionalized polymers or block copolymers with terminal group or one block (chemically or physically) binding to the substrate surface. These systems, however, usually have a rather low grafting density (Yamamoto *et al.*, 2000). Another commonly used method is through surface-initiated polymerization which can provide relatively high grafting density and well-controlled brush length.

Despite the fact that surface forces and lubrication of polymer brushes were largely investigated using SFA (Israelachvili, 2011; Zeng, 2013), AFM has also been employed for studying the morphology and lubrication behavior of polymer brushes. Takahara and his coworkers measured the swollen thickness of poly(2-methacryloyloxyethylphosphorylcholine) (PMPC) and poly[3-(N-2-methacryloyloxyethyl-N,N-dimethyl)ammonatopropane-sulfonate] (PMAPS) polymer brushes in solutions of various salt concentrations based on the force-distance curves from AFM measurements (Kobayashi *et al.*, 2013). Low

friction coefficients were measured by AFM using colloidal probes immobilized with high-density poly(methyl methacrylate) (PMMA) brushes in toluene (Yamamoto *et al.*, 2000). Takahara and coworkers have investigated the lubrication behavior of zwitterionic and cationic polyelectrolyte brushes using AFM. Polyelectrolyte brushes based on surface-initiated ATRP of 2-methacryloyloxyethyl phosphorylcholine (MPC) and 2-(N,N-dimethylamino) ethyl methacrylate (DMAEMA) show low friction coefficient and low adhesion force in both water and NaCl solutions of various concentrations (Kobayashi *et al.*, 2009).

The unique lubrication behaviors of polymer brushes shed new insights into liquid and polymer structures adjacent to surfaces, with important implications in different areas (*e.g.* coatings, lubricants, biosensors and functional polymers). Development of self-cleaning and antifouling surfaces is one of these research areas which have attracted much attention.

5. Conclusions

Understanding the nanorheology of fluids in confined geometries or porous media is important for various applications such as nanocomposites, lubricants, and MEMS/NEMS devices (Aoyagi *et al.*, 2001). The advent of advanced experimental techniques such as SFA, XSFA and AFM and computational methods such as molecular dynamics simulations provides powerful tools to study a wide range of rheological phenomena at molecular level and nano scale. Despite the significant progress made over the past few decades, the understanding of the fundamental principles of nanorheology, particularly the relationship between the rheological properties and structural evolution of the confined thin liquid films and particle suspensions, still remains incomplete. Some of the emerging research areas in the nanorheology field include, but are not limited to, the development of more advanced characterization techniques, design of multifunctional rheological fluids, bio-related nanorheology, and polymer brushes.

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