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Theory of depinning of monolayer films adsorbed on a quartz crystal microbalance

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In quartz crystal microbalance studies of the friction between an adsorbed monolayer film and a metallic substrate, the films are observed to slide relative to the substrate under inertial forces of order 10^{-14} dyn per film atom, a force much smaller than all existing theoretical estimates of the force that surface defects are capable of exerting on the film. We argue that defect potentials with a range comparable to an atomic spacing or more will produce a pinning force below the inertial force.

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Quartz crystal microbalance (QCM) studies of monolayers of molecules on metallic substrates [1] provide detailed information about friction at the atomic level. The QCM consists of a quartz oscillator of frequency $\sim 10^6$ Hz. Monolayer films adsorbed on the metallic surface of the quartz crystal oscillator are found to slip with respect to the surface during a period of the oscillator. Small changes observed in the frequency and in the associated Q factor allow us to gauge the friction between monolayer and substrate. The amount of dissipation generated under most conditions implies that sliding motion of more than a lattice constant occurs during a period of the QCM.

For film atom mass $m \approx 10^{-22}$ g, appropriate for xenon atoms, QCM frequency $\omega \approx 10^7$ rad/s and amplitude $A \approx 100 A^o$, which are appropriate parameters for a QCM experiment, the inertial force $m\omega^2 A$ is only about 10^{-14} dyn per film atom. Calculations of pinning of a monolayer film by defects, based on both perturbation theory [2] and molecular dynamic simulations [3], which gives a pinning force due to defects of at least 10^{-11} dyn per film atom, which already includes collective pinning effects [4], imply that this inertial force per atom due to oscillations of the substrate should not be sufficiently strong to depin the film.

Since the interaction of the film with a single defect is a periodic function of displacement of the film relative to the defect, it can be expanded in a Fourier series. Since for any smooth potential the Fourier coefficients fall off quite rapidly with increasing wave vector, it is argued that, even when the ratio of the film lattice spacing to the range of the potential is of order 1, the product of the magnitude of the smallest reciprocal lattice vector with the range of the potential, the argument of the Fourier transform, is sufficiently large to make the Fourier coefficient quite small. As a consequence, the net force on the film due to a single defect is found to be considerably smaller than the force that a defect would exert on a single atom if it were not part of the film by a sufficient amount to allow the inertial force to exceed the net pinning force due to the defects. In most treatments of an elastic medium interacting with a disordered potential [4], including Ref. [3], the range of the defect potential is assumed to be smaller than a film lattice spacing, so that it can interact with only one film atom at a time. Step and facet edges and grain boundaries clearly extend a number of lattice spacings along the length of the defect, and a vacancy extends more than a lattice constant because neighboring atoms displace toward the missing atom. The Larkin length [4], found from Ref. [3], which represents the length over which the film is able to distort, is long compared to a defect width.

Consider the potential energy of a rigid film of atoms interacting with a single defect potential $\Sigma_{\mathbf{R}} v(\mathbf{R}+\Delta\mathbf{r})$, where $v(\mathbf{R}+\Delta\mathbf{r})$ is the potential energy due to the defect of an atom located at the point $\mathbf{R}+\Delta\mathbf{r}$ in the film, $\Delta\mathbf{r}$ represents a displacement of the film relative to the potential, and $\mathbf{R}$ is an atomic position in the periodic lattice of the film. Since this quantity is a periodic function of $\Delta\mathbf{r}$ with the periodicity of the film lattice, it can be expressed as a Fourier series [6] in the coordinates in the plane parallel to the interface,

$$\sum_{\mathbf{R}} v(\mathbf{R}+\Delta\mathbf{r}) = \sum_{\mathbf{G}} \bar{v}(\mathbf{G}) e^{i\mathbf{G}\cdot\Delta\mathbf{r}} \qquad (1)$$

where the Fourier coefficient $\bar{v}(\mathbf{G}) = \Omega^{-1}\int d^2r\, e^{-i\mathbf{G}\cdot\mathbf{r}} v(\mathbf{r})$, where Ω is the unit cell area and $\mathbf{G}$ is a reciprocal lattice vector of the film. The integral is taken over the film unit cell. The z coordinate of the atom (z is the direction normal to the film) is assumed to always take on its equilibrium value as the atom moves along the film (i.e., in the x-y plane). This assumption is certainly valid for the slow-speed sliding motion of the film over the surface. For line defects, such as step and facet edges and grain boundaries, v($\mathbf{r}$) will vary quite slowly as a function of $\mathbf{r}$ along the length of the line defect (i.e., the distance over which the defect is relatively straight). As a consequence, we shall see that the Fourier coefficients $\bar{v}(\mathbf{G})$ are likely to be quite small for general directions of $\mathbf{G}$, such that $\mathbf{G}$ has a component along the length of the defect sufficiently large compared with 2π divided by the length of the defect, a condition that is easy to satisfy for any line defect long compared to a film lattice constant. The Fourier coefficients will also be very small for defects such as vacancies which are localized around a point on the substrate.

Numerical potentials commonly used to model defects [5] all possess discontinuities in either the potential or its derivatives, either because these potential functions are constructed

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[*] Deceased.

from piecewise continuous functions or because they are obtained using interpolation schemes, which generally have discontinuous derivatives. The Fourier transform of such a function falls to zero quite slowly as a function of wave vector, whereas the smooth function that it approximates, in contrast, must have a Fourier transform that falls to zero quite rapidly with increasing wave vector.

Since there do not exist smooth potential functions that precisely describe the defects, let us illustrate this effect by studying some simple smooth potentials, which qualitatively describe the defects and which drop off reasonably rapidly at large distances, in order to develop a picture of what one expects for defect potentials with a range comparable to a lattice spacing or larger. Let us consider two-dimensional Gaussian and Lorentzian potentials, which represent two extremes, as the Gaussian falls to zero very rapidly at large distances while the Lorentzian falls off relatively slowly (as is evidenced by the fact that its second moment is infinite). For an anisotropic Gaussian defect potential $v(\mathbf{r})=-Ve^{-[(x/b_1)^2+(y/b_2)^2]}$, where b_1 and b_2 are the range parameters, we obtain, for a triangular lattice, $\bar{v}(\mathbf{G})=-2V\pi[b_1b_2/(3)^{1/2}a^2]e^{-(G_x^2b_1^2/4+G_y^2b_2^2/4)}$. [Again, the x and y dependence of $v(\mathbf{r})$, where $\mathbf{r}=(x,y)$, assumes that z is always set equal to its equilibrium value for all values of (x,y).] For the two-dimensional Lorentzian potential $v(\mathbf{r})=-V[1+(x/b_1)^2+(y/b_2)^2]^{-1}$, $\bar{v}(\mathbf{G})$ on the right-hand side of Eq. (1) is equal to $-[4\pi b_1b_2/a^2(3)^{1/2}]VK_0(Q)$, where $Q=(G_x^2b_1^2+G_y^2b_2^2)^{1/2}$ and $K_0(Q)$ is the spherical Hankel function of the first kind with an imaginary argument [7], whose large-argument asymptotic form is $K_0(Q)\approx(2/\pi Q)^{1/2}e^{-Q}$. These forms can be used to model a line defect which runs along the x axis, if we take $b_1>b_2$, with b_1 representing the distance along the defect length that one must travel in order to reach a point at which the relatively straight section of the defect ends (e.g., because it changes directions there), and b_2 represents the width of the defect potential perpendicular to the direction of the line defect. We will assume the film's crystallographic axes and sliding direction to be at arbitrary angles with respect to the x and y axes. If we wish to model localized defects, such as vacancies or interstitials, we set $b_1=b_2$. Physically, the potential resulting from a line defect results in the case of a step, for instance, primarily from the fact that when a film atom lies against the side of the step, it is in contact both with atoms in the part of the substrate just below it and with atoms making up the wall of the step, whereas at all other locations it interacts only with atoms below it. There is an implicit assumption here that the film is sufficiently stiff so that the atoms belonging to the film will be able to be pulled across a step without being caught by the hard core repulsion with the substrate atoms that make up the step, so that the pinning comes about purely from the attractive potential between film and surface atoms. This becomes a problem only when there is a high density of steps oriented at arbitrary angles with respect to each other. For other line defects, such as facet edges, for which the topology of the surface is much more gentle, the present model is clearly applicable without any additional assumptions. In the case of a localized defect, such as a vacancy, the defect potential results from the change in the substrate potential resulting from the fact that an atom is missing from the substrate and from the fact that neighboring atoms displace toward the location of the missing atom. The negative gradient of Eq. (1) with respect to $\Delta\mathbf{r}$ gives a force on the film whose amplitude is approximately $|G\bar{v}(\mathbf{G},z)|$, since if $\bar{v}$ falls off rapidly with increasing $\mathbf{G}$, the smallest $\mathbf{G}$ terms in the Fourier series dominate, where $\mathbf{G}$ is one of the smallest reciprocal lattice vectors. The maximum force on the film for the Gaussian defect potential for $b_1=b_2=b=1.23a$ is $0.979\times10^{-7}V/b$ whereas for $b_1=b_2=b=0.5a$ it is $0.0248V/b$. The corresponding value for the maximum force for the two-dimensional Lorentzian potential is $0.00349V/b$ for $b_1=b_2=b=1.23a$ and $0.0729V/b$ for $b_1=b_2=b=0.5a$. The former estimate is about two orders of magnitude smaller than the maximum possible force that these model potentials can exert on a single film atom, which is $0.429V/b$ for the Gaussian and $0.5V/b$ for the Lorentzian. According to the estimates of the pinning force given in Ref. [3], this reduction of the defect force is of sufficient magnitude to suggest that the magnitude of the defect force can be reduced below that of the inertial force.

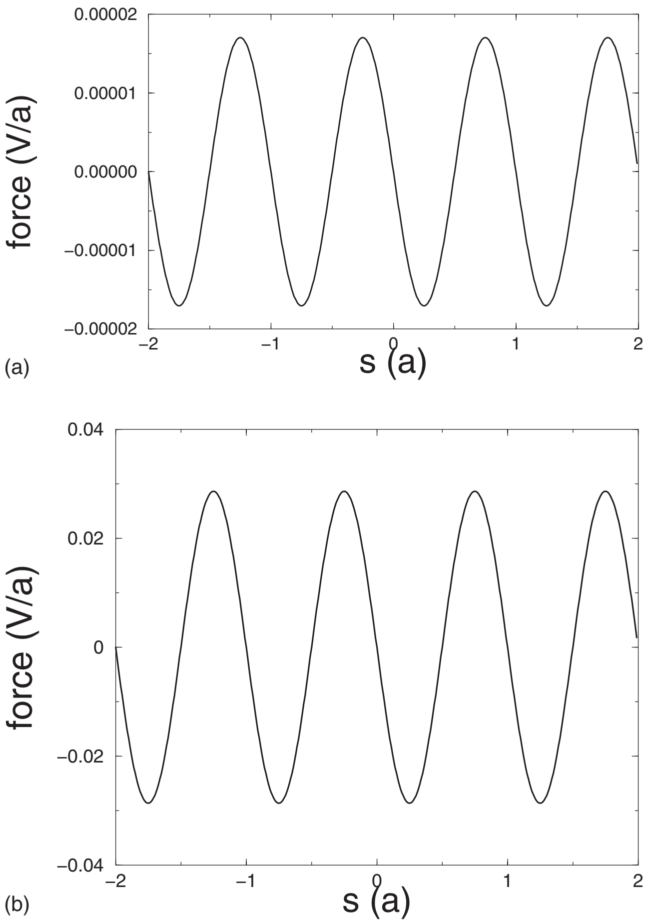

FIG. 1. Total force due to a Gaussian potential acting on a rigid lattice of atoms of spacing a is plotted as a function of the displacement of the film s for $b=1.236\,067\,978a$ in (a) and 0.834 334 9 in (b).

In order to illustrate numerically the high sensitivity of the pinning force on the range of the defect potential, consider a rigid two-dimensional simple square lattice sliding in

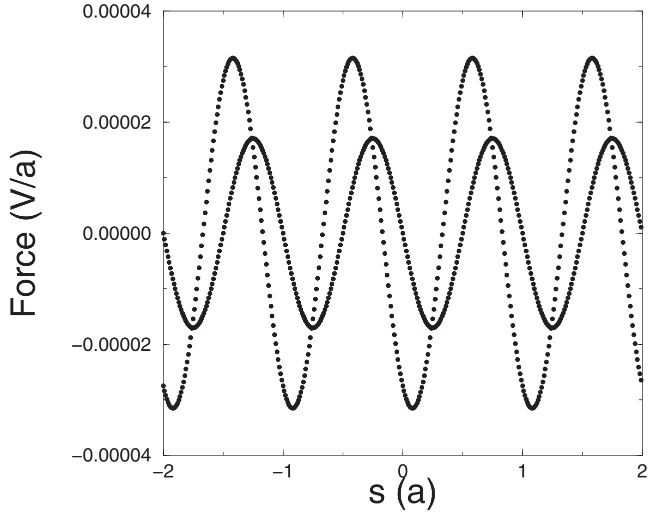

FIG. 2. Total force due to a Gaussian potential acting on a rigid lattice of atoms of spacing a is plotted as a function of the displacement of the chain s in the lower-amplitude curve for $b=1.236\,067\,978a$. The total force acting on a modulated lattice is shown in the higher-amplitude curve.

the potential $-Ve^{-r^2/b^2}$. The force on the lattice due to this potential is plotted as a function of the sliding distances in Fig. 1(a) for $b=1.236067986a$ and in Fig. 1(b) for $b=0.834\,334\,9a$. The amplitude of the force on the film is clearly considerably smaller in Fig. 1(a) than in Fig. 1(b).

For line defects, the effects can be even more dramatic. For example, for a line defect along the x axis, it is reasonable to assume that b_1 is a number of lattice spacings long, and hence considerably longer than a film lattice spacing. Hence, for virtually all orientations of the film axes, $|G_x b_1| \gg 1$, and hence we can see that for the two-dimensional Gaussian and Lorentzian potentials discussed in the last paragraph, their Fourier coefficients will be extremely small. Therefore, we see from Eq. (2) that the dependence of the interaction of the potential with the film on $\Delta\mathbf{r}$ will be extremely small compared to values for $b_1=b_2$ quoted in the last paragraph, implying that extremely small forces act on the film.

Even if the film is pinned with a pinning force greater than the inertial force, at zero temperature, we will see now that at nonzero temperature, lattice vibrations can depin it. At a given instant of time, a lattice vibration of wave vector $\mathbf{q}$ will add a term $\mathbf{A}\cos[\mathbf{q}\cdot(\mathbf{r}+\mathbf{R})-\omega t]$ to $\mathbf{R}$ in Eq. (1), where $\mathbf{A}$ is the amplitude (assumed to be much smaller than a lattice constant a), ω is the frequency of the vibrational mode, and t is the time. Then, if v is expanded in a Fourier series, Eq. (1) becomes

$$\sum_{\mathbf{R}} N^{-1}\sum_{\mathbf{k}} \bar{v}(\mathbf{k}) e^{i\mathbf{k}\cdot(\mathbf{R}+\Delta\mathbf{r})} e^{i\mathbf{k}\cdot\mathbf{A}\cos[\mathbf{q}\cdot(\mathbf{r}+\mathbf{R})-\omega t]}, \qquad (2)$$

where N is the number of atoms in the film. When the second exponential is expanded in Bessel functions, Eq. (2) becomes

$$N^{-1}\sum_{\mathbf{R}}\sum_{\mathbf{k}} \bar{v}(\mathbf{k}) \sum_{n=0}^{\infty} i^n J_n(\mathbf{k}\cdot\mathbf{A}) e^{(i\mathbf{k}-n\mathbf{q})\cdot(\mathbf{R}+\Delta\mathbf{r})} e^{-in\omega t}, \qquad (3)$$

which when summed over $\mathbf{R}$ becomes

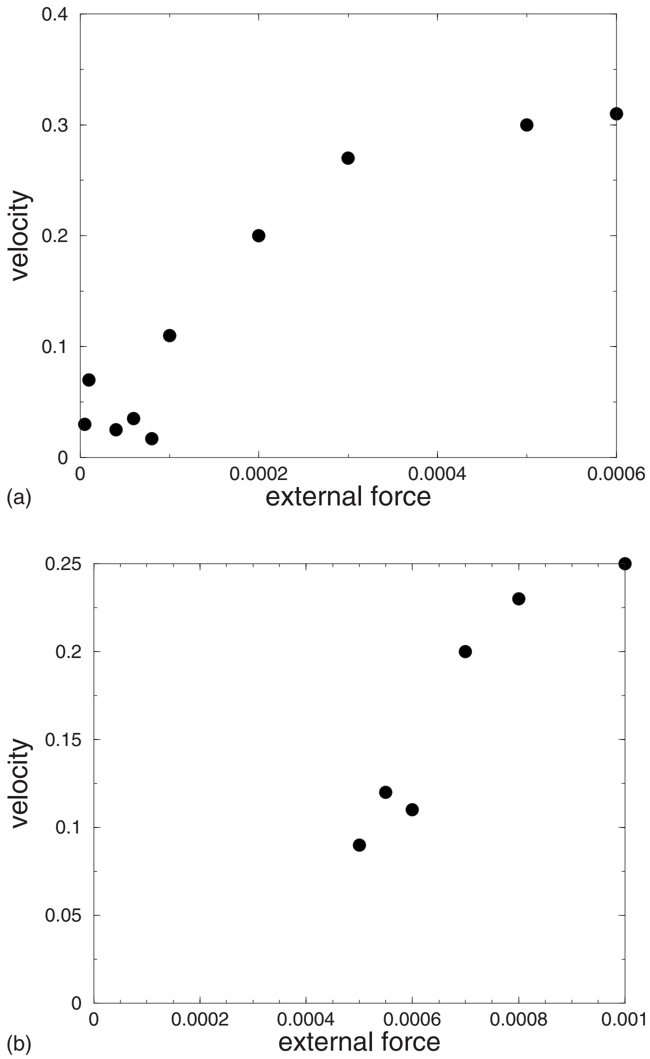

FIG. 3. Film sliding velocity found by molecular dynamics simulations of a xenon film on a silver substrate as a function of the external applied force per atom. The velocity is in units of σ/t_0 and the force is in units of ϵ/σ (where σ and ϵ are the length and energy parameters of the Lennard-Jones potential and t_0 is the time unit of the simulation, $(m\sigma^2/\epsilon)^{1/2}$, where m is the film atom mass. (a) shows the results of the run done with $b=1.25a$ and (b) shows a run done with $0.b=0.493a$.

$$\sum_{\mathbf{G}}\sum_{n} i^n J_n[(\mathbf{G}-n\mathbf{q})\cdot\mathbf{A}]\bar{v}(\mathbf{G}-n\mathbf{q}) e^{i(\mathbf{G}\cdot\Delta\mathbf{r}-n\omega t)}. \qquad (4)$$

For the $n=1$ term, which should be a good approximation for the small values of $|(\mathbf{G}-n\mathbf{q})\cdot\mathbf{A}|$ characteristic of lattice vibrations, we find that $\bar{v}(\mathbf{G}-\mathbf{q},z)$ for the Gaussian potential now contains a term $e^{-|\mathbf{G}-\mathbf{q}|^2b^2/2}$, which is comparable to or larger than $e^{-G^2b^2/2}$. As the former term oscillates in time for a lattice vibration, this term produces an oscillating term in the force on the film, which can be larger in magnitude than the force on the film that would occur if there were no vibrations [i.e., the $n=0$ term in Eq. (4)], implying that, at nonzero temperatures, the film will not be pinned by the defects because the film is pushed out of its total potential minimum by this oscillating force.

In order to illustrate this effect numerically, consider a stiff two-dimensional square lattice of atoms of lattice constant a interacting with a Gaussian potential $-Ve^{-r^2/b^2}$, where r is the distance from the center of the potential. We choose the range parameter of the potential, $b=1.236\,067\,978a$. The position of an atom in the lattice is then displaced by an amount x due to a lattice vibration with polarization in the x direction, where the position of a film atom is $(x_n,y_m)=(na,ma)$ with n and m integers, to simulate the effect of relatively short-wavelength vibrations. The modulation represents the lattice vibration at one instant of time. Here λ is taken to be equal to $1.64b$. The total force acting on the lattice is again plotted as a function of s for this case in Fig. 2 (the higher-amplitude curve). The total force acting on the lattice was found to be about twice as large for the modulated as for the unmodulated lattice. In this example, a static modulation was used. For a modulation due to actual thermally activated phonons, the modulation oscillates quite rapidly in time, resulting in a rapidly oscillating force, which overcomes any weak static pinning force due to the average interaction of the defect potential with the lattice. The effect of the oscillations in time of the modulation can be illustrated by adding a phase to the argument of the cosine in the above expression for the modulation, equal to ωt, where ω is the phonon frequency and t is the time. Thus, even if the inertial force is not large enough to depin a film without lattice vibrations, the oscillating force resulting from the lattice vibrations may depin it at sufficiently high temperature. One might even speculate that zero-point oscillations of the film might depin it at zero temperature [8].

Let us now repeat the molecular dynamics calculations of Ref. [3], but with a longer-range potential for point defects. The results are shown in Fig. 3. When we switch b from the value of about half a lattice constant used in Ref. [3] to 1.25 lattice constants, the threshold force for sliding drops from about $0.0005\epsilon/\sigma$ where ϵ and σ are defined in the caption to Fig. 3) to effectively zero, consistent with the results found earlier in this paper.

In conclusion, we have proposed a mechanism that may explain why defects, which must certainly be present on even the smoothest surfaces, might not prevent a stiff monolayer film from sliding under the extremely weak inertial forces that occur in a quartz microbalance experiment. What we have shown is that, if the defect potential has a range of a little more than one film lattice spacing, the resultant force on the film due to a single defect is a few orders of magnitude smaller than the maximum force that a defect can exert on a single film atom. Although we have only considered defects in the substrate, the arguments used here apply equally well to defects in the film, as long as the defects in both the film and substrate are sufficiently dilute, so that they will not interact with each other too often. We have also argued that, even if the pinning force due to defects is still greater than the inertial force, lattice vibrations can produce a rapidly oscillating force at each defect that will depin the film.

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