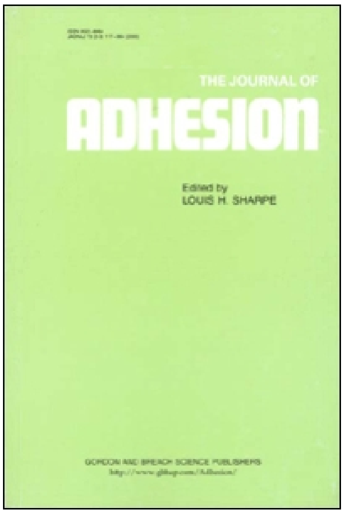

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Limit Cycles in Dynamic Adhesion and Friction Processes: A Discussion

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Limit Cycles in Dynamic Adhesion and Friction Processes: A Discussion

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Simple equations exist relating adhesion and friction forces. These apply to simple attachment-detachment processes and steady-state (smooth) sliding conditions. However, in the case of more complex, such as polymer, surfaces both the adhesion and friction can be very complex, irreversible, and nonlinear, exhibiting stringing and tack in the former and stick-slip sliding in the latter. We explore possible relationships between such nonlinear adhesion and friction processes. Based on recent experiments we find that certain types of "limit cycles," relating the (normal) adhesion and (lateral) friction forces, $F_\perp$ *and* $F_\parallel$*, to the relative velocities,* $V_\perp$ *and* $V_\parallel$*, of the surfaces during an attachment-detachment process or stick-slip sliding, bear a very similar resemblance to each other. We briefly discuss the theoretical and practical implications of describing such dynamic processes in terms of limit cycles.*

Keywords: Adhesion limit cycle; Friction limit cycle; Rate and state models

The relationship between adhesion and friction is a complex one. For simple systems—those that do not display complex nonlinear effects in their adhesion (*e.g.*, tack, stringing, fibrillation, crazing, fingering, cavitation) or friction (*e.g.*, stick-slip sliding)–there is a simple picture and relationship connecting the two processes. The physical scenario

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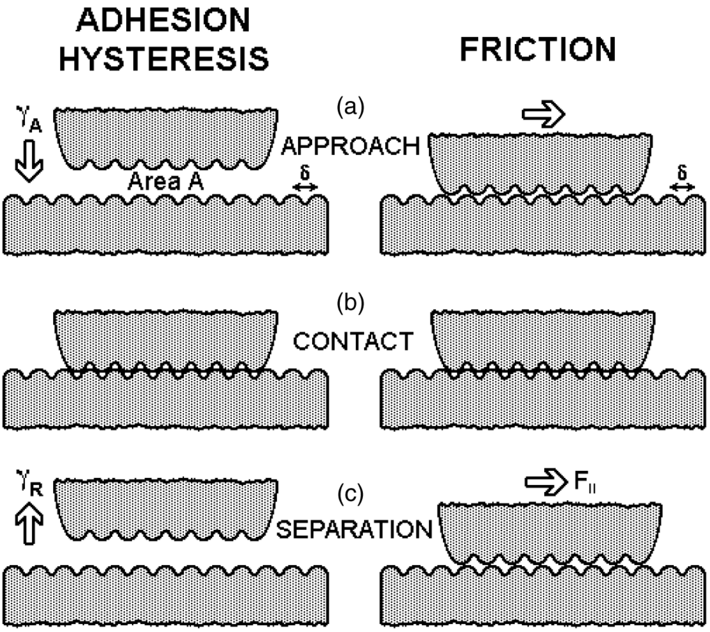


FIGURE 1 During an "adhesion cycle" (loading-unloading or attachment-detachment) of two surfaces (left), the two surfaces come into contact (a), new bonds are formed across the interface (b), which break when the surfaces are separated (c). During a "friction cycle" (right), as two surfaces move past each other, bonds are continually being formed and broken in a similar way as occurs during an adhesion cycle, except that the atoms are not separated to infinity in (c) so that the energy expended is less than the hysteresis during an adhesion cycle, $(\gamma_R - \gamma_A)$ per unit area [12,27].

is illustrated in Figure 1, which leads to the following equation for the steady-state (smooth, kinetic) friction force $F_{\parallel}$, for two surfaces of contact area A:

$$F_{\parallel} = \frac{(\gamma_R - \gamma_A)A\varepsilon}{\delta} + \text{terms related to } L \text{ (normal load)} \qquad (1)$$

where γ_A is the advancing surface energy on loading and γ_R is the receding energy on unloading or separation, and where $(\gamma_R - \gamma_A)$ is the adhesion energy hysteresis per unit area measured during a loading-unloading cycle. The first term is the so-called "adhesion-controlled friction," the second being the "load-controlled" contribution (typically given by μL where μ is the friction coefficient). Adhesion-controlled friction always dominates at low or zero loads, unless the force between the surfaces is repulsive ($\gamma = 0$), which can occur in liquids. The distance, δ, is the characteristic (molecular or asperity) length over which sliding must occur for the same number of bonds to be broken, that is, for the same amount of energy to be dissipated, in the two processes. This distance is expected to have molecular scale dimensions. Note, too, that when comparing the two processes, the time taken to slide laterally by a distance δ should be the same as the contact time in the adhesion cycle and the externally applied load or pressure should also be the same. The factor ε ($\varepsilon < 1$) accounts for the less than full breaking of the bonds during a sliding cycle (see Figure 1) and the less than full transfer of the energy to the lattice during molecular collisions (as heat). The computation of ε, which is not a constant independent of the interfacial shearing velocity V, remains one of the most challenging problems in the field.

Equation (1) shows that friction is expected to be correlated, not with the adhesion *per se*, but with the nonreversible or *hysteretic* part of the adhesion energy during an adhesion cycle. This simple equation has been found to predict the right qualitative trends in many systems [1–5] and to give better than order of magnitude quantitative agreement between measured friction forces and adhesion energy hysteresis of silica [3], polymer surfaces [1,2,5], and surfactant boundary lubricant surfaces [4]. Figure 2 shows an example of this good agreement. It shows the adhesion hysteresis (JKR plots) of two UV treated (partially bond-broken) polystyrene surfaces. The measured contact area, A, and friction force, $F_{\parallel}$, for this system measured at zero external load (results not shown) were $A = 1{,}260\,\mu\text{m}^2$ and $F_{\parallel} = 5.8\,\text{mN}$. Inserting these values into Equation (1), and assuming $\delta \sim 1.6\,\text{nm}$ for the estimated maximum interdigitation length at the PS surfaces [3], we obtain $\varepsilon \approx 0.55$, which is a reasonable value for the energy transfer factor. It is noteworthy that a small adhesion hysteresis can give rise to a large friction force, as found experimentally and predicted by Equation (1).

In many cases both the adhesion hysteresis and friction depend on the rates of the measurements: the speed of loading and unloading, $V_{\perp}$, or the sliding velocity, $V_{\parallel}$. In the case of adhesion this means that the surfaces are non-Newtonian and/or viscoelastic, while in the case of friction that it depends on the sliding speed. More complex dependencies are also usually implicated, such as the applied load, the previous history (*e.g.*, the contact time), the sliding distance, etc., none of which appear in Equation (1).

In the case of adhesion Figure 3(a) shows the normal force, $F_{\perp}$, as a function of surface separation velocity, $\dot{D}$ (top axis), for two polystyrene surfaces (crossed cylinder or, equivalently, sphere on flat

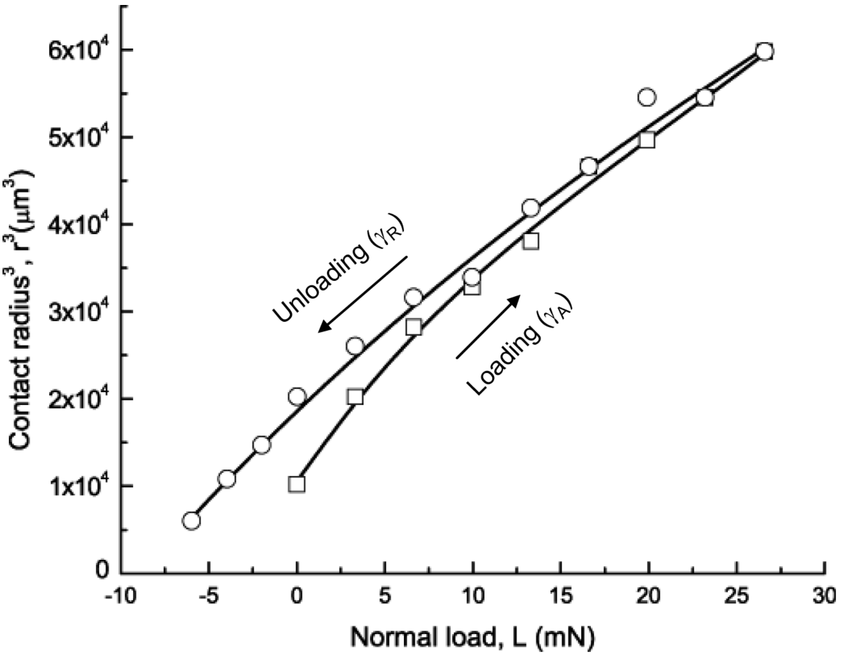
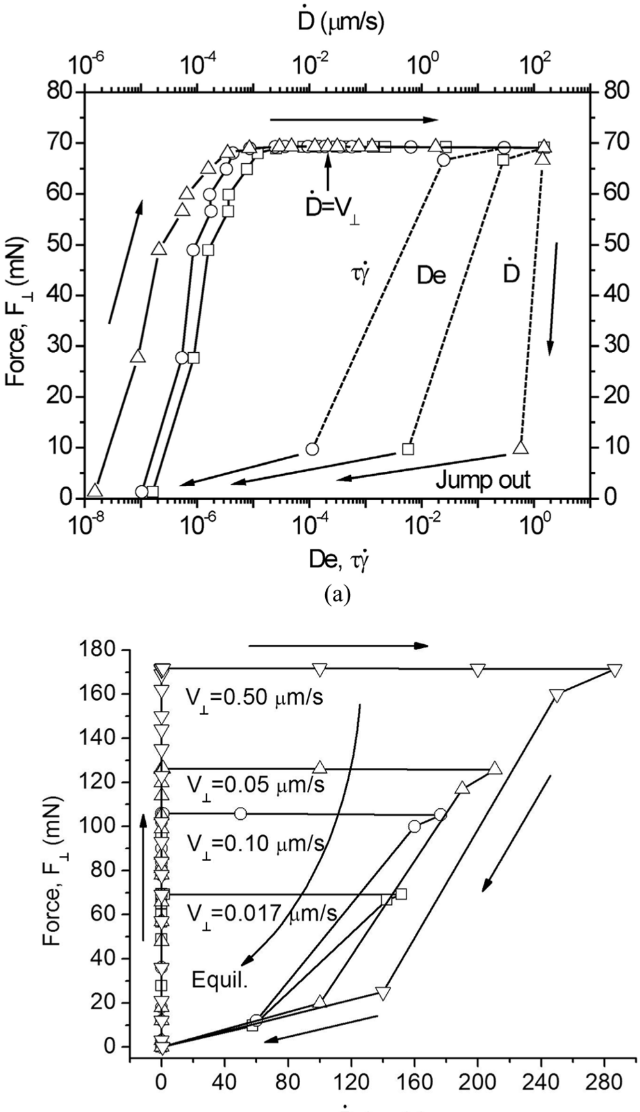


FIGURE 2 Loading-unloading JKR cycle for two polystyrene surfaces (MW 280,000, $T_g = 106°C$) measured at T = ~23°C, giving $(\gamma_R – \gamma_A) = 13.5 \pm 3.0$ mJ/m^2. (Adapted with permission from Chen, N. H., Maeda, N., Tirrell, M., Israelachvili, J., *Macromolecules* **38**, 3491–3503 [2005]. Copyright [2005] by the American Chemical Society.)

FIGURE 3 (a) Adhesion limit cycle for the normal force, $F_\perp$, *versus* the Deborah number, De, dimensionless shear rate, $\tau\dot{\gamma}$, and the velocity of surface-surface separation, $\dot{D} = dD/dt$, of two polymer surfaces near T_g at a fixed driving velocity of $V_\perp = 0.017\,\mu m/s$ of the spring supporting the moving surface, as measured in a Surface Forces Apparatus (SFA). De is defined in Eq. 3, τ is the relaxation time of the polymer at the experimental temperature, $\dot{\gamma}$ is the maximum shear rate in the fluid for normal motion of a sphere near a surface [6], $\dot{\gamma} = (1/2)(3/2)^{5/2}\dot{D}(R^{1/2}/D^{3/2})$, which occurs at $r = (2RD/3)^{1/2}$. Each cycle, starting at zero force, shows a slow increase in the separation, D, and velocity, $\dot{D}$, with increasing force, $F_\perp$, followed by a very rapid acceleration at almost constant force, followed by a decrease in both values as the surfaces slow down and come to a stop at zero force. The polymer was polystyrene (MW 1300, $T_g = 39–45°C$, experimental temperature 51°C). (b) Same as (a) but for four different separation velocities, $V_\perp$; the lowest cycle being the same as that shown in (a). (Figure 3[a] adapted with permission from Zeng, H. B., Maeda, N., Chen, N. H., Tirrell, M., Israelachvili, J., *Macromolecules* **39**, 2350–2363 (2006). Copyright [2006] by the American Chemical Society.)

geometry, with sphere radius R = 2 cm). The surfaces were pulled apart at a steady velocity of $V_{\perp} = 0.017\,\mu m/s$ (the pulling velocity on the spring supporting the movable surface) for a certain time. At first,



(a)

(b)

the surfaces separate very slowly ($\dot{D} << V_\perp$), *i.e.*, they are in a "stick" regime. They then accelerate until ($\dot{D} \approx V_\perp$), which coincides roughly with the maximum force—the measured adhesion force or pull-off force, $F_\perp = F_{\mathrm{ad}}$. This is analogous to the start of a "slip" during stick-slip sliding. The moving surface continues to accelerate rapidly (note the log axis for $\dot{D}$), then slows down, eventually coming to rest as the force $F_\perp$ also falls to zero. Limit cycles for the force can also be plotted against the Deborah Number, De, or shear rate, $\dot{\gamma}$ (bottom axis) [6], the time, *t*, or the surface separation, *D*. Figure 3(b) shows the same plot as in (a) but for four different separation velocities $V_\perp$, on linear scales.

Limit cycles have been studied and analyzed in great detail in the case of (stick-slip) friction, but not in the case of adhesion. Theoretical analyses have generally been in terms of rate and state models, chaos theory and Lyapunov exponents [7–13]. Specific analyses of friction limit cycles in the case of branched hydrocarbon and surfactant boundary lubricants have shown that the number of variables or system parameters needed to describe such cycles are at least three [7,14]. The most common parameters are the relaxation time τ (at least one, describing how the system relaxes to equilibrium after the externally applied normal or shear force is removed), the adaptation time τ_{a} (the time to reach steady-state conditions after the application of the external force, which is different from τ), and a state parameter, Θ, describing the state of the system as determined by the temperature, externally applied force, previous history (memory effect), a characteristic length scale, and the above two characteristic times of the system. All these determine the instantaneous rate of motion (shear rate, velocity) and the adhesion and friction forces, *i.e.*, the state of the system, Θ.

The same concepts may be expected to apply to adhesion cycles where the *normal* forces, distances and velocities replace the *lateral* or shear forces, velocities and distances. Thus, a "rate-and-state" model for adhesion cycles (Figure 1, left) can be established as for friction (Figure 1, right) [7–11]:

$$F_\perp = F(V_\perp, \Theta) \tag{2}$$

where Θ is the state variable, depending on all the experimental state parameters such as temperature, molecular relaxation time(s), characteristic length scales of the adhesive surfaces, and underlying substrate material [15]: assuming the adhesive contact area A consists of N independent bonds or adhesive "junctions," a junction can detach either spontaneously by thermal excitation or due to the external pull-off force. Let τ_0 be the mean time to break a junction due to thermal fluctuations under zero normal stress. A dimensionless Deborah Number during the adhesion cycle can be defined as [6]:

$$De = \tau_0 \frac{\dot{D}}{D} \tag{3}$$

In Surface Forces Apparatus (SFA) and most other types of adhesion experiments, the time-dependent force $F_\perp(t)$, and measured pull-off force, F_{ad}, can be calculated by solving

$$m\ddot{D} = K[V_\perp t - D(t) + D_0] - F_\perp(t) \tag{4}$$

where m is the mass of the adhesive surface, K is the spring stiffness, and D_0 is the initial surface separation. Usually the first inertial term on the left side of Equation (4) is small and can be neglected. Then the maximum force is always located at $\dot{D} = V_\perp$ during the adhesion cycle. The surface separation D is a function of time and depends on the previous history, spring constant, and separation rate. The previous history is in turn related to the lifetime of the adhesion junction and other system and experimental parameters. However, an adhesion junction is under a normal stress during the adhesion cycle. The lifetime of a stressed junction can be expressed as [7]:

$$\tau = \tau_0 \exp\left(-\frac{aF_\perp}{k_b T}\right) \tag{5}$$

where a is a constant with the dimension of a characteristic length and T is the temperature.

Based on the above discussion all these make the maximum pull-off force, $F_\perp = F_{ad}$, not only rate dependent but also state dependent, from which the effective surface energy, γ, and adhesion hysteresis, $\Delta\gamma$, can be estimated from Equations (6) and (7):

$$\gamma = \frac{F_\perp}{\beta\pi R} = \frac{F_{ad}}{\beta\pi R} \tag{6}$$

$$\Delta\gamma = \gamma_R - \gamma_A \tag{7}$$

where β is a constant. $\beta = 4$ is predicted by the Derjaguin-Muller-Toporov (DMT) theory; $\beta = 3$ is predicted by the Johnson-Kendall-Roberts (JKR) theory [6,15]. The adhesion hysteresis, $\Delta\gamma$, during the adhesion cycle can be also approximately established as the maxima pull-off force times the critical separation distance, δ_c, at pull-off [13]. However, it should be noted that the pull-off force $F_\perp = F_{ad}$ also depends on the characteristic molecular length scale, δ, of the adhesive surfaces (Figure 1) and the critical separation, δ_c, at pull-off.

In the case of friction a common manifestation of nonlinear behavior is the occurrence of stick-slip motion over certain velocity regimes. During stick-slip the surfaces are pushed by a force transmitted by a spring or elastic element, but they initially do not move (actually, they do move, but very slowly, *i.e.*, they *creep*). This is the stick regime. Then there is a rapid acceleration followed by a deceleration. This is the slip regime. The process then repeats itself, either with a well-defined periodicity (regular stick-slip) or with irregular frequencies and amplitude (irregular, intermittent or chaotic stick-slip). Plots of the friction force, $F_{\parallel}$ (analogous to the normal force $F_{\perp}$), *versus* the interfacial shearing velocity V (analogous to the rate of change in surface separation $\dot{D}$) during stick-slip cycles invariably look like the "limit cycles" shown in Figure 4.

The similarity in the shapes of the adhesion and friction limit cycles is striking when the force-velocity functions, $F_{\perp}(\dot{D})$ and $F_{\parallel}(V)$, are compared. Thus, Figure 4(a), which shows the limit cycle when the stick-slip was most pronounced and regular, is very similar to Figure 3(b), both plotted on linear scales. At higher velocities, the stick-slip disappears and the sliding is smooth. This is manifested by the cycle collapsing into a point, as shown in Figure 4(d), where the shear (sliding) velocity, V, equals the driving velocity $V_{\parallel}$. At driving velocities close to the critical velocity (Figure 4(c)) the stick-slip is often erratic or "chaotic," as also predicted by a number of theoretical models [16–20]. With decreasing sliding velocity, as $V_{\parallel} \to 0$, the stick-slip and friction force also tend to zero (not shown in Figure 4 because these ultra-low velocities were not attainable in these experiments), and the limit cycle collapses as at high velocities. A similar trend occurs in the adhesion cycles as the separation velocity is decreased: the cycles collapse from top to bottom as the system approaches equilibrium (nondissipative) conditions, as shown in Figure 3(b). At the opposite extreme of very high normal velocities, $V_{\perp}$, of approach *and* separation, and infinitesimally short contact times (not attained in these experiments), we again expected the cycles to collapse and the adhesion hysteresis to vanish.

As mentioned above, there are a number of ways to plot limit cycles; however, plotting the functions $F_{\perp}(\dot{D})$ and $F_{\parallel}(V)$ is particularly useful because the area of the cycle gives the (rate of) work done during each cycle.

Note that the two surfaces do not have to end up in precisely the same location to complete a cycle so long as they end up in the same *state*. Thus, in Figures 1 (right) and 4, the surfaces are at a different

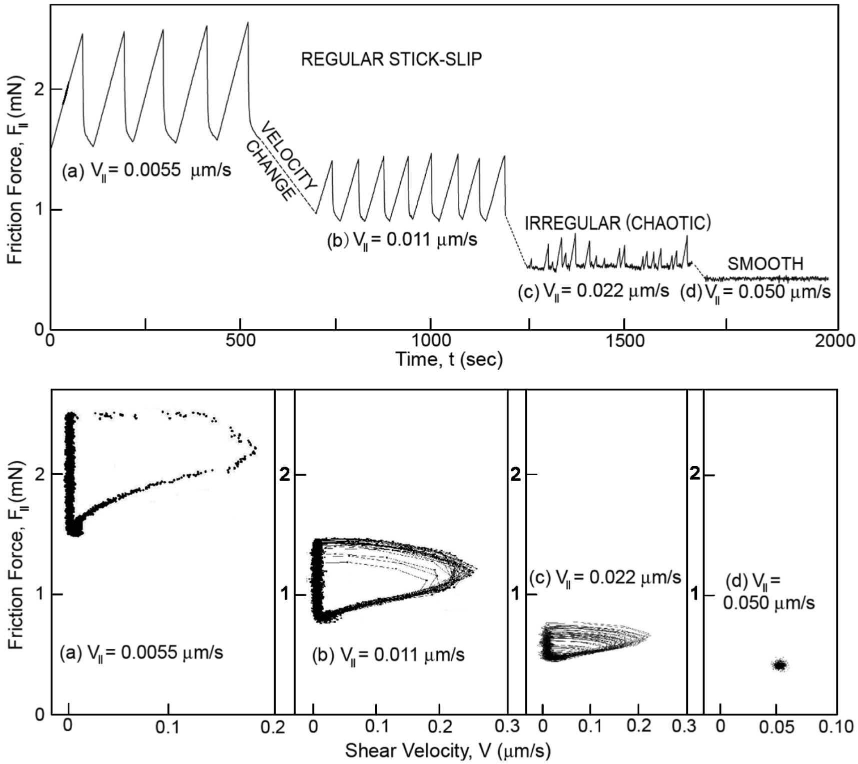


FIGURE 4 Limit cycles of shear (friction) forces, $F_{\parallel}$, *versus* time, t, and relative surface velocity, V, for ultra-thin squalane films between two mica surfaces at different driving velocities, $V_{\parallel}$, of the spring supporting the moving surface. For shear motion the relative surface velocity V and driving velocity $V_{\parallel}$ are analogous to the normal velocities $\dot{D}$ and $V_{\perp}$ in an adhesion cycle (Figure 3). Experimental conditions are load $L = 1.5\,\text{mN}$, lateral force-measuring spring stiffness $K = 1900\,\text{N/m}$ at 26°C. Note that the area of each cycle gives the rate of doing work (the power consumed) during each cycle [14].

location after each stick-slip event, but in the same thermodynamic or dynamic state. Likewise for the adhesion cycles shown in Figure 3, where the surfaces end in a different place after detachment, but with near zero velocity $\dot{D}$ as at the "start." After detachment only an infinitesimal force and velocity need be applied to bring the surfaces back into adhesive contact and restart the process from the same state to repeat or complete the cycle (as defined in Figure 1, left).

We may note other similarities and some differences in the limit cycles of adhesive and frictional processes:

(1) In both cases, the maximum (adhesion or friction) force occurs when the relative surface velocity equals the driving velocity. The surface velocity continues to increase after that point, but the force decreases. This occurs only when the inertial terms are negligible (*e.g.*, the $m\ddot{D}$ term in Equation [4]), as was the case in the two types of experiments analyzed in Figures 3 and 4.

(2) In both cases the forces are not uniquely determined by the velocity, for example, a simple "velocity-dependent friction" function $F_{\parallel}(V)$, where $F_{\parallel}$ increases then decreases with V. An additional variable has to be included to describe these systems, as described above and in Refs. [7] and [14].

(3) For viscous and viscoelastic fluids, such as polymers at temperatures, T, close to or greater than T_g, both bulk flow (which affects the bulk elastic modulus K appearing in the JKR equation) and surface interdigitation effects (which affect γ) modify the adhesion and friction forces, and their limit cycles, in a fundamentally similar way. Basically, both processes involve both bulk shear flow and surface motion—the differences being in the directions of these motions and, therefore, the different contributions they make to the measured adhesion and friction forces, and limit cycles. For the system analyzed here, where T was close to T_g, it is difficult and perhaps not possible to separate the two contributions. For systems in the glassy state ($T \ll T_g$), the effective surface energy, γ, as measured from the pull-off force, F_{ad}, using Equation (6), will dominate both processes, with important contributions coming from surface group interdigitation [1,5,21]. Surface heterogeneities such as roughness and lattice defects can also cause discontinuities (erratic motion, stick-slip jumps or steps) both in the adhesion [21–27] and friction [22]. In the other limit of $T \gg T_g$ and/or at very low pulling or sliding speeds, the situation is quite different: the adhesion force is now determined mainly by γ and the friction or lubrication forces by the bulk or thin film viscosity of the fluid.

Limit cycles provide information on the rate of energy dissipation (the power consumed) during hysteretic adhesion and energy-dissipating friction processes. They may, therefore, be a useful way to characterize or quantify such irreversible processes, in the way that the efficiency of a Carnot Cycle characterizes the total work done during a reversible cycle. "Dynamic" phase diagrams have recently been proposed for dissipative systems, for example, flowing colloidal or granular systems [28,29]. Plotting the forces *versus* the distances traveled or sheared (D rather than $\dot{D}$) may be another way to express the work done during such cycles.

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