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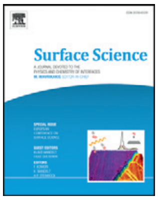

Force measurement reveals structure of a confined liquid: Observation of the impenetrable space

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ABSTRACT

Understanding of the structure of a confined liquid is an important subject for developments in surface science, tribology, biophysics, etc. In this study, we propose its measurement theory and conduct a test of the theory. The measurement theory uses a force curve obtained by surface force apparatus and transforms the force curve into the confined liquid structure. To check the validity of the measurement theory, we perform a verification test in a computer. It is found that the theory can semi-quantitatively reproduce the confined liquid structure. The theory will lead to the first step toward measuring a liquid structure confined between optically impenetrable substrates.

1. Introduction

Recently, structural analyses of nano-materials and nano-systems are important subjects. Similarly, the analysis of a confined liquid structure is also important, because it is related to surface science, tribology, biophysics, and so on. The confined liquid structure has been experimentally studied by several researchers using, e.g., surface force apparatus (SFA) and atomic force microscopy (AFM). The studies by SFA [1–6] have revealed the peculiar phenomena of the confined liquid: oscillatory force between the two surfaces, symptoms of evaporation and solidification, rapid increase of the liquid's viscosity. AFM has also revealed the confined liquid's property [7–9]. Although these instruments can detect the oscillatory force suggesting structural layering within the confined space between the probe and the sample surface, they have not directly measured the structure of the confined liquid itself. On the other hand, x-ray and neutron experiments are able to measure the confined liquid structure [10–12] as well as the structures of liquid/air [13,14], liquid/liquid [15], liquid/solid [16–18] interfaces by analyzing these experimental results. The x-ray and neutron experiments are useful for determination of the confined liquid structures; however, many of the structures have not been measured due to the difficulties of the experimental setup and condition. The confined liquid structure has been studied also by statistical mechanics of liquids [19–21], density functional theory [22,23], and simulations [24–28]. These theoretical studies have indicated the structural layering within the confined space and the local phase transitions. In this way, the confined liquid structures have been experimentally and theoretically studied much, and these studies are significant for elucidation of the properties of the confined liquids.

In this study, we present a measurement theory (a theory for the experiment) which calculates the confined liquid structure from the force curve obtained by SFA. Here, we call it the transform theory. The transform theory has two advantages. One is that one can obtain the liquid structure without x-ray and neutron. The other is that one can obtain the liquid structure even if the substrates are opaque, because recent SFA named twin-path SFA [6] can use opaque substrates in the measurement of the force curve. Of course, both the SFA and transform theory have weak points in accuracies at the present time. However, in our view, this measurement strategy is important to obtain the confined liquid structure between the opaque substrates. The transform theory plays an important role when the force curve is interpreted as or compared with the liquid structure.

Transformation from the force curve into the solvation structure (local liquid structure) is comparatively a new subject. In 2010, Kimura et al. [29] have derived a simple relationship between the force curve measured by AFM and the liquid structure on a single surface (not confined). In the theory, the tip apex is approximated by a delta function and there are no considerations about the volume of the probe and the solvent's entropy. According to the theory, the AFM probe receives zero force when it overlaps with the solid surface. (When the probe overlaps with the solid surface, it should receive strong repulsive force.) Then, recently, Watkins et al. [30] and Amano et al. [31] independently proposed a relational expression by approximating the probe as one solvent molecule (it is called the ideal probe). It has been found that the theory functions when the solvent molecule or a very similar one is located on the tip apex. Therefore, it has been concluded that a nearly ideal probe is required in the real experiment in order to precisely

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measure the solvation structure [31]. Just recently, the transform theory for SFA has also been proposed by Amano and Takahashi [32]. In the theory, the solvent molecule is approximated by a sphere and two-body potential between solvent molecules is arbitrary. However, two-body potential between the solvent molecule and solid surface (SFA probe) is approximated to rigid. Using the theory, the liquid structure on the single surface was reproduced from the force curve. It has been found that the force is proportional to the liquid density on the contact surface and the theory works better when the number density of the solvent is lower and the two-body potential between solvent molecule and solid plate is close to the rigid potential.

The outline of the paper is as follows. The theoretical and computational details of the transform theory are given in Chapters 2.1 and 2.2, respectively. To check the validity of the transform theory, its verification test is performed in a computer, results of which are shown in Chapter 3. In the test, a force curve between two walls is numerically calculated by using a traditional liquid theory. Then, the force curve is substituted into the transform theory as an input. This computational test is important for practical realization of the theory. It will be shown that the transform theory can semi-quantitatively reproduce the confined liquid structure. Finally, in Chapter 4, the conclusions are written.

2. Theory and computation

2.1. Theoretical details

To calculate the confined liquid structure from the force curve, two transform theories are used. One is an application of the theory written in [32]. In the theory, the two solid surfaces are rigid wall, and thus we call it RW theory. On the other transform theory, the two solid surfaces have soft potential with rigid wall with the solvent molecule, i.e., two-body potential between the solid surface and the solvent molecule is soft potential with rigid wall [33]. Therefore, we call it SPRW theory. Two key concepts for calculation of the confined liquid structure are (I) there is information about the confined liquid structure in the force curve, i.e., the force curve is determined by the confined liquid structure; (II) the information about the confined liquid structures are preserved in the liquid structure on a single wall calculated by RW and SPRW theories, because Kirkwood superposition approximation [34–36],

$$\rho(z;s)=\rho_0 g_{\mathrm{tot}}(z;s)\approx\rho_0 g_1(z)g_2(z-s),\tag{1}$$

used in RW and SPRW theories, cannot offset the compression phenomenon of the interlayer spacing caused by the sandwiching, i.e., the liquid structures on a single wall calculated by RW and SPRW theories essentially include properties of the confined liquid structures. Here, ρ is the number density of the confined liquid, ρ_0 is the bulk number density (which is constant), g_{tot} is the normalized number density of the confined liquid, and g_i ($i = 1$ or 2) is a pair correlation function between the solid i and solvent (g_i is the so-called normalized number density of the solvent or a solvation structure). We notify that g_i is that for an isolated solid i. In other words, the solid i immersed in the bulk solvent has the solvation structure g_i on its flat surface. z and s represent displacement from the center of the circular surface of solid 1 and separation between solid plates 1 and 2 (see Fig. 1). The key concepts above lead to the fact that the confined liquid structure can be calculated by the following procedure: (A) calculate the liquid structure on a single wall by using RW or SPRW theory; (B) calculate the confined liquid structure by reusing Kirkwood superposition approximation. (The confined liquid structure can be reproduced by mixing g_1 and g_2 because they, calculated by RW or SPRW theory, essentially contain information about confined liquid structure.)

The derivation process of the SPRW theory [33] is explained here. In our earlier work [32], the transformation is performed by modeling the two-body potential between the solid surface and the solvent molecule as the rigid potential. However, the approximation was very rough. It should be improved to a more realistic model. Hence, the two-body potential for SPRW theory is modeled as attractive (or repulsive) soft potential with rigid wall. SPRW theory is derived based on the statistical mechanics of simple liquids. The theoretical conditions are as follows: the two same solids with flat surfaces are immersed in the solvent; their flat surfaces are parallel; the thickness of the solid is sufficiently long; the diameter of the solvent molecule is d_S (arbitrary value); two-body potential between the solvent molecules is arbitrary in shape, whereas the two-body potential between the solid plate and the solvent molecule is attractive (or repulsive) soft potential with rigid wall. In SFA experiment, the force between two surfaces is measured, and the solvation force can be extracted from the crude force (total force) by subtracting the two-body force between the solid plates. That is, $f_{\mathrm{sol}} = f_{\mathrm{all}} - f_2$, where f_{sol}, f_{all}, and f_2 represent the solvation force, total force, and two-body force, respectively. The two-body force can be measured in the air (vacuum) or theoretically calculated. The solvation force along the z-axis (which acts on the cylindrical solid 2) has a relationship with the number density distribution of the liquid. It can be expressed as [24,32]

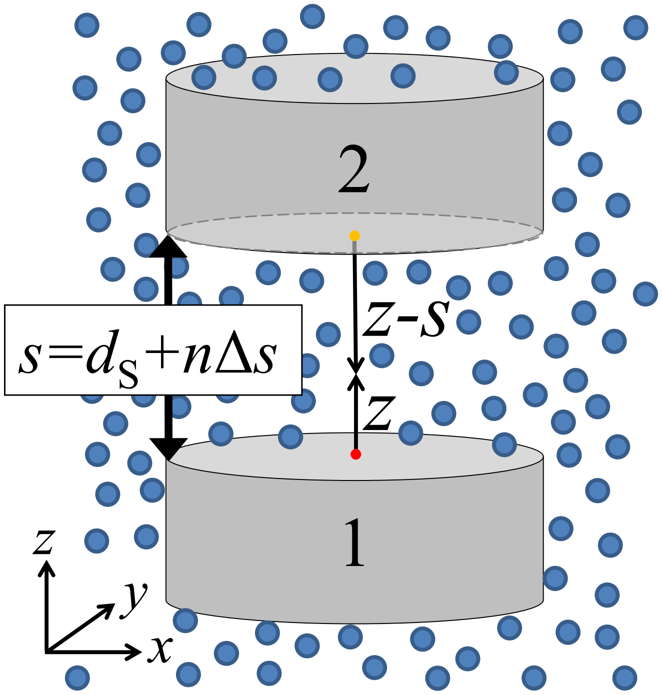

Fig. 1. Schematic view of the system.

$$f_{\mathrm{sol}}(s)=A\int_{-\infty}^{\infty}\rho(z;s)\frac{\partial u_2(z;s)}{\partial z}dz,\tag{2}$$

where A represents surface area of the flat surface i.e., circular surface area of the cylindrical solid 2 (see Fig. 1). $\rho(z;s)$ is the number density of the solvent at z, where the separation between the cylindrical solids is s. u_2 is the two-body potential between cylindrical solid 2 and the solvent molecule. Here, Kirkwood superposition approximation [24,32–36] is applied to ρ, and then Eq. (2) becomes

$$f_{\mathrm{sol}}(s)=A\rho_0\int_0^s g_1(z)g_2(z-s)u_2'(z-s)dz-PA,\tag{3}$$

where u_2' represents the partial differentiation of u_2 with respect to z, and P represents the solvent's pressure on a wall. $-PA$ represents the solvation force acting on the upside of the solid 2, the value of which