Gold Clusters Sliding on Graphite: 
a Possible Quartz Crystal Microbalance Experiment?

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A large measured 2D diffusion coefficient of gold nanoclusters on graphite has been known experimentally and theoretically for about a decade. When subjected to a lateral force, these clusters should slide with an amount of friction that could be measured. We examine the hypothetical possibility to measure by Quartz Crystal Microbalance (QCM) the phononic sliding friction of gold clusters in the size range around 250 atoms on a graphite substrate between 300 and 600 K. Assuming the validity of Einstein’s relations of ordinary Brownian motion and making use of the experimentally available activated behavior of the diffusion coefficients, we can predict the sliding friction and slip times as a function of temperature. It is found that a prototypical deposited gold cluster could yield slip times in the standard measurable size of $10^{-9}$ sec for temperatures around 450 – 500 K, or 200 C. Since gold nanoclusters may also melt around these temperatures, QCM would offer the additional chance to observe this phenomenon through a frictional change.

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I. INTRODUCTION

Understanding the diffusion mechanisms and the frictional properties of aggregates of atoms or molecules of nanometric size (nanoclusters) on surfaces is important from both fundamental and technological view points. Growth of new materials with tailored features, as, e.g., a structure controlled down to the nanometer scale, is one of the active research fields in physical science. Different experimental techniques can be used to build nanostructured systems; however the requisites of control (in terms of characterization and flexibility) and efficiency (in terms of quantity of matter obtained per second) are generally incompatible. The main advantage of the cluster-deposition technique is that one can carefully control the building block (i.e., the cluster) and characterize the formation processes. The behavior of these deposited nano-objects is often distinctive (mostly due to their large surface-to-volume ratio), being qualitatively different from those of their constituent parts and from those of bulk material. In particular, they may present properties that vary dramatically with size.

Under different circumstances, various individual mechanisms (single-atom-like processes) can be responsible for cluster motion, such as evaporation and/or condensation, diffusion of particles along the cluster edge, and motion of misfit dislocations. Differently, one of the remarkable experimental observations of the last decade is concerned with gliding-like dynamics of compact solid gold clusters as a whole (concerted jumps with conservation of size and shape).

After room temperature deposition, gold clusters, comprising typically 250 atoms (radius of $\sim 10$ Å), have been repeatedly observed to diffuse on Highly Ordered Pyrolytic Graphite (HOPG) surfaces with surprisingly large, thermally activated diffusion coefficients in the range $10^{-7} – 10^{-5}$ cm$^2$/sec already at room temperature [1]; a similar behavior was reported for Sb$_{2300}$ clusters. A large mobility was recently observed also for activated surface diffusion of close-packed hexagonal clusters Ir$_7$ and Ir$_{19}$ [2]. The detailed atomic mechanisms for diffusion of gold clusters, on which we focus here, was studied theoretically and simulated by Molecular Dynamics (MD) by Luedtke et al. [3], who pointed out the coexistence of short and long jumps, the latter assimilating the process to a Lévy flight. Later work by Lewis et al. [4] and by Maruyama [5] further explored the cluster diffusion mechanisms.

The observable diffusion of sizeable clusters as a whole raises an interesting question in the context of nanofriction. If one could manage to apply a sufficient lateral driving force to the clusters, they would drift under its action. By the fluctuation-dissipation theorem, the lateral cluster drift mobility should then be related (leaving Levy flights aside for the time being [6]) to diffusion through Einstein relation. The measurable diffusivity of deposited clusters could thus lead to a measurable frictional dissipation in experimental apparatuses such as a Quartz Crystal Microbalance (QCM) [7, 8]. This is precisely the issue we propose to explore synthetically in this paper.

Specifically, we wish to examine a hypothetical, yet very practical, QCM experimental case where sliding friction could be measured for gold clusters adsorbed
on graphite, for sizes around 250 atoms and temperatures between room temperature and about 600 K. As it will turn out, the experimentally observed temperature dependence of the diffusion coefficients (obeying an Arrhenius-type activated law) predicts, through Einstein's relation, easily measurable QCM slip times at temperatures of the order of 450–500 K, possibly even lower, which anyway appear well within the reach of existing QCM setups.

An additional interesting effect is that small gold clusters will tend to “premelt” already at much lower temperatures than the bulk \( T_m = 1336 \) K. Buffat and Borel \cite{8} analyzed free gold clusters for premelting. Their data actually suggest melting not too far from room temperature for sizes around \( \text{Au}_{250} \) or thereabout. In addition one may expect the solid to acquire some additional stability against the liquid when adsorbed on the flat graphite substrate. So the actual temperature where the adsorbed Au cluster melts into a (partly) wetting Au droplet is difficult to predict and will have to await experimental scrutiny. Our point however is precisely that a sudden change of QCM sliding friction as \( T \) increases should be generically observable, and will signal that the cluster has melted.

II. MODELLING

The simplest theoretical model for cluster diffusion could be a model of jump over simple monatomic steps. A single jump mechanism predicts diffusion coefficients given by

\[
D(T) = \frac{\nu a^2}{4} \exp \left( -\frac{E_d}{k_B T} \right)
\]

where \( a \) is the jump step, \( \nu \) is the attempt frequency, and \( E_d \) is the energy barrier to be overcome. However, even if \( \nu \) is taken as large as the Debye frequency \( (\nu \approx 10^{12} \, \text{s}^{-1}) \), with \( a \sim 0.3 \, \text{nm} \), the prefactor is \( 10^{-3} \, \text{cm}^2/\text{sec} \), many orders of magnitude smaller than experimental value of \( 10^3 \, \text{cm}^2/\text{sec} \).

Luedtke et al. \cite{9} simulated gold cluster diffusion numerically using a many-body embedded atom (EAM) potential for the interaction among the gold atoms, and a two-body Lennard-Jones (LJ) potential for the interaction between gold and carbon atoms. The LJ potential parameters were \( \epsilon_{\text{Au-C}} = 0.01273 \, \text{eV} \) and \( \sigma_{\text{Au-C}} = 2.9943 \, \text{Å} \). The \( \text{Au-C} \) LJ potential was given different parameters \( \epsilon_{\text{Au-C}} = 0.022 \, \text{eV} \) and \( \sigma_{\text{Au-C}} = 2.74 \, \text{Å} \) in a later simulation by Lewis et al. \cite{10}. Both works uncovered a cluster diffusion mechanism that has a very interesting nature. There are long “sticking” periods of short-range local dwelling without too much diffusion of the cluster. Every now and then, there appear rare but important events where the cluster “slips” – it actually glides – over relatively long distances. The sticking plausibly corresponds to trapped cluster configurations, occasionally abandoned thanks to large and rare fluctuations. During one such fluctuation the two crystalline surfaces in contact, the gold cluster and the graphite plane, behave as hard incommensurate sliders \cite{11}, and thus slip for a while essentially freely.

This reasoning is supported by existing numerical results based on molecular dynamics simulations. Many-particle clusters that are incommensurate with the substrate were shown \cite{12} to exhibit very rapid diffusion, with their paths akin to a Brownian motion induced by the internal vibrations of the clusters and/or the vibrations of the substrate. The behavior of an incommensurate object moving “as a whole” is in striking contrast with other diffusion mechanisms, especially observed for clusters epitaxially oriented on the surface, where the cluster motion results from a combination of single-atom processes (e.g., evaporation, condensation, edge diffusion, etc.). The latter mechanisms, giving rise to relatively low diffusion coefficients \( (D \sim 10^{-17} \, \text{cm}^2/\text{sec}) \), are likely not significant in cases where the mismatch between cluster and substrate is large and/or their mutual interaction is weak. In this view, a gold cluster adsorbed with a (111) face onto a graphite substrate forms an ideal mismatched (incommensurate) system with too many still mating surfaces that interact only weakly, thus representing a desirable sliding situation.

As shown by the simulation work by Lewis et al. \cite{10}, this stick-slip type dynamics still leads – despite its large difference from the simple jump model over monatomic barriers – to an activated diffusion coefficient of the form \( 4 \) above, although now with different coefficients from monatomic diffusion. That work however also clarifies the quantitative inadequacy of the LJ interaction model, which for a 250 atom cluster leads to a prefactor of about \( 2 \times 10^{-3} \, \text{cm}^2/\text{sec} \) and an effective barrier of 0.17 eV, against experimental values of \( 10^3 \, \text{cm}^2/\text{sec} \) and 0.5 eV \cite{1}. The Arrhenius activated behavior fit to these experimental data is shown in Fig. \( 4 \) The discrepancy between simulation and experiment was highlighted by Maruyama \cite{3}.

The source of discrepancy between simulations and experiment is probably related to a large error in the adsorption energy. An experimental estimate for adsorption energy of Au on graphite is \( E_a = 0.64 \, \text{eV} \). \textit{Ab-initio} calculations suggested even larger values for the adsorption energy of about 0.9 eV \cite{13}. On the other hand the LJ model potentials imply a much smaller adsorption energies \( E_a \sim 0.15 \, \text{eV} \). With this smaller adsorption energy, a cluster could experience a smaller effective energy barrier when trying to disentangle itself from the graphite substrate. Thus the adsorption energy error, at first sight irrelevant, might we suspect be at the origin of the large discrepancy of effective barriers in cluster diffusion (0.5 eV against 0.17 eV in Lewis’s LJ modeling, and probably even smaller in Luedtke’s).

While it will be important to fix these problems in future simulations, we can for the time being content ourselves with this qualitative understanding, and simply...
discuss cluster diffusion as a regular Brownian diffusion, although with a rather unusual activation mechanism.

III. ESTIMATE OF THE SLIP TIME THROUGH EINSTEIN’S RELATION

When an adsorbate island or a cluster is forced to slide on a substrate, the dissipation of energy due to kinetic friction can be characterized by a specific tribological quantity, the *slip time* $\tau$, defined as the time taken by the cluster speed, initially set to be nonzero, to drop to $1/e$ of its original value. This is a relaxation time associated with the cluster-momentum fluctuation, and is connected to the interfacial friction coefficient $\eta$ through the relation $\eta = \rho/\tau$, where $\rho$ is the mass per unit area of the cluster. Thus, defining $\rho = m_{Au} N/A$ ($N$ denoting here the number of gold atoms of the cluster in direct contact with the graphite substrate over an area $A$), the interfacial friction coefficient can be rewritten as

$$\eta = m_{Au} N/A \tau. \tag{2}$$

Our assumption that cluster diffusion enjoys the properties of Brownian motion implies the applicability of the fluctuation-dissipation theorem, which in turn causes the force free diffusion and the friction under a sliding force to be connected through Einstein’s relation

$$D \eta A = k_B T. \tag{3}$$

By substituting expression (2) for the interfacial friction coefficient in (3), we obtain for the slip time

$$\tau = D m_{Au} N/k_B T. \tag{4}$$

Through this relation, assuming approximately $N = 50$ atoms directly touching the graphite substrate and, from the experimental data of Bardotti et al. [1], a diffusion coefficient $D \sim 10^{-5}$ cm$^2$/sec for Au$_{250}$ nanoclusters at 300 K, we get a rough estimate of the room temperature slip time $\tau \sim 10^{-12}$ sec. While this value is at least two orders of magnitude too small to be observed by QCM, the situation, as discussed below, can change drastically upon heating.

IV. A POSSIBLE QCM EXPERIMENT

The problem of how to measure interfacial friction in a quantitative manner has remained long unsolved, while knowledge of this property would provide important information relevant to a wide variety of problems. Sliding friction of adsorbed films are very effectively probed by QCM. In a QCM experiment, a substrate is laterally oscillated with typical frequencies $f \sim 15$ MHz and amplitudes of $a \sim 100$ Å. This exerts on a $N$-atom adsorbate island to a typical inertial force $F = N(2\pi)^2 M f^2 a$, which when sufficiently large can depin the island and make it slide. The sliding frictional dissipation lowers the oscillator’s quality factor $Q$, and the result is conventionally measured by the slip time $\tau = d(Q^{-1})/df$. As was said earlier, the interfacial friction coefficient may then be derived from Eq. 2. Sliding friction vanishes in both limits $\tau = 0$ (film locked to the substrate), and $\tau = \infty$ (superfluid film), and typical measurable slip times are in the order of $10^{-8} - 10^{-9}$ sec [15].

For low speed, hard sliders on hard flat substrates far from their melting points, there is no wear, and all frictional dissipation occurs via phonon creation (in metals, also creation of electron hole pairs). We concentrate here on phononic dissipation, whose origin stems from the oscillatory potential energy variation associated with lateral cluster displacement, the so-called “corrugation”. A recent analysis of solid xenon monolayers sliding over different substrates suggested for example that the viscous friction coefficient $\eta$ increases quadratically with corrugation [16]

$$\eta = \eta_{subs} + b U_0^2 \tag{5}$$

where $\eta_{subs}$ is the dissipation arising from both phononic and electronic friction, $b$ is a coefficient which depends weakly from the substrate surface, and $U_0$ is the potential corrugation amplitude between adsorbate layer and substrate, controlling the phononic dissipation. Experimental upper bounds for $\eta_{subs}$ are 0.08 ns$^{-1}$ (for Xe/Cu(111), Xe/Ni(111), and Xe/graphite).
We propose here a possible QCM experiment to study the frictional dissipation of gold nanoclusters sliding on a graphite substrate heated above room temperature. Raising temperature will bring about QCM-measurable slip times. Working at temperature even as high as ~ 600 K does not affect the structural properties of graphite, and should be entirely possible. Assuming for the moment the Au clusters to remain solid, we can simply extrapolate at higher temperatures the diffusion and slip times as done in Fig. 2. The predicted cluster slip time should for a 250 atom cluster reach QCM measurable values of $10^{-9}$ sec between $T = 450$ and 500 K, where the corresponding diffusion coefficient $D \sim 10^{-2}$ cm$^2$/sec.

V. AU CLUSTERS MELTING AND NANOFRICTION

As was recalled in the introduction, small clusters of radius $R$ have a premelting temperature $T_m(R)$ well below the bulk melting temperature of the same material. Figure 3 reproduces the original data by Buffat and Borel [9], showing that a small gold cluster of diameter $\sim 20$ Å will generally melt at room temperature or below. Premelting of gold clusters has also been extensively simulated, notably by Ercolessi et al. [17].

The premelting temperature data for free gold clusters are well fit by the Gibbsian formula [18]

$$T_m(R) \approx T_m(\infty) \left( 1 - \frac{2}{\rho_l L R} \Delta \gamma \right),$$

with $T_m(\infty) = 1336$ K, and

$$\Delta \gamma = \gamma_{SV} - (\gamma_{SL} + \gamma_{LV}) \approx 600 \text{ mJ/m}^2.$$

Here, $\rho_l$ is the density of the liquid, $L$ is the latent heat of melting per unit mass, and the $\gamma$'s denote the free energies of the three solid-vapor (SV), solid-liquid (SL), and liquid-vapor (LV) interfaces.

Even though a deposited cluster might generally be more stable than a free one due to the stabilizing effect of a hard substrate, it will still premelt very readily upon heating. At melting, one should expect the nanocluster friction to change very significantly. In fact the nanocluster will turn into a droplet, with some characteristic wetting angle, and obviously losing its original rigidity. The droplet dissipation should be dominated by viscosity, with a damping whose magnitude is at this stage difficult to anticipate. The jump between rigid cluster sliding and viscous droplet dissipation should nonetheless be a strong feature, readily observable by QCM, taking place below or near 600 K, depending on size, for clusters below 20 Å in diameter.

In summary, we predict that QCM measurement of small gold clusters on a graphite substrate should lead to observable inertial sliding friction with measurable slip times at temperatures of a couple hundred centigrade's. The relatively sudden melting of deposited clusters should also become measurable in the form of a sudden jump of slip time upon heating, at temperatures that should depend very strongly on cluster size.

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[1] L. Bardotti, P. Jensen, A. Hoareau, M. Treilleux, B. Cabaud, A. Perez, F. Cadete Santos Aires, Surf. Sci. 367, 276 (1996).
[2] S. C. Wang, U. Kürpick, and G. Ehrlich, Phys. Rev. Lett. 81, 4923 (1998); S. C. Wang and G. Ehrlich, Phys. Rev. Lett. 79, 4234 (1997).
[3] W. D. Luedtke and U. Landman, Phys. Rev. Lett. 82, 3835 (1999).
[4] L. J. Lewis, P. Jensen, N. Combe, and J-L Barrat, Phys. Rev. B 61, 16084 (2000).
[5] Y. Maruyama, Phys. Rev. B 69, 245408 (2004).
[6] A thermodynamical formalism of anomalous diffusion has been published, and the Einstein relation of diffusivity generalized for random walks of the Lévy-flight type. D.H Zanette and P.A. Alemany, Phys. Rev. Lett. 75 366 (1995).
[7] J. Krim and A. Widom: Phys. Rev. B 38, 12184 (1988).
[8] See, e.g., L. Bruschi, A. Carlin, and G. Mistura, Phys. Rev. Lett. 88, 046105 (2002).
[9] Ph. Buffat and J.P. Borel, Phys. Rev. A 13, 2287 (1976).
[10] C. DeW. Van Siclen, Phys. Rev. Lett. 75, 1574 (1995).
[11] M. Dienwiebel, G.S. Verhoeven, N. Pradeep, J.W.M. Frenken, J.A. Heimberg, and H.W. Zandbergen, Phys. Rev. Lett. 92, 126101 (2004).
[12] P. Deltour, J-L Barrat, and P. Jensen, Phys. Rev. Lett. 78, 4597 (1997).
[13] R. Anton and P. Kreutzer, Phys. Rev. B 61, 16077 (2000).
[14] P. Jensen and X. Blase, Phys. Rev. B 70, 165402 (2004).
[15] B.N.J. Persson, Sliding Friction: Physical Principles and Applications, Springer-Verlag, Berlin, (1998).
[16] T. Coffey and J. Krim, Phys. Rev. Lett. 95, 076101 (2005).
[17] F. Ercolessi, W. Andreoni and E. Tosatti, Phys. Rev. Lett. 66, 911 (1991).
[18] U. Tartaglino, T. Zykova-Timan, F. Ercolessi, and E. Tosatti, Phys. Rep. 411, 291 (2005).