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PHONON-INDUCED ANISOTROPIC DISPERSION FORCES ON A METALLIC SUBSTRATE

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Surfactant micelles (cetyltrimethylammonium chloride) adsorbed on Au(111) exhibit orientational order dictated by the gold crystal axes. To explain this phenomenon, we take into account the ionic contribution to the dielectric response of the metal. Since the motion of an ion inside the metallic lattice is restricted by its neighbors in an anisotropic way, the total dielectric response of the metal acquires directional dependence. A crystalline substrate is thus able to generate both torque and attraction on geometrically asymmetric objects. Numerical calculations show that the resulting anisotropic van der Waals force is indeed capable of orienting rod-like dielectric micelles on a Au(111) surface.

Keywords: van der Waals force; Lifshitz theory; orientational order.

1. Introduction

Self-assembly is a powerful tool for "bottom-up" production of organized structures down to molecular scales.[1–3] Using crystalline surface templates has proven a very promising approach to achieve long-range order in such systems,[2] which is important for many applications. The underlying mechanism, however, is still unclear. In this paper, we report a study of the orientational order of micelles adsorbed on a metal. Motivated by our observations of the micellar assembly pattern on gold, we propose a novel mechanism that introduces anisotropic van der Waals forces exerted by a metallic crystalline substrate. Our approach links templated molecular alignment to phonon modes of the substrate, two seemingly unrelated physical processes.

In micellar coatings of surfactants at solid−liquid interfaces, the substrate not only exerts attractive forces on the molecular adlayers but also determines the observed structures and patterns of surfactant surface aggregates.[4–7] In systems with covalent bonds, the valence electronic structure has strong directional character, and we previously showed
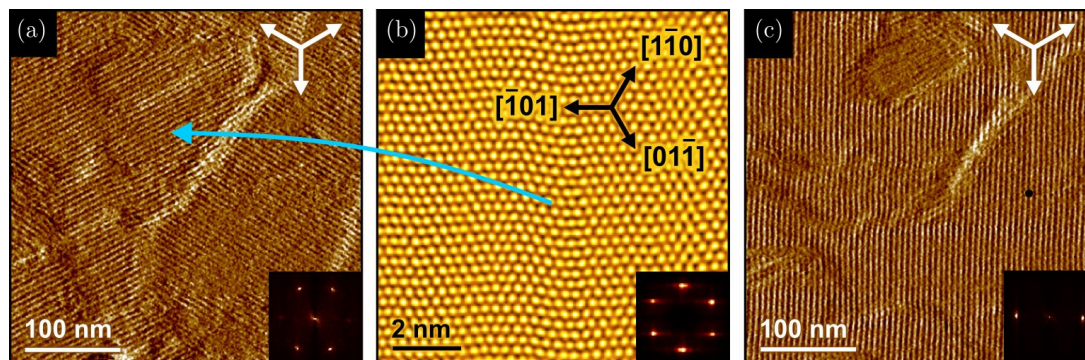
Fig. 1. (a) AFM deflection image of cylindrical micellar aggregates of CTAC surfactant on a flame-annealed Au(111) surface. (b) High-force, high-resolution image revealing the Au(111) lattice. (c) Same area as in (a) after tip-induced re-orientation.

that template-directed molecular self-assembly on graphite, where electrons form directional covalent bonds, can be understood in terms of anisotropic van der Waals forces.[8] However, it is unclear why micelles adsorbed on a metallic surface, such as gold, should align along crystallographic directions of the substrate.[7,9−12] The delocalized metallic electrons in the close-packed structure of gold do not display directional preference. Furthermore, in cubic crystals, including noble metals, all three principal values of the dielectric tensor are equal i.e. this class of crystals has isotropic dielectric properties. As a consequence, the van der Waals force from the gold substrate is expected to be isotropic. Atomic-scale mechanisms, such as epitaxy, for micelle orientation are difficult to substantiate, as the molecular structure of surfactant micelles cannot be determined experimentally, yet. Furthermore, the orientational order that we discuss in this paper has been observed for a wide range of substrate lattice constants,[4] which indicates that epitaxy may not be its main cause. The mystery deepens.

2. Experiments

The orientational adsorption can be readily observed using fluid-cell atomic force microscopy (AFM). In Fig. 1, AFM images were taken in a 1 mM solution of cetyltrimethylammonium chloride (CTAC) surfactant on a flame-annealed Au(111) surface of faced-centered cubic (fcc) crystal with a lattice constant $a = 0.40782$ nm. The surfactants form rod-like micellar aggregates[4,9,11] oriented in one of three preferred directions (Figs. 1(a) and 1(c)). Figure 1(b) shows a high-resolution AFM scan performed at the same sample location at

high[12] tip-sample force, revealing the (111) lattice structure of the gold substrate. The micelles are oriented perpendicular to $\langle 1\bar{1}1 \rangle$ i.e. the K directions of an fcc crystal. It has been demonstrated that surface micelles can be re-oriented using the AFM probe.[11] Only micelle orientations perpendicular to one of the three directions within the (111) plane can be achieved using this technique.[11] Figure 1(c) shows the same area as Fig. 1(a) after such a procedure. The insets of all panels in Fig. 1 show Fourier transforms of the AFM images, revealing their dominant orientations.

When atomic-scale effects can be neglected, the observed preferred orientation should indicate the most polarizable direction on the gold surface. Hence an interesting question emerges: Are there directions of enhanced screening response on a metallic substrate?

3. Theory and Calculational Methods

We consider the van der Waals interaction between rod-like molecules and metal surfaces. As the interaction is contingent upon the dielectric screening,[13] we shall consider screening of a metal by including *both* the effect of the conduction electrons and of the dressed ions. Then the total dielectric function of the metal, $\epsilon(\omega, \mathbf{k})$, can be written as $\epsilon(\omega, \mathbf{k}) = \epsilon^{\text{el}}(\omega, \mathbf{k})\epsilon^{\text{ion}}(\omega, \mathbf{k})$, in terms of the electronic dielectric function ϵ^{el} and of that of the dressed ions ϵ^{ion}.[14] In a metal with a nearly spherical Fermi surface ϵ^{el} is, to a very good approximation, isotropic, i.e. it only depends on the modulus of $\mathbf{k}$, not on its direction. The essential point is that, due to the spatial dispersion of the ionic dielectric response, the polarizability, and thus the resulting van der Waals force, becomes anisotropic.

In the Lifshitz theory of dispersion forces[15] one focuses on the long-wavelength fluctuations of the electromagnetic radiation field. In the small wave-vector regime the dielectric function of the dressed ions is well approximated by:

$$\epsilon^{\mathrm{ion}}(\omega, \mathbf{k}) = 1 - \frac{(c_s(\hat{\mathbf{k}})\mathbf{k})^2}{\omega^2} \qquad (1)$$

where $c_s(\hat{\mathbf{k}})$ is the sound velocity in the direction $\mathbf{k}$.[14] Equation (1) has the simple Drude form which is valid when the frequency ω is much larger than typical inverse electron relaxation times, a condition that is well satisfied by the finite Matsubara frequencies that enter the formalism of the van der Waals forces. Moreover at these frequencies $(c_s(\hat{\mathbf{k}})\mathbf{k})^2 \ll \omega^2$. We now apply Eq. (1) to gold. The measured sound velocity in the two high symmetry directions $\hat{K} \equiv (1/\sqrt{2})(1,1,0)$ and $\hat{X} \equiv (100)$ is $c_s(\hat{K}) = 5273\,\mathrm{m/s}$ and $c_s(\hat{X}) = 3921\,\mathrm{m/s}$, respectively.[16] Because of the directional dependence of the sound velocity, the dielectric response of the dressed ions is larger along $\hat{X}$ than along $\hat{K}$, reflecting a larger polarizability of the ionic system along the former direction. The effect is small but is amplified by the large value of ϵ^{el} in the relevant frequency range, because the total dielectric function of the metal is given by the product $\epsilon^{\mathrm{el}}\epsilon^{\mathrm{ion}}$. As we will argue in the following, this small anisotropy in the screening response induced by phonon modes may be sufficient to generate a van der Waals torque that is strong enough to orient adsorbed dielectric rods on smooth surfaces. According to this argument, the alignment of molecular assemblies (minimum energy configuration) should correspond to the most polarizable direction given by the direction of slowest sound propagation in a metallic system according to Eq. (1). Quite remarkably, this is what we observe for micelles adsorbed on the (111) surface of gold.

In this simple model, the anisotropy in the dielectric screening stems entirely from that of the normal modes of the ionic lattice in the long wavelength limit. Its origin can be traced back to the elastic properties of a crystal. According to continuum mechanics, in a system with mass density ρ, the sound velocity c_s satisfies

$$c_s^2(\hat{\mathbf{k}}) = \left(\frac{\partial p}{\partial \rho}\right)_{S,V} = \left(\frac{\partial p^{\mathrm{el}}}{\partial \rho}\right)_{S,V} + \left(\frac{\partial p^{\mathrm{ion}}}{\partial \rho}\right)_{S,V} \qquad (2)$$

where we attribute the pressure p in a solid to compression of electrons and ions. In Eq. (2) the main source of anisotropy is in the second term related to the ionic compressibility, which arises primarily from the ionic core-core repulsion of the lattice structure. Below we give a simple order-of-magnitude estimate of the effect to explain the orientational order of micelles adsorbed on an Au (111) surface.

For a micelle (represented as a cylindrical rod) of the radius a_m, length ℓ_m, at a height R from the gold substrate,[17] the interaction potential $V(R)$ between them can be written as

$$V(R) = -\frac{A_H a_m^2 \ell_m}{6R^3} \qquad (3)$$

where A_H is the Hamaker coefficient between a rod and the substrate. We may deduce A_H by constructing a composite semi-infinite slab in the configuration shown in Fig. 2. Using the Lifshitz theory set out by Parsegian and Weiss,[18] the anisotropic van der Waals energy between the two slabs is dictated by the dielectric tensors $\overleftrightarrow{\epsilon}^{\mathrm{R}}$ and $\overleftrightarrow{\epsilon}^{\mathrm{L}}$. On the Au(111) surface we have

$$\overleftrightarrow{\epsilon}^{\mathrm{R}}(\omega, \mathbf{k})$$

$$= \epsilon^{\mathrm{el}}(\omega) \begin{pmatrix} \epsilon_x^{\mathrm{ion}}(\omega, \mathbf{k}) & 0 & 0 \\ 0 & \epsilon_y^{\mathrm{ion}}(\omega, \mathbf{k}) & 0 \\ 0 & 0 & \epsilon_z^{\mathrm{ion}}(\omega, \mathbf{k}) \end{pmatrix} \qquad (4)$$

where we chose principal axes as $\hat{k}_x = (1/\sqrt{2}, -1/\sqrt{2}, 0)$ and $\hat{k}_y = (1/\sqrt{6}, 1/\sqrt{6}, -2/\sqrt{6})$. Aligned along $\hat{k}_x$, the dielectric tensor of the composite rod
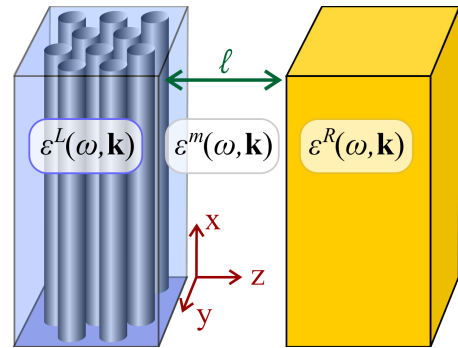

Fig. 2. On the left, a composite semi-infinite slab is made of arrays of rods whose dielectric properties are isotropic embedded in the isotropic medium of dielectric function $\epsilon^m(\omega, \mathbf{k})$. On the right, an Au(111) surface is an anisotropic semi-infinite slab. The distance between the two slabs is ℓ.

materials is

$$\epsilon_x^L(\omega) = \epsilon^m(\omega) + v[\epsilon^{\mathrm{rod}}(\omega) - \epsilon^m(\omega)] \quad (5)$$

$$\epsilon_y^L(\omega) = \epsilon_z^L(\omega) = \epsilon^m(\omega) + 2v\epsilon^m$$
$$\times (\omega)\Delta_{rm}/(1 - v\Delta_{rm}) \quad (6)$$

where $\Delta_{rm} = (\epsilon^{\mathrm{rod}} - \epsilon^m)/(\epsilon^{\mathrm{rod}} + \epsilon^m)$ and $v = \rho_r \pi a_m^2 \ell_m$ is the volume fraction of rod material. Here ρ_r stands for the number of rods per unit volume. Note that we only keep track of wave-vector dependence in the dressed ion screening, which is crucial in generating anisotropy in the long wave-length limit. Taking the limit $v \to 0$ in the van der Waals energy between the two slabs yields the interaction potential $V(R)$ between a single rod and the substrate.[19,20] We thus obtain the Hamaker coefficient A_H in Eq. (3):

$$A_H = \frac{3k_B T}{8\pi} \sum_{n=0}^{\infty}{}' \sum_{m=1}^{\infty} \int_0^{2\pi} d\theta \int_0^{\infty} x^2\, dx$$
$$\times \lim_{v \to 0} \frac{\Delta^{2m}(\xi_n, (2R)^{-1}x, \theta)}{v} e^{-mx}. \quad (7)$$

The variable Δ^2 is a function of the dielectric tensors, Eqs. (4)–(6), and $\xi_n = 2\pi n k_B T/\hbar$.[21]

4. Results and Discussion

The numerical integration in Eq. (7) can be performed with a few assumptions: the dielectric screening of rod materials is taken as that of hydrocarbons,[22] the parameters of the electronic dielectric screening of gold are obtained by fitting against optical data,[23] and the intervening medium between rods and gold is vacuum (no water in the interstitial region). At the separation $R = 0.4$ nm,

$$A_H = 20.5554534 \, k_B T \quad (8)$$
$$\delta A_H = -1.2 \times 10^{-5} k_B T \quad (9)$$

where δA_H is the difference in Hamaker coefficients when one rotates the composite rod materials to the $\hat{k}_y$ direction. Though δA_H is small, the relevant quantity is the potential in Eq. (3), which can be substantial for long rods close to the gold surface. As the size of molecular assembly grows larger, small energy differences at the molecular scale are thereby assembled into a collective effect. It has been shown that the difference of the order of $\delta A_H \approx 10^{-5} \, k_B T$ is sufficient to induce orientational ordering of micelles
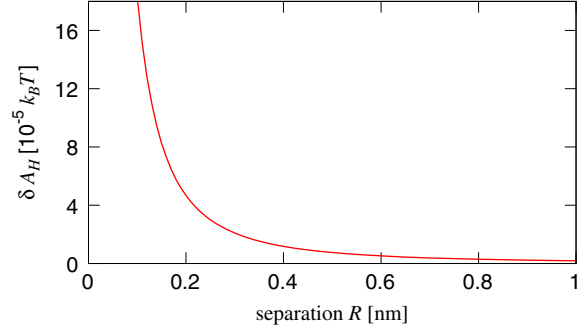

Fig. 3. The difference of Hamaker coefficients $\delta A_H(R)$ between a dielectric rod and a Au(111) surface.

on a substrate.[8] It should come at no surprise that the closer the separation, the larger the anisotropy in the Hamaker coefficient (Fig. 3).

The difference δA_H increases rapidly as the separation R approaches zero. We shall make a quick estimate to see the effect of δA_H at a reasonable adsorption separation.[24] For a rod of the length $\ell_m = 500$ nm, radius $a_m = 2$ nm, the van der Waals energy difference $\delta V(R)$ between two orientations is $\sim 2k_B T$ at $R = 0.2$ nm and becomes more than $\sim 60 k_B T$ at $R = 0.1$ nm.[25] This means, when a rod is physisorbed on gold, the van der Waals torque is strong enough to counter rotational Brownian motion; the anisotropy induced by phonon modes results in the orientational adsorption in Fig. 1.

Some approximations of the current colloidal approach and their justification, such as flexibility of micelles and interactions between them, are discussed in Refs. 8 and 20. In addition, we have considered the reconstruction of Au(111) surfaces in aqueous solutions, forming a characteristic herringbone structure that changes direction roughly every 20 nm and breaks the three-fold symmetry of Au(111).[26] It has been suggested that the reconstruction of Au(111) induces directional adsorption of alkanes.[27] For surfactant micelles, however, the tip-induced orientation of micelles perpendicular to any of the three $\langle 1\bar{1}0 \rangle$ directions can be achieved.[11] We conclude that the surface reconstructions cannot be the deciding element in the orientation of the surfactant micelles.

In conclusion, spatial dispersion of lattice vibrations in a metallic system is brought to the theory of van der Waals forces. The model we used for metallic screening links the sound propagation to the essential feature of electronic and ionic dielectric response. The mechanism only invokes the most elementary treatment of screening in metals and is

expected to be robust for a broad range of conditions on other metallic substrates. With a suitable choice of parameters, the origin of orientational order of molecular assemblies on a gold surface is shown to be caused by phonon-induced anisotropy, which is a bulk (not a surface) effect, stemming from the fact that electromagnetic fluctuations penetrate sufficiently inside the metallic substrate. We suggest that by exploiting the directional dependence of sound speed, either by a way of the intrinsic structural property or induced by an external constraint such as applied pressure or substrate boundary effect, the mechanism can be utilized to explain and control ordered molecular assemblies on a metallic substrate.

Acknowledgments

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