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for Research Supported by the
Office of Naval Research

Title: Adhesion Measurements of Physisorbed
Layers on Metal Surfaces

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I. Scientific Progress and Student Support

At this writing, the ONR grant has been in effect for three years. The work sponsored by this grant is now receiving both outside and internal recognition. Largely due to the research sponsored by ONR, J. Krim was nominated this year to be promoted to the position of Distinguished Professor of Arts and Sciences at Northeastern University. A sample letter in support of this nomination, e-mailed by J. Ferrante to J. Krim, is attached.

During the recent year, two graduate students have been partially supported: David Solina and Chris Daly. Solina completed an investigation of relationship between van der Waals interaction strength at a film-substrate interface and the observed interfacial friction. Friction levels were monitored for variations in the Van der Waals attraction energy due to both film thickness and interface chemistry. We observed systematic increases in interfacial friction levels with van der Waals attraction energy and also with film thickness. We are now studying these results within the context of available theory and computer simulation. We hope to not only publish the experimental results, but also to be able to identify the fundamental mechanisms governing the observed behaviors.

Daly completed the construction of a controlled environment scanning tunneling microscope which operates in conjunction with a quartz crystal microbalance. (See attached photos) With this setup we are able to record the drag of the STM tip on the oscillator as a function of adsorbed film thickness in addition to being able to image the surface as it shakes back and forth. We are currently carrying out studies of adsorbed water layers whose thickness ranges from one to ten angstroms. An unexpected and interesting result of these experiments is the fact that an adsorbed water layer only a few angstroms in thickness can enhance the STM image enormously (See attached Photos). We attribute this to the damping out of STM tip vibrations on account of the capillary effects of the film between the tip and the surface.

Both Daly and Solina have worked on studies of the effect of surface corrugation

Statement A per telecon
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on adhesive effects in adsorbed xenon monolayers. To date, we have been examining incommensurate xenon layers and have observed no dependence on substrate corrugation at all. We will repeat some of the incommensurate film studies to confirm this result, and then go on to study films which are commensurate with the substrate.

II. New Developments

The most significant new development this year was a suggestion by M. Persson and also B. Persson (Chalmers University, Sweden; attached), that the friction levels which we have been observing could be entirely explained in terms of an electron-hole mechanism. This suggestion explains the observed friction level to within a factor of two, and also the correct trend in the friction levels as the adsorbate gas is changed from Xe to Kr to Ar. If correct, this suggestion would explain why to date we have observed little effect of surface corrugation levels on friction: the electronic contribution is nearly the same for all of the metals which we have studied. The phonon contribution, which is quite sensitive to corrugation, may be orders of magnitude smaller than the electronic contribution, for the incommensurate films which we have studied.

III Summary of Upcoming Work

In the six months which remain on this grant, we plan to complete our studies of the effect of surface potential corrugation on the slippage of xenon monolayers. We expect the most interesting results of this study will to from the measurements carried out on commensurate films, where phonon contributions to friction are expected to play a major role. We will also carry out systematic experiments of the effect of a liquid film for measurements carried out in a tip-substrate geometry. Other ongoing work includes joint measurements with Dawn Dominguez at NRL concerning the slippage of physisorbed films adsorbed on polymer films which are used as "macroscopic" lubricants, and the controlled formation of nanostructures (through sliding

of material into place), in collaboration with Y. Bruynseraede's group in Leuven, Belgium.

IV. Invited Talks on Research Supported by this ONR Grant:

Meetings and Conferences

- (1) NATO Advanced Study Institute on "Phase Transitions in Surface Films", Erice, Italy (June 1990)
- (2) Materials Science Workshop on "Surface Physics in Materials Science", El Paso, Texas (July 1990)
- (3) General Meeting of the American Physical Society, Symposium on "Nanotribology", Cincinnati, Ohio (March, 1991)
- (4) Fall Meeting of the Materials Research Society, Joint Symposium on "Adhesion and Friction", Boston, MA (Dec. 1991)
- (5) Workshop on "Statistical Mechanics of Soft Condensed Matter", Florence, Italy (May 1992)
- (6) North Coast Symposium of the American Vacuum Society, on "Friction and Adhesion at Interfaces", Cleveland, OH (June 1992)
- (7) Japanese Society of Tribologists, International Workshop on "Microtribology", Morioko, Japan (Oct. 1992)

Seminars and Colloquia

- (1) Physics Colloquium, Univ. of California, Santa Barbara, CA (April 1990)
- (2) Physics Colloquium, Univ. of Virginia, Charlottesville, VA (Sept. 1990)
- (3) Condensed Matter Theory Seminar, Harvard University, Cambridge, MA (Oct. 1990)
- (4) Chemistry Division Seminar, Naval Research Laboratory, Washington D.C. (Feb. 1991)
- (5) Condensed Matter Seminar, Brandeis Univ., Waltham, MA (Oct. 1991)
- (6) Chemical Eng. Colloquium, Univ. of South Florida, Tampa, FL (Jan. 1992)

(7) Physics Dept. Colloquium, Worcester Polytech. Inst., Worcester, MA (Jan. 1992)

(8) Theoretical Physics Seminar, I.F.F., Julich, Germany (Feb., 1992)

(9) Physics Dept. Seminar, Univ. d'Aix-Marseille II, Marseille, France (1992)

VI. Publications Acknowledging Support by this ONR Grant:

(1) "Slippage of Simple Liquid Films on Silver and Gold Substrates", J. Krim, E.T. Watts and J. Digel, J. Vac. Sci. Tech. A8(4), 3417 (1990)

(2) "Probing Film Phase Transitions through Measurements of Sliding Friction", J. Krim, in *Phase Transitions in Surface Films*, H. Taub, Ed. (Plenum, New York, 1991)

(3) "Nanotribology of a Kr Monolayer: A Quartz Crystal Microbalance Study of Atomic-Scale Friction", J. Krim, D. Solina and R. Chiarello, Phys. Rev. Lett. 66, 181 (1991)

(4) "Sliding Friction Measurements of Molecularly Thin Films", J. Krim and R. Chiarello, J. Vac. Sci. Tech. B 9, 1343 (1991)

(5) "Sliding Friction Measurements of Molecularly Thin Films", J. Krim and R. Chiarello, J. Vac. Sci. Tech. A 9, 2566 (1991)

(6) "Surface Diffusion of an Adsorbed Layer Probed by a Quartz Crystal Oscillator", A. Widom and J. Krim (preprint)

(7) "Determination of Frictional Force Law from the Damping of a Quartz Crystal Microbalance", J. Krim, J.B. Sokoloff and A. Widom (preprint)

(8) "Combined Scanning Tunneling Microscopy and Quartz Microbalance Studies of Atomic-Scale Friction", C. Daly and J. Krim (manuscript in preparation)

4/14/92

Prof. Robert Lowndes
Dean of Arts and Sciences
Northeastern University

Dear Prof. Lowndes.

This is in response from a request from Prof. Jacqueline Krim for a letter of reference concerning a position as distinguished professor. First, I would like to say that I highly support this promotion based on Prof. Krim's research contributions. My background is as a long time contributor to the fields of Tribology, Surface Science and Condensed Matter Theory. Having struggled with the problems faced by a more fundamental scientist in order to make contributions to Tribology, I have had a particular appreciation for Prof. Krim's research. She has tackled problems that have been an enigma for years regarding gaining a fundamental understanding of friction. Dr. Krim has designed clever experiments to study these phenomena and made the first substantial contribution to this subject in decades. We at the N.A.S.A. Lewis Research Center have a particular appreciation for her work, since this has been the leading research organization in the country in fundamental studies in Tribology. Prof. Krim has gained substantial recognition for her research as is evidenced by her recent invited paper to the March Meeting of the American Physical Society. As you are undoubtedly aware such an invitation is highly prestigious in the Physics research community. This year we have invited Prof. Krim to give an invited paper at our regional meeting of the American Vacuum Society. Our symposium has been gaining recognition over the years as one of the more important regional meetings and has participation from a six state area. In conclusion, I feel that Prof. Krim's research has added to the reputation of Northeastern University and as a consequence she deserves the recognition for which you are considering her.

Sincerely,

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POSSIBLE ELECTRONIC MECHANISM BEHIND NANOTRIBOLOGY OF A RARE-GAS MONOLAYER

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(Received 17 September 1991 by B. Lundqvist)

The contribution from excitation of electron-hole pairs in the substrate to the sliding friction of an adsorbed monolayer of rare gas atoms on a metal surface is estimated from surface resistivity data. This contribution is found to be consistent with some recent measurements of the sliding friction of a Kr monolayer on a "smooth" Ag surface using a quartz-crystal microbalance.

A basic understanding of the processes behind friction, wear, and lubrication requires theoretical and experimental studies on an atomic level of the sliding surfaces. During the last few years there have been an intense activity in this emerging area of physics that sometimes is referred by the term "nanotribology". In a recent letter, Krim, Solina and Chiarello¹ presented some remarkable measurements of the sliding friction of adsorbed Kr monolayers on evaporated Au and Ag surfaces using a quartz-crystal microbalance. They noted that a theory by Sokloff², based on excitation of lattice vibrations in the substrate, gave values for the sliding friction η , which for an incommensurate overlayer was 4 orders of magnitude too small compared to the measured value and 8 orders of magnitude too large for a commensurate overlayer. The obvious contribution to η from the characteristic substrate excitations of a metal – the electron-hole pairs – was not considered or mentioned in the letter. This short communication points out that the estimated magnitude of the sliding friction of a rare gas atom on a metal surface due to excitation of electron-hole pairs in the substrate is consistent with the measured sliding friction for a solid Kr film on a "smooth" Au surface³.

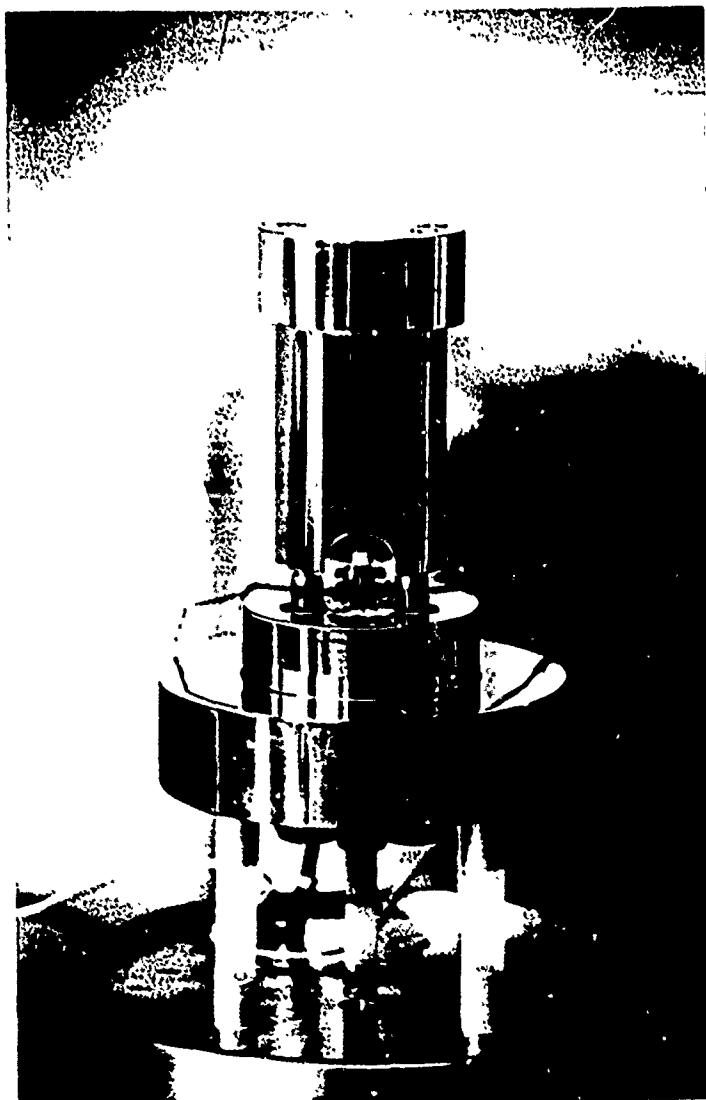
The electronic friction experienced by an adsorbate in vibrational motion on a metal surface due to excitation of electron-hole pairs has been discussed extensively in the literature⁴. In the case of adsorbate modes with vibrational energies well above the bulk phonon band this electronic mechanism is now widely believed to be the dominant mechanism for energy relaxation⁵. This conclusion is based on both experimental and theoretical studies. In particular, the recent direct measurements by picosecond infrared pump-probe techniques of the vibrational lifetime of the stretch mode of CO on some metal surfaces give strong additional support for this mechanism^{6,7}. The experience obtained in the field of vibrational spectroscopy can be applied in the present context due to the direct relation,

$$\eta_{el} = m_a / \tau_{eh} \quad (1)$$

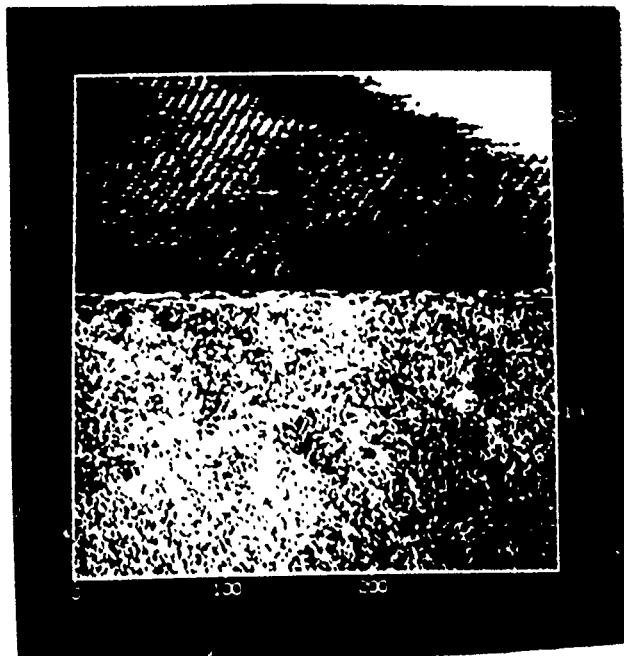
between the friction coefficient η_{el} for a single adsorbate with mass m_a and its vibrational life time τ_{eh} due to excitation of electron hole pairs⁴. This relation gives that the relaxation time τ of the adsorbate translational momentum is given by $\tau = \tau_{eh}$. The coupling to electron-hole pairs can give rise to a friction coefficient that is independent of the adsorbate velocity. This is due to the fact that the electron-hole pair density of states increases linearly with the excitation energy^{8,9}.

In general it is hard to do accurate calculations of τ_{eh} but recently it has been shown that it is possible to extract τ_{eh} directly from surface resistivity data¹⁰. This is based on an interesting relation between τ_{eh} for the frustrated adsorbate translation and the initial increase of the surface resistivity with adsorbate coverage. At present there exists only resistivity data for the rare-gas-metal adsorbate system: Xe on a "smooth" Ag surface¹¹, where this relation gives $\tau_{eh} \approx 3 \times 10^{-9}$ s. This value gives a sliding friction $\eta \approx 50$ dyns/cm², ($\eta = n\eta_{el}$), for a film of Xe atoms on Ag with the same density $n \approx 7.8 \times 10^{14}$ /cm² as the solid film of Kr. This value compares favourably in magnitude with the measured value $\eta \approx 5$ dyns/cm² for the solid film of Kr on the "smooth" Au surface¹, considering the uncertainties in both experiments. A larger value for η_{el} is expected for Xe than Kr since the physisorption interaction of Xe with a metal surface is known to be stronger than for Kr. The latter uncertainty could possibly be clarified by detailed electronic structure calculations of the coupling to the electron-hole pairs. Another effect is that not all adsorbed atoms will contribute to η . There will be no contribution from adsorbed atoms pinned to surface defects since the corresponding restoring force will make these atoms to follow the slow motion of the substrate almost instantaneously, i.e. essentially no sliding motion.

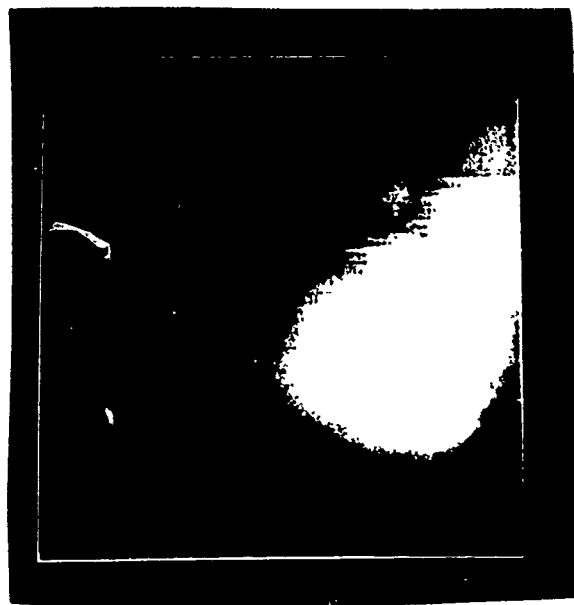
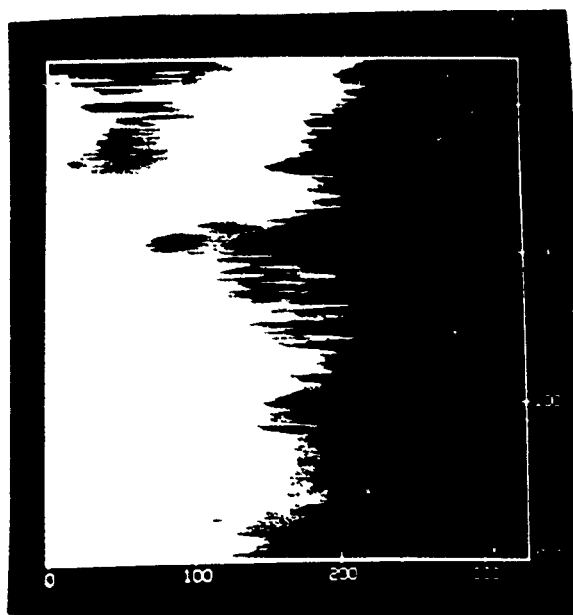
There are other conceivable contributions to η , like scattering of finite clusters of Kr atoms from surface defects and also the earlier mentioned dissipation to substrate phonon excitations which needs to be scrutinized. The studies of adsorption of rare gas atoms like Ar, Kr



Quartz crystal microbalance operating in conjunction with the scanning tunneling microscope. This is placed in a controlled environment chamber for water adsorption studies. The microbalance can also be operated beneath the tip of our ultra-high-vacuum tunneling microscope.



STM images of the gold electrode on a quartz crystal microbalance recorded in constant current (left) and constant height (right) mode. The oscillation is turned off on the lower half of each image and turned on for the upper half of each image. The lines in the constant height image are related to the amplitude of vibration of the surface, which is shaking from left to right.



STM images of the gold electrode on a quartz crystal microbalance with(right) and without (left) 8 Angstroms of adsorbed water. Image quality is always improved by the presence of thin adsorbed water layers, perhaps on account of the damping of tip vibrations by the capillary effects of the water.