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Excess thermodynamic properties of thin water films confined between hydrophobized gold surfaces

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ABSTRACT

Surface forces between gold surfaces were measured in pure water at temperatures in the range of 10–40 °C using an atomic force microscope (AFM). The surfaces were hydrophobized by self-assembly of alkanethiols (C_nSH) with $n = 2$ and 16 in ethanol solutions. The data were used to determine the changes in excess free energies (ΔG^f) of the thin water films per unit area by using the Derjaguin approximation [1]. The free energy data were then used to determine the changes in excess film entropy (ΔS^f) and the excess film enthalpy (ΔH^f) per unit area. The results show that both ΔS^f and ΔH^f decrease with decreasing film thickness, suggesting that the macroscopic hydrophobic interaction involves building some kind of structures in the intervening thin films of water. It was found that $|\Delta H^f| > |T\Delta S^f|$, which is a necessary condition for an attractive force to appear when the enthalpy and entropy changes are both negative. That macroscopic hydrophobic interaction is enthalpically driven is contrary to the hydrophobic interactions at molecular scale. The results obtained in the present work are used to discuss possible origins for the long-range attractions observed between hydrophobic surfaces.

1. Introduction

The DLVO theory has served colloid science and technology well for the past 70 years. It can predict the stability of colloidal suspensions and wetting films on the basis of balancing the attractive van der Waals-dispersion and repulsive double-layer forces. However, many investigators, including Derjaguin himself, found that the theory fails to predict the stability of very hydrophilic and very hydrophobic particle suspensions [2–5]. According to Churaev [6], it works well for particles whose contact angles (θ) are in the range of 20–40°. Outside this narrow range of surface hydrophobicity, structural forces play a role. These non-DLVO forces are repulsive when $\theta < 20°$ and attractive when $\theta > 40°$.

The structural forces are considered to originate from overlapping boundary layers possessing special features related to long-range molecular forces [2,7]. The presence of the repulsive structural force was first recognized by the large positive disjoining pressures measured for the wetting films of water formed on hydrophilic substrates such as mica [8] and silica [9]. Israelachvili and Pashley [10] were the first to measure attractive forces between hydrophobized mica surfaces with $\theta = 64°$ that were about an order of magnitude larger than the van der Waals-dispersion force. This non-DLVO force was called hydrophobic force. Rabinovich and Derjaguin [11] measured even larger and longer-range hydrophobic forces between silica filaments with $\theta = {\sim}100°$. These investigators considered the hydrophobic force to originate from the structural changes in the overlapping boundary layers as two surfaces approach each other. Eriksson et al. [12] attributed the hydrophobic force to the presence of the surface-induced water structure, which decays with the separation distance between two hydrophobic surfaces.

Follow-up measurements conducted by numerous other investigators confirmed the presence of the non-DLVO attractive forces as summarized in review papers [13,14]. Some investigators suggested that they are 'true' hydrophobic forces [15,16], while others presented rather convincing evidence that the long-range attractions are caused by the bubbles adhering to hydrophobic surfaces [17–19]. More recent work [20,21] showed, however, that long-range attractions are still being observed in degassed solutions, which reduces the possibility of bubbles or cavities causing the long-range attractions. Many investigators measured hydrophobic forces while there were no signs of bubbles present on hydrophobic surfaces [21–23]. The most recent view on the subject is that while the short-range attractions observed at film thicknesses below approximately 20 nm are true hydrophobic force, the longer-range attractions may not be related to surface hydrophobicity [20,24]. It has been shown, however, that the range of hydrophobic

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force increases with increasing chain length of *n*-alkane homologs [25] and water contact angle [26,27].

Miklavic et al. [28] proposed a model for the long-range hydrophobic forces based on the concept that an ionic surfactant adsorbs on a surface and forms patches (or hemi-micelles), leaving part of the surface unoccupied. In this case, the surface would have a mosaic structure consisting of patches of positive and negative charges, which can then correlate to give rise to a long-range attractive force. For this mechanism to work, the surfactant would have to adsorb physically so that the patches can have sufficient lateral mobility to enable charge correlation. According to this approach, long-range attractions should not be observed between surfaces hydrophobized with chemisorbing surfactants such as alkanethiols. However, long-range attractions were still observed between gold surfaces coated with 1-hexadecanethiol with no signs of bubbles causing them [22].

Several theoretical chemists carried out molecular simulations to explore the possibility that the hydrophobic force arises from structural changes in the interlayer of water relative to that of bulk water [29–32]. The results invariably showed, however, that the structural changes are limited to only a few molecular distances away from surface, while long-range attractions are measured in experiment at separations as large as 80 nm. It may be useful to note here that the excess free energies per molecule related to the long-range attractions are in the range of 10^{-5}–10^{-3} kT [12], while molecular dynamics simulations would have difficulties in detecting changes in energy below ~0.1 kT per molecule due to limitations in accuracy.

In the present work, we have measured hydrophobic surface forces at different temperatures to determine the changes in excess thermodynamic properties, *i.e.*, free energy, enthalpy, and entropy, associated with the hydrophobic interaction between macroscopic surfaces. The measurements were conducted using an atomic force microscope (AFM) capable of controlling the temperature of the liquid cell. The force measurements were conducted between gold surfaces hydrophobized with alkanethiols (C_nSH) with $n = 2$ and 16. Thermodynamic analysis of the results shows that the hydrophobic interaction at macroscopic scale is predominantly enthalpic, contrary to the largely entropically driven hydrophobic effect at molecular scale [33]. The results seem to support the structural origin of the hydrophobic force.

2. Materials and methods

2.1. Materials

Two alkanethiols, *i.e.*, ethanethiol (C_2SH, 98%) and 1-hexadecanethiol ($C_{16}SH$, ≥97%), from TCI America were used as hydrophobizing agents for gold substrates without further purification. Both were used as solutions in pure ethanol from Decon Laboratories, Inc. The gold substrates were cleaned before hydrophobization with H_2SO_4 (98%) and H_2O_2 (29.0–32.0%) from VMR International and Alfa Aesar, respectively. A Millipore Direct Q-3 (Millipore, MA) water purification system was used to obtain conductivity (Ultrapure) water with a resistivity greater than 18.2 MΩ/cm at 25 °C.

2.2. Preparation of flat gold surfaces and spherical gold probes

Flat gold surfaces (0.5 × 0.5 in.) were prepared by coating smooth glass plates with thermally evaporated gold (~500 Å thickness, 99.9% Au) in a vacuum evaporator. Prior to the gold coating, a glass plate was coated first with a layer of chromium (~50 Å thickness) to promote the adhesion of gold on glass plate. The AFM images of the gold-coated plates showed root mean square (rms) roughness of approximately 0.8 nm over an area of 1 × 1 μm^2. Gold spheres were produced by short-circuiting a gold wire (12.7 μm diameter, 99.9% Au, Alfa Aesar) at 120 V AC over a glass tray as described by Raiteri et al. [34]. Of the various sizes of gold spheres produced, only those with radius of 3–7 μm were used for surface force measurements.

Gold spheres were attached onto the tips of AFM cantilevers with a solid polymer glue (Epon 1004, Shell Chemical Co.) by means of a three-dimensional translation stage equipped with a hot plate and an optical microscope (BH2, Olympus). The radius of the gold sphere was measured under the optical microscope. Before gluing a gold sphere onto a cantilever tip, the latter had been cleaned thoroughly by ethanol, followed by UV irradiation for 10 min.

2.3. Cleaning and hydrophobization of gold surfaces

The gold-coated glass plates were cleaned of carbonaceous impurities by soaking them in a boiling piranha solution (1:2 mixture of H_2O_2 and H_2SO_4 by volume) for 20 min, followed by washing in Ultrapure water for 1 min and subsequently in ethanol for 2 min. The gold spheres, on the other hand, were cleaned by ethanol wash after they had been glued onto AFM cantilevers, followed by UV irradiation for 2 h and another ethanol wash. Washing them in boiling piranha solutions would have unglued the spheres.

After the cleaning procedure, a set of gold sphere and plate was immersed in a 10^{-5} M C_2SH-in-ethanol (or $C_{16}SH$-in-ethanol) solution for 15 min, so that thiols form self-assembled monolayers on the gold substrates and hydrophobize them. After the hydrophobization, the surfaces were rinsed thoroughly with pure ethanol, Ultrapure water, and then blow dried in an ultra high purity N_2 stream before AFM force measurements.

2.4. AFM surface force measurement

Surface force measurements were conducted using a NanoScope IVa AFM (MultiMode, Digital Instruments, Inc.). The instrument was equipped with a heater/cooler accessory, which enabled force measurements at controlled temperatures. Primary components of the temperature control system included a Peltier element, a high-temperature piezoelectric scanner "J" with a cooling system, and a thermal applications controller (TAC) that controls the temperature of the liquid in a fluid cell.

The force measurements were conducted with the triangular silicon nitride cantilevers (NP-20, Veeco Probes, Inc.), whose spring constants were determined using the resonant frequency technique [35]. The closest separation distances (h) between a gold sphere and a gold-coated glass plate were measured by monitoring the deflection of the cantilever on which the gold sphere was attached. Measured forces (F) were normalized by the radius (R) of gold sphere and plotted vs. h.

In the present work, surface forces between thiolated gold plate and sphere were measured in pure water at temperatures in the range of 10–40 °C. A given pair of sphere and plate was used to complete a temperature cycle. Initially, the measurements were conducted at 10 °C first and subsequently at 20, 30, and 40 °C. It usually took 15 min for the temperature to rise by 10 °C and reach equilibrium. After the measurement at 40 °C, the temperature was brought back to 20 °C and the force measurement was repeated to check the reproducibility and the stability of the hydrophobic surfaces at the higher temperatures. It was found that the force measurements were reproducible in the temperature range investigated, and the data presented here are the most representative of 2–3 repeat experiments conducted at a given temperature.