

Chapter 8

Atomic Force Microscope (AFM)



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Abstract Atomic force microscope (AFM) evaluates morphology of surfactant layer formed at a solid/liquid interface as well as additional information of the adsorption layer such as thickness and compressibility. The morphology can be visualized when a probe tip (cantilever) is scanned at a given repulsive set-point force arising from the adsorbed surfactant layer. This AFM observation method is called “soft contact method” due to its non-distractive nature to the soft materials. In force curve measurement, the separation “0” is defined as the constant compliance region where the cantilever and base substrate move together. Special care is required for the separation definition; if the adsorption layer is stacked like a sandwich between the cantilever and the base substrate, it would not be pushed out by compression. Spherical particles can be placed on the cantilever tip to measure the force and friction curves. This procedure is called “colloid probe method” and is useful in determining the interaction surface energy under the Derjaguin approximation.

Keywords Atomic force microscope (AFM) · Force curve · Adsorption

8.1 Introduction

Evaluation of amphiphilic molecule adsorption that occurs at solid/liquid interfaces has commonly been evaluated by measuring adsorption isotherm or zeta potential. Several adsorption models for the self-assembly of small amphiphilic molecules on the solid surface such as the reverse orientation model, surface bilayer model, and surface micelle model have been proposed [1]. In addition to these indirect methods, direct measurement by means of atomic force microscope (AFM; Fig. 8.1) was developed in the late 1990s. AFM observation can be performed using a sharp probe

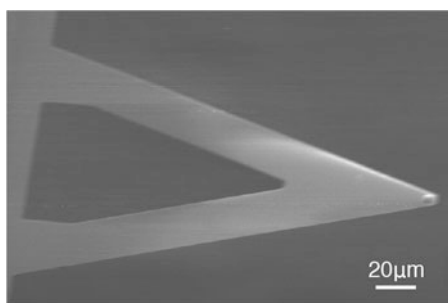
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Fig. 8.1 AFM instrument.
(Photo credit Hitachi High-Tech Science Corporation)



Fig. 8.2 SEM image of
AFM cantilever



tip called a cantilever (Fig. 8.2), which can detect very weak repulsive force between the probe tip and molecular layers adsorbed on the solid surface in situ. Then the topographic information can be visualized when the cantilever is scanned at a given set-point force detected here [2]. This AFM observation method is classified as a type of contact method and is even called a soft contact method due to its non-distractive nature to the soft materials.

Additionally, the morphology of the adsorbed layers can be observed by nondestructive scanning of the cantilever under a certain oscillation. Structural evaluation of the adsorbed layers has previously been performed mostly in equilibrium, but now thanks to the recent technological advancement of AFM, we can observe and discuss the formation process of the adsorption layers [3, 4].

Forces between the cantilever and the adsorbed surfactant layers involve electrostatic interactions, steric repulsions, van der Waals attractions, hydrophobic interactions, etc. The soft contact method generally utilizes electrostatic interactions and steric repulsions. The force curve can be obtained by plotting the detected interactions vs. apparent surface separation. When the experimental condition results in attractive forces working between the probe and adsorbed layer, visualization of

surface morphology is difficult in principle, even though valuable information for the adsorbed layer structure can be obtained from force curve measurements. The use of AFM allows us to get the visualized morphology of the adsorbed layer as well as further additional information through force curve interpretation.

As there are plenty of useful books available for the instrumental principles of AFM measurement, this chapter introduces some important points for the evaluation of adsorbed surfactants by AFM through the author's experiences.

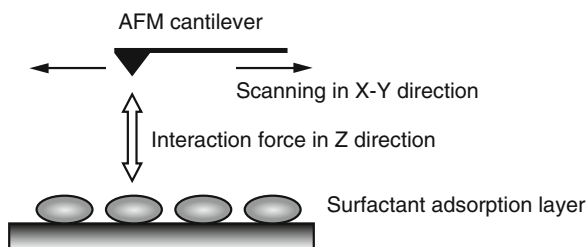
8.2 What You Get

1. In situ evaluation for the morphology of the surfactant layer adsorbed on the solid surface such as spherical, globular, cylindrical (rod or thread), or planar (lamellar) morphology.
2. Information of adsorbed layers in depth direction such as the thickness and compressibility can be discussed from the force curve.
3. The dual force curve can be obtained by the movement direction of the cantilever; one is toward the substrate (approach), and the other is from it (retraction). The latter data give adhesive force of the cantilever to the adsorbed layer, but statistical processing is preferable in evaluating the attractive force since the fluctuation in data is quite high.
4. The friction curve (friction coefficient) can be measured for the adsorbed surfactant layer by measuring the twist amount (torsional response) under the constant vertical load on the cantilever. The friction coefficient as a nano-tribological parameter can be determined from the slope of the line plotted for the vertical load on the horizontal axis and the frictional force on the vertical axis.

8.3 Essentials and Tips

1. The main unit of AFM equipment should be placed on an anti-vibration table as external vibration would cause noise generation during the measurement.
2. The surface of the cantilever and the solid should be clean for the measurement, and the tweezers to hold the cantilever and cell for the sample solution should also be clean to avoid contamination.
3. The surface of the solid substrate should be as flat as possible to get accurate data and precise interpretation.
4. The thickness of the surfactant layer formed on the solid surface will be several nanometers, sometimes much smaller than the surface roughness of the solid substrate. As a result, the topographic image of the adsorbed layer based on the height profile becomes blurred (unclear). From this point, deflection or error signal image with enhanced edge morphology is usually used for the soft contact method.

Fig. 8.3 Schematic representation of soft contact AFM method



5. For the soft contact method, the image of the adsorbed layer morphology is obtained by detecting weak repulsive forces between the cantilever tip and the adsorbed layer (Fig. 8.3). The adsorbed layer could be collapsed if excess force is applied to the adsorbed layer. If the applied force is too weak, the image would be too blurry since the cantilever scans the position far from the adsorbed layer. Hence, it is important to find the best set point to get an image with the highest resolution by measuring the force curve. Scanning at the point just before the cantilever jumps into contact gives the highest resolution since the force sensitivity to the distance becomes maximum. Caution should be paid for the thermal drift which causes shifting of the set-point force during the scanning, while this drift can be tactically utilized to observe morphology change of the adsorbed layer in response to the applied force. An example image for the surfactant layer with the soft contact AFM method is shown in Fig. 8.4.
6. It is important to change the area and direction of scanning when periodical image is found in the cylindrical structure in order to distinguish from electric noises.

8.4 Understanding Your Data

In situ observation and analysis are required to measure the adsorbed layers in solution, as its structure would change during the drying process. This should be sensibly kept in mind as we can find experimental reports trapped into this pitfall on the adsorbed structures of surfactants, especially polymer surfactants, observed under open atmosphere after evaporation of solvents.

AFM measurement gives force output change as electric voltage or current along with the piezo movement. By taking the spring constant and deflection amount of cantilever into account, the force curve can be obtained by plotting the detected interaction force against apparent surface separation (Fig. 8.5). Special caution should be paid here for the separation “0” is defined as the constant compliance region where the cantilever and base substrate move together. If the adsorbed layer is stacked like a sandwich between the cantilever and the base substrate, it would not be pushed out by compression, and the definition of separation “0” becomes obscure. On the other hand, when using surface force apparatus (SFA) [5], the distance

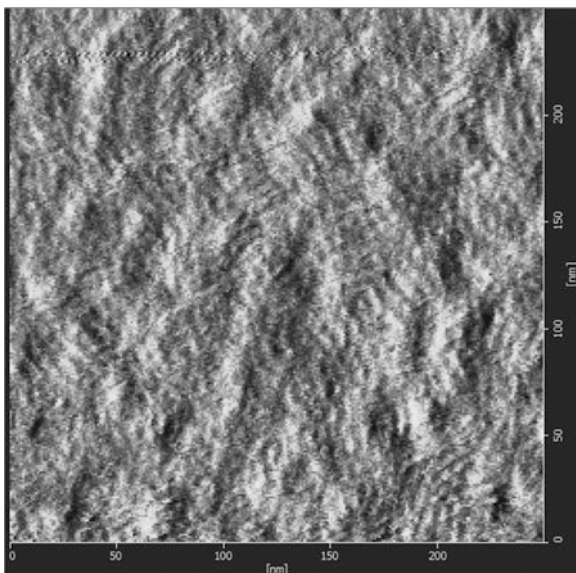


Fig. 8.4 Typical soft contact AFM image: adsorbed layer morphology of a cationic surfactant (hexadecyltrimethylammonium bromide, HTAB or CTAB) on silica in the presence of NaBr (250 nm image)

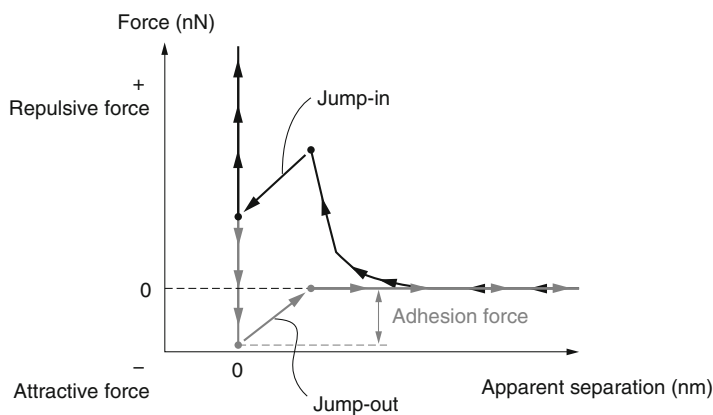


Fig. 8.5 Schematic representation of force curve data

between surfaces is strictly defined, and it causes a mismatch between the AFM and SFA data. Additionally, the interpretation of the spring constant can cause errors in force calculation.

Adsorption of surfactants onto the cantilever can be easily overlooked. Materials commonly used for cantilever are silicon or silicon nitride with negative charge in aqueous solutions under neutral pH. This causes adsorption of cationic surfactants

on the cantilever and generates attractive force with the base substrate when the surfactant concentration is low while generating electrostatic repulsive force at high concentrations. The surfactant layer adsorbed on the cantilever is considered weak against compression, and two steps of repulsive force can be observed when the cantilever approaches toward the base substrate when the surfactant concentration is relatively high. The jump-in as a discrepancy of the first repulsion at longer distances and the second repulsion at shorter distances is interpreted as the adsorbed layer collapsing on the cantilever or base substrate [6]. The distance of the “jump-in” in the latter case corresponds to the thickness of the adsorbed layer [7], as shown in Fig. 8.5. There is another interpretation reported for the stepwise repulsion as derived from the double layers built up on the substrate surface [8]. It is recommended to apply other analytical methods such as ellipsometry for better understanding the phenomena.

8.5 Useful Hints

In relation to two to four of **What You Get**, spherical particles can be placed on the cantilever tip to measure the force and friction curves. This procedure is called the “colloid probe method” [9, 10]. Although common materials for the cantilever are silicon or silicon nitride, this spherical particle tip offers a wide choice of materials. Normalization using the curvature radius can convert the force data into the energy dimension with the Derjaguin approximation [5].

The curvature radius for the cantilever is usually provided from the manufacturer, but due to fluctuations between individual tips and unavoidable wearing, it is impossible to determine the accurate interaction energy from the provided radius. Furthermore, the Derjaguin approximation should be considered since it is applicable only when the distance of the surface force is negligibly smaller than the curvature radius of the tip [5]. Hence it is not desirable to determine the surface force (interaction energy) using the curvature radius of the tip. In contrast, for the colloid probe method, the curvature radius of the colloid probe can be measured, and its size is much greater than the force-detectable distance. From these points, the colloid probe method is useful in determining the interaction energy as a function of apparent surface separation.

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