4.6. Nano-Rheology of Confined Simple Liquids

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The rheological properties of liquids depend on external parameters such as pressure, shear rate, and temperature. If a homogeneous liquid is confined between two structureless surfaces of infinitesimal stiffness, direct correlations between the rheological properties and the external parameters can be drawn. These boundary conditions are usually made in the hydrodynamic regime of lubrication, and described for incompressible Newtonian fluids with the Reynolds equation. At higher pressures and thinner films more sophisticated theories are necessary to explain the complex shear force behavior which is reflected in the multidimensional Stribeck curve. Assumptions of structureless and hard surfaces should be dropped and new parameters included; e.g., statistical parameters for roughness and Young's and shear modulus.

The complexity of the shear behavior of an ultrathin film demands the breakdown of the problem into very distinct regimes:

(a) How do rheological properties and shear properties of a homogeneous simple fluid change if it is normally confined between two "nearly" structureless solid surfaces?
(b) How does a rheological or structural complex but homogeneous liquid behave if it is normally confined between two "nearly" structureless solid surfaces?
(c) How does a surface adsorbed liquid or polymer melt or brush behave under shear?
(d) What is the impact of interfacial confinement on the material properties of a liquid or liquid-like polymer film?
(e) What is the effect of roughness on the rheological or structural properties of a thin liquid film? And,
(f) how are viscous properties of single phase liquids influenced by interfacial interactions?

This section will deal with these problems by reviewing recent surface forces apparatus (SFA) and scanning force microscopy (SFM) studies and theoretical models and simulations.
4.6.1 Dynamic Surface Forces Apparatus Studies on Confined Liquids

Liquids are in many practical applications confined to ultrathin films. The study of ultrathin confined liquids is relevant, for example, for lubrication, flow of liquids through porous media, flow of liquids in biological systems, formation of polymer composites, and thin film castings.

In the previous paragraphs, the viscosity of liquids has been discussed in terms of the Navier-Stokes equations of continuum hydrodynamics. This theory has been extended to viscoelasticity by introducing Boltzmann’s linear superposition principle and simple mechanical models consisting of springs and damping terms.

Montfort and Hadziioannou applied corresponding phenomenological theories to their surface forces apparatus (SFA) experiments of ultrathin confined films of long chain molecules (13), Fig. 4.1.

![Diagram](image)

Figure 4.1: (a) SFA schematic. Upper surface moves with $y(t)$, and lower surface responds with $x(t)$. (b) The liquid thickness, $D$, is chosen to be much smaller than the effective radius, $R$, and hence $r \ll R$.

Pure polymer liquids, perfluorinated polyether \((CF_2CF_2O)_m-(CF_2O)_n\), were confined between two mica surfaces. Static forces were measured as the surfaces approached each other very slowly, Fig. 4.2. Repulsive forces were found to extend out to separations greater than 10 times the radius of gyration, $R_g$, of the sample polymer in the bulk. The steep repulsive slope in the force at small separation distances is due to a hard wall effect. The separation can be decreased no further because of the softness of the SFA spring, or in other words, the stiffness of the confined sample exceeds the spring constant of the double cantilever. The authors conclude, based on the high wettability of perfluorinated polyether to clean mica surfaces, that the formation of surface films on each side, plus unattached chains in between, are causing the measured long-range repulsive forces.
Figure 4.2:
Logarithmic force/(radius of curvature), plot vs. distance, d, of perfluor-inated polyether liquid at 25 °C (· droplet between the surfaces) (∎ immersed surfaces in the liquid). (From (13)).

Montfort and Hadziioannou considered the following forces acting on the lower surface (with mass m) of their SFA, Fig. 4.1:

(a) the inertial force, \( F_I = m \frac{d^2 x}{dt^2} \),
(b) the restoring force of the spring, \( F_R = -kx \),
(c) the surface forces, \( F_S \), and
(d) the hydrodynamic forces, \( F_H \).

The surface force can be assumed to corresponds with the static forces as discussed above as long as the perturbation of the distance, \( D \), around the mean distance, \( \bar{D} \), is small. Hence, the surface forces can be described, in a first order approximation, as:

\[
F_S (D) = F_S (\bar{D}) + k_{\text{eff}} \times (D - \bar{D}),
\]

where the slope, \( k_{\text{eff}} \), is determined from static force-distance measurements. The slope is a measure of the effective stiffness of the systems which includes the sample liquid and the SFA. The hydrodynamic force \( F_H \) of the confined liquid has been treated by Montfort and Hadziioannou as a first-order linear, viscoelastic fluid by combining the continuity equation and the equation of motion for incompressible liquids with the Maxwell model. In the crossed cylinder configuration of the SFA experiment, the equations are:

\[
\frac{1}{r} \frac{\partial}{\partial t} (rv_r) + \frac{\partial v_z}{\partial z} = 0 \quad \text{(equation of continuity),}
\]

\[
\frac{dp}{dr} = \frac{\partial \tau_{rz}}{\partial z} \quad \text{(equation of motion),}
\]

assuming that the local radii of curvature of the SFA are large in comparison with the distance between the surfaces. In this approximation, the flow is similar to that between parallel plates. The stress tensor \( \tau \) for a viscous liquid without any “memory” can be expressed by

\[
\tau(t) = \eta \frac{dy}{dt},
\]
which is also predicted by the Maxwell model for very slow motion. Chan and Horn obtained for the hydrodynamic force, \( F_H \), based on the following relation for a plane-sphere geometry (14)

\[
F_H = -\frac{6\pi R^2}{D} \eta \frac{dD}{dt}.
\]

This relation was extended by Montfort and Hadziioannou to viscoelastic liquids with Boltzmann’s superposition principle which yield a hydrodynamic force of

\[
F_H = -\frac{6\pi R^2}{D(t)} \int_{-\infty}^{t} G(t-t') \frac{dD}{dt'} dt'.
\]

Hence, the equation of motion of the lower SFA surface is

\[
m \frac{d^2x}{dt^2} + kx - \frac{6\pi R^2}{D(t)} \int_{-\infty}^{t} G(t-t') \frac{dD}{dt'} dt' + F_S(D) + k_{\text{eff}} (D - \overline{D}) = 0.
\]

This differential equation can be solved for a sinusoidal movement of amplitude \( A_{in} \) and frequency \( \omega \) that is applied to the upper surface, Figure 4.1, by using the complex notation

\[
\int_{-\infty}^{t} G(t-t') \frac{dD^*}{dt'} dt' = i\omega \eta^* (D^* - \overline{D}),
\]

with the complex quantities \( D^* = \overline{D} + (A_{in} - A_{out}) e^{i(\phi+\varphi)} \), where \( A_{in} \) and \( A_{out} \) are the input and output modulation amplitudes at the upper and lower surface, respectively, and \( \eta^* = \eta^\vee + i\eta^\wedge \). The solution yields a viscous component of the complex viscosity,

\[
\eta^\vee = -\frac{D}{6\pi R^2 \omega} \left( k - m\omega^2 \right) A^\prime \sin \phi,
\]

and an elastic component,

\[
\eta^\wedge = -\frac{D}{6\pi R^2 \omega} \left[ (k - m\omega^2) (A^\prime \cos \phi - 1) + k_{\text{eff}} \right] = \frac{G^\vee}{\omega},
\]

where \( A^\prime = A_{in}/(A_{in} - A_{out}) \) and \( \phi \) is the phase lag in regard to the input modulation. For purely viscous liquids the viscosity, \( \eta \), is equal to the dynamic viscosity, \( \eta^\vee \), which can be rewritten in the form

\[
\eta = -\frac{D}{6\pi R^2 \omega} \left( k - m\omega^2 \right) \sqrt{(A^\prime)^2 - \left( \frac{k_{\text{eff}} - m\omega^2}{k - m\omega^2} \right)^2},
\]

Israelachvili used a simplified form of this equation, i.e.,

\[
\eta^* = -\frac{D k}{6\pi R^2 \omega} \sqrt{(A^\prime)^2 - \left( \frac{k_{\text{eff}} - m\omega^2}{k} \right)^2},
\]

for viscous liquids probed by SFA under low frequency conditions by neglecting the inertial terms of equation (4.9), i.e., by setting \( k = k - m\omega^2 \) (15).

The complex response function, \( \eta^* \), is connected to the relaxation function \( G(t) \) through the superposition principle as follows:

1 Note that \( kx + F_S(D) = 0 \) for one full period.
which leads, together with the Maxwell model for $G(t)$, to:

$$
\eta^* = \frac{\eta_0}{1 + i\omega\tau},
$$

with the relaxation time, $\tau = \frac{\eta_0}{G_0}$.

Montfort and Hadziioannou combined equations (4.8a), (4.8b) and (4.12) to obtain

$$
\frac{1}{A'} = \frac{1}{A'} = \frac{1}{\alpha} \left( \frac{\omega\eta_0}{\alpha (1 + \omega^2\tau^2)} \right)^{-1} \left( \sqrt{1 + \left( \omega t + \alpha \left( 1 - \frac{k_{eff}}{k} \right) \frac{1 + \omega^2\tau^2}{\omega\eta_0} \right)^2} \right)^{-1}; \quad \alpha = \frac{kD}{6\pi R^2},
$$

and studied the functional behavior of the amplitude of oscillations for a Maxwell fluid in the presence of surface forces, Fig 4.3. They found that in the case of repulsive forces ($k_{eff} < 0$), the variation in $A'$ are comparable to the variations observed without surface forces (13).

Figure 4.3: Amplitude of oscillations for a Maxwell fluid in the presence of surface forces: (a) $k_{eff} < 0$, (b) no surface forces: $k_{eff} = 0$, (c) $0 < k_{eff} < 1$, (d) $k_{eff}/k = 1$, (e) $k_{eff}/k = 1 + G_d/\alpha$, (f) $k_{eff}/k = 1 + G_d/\alpha$; for $G_d/\alpha = 1$.

With the asymptotic behavior

$$
\lim_{\omega \to 0} \frac{1}{A'} = \left( \frac{1}{A'} \right)^{(0)} = \left( 1 - \frac{k_{eff}}{k} \right)^{-1},
$$

(4.14)
\[
\lim_{\omega \to \infty} \frac{1}{A'} = \left( \frac{1}{A'} \right)^{(-\infty)} = \frac{G_o}{\alpha} + 1 - \frac{k_{\text{eff}}}{k}, \tag{4.15}
\]
the effective spring constant, \(k_{\text{eff}}\), and the elastic modulus, \(G_o\), can be calculated. In the case of attractive surface forces, different classes should be distinguished, Fig. 4.4. It is important to note that depending on the strength of the attractive surface forces the response amplitude increases, decreases or remains constant with the frequency. The different qualitative behavior of the amplitude variation is found in the frequency dependence of the phase shift, \(\phi\), which is
\[
\tan \phi = \omega t_o + \alpha \left( 1 - \frac{k_{\text{eff}}}{k} \right) \frac{1 + \omega^2 t_o^2}{\omega \eta_o}, \tag{4.16}
\]
and presented in Figure 4.4. While for the amplitude the asymptotic behavior is interesting, it is the minimum in the phase shift, \(\phi_m\), expected for
\[
\omega_m^2 t_o^2 = \left( \frac{1}{A'} \right)^{(-\infty)} = \left( \frac{1}{A'} \right)^{(0)}, \tag{4.17}
\]
where \(\omega_m\) is the frequency to the minimum phase shift, which provides additional information about the Maxwell relaxation time \(t_o\).

**Figure 4.4**: Phase shift for a Maxwell fluid in the presence of surface forces:
(a) \(k_{\text{eff}}<0\), (b) no surface forces: \(k_{\text{eff}}=0\), (c) \(0<k_{\text{eff}}/k<1\), (d) \(k_{\text{eff}}/k=1\), (e) \(k_{\text{eff}}/k=1+G_o/\alpha\), (f) \(k_{\text{eff}}/k.1+G_o/\alpha\); for \(G_o/\alpha=1\).

Montfort and Hadziioannou found equation (4.10) experimentally confirmed for a polymer liquid of perfluorinated polyether, until a mean separation distance of around 200 nm (13). The measured viscosity of the confined film was reported to be 2.47 P, which is in correspondence to the bulk polymer. At a distance of 84 nm, the viscosity was found to increase to a value of 3.32 P. The authors claim that as the gap
decreases to a size comparable to the dimensions of the pinned chains, the mobility of
the chains decreases and, as a result, the viscosity increases. The first finding of
Montfort and Hadzioannou was that the phenomenological theory developed above
predicts well the viscoelastic behavior of liquids, e.g., semidilute polymer solutions
up to a certain thickness. Their second important finding deals with ultrathin liquid
films below a certain critical thickness where interfacial interactions and molecular
dimensions become noticeable. Also other groups observed, at lesser separations, that
hydrodynamic forces are larger than expected from the phenomenological
calculations discussed above (16-18).

The extended theories of lubrication, for instance the exponential relationship
of the viscosity with hydrostatic pressure, equation (6.51), were found to predict
viscosity values larger than experimentally encountered. Thus, an adsorbed polymer
layer or a brush is not well described by a rigid film. Further theories were developed
by Milner (19) and Pincus (20) who were modeling the complex flow of solvents
between grafted polymer layers. Their theories are in analogy of flow through porous
media.

4.6.2 Dynamic Force Microscopy Study on Liquids

Dynamic viscoelastic properties of ultrathin liquid films have also been
studied with another technique, the scanning force microscope (SFM) (21, 22).
Friedenberg and Mate applied the SFM to a low-molecular-weight polymer liquid,
poly(dimethylsiloxane) (PDMS), by using spherical glass beads of 22 µm radius, R, at
the end of a tungsten wire with a calculated spring constant of 40 N/m, k_L from a
measured resonance frequency of 7.8 kHz, Fig. 4.5. Also Friedenberg and Mate used
Maxwell’s steady creep model consisting of a Newtonian damping term b_p for the
polymer sample at small shear rates, by setting the samples elastic response k_P to
zero, and connecting the cantilever spring constant in series, Fig. 4.5. The authors
further assumed that the surface force between the glass bead and the polymer surface
is dominated by the meniscus force, F,

\[ F \equiv -4\pi R \gamma_L \left( 1 + \frac{\delta}{2r} \right), \tag{4.18} \]

where \( \gamma_L \) is the surface tension, \( \delta > 0 \) is the average penetration depth of the sphere in
the polymer liquid, \( \delta < 0 \) is the distance between the sphere and the original film
surface, and \( r \) is the capillary radius - with \( r \) much smaller than the radius of the
sphere, \( R \), (23), Fig. 4.5.
Because the meniscus force is linear with displacement, a *meniscus spring constant* can be introduced as:

$$-k_M = \frac{dF}{d\delta} \equiv -2\pi \gamma_L \frac{R}{r}, \quad (4.19)$$

which is assumed to be independent of both frequency and separation. The meniscus spring constant $k_M$ corresponds to the effective spring constant, $k_{\text{eff}}$ introduced above, and hence, can be determined at low frequencies and at large separations where viscous forces are negligible.

The viscous forces, $F_v = bv = b*dh/dt$ are measured at small surface deformations, where $v$ is the relative velocity of the surfaces, $b = 6\pi R^2 \eta / h = k_L \eta / \alpha$ is the viscous drag coefficient (24), and $h$ is the distance between the sphere and the wall. Friedenberg and Mate's measurements provide, as expected, a linear relationship between $\alpha = k_L \eta / b$ and the separation distance, $h$, Fig. 4.6.

The damping coefficient, $b$, can be determined from

$$A = \frac{A_{\text{out}}}{A_{\text{in}}} = \frac{\omega b \sin \phi - k_M \cos \phi}{k_L - k_M - m\omega^2} \quad (4.20)$$

where $A$ is the amplitude ratio, $A_{\text{out}}$ is the response amplitude of the cantilever spring, $A_{\text{in}}$ is the input modulation, $\phi$ is the phase shift between input and response, $k_M$ is the meniscus spring constant which is determined independently from the lever response at low frequency and large separation, $k_L$ is the lever spring constant, and $m$ is the mass of the cantilever probe (21). The expression for the amplitude ratio reduces to

$$A = \frac{\omega b \sin \phi}{k_L} \quad (4.21)$$

for very low modulation frequencies, i.e., $k_L \omega^2 \ll k_L$ and neglecting capillary forces.²

² Note that equations developed by Montfort and Hadziioannou for SFA, e.g., equation (4.8a), and equations developed for SFM, e.g., equation (4.21), are related by

$$-A' \sin \phi_1 = \frac{A}{\sin \phi_2},$$

where $\phi_1$ and $\phi_2$ are the phase shift of the lower plate and the cantilever spring, respectively.
The sharp decrease of the reciprocal damping coefficient in Figure 4.6 is believed to arise from hard-wall contact, and hence, serves as the critical point to define zero separation (21). A viscosity of 430±40 cP could be determined from the linear extrapolation in Figure 4.6 and the radius of curvature of the sphere, and was found to be close to the bulk value of 350 cP (21).

One of the most fundamental questions in thin film applications is the interaction strength of films with their substrates. Friedenberg and Mate suggest using the capillary pressure, \( P = \gamma L/r \), which is assumed to be in equilibrium with the pressure of the liquid film on the substrate surface, as a quantitative measure for the interaction strength. Low pressure would indicate a weak interaction force. The capillary pressure is determined from the experimental determination of the stiffness of the meniscus, \( k_M \), and the equation (4.19). In this particular example of PDMS, a disjoining pressure of 14 kPa for a 32 nm film, 5.8 kPa for a 92 nm film, and 2.5 kPa for a 128 nm film were found (21).

![Figure 4.6](image)

Figure 4.6: Reciprocal of the viscous damping coefficient, \( b \), as a function of separation for a 92 nm PDMS film. The dotted line is a linear extrapolation. (From (21) with permission of C.M. Mate)

The frequency response of the amplitude ratio at large separation were found to be finite and non-zero at low frequency which was attributed to the capillary force (21). As the frequency increases, the amplitude ratio was found to increase to unity because of enhanced viscous coupling between the cantilever and the polymer liquid (21). Friedenberg and Mate claim that this is an important difference between SFM and SFA measurements (21).

The significant difference between the SFM and SFA approach to confinement measurements of ultrathin films are the surface forces. In SFA measurements, capillary interactions are negligible compared to other forces due to the low curvature of the large contact area. This is however different for SFM measurements where the contact area is small and capillary forces at large separations are significant.
4.6.3 Viscous Friction Force Measurements between Lubricated Surfaces

In the two previous paragraphs, viscous drag forces and interfering surface forces were discussed in experimental setups of two adjacent surfaces which are moving perpendicular to each other. In the event of lateral motions of two surfaces which confine a ultrathin film in between, typically referred to as lubricated frictional motion, it is expected that the overall friction is reduced and the surfaces slide smoothly relative to one another. Hence, the acting viscous forces for a Newtonian fluid can be expressed as $F = \eta v$ as already introduced above with the viscous damping coefficient for surface perpendicular motions. It was, however, found that for very thin lubricant films the forces become much larger than those measured in the bulk liquid. Considering that the degree of freedom of motion in a confined "two-dimensional" fluid is significantly reduced in comparison to a three-dimensional bulk fluid, it is reasonable to assume that the characteristic relaxation times become orders of magnitude greater than those of the bulk (6). Hence, increased viscous friction in an ultrathin film could be understood from the standpoint of entropy only, without considering the effect of surface interactions which will be discussed in more detail below.

Israelachvili and co-workers found that thin lubricant films can exhibit solid-like properties, including a critical yield stress and a dynamic shear melting transition, which can lead to stick-slip motions (4, 25-27). The generic shape of an overdamped stick-slip behavior is illustrated in Figure 4.7 which has been observed with SFA experiments as sketched in Figure 4.8 (27). The spring force, $F = -k(u-vt)$, results from the difference of the relative displacement of the block to the stationary lower surface, $u$, and the drive distance, $vt$, in conjunction with the spring constant $k$.

![Figure 4.7: Illustration of a generic stick-slip motion of an overdamped spring system for increasing pulling velocities. Below the critical values for temperature, $T_c$, and shear rate, $\nu_c$, dominant stick-slip motions have been observed for hexadecane films (27). The stick-slip spikes disappear as the velocity is increased above $\nu_c$.](image-url)
There are three possibilities which result in stick-slip motion of a measuring system which is based on springs:

(a) Spring instabilities occur due to the choice of soft measuring springs. It is not the liquid but the spring system which is measured.

(b) The confined liquid film is "frozen" and the measuring spring is stiff enough so that the yield of the confined film due to lateral displacement occurs before any spring instabilities. Further, it is assumed that the film material yields three-dimensionally. That process is called shear-melting. The force which is measured can be described by a viscous force.

(c) Due to the fact of confinement the exerted force is initially too small to deform the highly viscous film (stick regime). Yielding of the film occurs two-dimensionally along a slip plane either between the film and the solid mica surface or in between the film. This process - where again a stiff spring is assumed - is better described by solid friction.

Yoshizawa and Israelachvili claim that their observation of stick-slip behavior is associated with some sort of melting transition (27). They support their statement by start-stop experiments with varying stopping times and sliding velocities above the critical stick-slip velocity, $v_c$. As mentioned above for sliding velocities, $v>v_c$, sliding occurs steadily. Yoshizawa and Israelachvili observed for hexadecane at $T = 17$ °C, if sliding is discontinued for a time $t_s$ smaller than a critical time $t_c$, the spring force $F$ returns smoothly to the value it had prior to the stopping interval, while for a time $t_s \geq t_c$ a stiction spike is produced before the friction force returns to the value it had taken prior to the stopping interval. Yoshizawa and Israelachvili find the sharp onset for a stiction spike at $t_s = t_c$ sufficiently different from macroscopic dry friction experiments (28, 29), which leads them to refer to $t_c$ as the nucleation time of the frozen state. The generic behavior of friction at dry interfaces is that the stiction spikes increase logarithmically with time with no sharp transition time (30).
4.6.4 Theoretical shear simulations and mechanical models

In molecular dynamic (MD) simulations of Gao, Luedtke and Landman, it was found that the shear motion of a confined ultrathin hexadecane film can be visualized with the average motion of a single card in a stack of cards (31). Previous drainage experiments of hexadecane films, performed experimentally and by MD simulation (32), confirm a layered density oscillation of surface-confined n-hexadecane (32). The solvation force oscillations observed during normal compression are found to be very pronounced in n-hexadecane because of their strong repulsive and attractive regions which are due to the simple linear structural form of the molecules. Landman et al. showed that for a slightly more complex structure of a branched alkane, such as squalane, the solvation forces are mostly repulsive which exhibit a monotonic continuous decrease in the number of confined segments contrary to the step-like variations observed with n-hexadecane films. In friction experiments, the confined hexadecane film can be pictured as being built up of discrete molecular layers which move statistically either in registry with the top or the bottom shear surface. The thicker the film the higher are the statistical possibilities of shear motions so that after five molecular layers no stick-slip motions can be found in the averaged lateral shear stress. Note that Landman’s MD simulation of shear does not suggest a melting transition to be responsible for the stick-slip motion. The statistical sliding between layers determines the overall friction force. Sliding occurs in two-dimension, which is in contrast to viscous sliding where deformation occurs more or less isotropic in three dimensions depending on the complexity of the fluid and interfacial interactions.

Various groups motivated by SFA or SFM experiments used simple mechanical models to investigate the stick-slip behavior (33, 34). It is important to note that all of these attempts are phenomenological in nature by using differential equations where a spring and a viscous damping term are involved. Depending on the Ansatz of the differential equation, the character of dissipation is already implied. For instance, an equation of motion of the simple form

\[ m\ddot{x} + kx + \eta\dot{x} = f(t) \]  \hspace{1cm} (4.22)

implies a Newtonian viscous dissipation.\(^3\) Carlson and Batista proposed a phenomenological constitutive relation to describe the frictional forces as function of the macroscopic variables, position, velocity and time (34). Constitutive equations are referred to as rate and state laws, where the rate variable refers to the sliding velocity, and the state variable is meant to capture all memory dependent effects. Carlson and Batista based their spring model calculation on Yoshizawa and Israelachvili's friction measurement of hexadecane lubricated surfaces as discussed above and sketched in Figure 4.8. Hence, it was assumed that the state variable represent the degree of "melting", as suggested by Yoshizawa and Israelachvili. Carlson and Batista setup a single degree of freedom equation of motion of the form

\[ m\ddot{U} = -k(U - vt) - F_o \]  \hspace{1cm} (4.23)

where \(U\) is the displacement of the block, and the other parameters are defined as in Figure 4.8. The friction force \(F_o\) was introduced in its dimensional form, containing the rate \(dU/dt\) and state \(\theta\) of the system, as follows (34):

\[ F_o = \theta + \beta\dot{U} \]  \hspace{1cm} (4.24)

\(^3\) Dots denote time derivatives.
with
\[
\dot{\theta} = \frac{(\theta - \theta_{\min})(\theta_{\max} - \theta)}{t^*} - \alpha(\theta - \theta_{\min})U
\] (4.25)

The state of the system has been arbitrarily constrained between \(\theta_{\min}\) and \(\theta_{\max}\), corresponding to the "fully melted" and "frozen" states, respectively. The friction force \(F_o\) corresponds to the maximum static friction when \(dU/dt = 0\), and to the dynamic friction when \(dU/dt \geq 0\). Equation (4.25) describes the evolution of the state variable. A characteristic time \(t^*\) is introduced which makes the film freeze from any initial state \(\theta \neq \theta_{\min}\). The inverse of \(\alpha\) plays the role of a characteristic melting length (i.e., slip distance over which the melting transition takes place). Like the experimental system, the model exhibits a transition from stick-slip to steady sliding at a critical velocity (34).

Carlson and Batista concluded that rate and state constitutive relations, while purely phenomenological, can provide some important guidelines for the design of mechanical systems, in terms of both material choices and operating conditions. More work remains to be done in the choice and the evaluation of particular constitutive relations. Considering the very recent MD simulations by Landman and co-workers, it seems reasonable also to consider rate and state laws for interfacial sliding in between liquid layers or at the liquid-solid interface.

In summary, it was found that even "simple liquids" such as short-chain alkanes behave quite complex under confinement. In recent studies it was also found that spherical molecules, such as octamethylcyclotetrasiloxane (OMCTS) and low molecular polymer melts, cease to behave as bulk liquids if confined to a film of less than 2.5-5.0 nm in thickness (4-7).

References