

## Control of friction by shear induced phase transitions

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Controlling frictional behavior can be made possible when relationships are established between the macroscopic frictional response and the microscopic properties of sheared molecular systems. Here an approach is suggested for modifying the frictional response through shear induced phase transitions in a mixed lubricant monolayer of a base solvent and an additive. The solvent-additive intermolecular interaction and relative concentration are shown to be the major parameters in determining the friction force magnitude and the nature of the response (stick-slip or sliding).

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Interfacial friction is one of the oldest problems in physics and chemistry and certainly an important one from a practical point of view. With the recent introduction of new experimental tools that allow for detailed investigations of friction at nanometer scales, there has been a major increase in activity in the study of nanotribology: namely, interfacial friction on the microscopic level.<sup>1–9</sup> Nanotribology offers a meeting ground for practical aspects with new and fascinating physical phenomena such as dynamic phase transitions, giant enhancement of an effective viscosity in nanoscale confinements, shear induced chaos, memory effects, and more.<sup>10–15</sup>

Controlling frictional forces has been traditionally approached by chemical means, usually supplementing base lubricants by friction modifier additives.<sup>16,17</sup> Each additive in such molecular mixtures serves a different role: some decrease static friction and eliminate undesirable stick-slip motion, some influence the temperature dependence of viscosity, and others inhibit corrosion.<sup>16,17</sup> While the behavior of single-component lubricants in nanoscale confinements has been extensively studied both experimentally and theoretically,<sup>1–3,6–8,10,11,15</sup> investigations of the behavior of molecular mixtures under similar conditions are in their early stages.<sup>18,19</sup>

In this paper we suggest an approach which might help decide how to tailor molecular mixtures so that they provide desirable frictional properties. Modifying friction is achieved here through shear induced phase transitions in the mixed embedded system. Understanding the molecular picture could help create desirable phases of motion and thereby modify frictional forces.

In order to mimic surface forces apparatus experiments on sheared confined liquids<sup>1–4</sup> we introduce a model which consists of two noninteracting rigid plates, with a monolayer of  $N$  particles each of mass  $m$  at coordinates  $\mathbf{r}_i = \{x_i, y_i\}$  embedded between them. One of the plates of mass  $M$  and center-of-mass coordinate  $\mathbf{R} = \{X, Y\}$  is pulled with a linear spring of spring constant  $K$ . The spring is connected to a stage which moves with velocity  $\mathbf{V}$ . This system is described by  $2N + 2$  equations of motion:

$$\frac{M \partial^2 \mathbf{R}}{\partial t^2} + \sum_i^N \frac{\eta \partial(\mathbf{R} - \mathbf{r}_i)}{\partial t} + \sum_{i=1}^L \frac{\partial U^A(\mathbf{r}_i - \mathbf{R})}{\partial \mathbf{R}} + \sum_{i=L}^N \frac{\partial U^B(\mathbf{r}_i - \mathbf{R})}{\partial \mathbf{R}} + K(\mathbf{R} - \mathbf{V}t) = 0, \quad (1)$$

$$\frac{m \partial^2 \mathbf{r}_i}{\partial t^2} + \frac{\eta \partial(2\mathbf{r}_i - \mathbf{R})}{\partial t} + \frac{\partial[U^{A,B}(\mathbf{r}_i - \mathbf{R}) + U^{A,B}(\mathbf{r}_i)]}{\partial \mathbf{r}_i} + \sum_{i \neq j}^N \frac{\partial \Phi(\mathbf{r}_i - \mathbf{r}_j)}{\partial \mathbf{r}_i} = f_i(t),$$

$$i = 1, \dots, N. \quad (2)$$

Here we consider a mixed monolayer consisting of two types of molecules  $A$  and  $B$ : a “base solvent”  $A$  and an “additive”  $B$ . Molecules  $A$  are numbered from 1 to  $L$  and molecules  $B$  from  $L$  to  $N$ . Molecules  $A$  and  $B$  are chosen in such a way that they tend to occupy different sites on the surfaces of the plates—for instance, on top of a substrate atom and at the center of the substrate lattices. Correspondingly, the interactions between the molecules  $A$  and  $B$  and each of the plates are given by different periodic potentials: namely,  $U^A(\mathbf{r}) = U^A\{\cos(2\pi x/a) + \cos(2\pi y/a)\}$  and  $U^B(\mathbf{r}) = -U^B\{\cos(2\pi x/a) + \cos(2\pi y/a)\}$ , where  $a$  is the periodicity of the substrate lattices. For simplicity, we chose the same periodicity of  $U^A$  and  $U^B$ . The intermolecule interaction is described by a potential  $\Phi$  which includes a short-range repulsion  $C \exp[-(\mathbf{r}_i - \mathbf{r}_j)^2/c^2]$  and a regularized Coulomb interaction  $q_A q_B / [b^2 + (\mathbf{r}_i - \mathbf{r}_j)^2]^{1/2}$ , where for the effective charges we assume  $q_B = -q_A = q$ , and  $b$  is a cutoff parameter. The chosen Coulomb interaction provides an attraction between different type molecules and repulsion between identical molecules. The parameter  $\eta$  accounts for the dissipation of the kinetic energy of each particle due to interactions with excitations in the plates. Again, for simplicity we assume that all molecules have an identical mass  $m$  and dissipation constant  $\eta$  and that  $U^A = U^B = U_0$ . The effect of the thermal motion of the embedded molecules is given by a random force  $f_i(t)$ , which is  $\delta$  correlated,  $\langle f_i(t) f_j(0) \rangle$

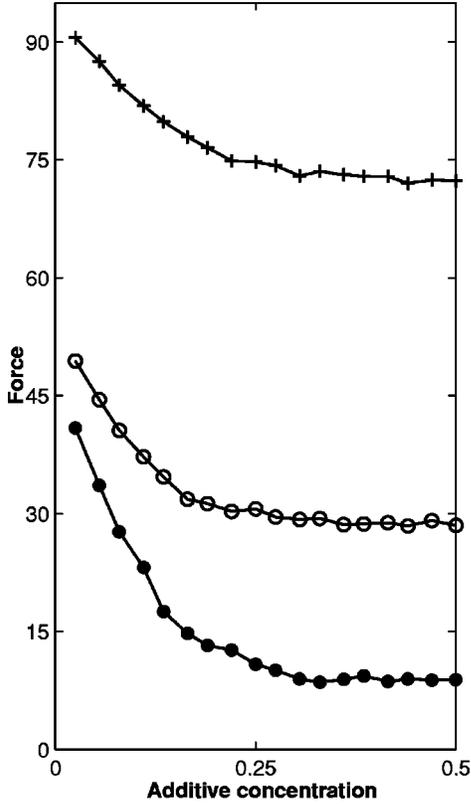


FIG. 1. Dependence of the average spring force on the concentration of additives for driving velocities  $V/\omega a = 0.04, 0.3, 0.7$ , corresponding to stick-slip (bold symbols), intermittent type (circles), and sliding (plus signs) motions. The force, time, and distances are presented in units of  $2\pi U_0/a$ ,  $\omega^{-1} = (a/2\pi)(M/U_0N)^{1/2}$ , and  $a$ . Parameter values:  $N = 200$ ,  $M/m = 0.7N$ ,  $\eta = M\omega/N$ ,  $q = 0.9(U_0a)^{1/2}$ ,  $K = 80U_0/a^2$ ,  $c = a$ ,  $C = 2U_0$ ,  $k_B T = 10^{-3}U_0$ , and  $b/a = 0.1$ .

$= 2mk_B\eta T\delta(t)\delta_{ij}$ . Here  $T$  is the temperature and  $k_B$  is the Boltzmann constant. It should be noted that the particular form of interactions chosen here serves only as an example to demonstrate the suggested mechanism for modifying friction. However, our conclusions are mostly independent of the particular form of potentials. For instance, similar results have been obtained for the van der Waals attraction between molecules.

Before analyzing the model and describing the mechanism of how to modify friction, we present in Fig. 1 an example of dependence of the time-averaged spring force on the concentration of the additive molecules  $B$ :  $\xi = (N - L)/N$ . The total number of embedded molecules is kept constant. The calculations have been done for three values of driving velocities, which correspond to periodic and chaotic stick-slip behaviors typical of low driving velocities,<sup>1-3,6,8,11-15</sup> and to steady sliding typical of higher velocities. Figure 1 demonstrates a decrease in friction with an increase in the concentration of the additive. More than a fourfold lowering of friction has been observed when the concentration of the additive changed from 0 to 0.5. We observe a decrease in friction for all regimes of motion, but with the strongest effect at low driving velocities, where the

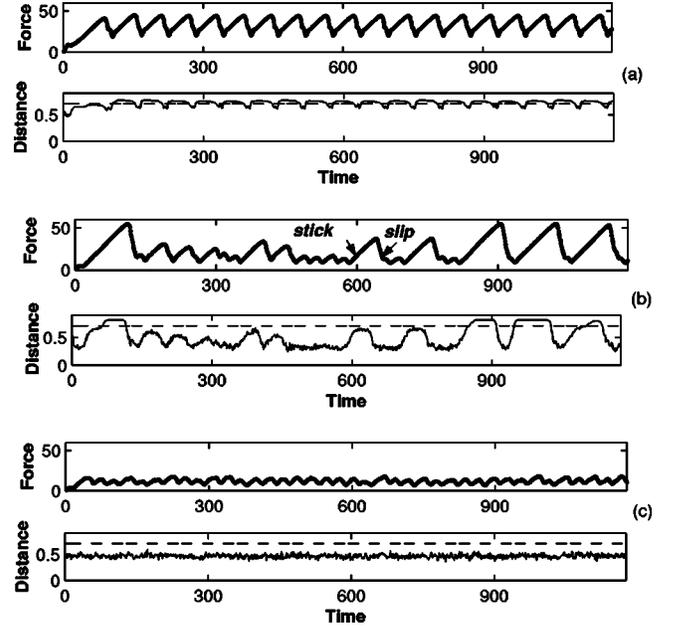


FIG. 2. Time dependence of the spring force for (a) weak  $q/(U_0a)^{1/2} = 0.5$ , (b) intermediate  $q/(U_0a)^{1/2} = 0.9$ , and (c) strong  $q/(U_0a)^{1/2} = 1.4$  attractions between  $A$  and  $B$  molecules. Bottom panels show the corresponding time dependences of the ensemble-averaged distances between neighboring  $A$  and  $B$  molecules. Parameter values:  $V = 0.07\omega a$ ,  $\eta = 2.6M\omega/N$ , and  $N = 50$ ; other parameters are the same as in Fig. 1.

stick-slip motion occurs. Under our assumptions the spring force versus the concentration of the additive molecules is symmetric with respect to  $\xi = 0.5$  with a minimum at equal concentrations of molecules  $A$  and  $B$ .

In order to clarify the mechanism of modifying friction by adding an additive we have performed a detailed study of the geometrical structure of the mixed embedded molecular layer under shear and have established the relationship between geometry and frictional response. Here we present results obtained for the case  $\xi = 0.5$ , which corresponds to an equal number of  $A$  and  $B$  molecules. Figure 2 shows the time series of the spring force and of the ensemble-averaged distance between molecules  $A$  and  $B$ , both calculated for weak, intermediate, and strong attractions between the solvent and additive molecules. In our model the strength of the attraction is determined by the “effective charge” of the molecules,  $q$ . All curves in Fig. 2 have been obtained for the same driving velocity corresponding to stick-slip motion for the base solvent  $A$ . In addition, Fig. 3 presents the snapshots of the embedded system observed during stick (a) and sliding (b) states of motion for the intermediate strength of attraction. The instants corresponding to the snapshots are marked on the time series of the force by arrows: see Fig. 2(b). The snapshots are complemented by the two-dimensional (2D) Fourier transforms of the instantaneous correlation function for the sheared monolayer, which are also shown in the insets to Fig. 3.

Our results clearly demonstrate that for weak and intermediate strengths of the  $A$ - $B$  attraction the monolayer in the stick state has a *tetragonal* symmetry, for which the distances

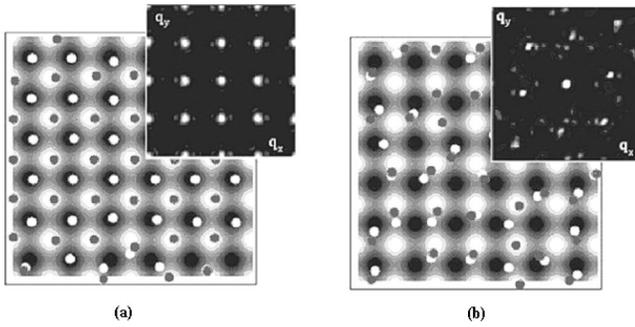


FIG. 3. Snapshots of the sheared monolayer showing tetragonal lattice (a) for the locked states and hexagonal one (b) for the sliding states. Insets present corresponding correlation functions. Parameter values:  $V=0.3\omega a$  and  $\omega=2\pi(U_0 N/M)^{1/2}/a$ ; other parameters are the same as in Fig. 1.

between neighboring  $A$ - $A$  and  $A$ - $B$  molecules equal  $a$  and  $a/\sqrt{2}$ , respectively. For the weak attraction the monolayer retains tetragonal symmetry also in the sliding state where the monolayer molecules move mostly while remaining in the corresponding minima of the molecular-plate potentials. This is reflected by the time series of the averaged distance between  $A$ - $B$  neighbors, which only slightly fluctuates around the value of  $a/\sqrt{2}$  [Fig. 2(a)]. The same is true for a one-component monolayer.

In contrast, for the intermediate  $A$ - $B$  attraction a new *hexagonal* symmetry arises during sliding. Here the different kind molecules group into  $A$ - $B$  pairs and form a lattice with well-defined hexagonal symmetry, ignoring essentially the symmetry of underlying potential (see Fig. 3). The effect of pair formation is seen in Fig. 2(b), which shows a significant decrease of the  $A$ - $B$  distances during sliding compared to the value  $a/\sqrt{2}$ , which is typical of the tetragonal lattice. Sliding and stick states can be easily distinguished according to the time series of the spring force, presented in Fig. 2. Our calculations also demonstrate that being in the sliding state the molecules are, on average, equally distant from the minima of the plate potentials,  $U^A(\mathbf{R})$  and  $U^B(\mathbf{R})$ , and move within the channels between them. Thus, due to the attraction between the base and additive, the molecules “pull” each other out of the minima of the corresponding potentials  $U^A$  and  $U^B$ , thereby effectively decreasing the potential barriers to sliding. This leads to a significant reduction of friction force in the sliding state and to an increase of time intervals that the system spends in motion. This complements the idea introduced in Ref. 7 for one type of molecule.

As we already noted above, for intermediate strengths of attraction the embedded monolayer has mostly tetragonal symmetry in the stick state. However,  $A$ - $B$  attraction causes the formation of defects: pairs, pair chains, and domains of a foreign phase within the tetragonal lattice. The presence of defects leads to a decrease of the external force needed to initiate motion (static friction force) as compared with the cases of weak attraction and of a monolayer containing only one kind of molecule. This way the  $A$ - $B$  attraction reduces the time-averaged static friction and transforms the almost periodic stick-slip motion into an erratic one [compare Figs. 2(a) and 2(b)]. However, Fig. 2(b) shows that from time to

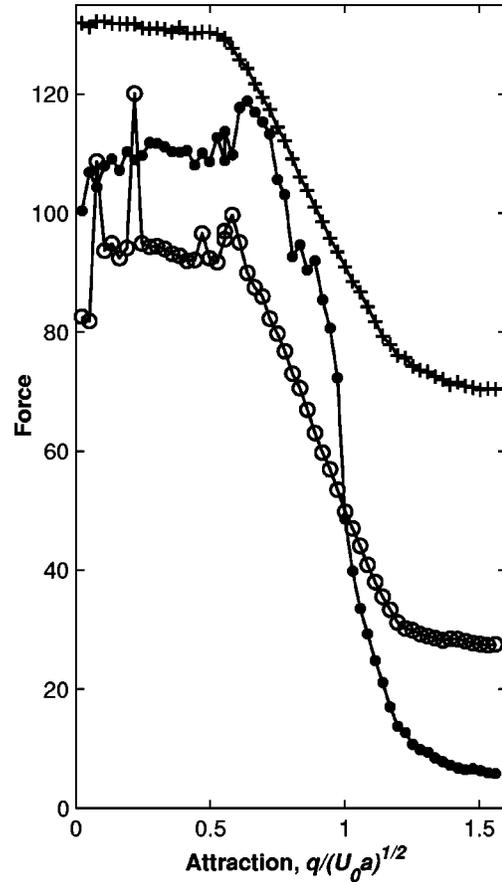


FIG. 4. Time-averaged spring force as a function of attraction for driving velocities  $V/\omega a=0.04, 0.3, 0.7$ , corresponding to stick-slip (bold symbols), intermittent type (circles), and sliding (plus signs) motions. Parameter values as in Fig. 1.

time an almost ideal tetragonal structure with  $A$ - $B$  neighboring distances close to  $a/\sqrt{2}$  builds up, accompanied by an enhancement of the instant depinning force. This occurs as a result of the effective stirring of the system during long intervals of sliding motion. Such a motion induces annealing which removes defects that always arise during preparation of the system.

For strong  $A$ - $B$  attraction we find that the embedded molecules at all times form a nonideal hexagonal lattice, which includes pair chains and dislocations. Figure 2(c) shows that at all times the molecules coalesce into  $A$ - $B$  pairs drastically reducing frictional force. In this case the system executes sliding motion even in the range of low driving velocities, where a stick-slip motion has been observed for weak and intermediate strengths of attraction.

Shear-induced transitions between tetra and hexa phases observed here resemble the Kosterlitz-Thouless transitions in 2D systems with Coulomb interactions, where pairing and unpairing of oppositely charged particles occur under change of the balance between interaction and temperature.<sup>20</sup> In our case the pairing and unpairing process is mainly controlled by the balance between the periodic potentials and interaction strength. Here an external force pushes the particles out of the potential minima and so the plate velocity rather than

temperature plays the role of the characteristic parameter which triggers the transition. The driven system resides alternately in both phases, and their contributions to the average are dictated by the duration of the stay in each phase. Coexistence of the tetra and hexa phases has been also observed here at every instant in the form of domains of one phase inside another.

In order to characterize quantitatively the effect of  $A$ - $B$  attraction on the frictional force, we present in Fig. 4 the time-averaged frictional forces in three typical regimes of motion: stick-slip, intermittent motion, and sliding as a function of the attraction parameter. A significant reduction in friction with an increase in attraction has been found for all the regimes. However, the strongest effect (a 12-fold reduction of the force for the chosen parameters) has been observed for the smallest driving velocity, which corresponds to a periodic stick-slip motion in a one-component system.

This observation can be understood taking into account that there are two contributions to the frictional force: the potential one given by the  $U^A$  and  $U^B$  terms in Eq. (1) and the viscous one given by the  $\sum_i^N \eta \partial(\mathbf{R} - \mathbf{r}_i)/\partial t$  term. The potential terms  $U^A$  and  $U^B$  dominate in the stick-slip regime. For the tetragonal structure their contribution to the averaged force can be estimated as  $\pi U_0 N/b$ . The attraction between  $A$  and  $B$  molecules reduces the effective potential barriers, which leads to a significant decrease in friction, which can be viewed as a decrease in the stiffness of the molecular system

relative to the mechanical stiffness  $K$  in Eq. (1). The viscous contribution is constrained in the range between  $\eta VN$  and  $\eta VN/2$ .<sup>6</sup> Thus, at low driving velocities, the reduction of friction can be as large as  $(\pi U_0/b + \eta V)/(\eta V/2)$ .

The viscous term dominates in the sliding regime. The  $A$ - $B$  attraction also influences the viscous contribution by suppressing the velocity fluctuations of the embedded molecules due to an effective decrease of the potential corrugation. However, due to the above-mentioned constraints on the value of the viscous term, this effect is less pronounced than the effect of the attraction on the potential contribution. As a result, for high driving velocities the reduction does not exceed the factor of 2.

In summary, mixing the embedded layer with additives does not only reduce friction, but it also makes it possible to control the regimes of motion. Namely, tuning the concentration of additives and/or the attraction between the additive and the base solvent allows to eliminate stick-slip motion and to achieve sliding at low driving velocities [see Figs. 2(a) and 2(c)]. Such a control can be of high technological importance for micromechanical devices, where the early stages of motion and the stopping processes, which exhibit stick and slip, pose a real problem.

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