Creeping Friction Dynamics and Molecular Dissipation Mechanisms in Glassy Polymers

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The dissipation mechanism of nanoscale kinetic friction between an atomic force microscopy tip and a surface of amorphous glassy polystyrene has been studied as a function of two parameters: the scanning velocity and the temperature. Superposition of the friction results using the method of reduced variables revealed the dissipative behavior as an activated relaxation process with a potential barrier height of 7.0 kcal/mol, corresponding to the hindered rotation of phenyl groups around the C-C bond with the backbone. The velocity relationship with friction $F(v)$ was found to satisfy simple fluctuation surface potential models with $F \propto \text{const} - \ln(v)$ and $F \propto \text{const} - \ln(v)^{2/3}$.

In the latest ambient scanning force microscopy (SFM) experiments and computer models, such as molecular dynamic and Monte Carlo simulations, molecular-scale friction was discussed in terms of mechanical relaxations and internal conformational changes [1–4]. These studies involved highly structured model systems, which were prepared by either self-assembly or Langmuir-Blodgett techniques [5]. Such monolayered or multilayered systems provide convenient access for investigations of molecular-scale dissipation mechanisms; e.g., load-induced molecular tilts [1] and reversible and irreversible conformation changes [1–3]. Simple frictional models, such as the Tomlinson-Prandtl model [6], could be tested, and the corrugated molecular surface potential compared to the magnitude of discontinuous molecular stick-slip sliding [2,4]. The jump distances were found to be stochastic above a critical sliding velocity, which led to a discussion of molecular friction in terms of fluctuations around discrete attractors [4]. This corresponds to recent theoretical treatments, i.e., *creep models,* that consider *barrier-hopping fluctuations* of periodic surface potentials with slips occurring at lower energy values than prescribed by the potential barriers [7–9]. With this Letter, we investigate the possibility that *hindered,* or *frozen,* relaxation states of an amorphous polymer, atactic polystyrene, could be activated in the course of a frictional sliding process and thus give rise to a barrier-hopping fluctuation not unlike the one observed for highly ordered surfaces.

Atactic polystyrene (PS) (Polymer Source, Inc., $M_W = 96.5$ K, $M_W/M_N = 1.04$) was selected as a model polymer for its high monodispersity and phase homogeneity. The PS film was spin cast from a toluene solution onto a silicon wafer $\langle 1, 1, 1 \rangle$ and thermally annealed at 150 °C for 2 h under vacuum. The PS film thickness was ~220 nm, and the near surface glass transition temperature T_g was 373 K, measured with shear-modulated SFM [10]. SFM friction measurements were conducted with a commercial SFM instrument (Explorer, Vecco) using a bar-shaped silicon cantilever (Nanosensors, $k_N =$

0.139 N/m, $k_T \sim 80$ N/m) and under nitrogen with the relative humidity below ~7%. The instrument and cantilever were calibrated on a silicon wafer $\langle 1, 1, 1 \rangle$ according to the procedure by Buenviaje *et al.* [11]. Measurements were performed over a 2.0 μm scan range with a 20 nm line spacing to avoid memory effects from previous scans.

Isothermal friction-velocity curves are presented in Fig. 1 for temperatures between 300 and 365 K. Quasilogarithmic friction-velocity relationships are found, which is in accordance with recently developed theoretical models [7–9,12], and resemble SFM experiments on ionic crystals in ultrahigh vacuum [13] and in lubricated sliding [14].

Based on the *linear creep model* by Heslot, the friction between two contacting surfaces with constant potential bias depends logarithmically on the sliding velocity, i.e.,
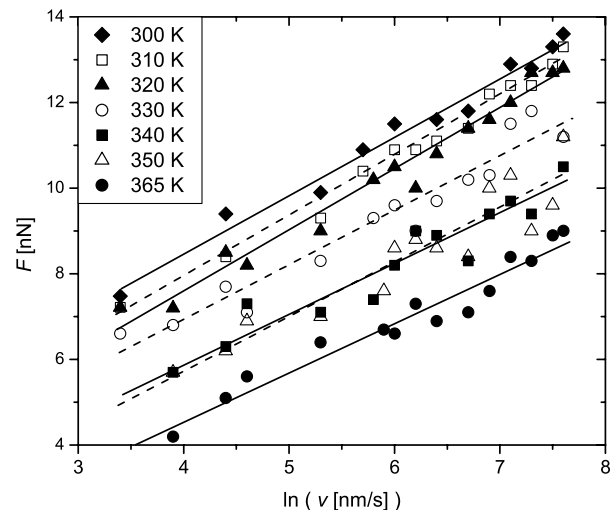

FIG. 1. Friction force−scan velocity relationship on glassy polystyrene at various temperatures [K] indicated in the legend and under a normal force of 15 ± 2 nN. The scan velocity was varied between 30 and 2000 nm/s at each temperature, over a range of 300 to 365 K.

$F \propto \text{const} + \ln(v)$, where v represents the slider support velocity [9]. An extension to this model, the *ramped creep model,* independently proposed by Dudko *et al.* and Sang *et al.* [7,8], considers that the SFM tip support is also moving, resulting in a potential bias that is continuously ramped up. Thus, the barrier height becomes proportional to a 3/2-power law in the friction force [7,8]. This modification to the linear creep model leads to a logarithmically power-law distorted friction-velocity relationship of $F = F_c - \Delta F |\ln v^*|^{2/3}$. From Sang, $v^* \propto v/T$ represents a dimensionless velocity, and $\Delta F \propto T^{2/3}$. F_c is an experimentally determined constant that contains the critical position of the cantilever support. F_c is determined from the intercept of F versus $T^{2/3}$ and from F versus T for ramped and linear creep, respectively, both at a fixed ratio $T/v = 1$ K/(nm/s) [8]. The combination of these relationships suggests the collapse of $F(v)|_T$ curves obtained at different temperatures.

This scaling model was shown to be in accordance with the solution of the Langevin equation

$$M\ddot{x} + M\beta\dot{x} + \frac{\partial E(x,t)}{\partial x} = \xi(t), \quad (1)$$

where x is the position of the tip on the surface, M is the mass of the SFM tip, and β is a linear dampening factor (*microscopic friction coefficient*). Equation (1) assumes a sinusoidal surface potential and perfect cantilever oscillator in the total potential energy E, with thermal noise in the form of the random force $\xi(t)$, where $\langle\xi(t)\xi(t')\rangle = 2M\beta k_b T\delta(t - t')$ [7,8]. We successfully tested the scaling models with our amorphous glassy PS friction measurements in Fig. 1. The results are presented in Figs. 2 and 3.

The ramped creep model, Fig. 2, provides a marginally better fit compared to the linear creep model, Fig. 3. The fit quality of the ramped creep model relative to the linear creep model is expected to increase for a system that is less overdamped, i.e., a stiffer spring with respect to β [15], and with measurements over larger velocity and temperature ranges.

At this point, it would be desirable to identify the potential barrier responsible for frictional losses of a nanoscopic SFM tip sliding over the amorphous PS surface. Recognizing the *quasiparallelism* of the $F(v)|_T$ curves in Fig. 1, we employed the method of reduced variables to superpose the data into a master curve [16]. This *linear* approach serves to decouple the thermal and rate contributions to the friction force, similar to the well known Williams-Landel-Ferry equation applied to viscoelastic behaviors of polymers above the glass transition [16]. The superposed data, from a single horizontal shift defining the a_T shift factor, are shown in Figs. 4(a) and 4(b). The thermal dependence of the a_T shift factor in Fig. 4(b) identifies the frictional process as an activation process. From the Arrhenius behavior of a_T, the representative barrier height U_o is 7.0 kcal/mol. This value corresponds to the activation energy of the phenyl rotation around the C-C bond to the backbone chain in atactic PS, 7.0 kcal/mol [17]. Thus, the primary dissipation mechanism for *dry* sliding of a nanoscopic tip on glassy PS is through rotation of the phenyl groups.

Considering that the creep models (a) fit the friction data reasonably well and (b) are in accordance with a fluctuation model based on a Gaussian fluctuation distribution, we may conclude that there is little or no
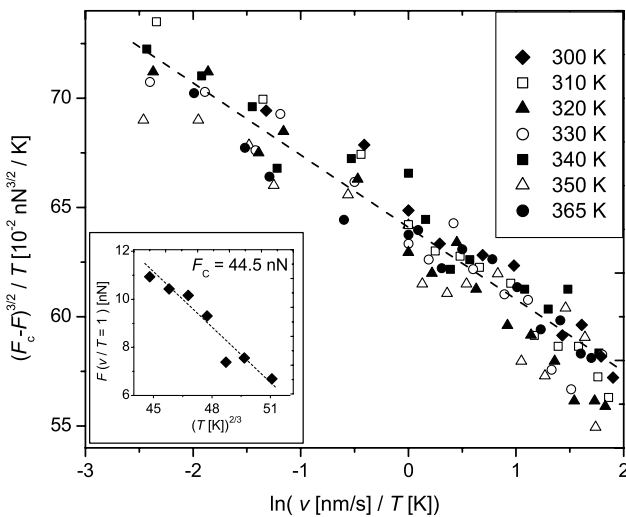
FIG. 2. Collapse of the friction data from Fig. 1 using a ramped creep scaling model [8]. The regression parameters from the linear fit (dashed line) are $-2.158 \times 10^{-2} N^{3/2}$ s/m and 40.186×10^{-2} nN$^{-3/2}$/K ($R^2 = 0.9124$). Inset: the constant F_c is determined from the intercept of F versus $T^{2/3}$ for a fixed ratio $T/v = 1$ K/(nm/s) [8]: $F_c = 44.5$ nN.
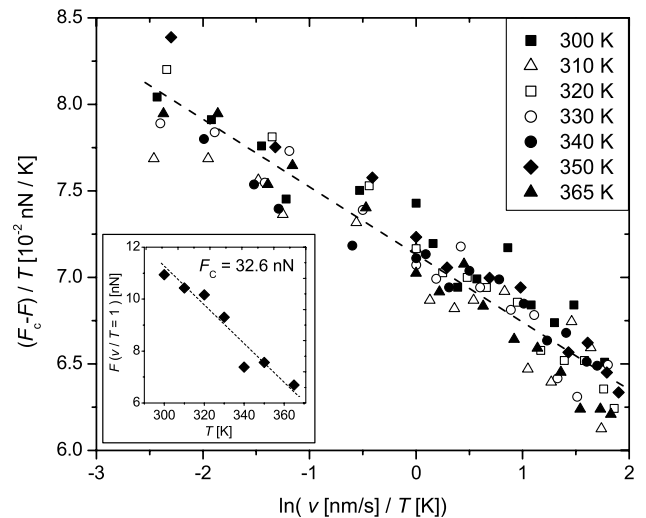
FIG. 3. Collapse of the friction data from Fig. 1 using a linear creep scaling model [9]. The regression parameters from the linear fit (dashed line) are $-0.385 \times 10^{-2} N$ s/m and 7.125×10^{-2} nN/K ($R^2 = 0.909$). Inset: the constant F_c is determined from the intercept of F versus T for a fixed ratio $T/v = 1$ K/(nm/s) [8]: $F_c = 32.6$ nN.
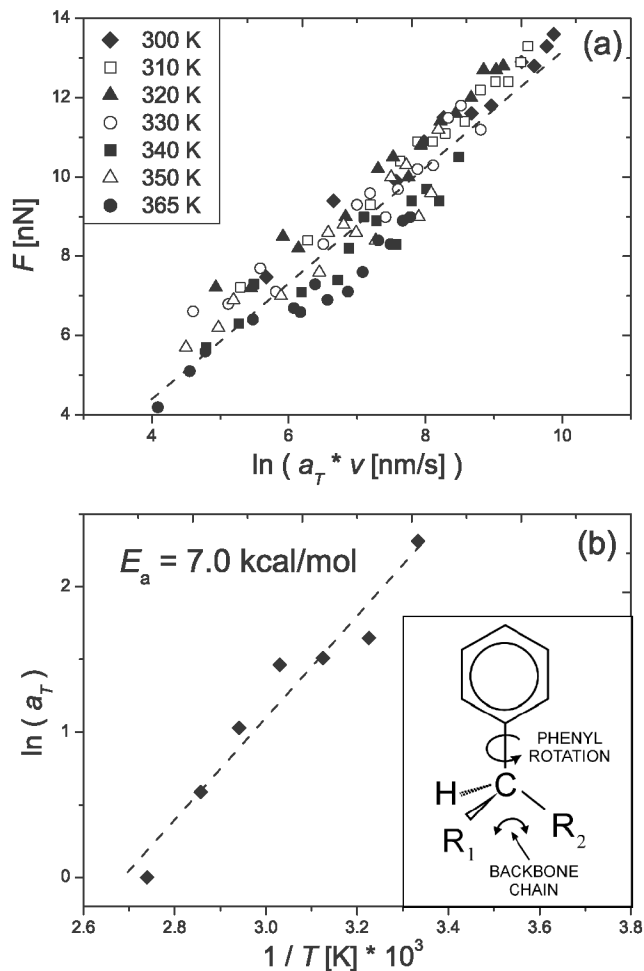
FIG. 4. (a) Superposed friction master curve from data of Fig. 1. (b) Thermal a_T shift factor. An activation energy E_a of 7.0 kcal/mol is deduced from the slope of the regression line, corresponding to the activation of phenyl rotation in atactic PS (inset).

correlation between the individual phenyl rotations that are *relaxed* during the sliding motion. It is because of this weak correlation that similar frictional dissipative behaviors are observed on both highly structured (crystalline) surfaces and the unstructured (amorphous) PS surface.

The rotation of phenyl groups in atactic PS has been attributed to the γ relaxation [18]. Considering that other relaxations are possible (e.g., δ, β, and α with respective activation energies of $2-3$, 35, and 90 kcal/mol) [19], one would expect that depending on the load and contact area, i.e., the degree of size and pressure confinement, friction could also originate from other relaxations. For example, Hammerschmidt et al. have identified the β relaxation as the primary dissipation mechanism in SFM friction measurements on poly(methyl methacrylate) [20]. As long as the individual relaxation processes are uncorrelated, it is reasonable to assume that the current creep models will apply to describe friction on a broad range of polymer

molecules. Any deviations from the model could be attributed to memory effects within the system.

These results and the associated discussion of molecular friction mechanisms on a glassy polymer system illustrate the effectiveness of rudimentary nonequilibrium models that incorporate simple potentials with thermal fluctuations. The combination of polymer relaxation data, available from transition studies, with either of the two creep models should provide a vast array of possible outcomes for friction values involving single asperity contacts. Deviations from the models are expected, particularly for correlated fluctuations, i.e., memory effects in relaxation processes. Addressing the issue of the so-called non-Markovian behavior of sliding systems demands a more rigorous theoretical treatment, such as the generalized Fokker-Planck equation with a system specific statistical kernel [21–24]. It is interesting to note, for Gaussian systems, Dudko et al. showed that a force reconstruction approach from the density of states, accumulated from the corresponding Fokker-Planck equation, is equivalent with the solution of the Langevin equation, Eq. (1) [7]. The applicability of this work reaches beyond the scope of traditional tribology. It promises groundbreaking nanorheological analysis of molecular systems, in which there is a competition between the rate of thermally assisted escape from the trapped state and the pulling rate, as found, for instance, in the study of bond rupturing and unfolding of complex biological molecules [25].

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