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Gold clusters sliding on graphite: a possible quartz crystal microbalance experiment?

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Abstract

A large measured two-dimensional (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 can be measured. We examine the hypothetical possibility of measuring 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 behaviour 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 at the standard measurable size of 10^{-9} s for temperatures around 450–500 K, or 200 °C. Since gold nanoclusters may also melt at around these temperatures, QCM could offer the additional chance of observing this phenomenon through a frictional change.

(Some figures in this article are in colour only in the electronic version)

1. 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. The growth of new materials with tailored features, such as a structure controlled down to the nanometre scale, is one of the active research fields in physical science. Different experimental techniques can be used to build nanostructured systems; however, the prerequisites for control (in terms of characterization and flexibility) and efficiency (in terms of the 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 behaviour 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. Alternatively, one of the remarkable experimental observations of the last decade is concerned with the 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 (with a radius of ~ 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} cm² s⁻¹ already at room temperature [1]; a similar behaviour was reported for Sb₂₃₀₀ clusters. A large mobility was also recently observed for activated surface diffusion of close-packed hexagonal clusters Ir₇ and Ir₁₉ [2]. The detailed atomic mechanisms for the 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 Lévy flights aside for the time being⁵) to diffusion through the 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 that 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 of 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, and 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 ‘pre-melt’ already at much lower temperatures than the bulk $T_m = 1336$ K. Buffat and Borel [9] analysed free gold clusters for pre-melting. Their data actually suggest melting not too far from room temperature for sizes of around Au₂₅₀ or thereabouts. 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.

⁵ A thermodynamical formalism of anomalous diffusion has been published, and the Einstein relation of diffusivity generalized for random walks of the Lévy-flight type [6].

2. Modelling

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

$$D(T) = \frac{\nu a^2}{4} \exp\left(-\frac{E_d}{k_B T}\right) \quad (1)$$

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

Luedtke *et al* [3] 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 $\sigma_{\text{Au-C}} = 2.9943 \text{ \AA}$. The Au–C LJ potential was given different parameters, $\epsilon_{\text{Au-C}} = 0.022 \text{ eV}$ and $\sigma_{\text{Au-C}} = 2.74 \text{ \AA}$, in a later simulation by Lewis *et al* [4]. 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 [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 [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 behaviour 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 ($D \sim 10^{-17} \text{ cm}^2 \text{ s}^{-1}$), 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 two very stiff mating surfaces that interact only weakly, thus representing a desirable sliding situation.

As shown by the simulation work by Lewis *et al* [4], 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 (1) 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 $2 \times 10^{-3} \text{ cm}^2 \text{ s}^{-1}$ and an effective barrier of 0.08 eV, against experimental values of $10^3 \text{ cm}^2 \text{ s}^{-1}$ and 0.5 eV [1]. The Arrhenius activated behaviour fit to these experimental data is shown in figure 1. The discrepancy between simulation and experiment was highlighted by Maruyama [5].

The source of discrepancy between simulations and experiment is probably related to a large error in the adsorption energy. An experimental estimate for the adsorption energy of Au on graphite is $E_a = 0.64 \text{ eV}$ [13]. *Ab initio* calculations suggested even larger values for the adsorption energy of about 0.9 eV [14]. On the other hand, the LJ model potentials imply much

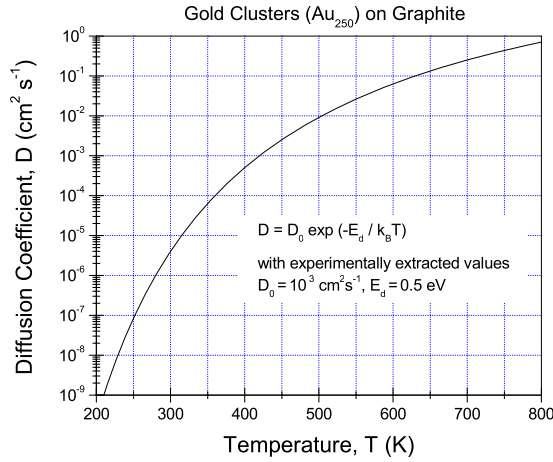


Figure 1. Temperature dependence of the diffusion coefficient of Au₂₅₀ on graphite. The values of D_0 and E_d are chosen to fit the experimental data by Bardotti *et al* [1] with an Arrhenius-type law.

smaller adsorption energies, $E_a \sim 0.15$ 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, which is at first sight irrelevant, might, we suspect, be at the origin of the large discrepancy in effective barriers in cluster diffusion (0.5 eV against 0.08 eV in Lewis's LJ modelling, 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.

3. 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* τ , 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 η through the relation $\eta = \rho/\tau$, where ρ is the mass per unit area of the cluster. Thus, defining $\rho = m_{\text{Au}}N/A$ (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

$$\eta = m_{\text{Au}}N/A\tau. \quad (2)$$

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,

$$D\eta A = k_B T. \quad (3)$$

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

$$\tau = Dm_{\text{Au}}N/k_B T. \quad (4)$$

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

$D \sim 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ for Au_{250} nanoclusters at 300 K, we get a rough estimate of the room-temperature slip time, $\tau \sim 10^{-12} \text{ s}$. 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.

4. 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 $f \sim 15 \text{ MHz}$ and amplitudes of $a \sim 100 \text{ \AA}$. This exerts on a N -atom adsorbate island a typical inertial force $F = N(2\pi)^2 M f^2 a$ which, when sufficiently large, can de-pin 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 equation (2). Sliding friction vanishes in both the limits $\tau = 0$ (film locked to the substrate) and $\tau = \infty$ (superfluid film), and typical measurable slip times are on the order of 10^{-8} – 10^{-9} s [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 the 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 η increases quadratically with corrugation [16]:

$$\eta = \eta_{\text{subs}} + bU_0^2 \quad (5)$$

where η_{subs} is the dissipation arising from both phononic and electronic friction, b is a coefficient that depends weakly from the substrate surface, and U_0 is the potential corrugation amplitude between the adsorbate layer and substrate, controlling the phononic dissipation. Experimental upper bounds for η_{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 temperatures even as high as $\sim 600 \text{ K}$ does not affect the structural properties of graphite, and should be entirely possible. Assuming for the moment that the Au clusters remain solid, we can simply extrapolate the diffusion and slip times at higher temperatures, as done in figure 2. The predicted cluster slip time should, for a 250 atom cluster, reach QCM-measurable values of 10^{-9} s between $T = 450$ and 500 K , where the corresponding diffusion coefficient $D \sim 10^{-2} \text{ cm}^2 \text{ s}^{-1}$.

5. Au clusters melting and nanofriction

As was recalled in the introduction, small clusters of radius R have a pre-melting 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 $\sim 20 \text{ \AA}$ will generally melt at room temperature or below. Pre-melting of gold clusters has also been extensively simulated, notably by Ercolessi *et al* [17].

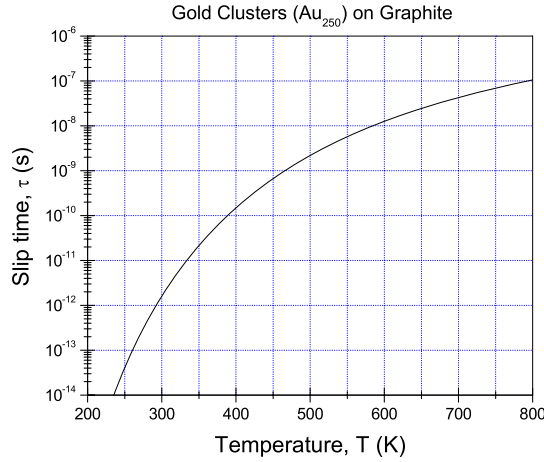


Figure 2. Predicted temperature dependence of the slip time of Au₂₅₀ on graphite. τ is evaluated considering an interfacial contact area of $N = 50$ Au atoms.

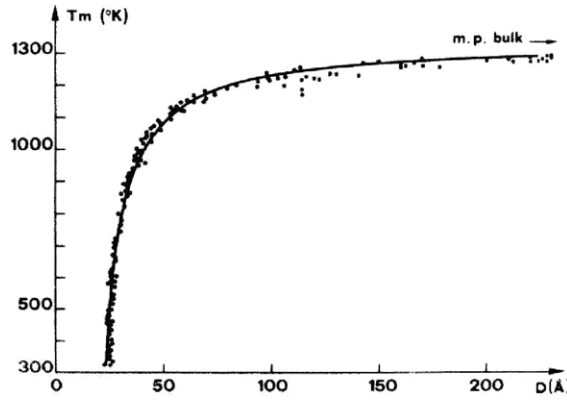


Figure 3. Experimental values of the melting point temperature of free gold clusters as a function of their diameter. From [9].

The pre-melting temperature data for free gold clusters are fitted well by the Gibbsian formula [18],

$$T_m(R) \approx T_m(\infty) \left(1 - \frac{2}{\rho_l L R} \Delta\gamma \right), \quad (6)$$

with $T_m(\infty) = 1336$ K and $\Delta\gamma = \gamma_{SV} - (\gamma_{SL} + \gamma_{LV}) \approx 600$ mJ m⁻². Here, ρ_l is the density of the liquid, L is the latent heat of melting per unit mass, and the γ s denote the free energies of the three solid–vapour (SV), solid–liquid (SL), and liquid–vapour (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 pre-melt 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, that takes 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 of hundred centigrade. 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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