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Effect of surface hydrophobicity on short-range hydrophobic attraction between silanated silica surfaces[☆]

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ABSTRACT

The interaction forces between silanated silica surfaces without nanobubbles were measured using colloidal probe atomic force microscopy (AFM). To obtain hydrophobic surfaces without nanobubbles, an aqueous solution was introduced between the surfaces following an exchange process involving several solvents. In the obtained approaching force curves, an attractive force was observed from a distance of 10–20 nm, which is an additional attractive force stronger than typical van der Waals attractions. When the surface hydrophobicity decreased, the range of this attraction decreased slightly; the attraction disappeared when the surface contact angle was below 90°. In contrast, measurements in the water–ethanol mixtures revealed that the attraction persisted even when the contact angle was well below 90°. The possible origin of this force was discussed on the basis of the obtained results.

1. Introduction

Suspensions of micro- and nanoscopic particles in liquids are very important in a wide variety of industrial fields because they are used in various manufacturing processes. Upon handling the suspensions, it is crucial to evaluate and control the dispersing/aggregating behavior of the particles. Generally, the dispersing/aggregating behavior of particles in liquids is dominated by the interaction forces acting between the surfaces of the particles. Thus, precise measurement of the interaction forces between particle surfaces in liquids is a key for the adequate evaluation of particle behaviors. To this end, the direct measurements of surface interactions in liquids, using atomic force microscopy (AFM) in particular, have been conducted in various fields of research.

Among the interaction forces in liquids, hydrophobic attraction, the long-range and strong attractive force between hydrophobic surfaces in aqueous solutions, plays a critical role. Hydrophobic attraction has a significant effect not only on the dispersing/aggregating behavior of particles but also on various phenomena such as the attachment of particles onto bubbles and the formation of lipid bilayers and micelles. The direct measurements of the hydrophobic attraction have been conducted by many researchers using different experimental systems ever since the first direct measurement by Israelachvili and Pashley in 1982 [1]. The results of these experiments have revealed [2–8] that the hydrophobic attraction is an anomalously long-range force whose range is sometimes more than 300 nm [9], whereas the effective range of normal interaction forces is 10 nm at most. Because such a long-range attraction cannot be explained by conventional thermodynamics, the origin of the hydrophobic force has been regarded as a mystery in colloid chemistry.

Now, however, the mechanism of the hydrophobic attraction is being gradually clarified. The mechanism of the hydrophobic force is assumed to depend on the system employed to measure the force [10,11]. Among the mechanisms, the interaction between chemisorbed hydrophobic surfaces, which usually exhibit a robust monolayer with a high surface contact angle, is attributable to small bubbles (nanobubbles) that can attach stably on the surfaces [12,13]. When the surfaces come close, the nanobubbles, which have sizes on the order of 10–100 nm, form a bridge between the surfaces and generate a long-range attraction. On the other hand, recent studies have found attractive forces with a range longer than that of the van der Waals force acting at a distance of 10–25 nm between the hydrophobic surfaces without any nanobubbles [14], indicating that another type of hydrophobic attraction can act even in the absence of bridging bubbles. This "short-range" hydrophobic attraction is assumed to be a more

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genuine hydrophobic attraction because it is produced not by the intervention of a phenomenon such as bridging bubbles. However, the origin of this force is still unclear.

The aim of this study was to investigate the interaction forces between silanated silica surfaces on which there are no nanobubbles using AFM, in terms of the affinity between the surfaces and the solution. We changed the affinity of the surfaces to the solution using two different methods: a change in the surface hydrophobicity by varying the density of a hydrophobizing reagent on the surfaces and the use of a mixture of water and ethanol to change the affinity. By comparing the interaction forces obtained using these methods, we hoped to obtain clues into the origin of the hydrophobic attraction.

2. Materials and methods

2.1. Materials

Force measurements were conducted between a Si wafer (Nilaco, Japan) and a silica particle (MSV-25, Tatsumori, Japan). The average diameter of the silica particle was 15 μm. The silica particle was attached onto the top of an AFM probe (OMCL-AC240TS, Olympus, Japan) to make a colloid probe [15]. Octadecyltrichlorosilane (OTS, Shin-etsu Chemicals, Japan), a silane coupling reagent with a C18 hydrocarbon chain, was used as received to prepare the hydrophobic surfaces.

2.2. Surface preparation

The silica particles were sonicated in a warm ethanol solution and in a 5 vol% H_2O_2 solution for 10 min respectively. and then. It was then sonicated in a 5 mM NaOH solution for another 10 min and sonicated twice with warm pure water, and dried in vacuum. A cleaned silica particle was first attached to the top of the AFM cantilever using epoxy glue (Araldite, Ciba-Geigy, Switzerland) using a manipulator under observation with an optical microscope. The silicon wafers were sonicated in ethanol and then cleaned in a plasma cleaner (PDC-32G, Harrick Plasma, USA) operating at 12 W under reduced pressure for 10 min. The silica particles and silicon substrates were hydrophobized simultaneously by immersing them in the OTS solution in toluene. The surface hydrophobicity was altered by varying both the concentration of OTS (0.01–1 mM) in toluene and the immersion time. It was then evaluated using the contact angle, θ, of a drop of solution measured by the sessile drop method using a custom-made contact-angle goniometer built in our lab.

2.3. Force measurement

Force measurements were performed using an AFM (Nanoscope IIIa, Veeco Instruments, USA) with a quartz fluid cell. The cantilevers mainly used were the stiff and rectangular silicon cantilevers (NCH, Nanosensors, Switzerland). In the force measurements, the colloid probe was brought close to the sample plate and the displacement of the probe by interaction forces was recorded against the driving distance of the probe toward the plate. Then the data were converted to force-separation distance curves following the method by Ducker et al. [15]. The approaching velocity of the surfaces was set to 100 nm/s.

3. Results and discussion

3.1. Interaction between surfaces with varied hydrophobicity

The approaching force curves between the OTS-hydrophobized surfaces in water without the removal of surface bubbles are shown in Fig. 1. The contact angle of the surface against water was 106°, and the force curves were measured at three different points on the silicon wafer surface. In the same figure, the theoretical curve for the van der Waals force between a sphere and a plate is also shown for comparison. The van der Waals force was calculated by

$$\frac{F_{\mathrm{vdW}}}{R} = -\frac{A}{6h^2}, \tag{1}$$

where h, R and A are the separation distance, particle radius of the colloid probe and the Hamaker constant respectively. The value of the Hamaker constant used was 0.8×10^{-20} J, which is for a hydro carbon–water–hydrocarbon system [16].

In all the force curves, long-range attractive forces with a range of 50–150 nm appeared with steps at the points where the attractive forces appeared, as shown by the arrows in Fig. 1. The origin of these attractive forces is attributed to the bridging of the nanobubbles on the surfaces because the attractive forces were much longer-ranged than the van der Waals force and because the step is a specific feature observed usually with the bubble-bridging force [12]. The differences in the strengths and ranges of the forces depending on the measurement point are suggested to reflect differences in the sizes of the nanobubbles on the surfaces.

In order to remove the bubbles attached onto the hydrophobic surfaces, the solution-exchange method was used [14]. In this process, ethanol, which can completely wet a hydrophobic surface, was introduced into the AFM liquid cell. Then, the ethanol was replaced by an ethanol–dimethyl sulfoxide (DMSO) mixture. The solution was further replaced by DMSO, followed by a DMSO–water mixture. Finally, the surfaces were rinsed repeatedly by flushing copious amounts of water into the cell. The reason why DMSO was used together with ethanol is because mixing ethanol directly with water often produces large amounts of bubbles in bulk solution, thus increasing the probability of bubbles attaching to the surfaces [19]. Because DMSO has a surface tension value between those of water and ethanol, the use of DMSO can prevent the production of bubbles in the solution.

The approaching force curves measured at three different points after the bubble-removing process are shown in Fig. 2. The attractive forces become shorter-ranged and appear at approximately

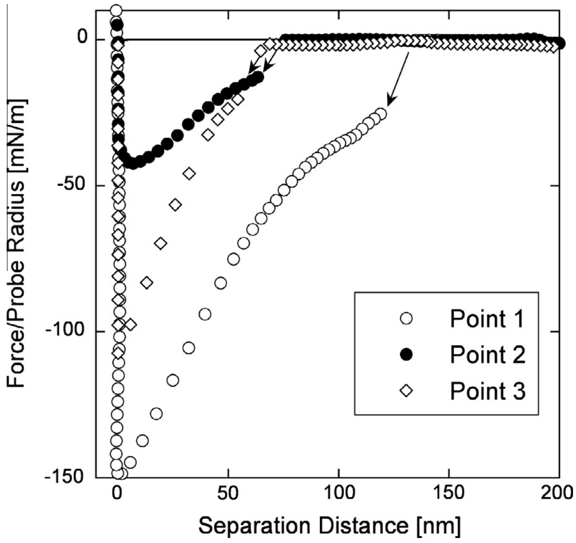

Fig. 1. Approaching force curves between OTS-coated surfaces with a contact angle of 106° measured in water. The force curves measured at three different points on the sample plate are shown. The solid line shows the van der Waals force.