



# Simple transform methods of a force curve obtained by surface force apparatus to the density distribution of a liquid near a surface



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## HIGHLIGHTS

- Measurement theory for SFA (Surface Force Apparatus) is proposed.
- Solvation structure can be obtained experimentally by using the theory proposed here.
- Verification tests of the theory are conducted.

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## ABSTRACT

We propose two simple methods that transform a force curve obtained by a surface force apparatus (SFA) into a density distribution of a liquid near a surface of the SFA probe. The transform methods are derived based on the statistical mechanics of simple liquids, where the liquid is an ensemble of small spheres. The solvent species is limited to only one component and two-body potential between the solvent spheres is arbitrary. However, two-body potential between the SFA probe and the solvent is restricted to rigid potential (i.e., the transform methods are derived within the restriction of the rigid potential). In addition, Kirkwood and linear superposition approximations are applied in order to derive the transform methods. The transform methods are simply tested in both hard-sphere fluid and Lennard-Jones (LJ) fluid with hard core potential. The tests are computationally practiced using a three-dimensional integral equation theory. It is found that the transform method with Kirkwood superposition approximation (transform method 1) generally reproduces the more precise solvation structure than that with linear superposition approximation (transform method 2). In the test of the hard sphere solvent, it is found that the reproducibility becomes better as the number density of the solvent is lower. Furthermore, it is found in the test of the LJ fluid that the reproducibility becomes better as the two-body potential between the SFA probe and the solvent approaches rigid potential. This is because, the transform methods are derived within the model of the rigid potential. It is verified that the transform methods are useful for obtaining of a rough image of the solvation structure. (However, if evaporation or solidification, a phase transition in a local space sandwiched between the two surfaces, occurs while the experiment, the transform methods should not be used.)

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## 1. Introduction

The surface force apparatus (SFA) has been used to measure the force acting between arbitrary two surfaces in solvents [1,2]. The two surfaces are the force probes for the experiment of SFA, and they can confine various types of the solvents. The force obtained by SFA is usually shown as the *force curve* whose vertical line is force and horizontal line is separation between the two surfaces. In the force curve, there are mainly two origins of the force factors. One is two-body interaction between the two SFA probes themselves, and the other is the solvation force between them. The solvation force is originated from the many-body interaction of the confined solvent particles, and it is the origin of the oscillation in the force curve. In order to understand why the force curve has such an oscillatory shape, several theoretical studies have been performed in the past decades [3–6]. Due to their studies, the mechanism of the oscillatory shape has already been elucidated, however, there is not the method for transforming the force curve obtained with SFA into the (intrinsic) solvation structure on the surface of the SFA probe. In the present study, hence, we propose two transform methods based upon a theory of statistical mechanics of simple liquids. To derive the two transform methods, we take advantage of Kirkwood [7–9] and linear [3] superposition approximations. In this paper, we call the transform method derived by using the Kirkwood superposition approximation and that derived by using linear superposition approximation transform methods 1 and 2, respectively. To test the validity of the both methods, we computationally perform simple tests in both hard sphere fluid and Lennard-Jones (LJ) fluid with hard core potential.

Recently, M. Watkins et al. [10] and Amano et al. [11] proposed a method for transforming the force distribution measured by atomic force microscopy (AFM) in a solvent [12,13] into the (intrinsic) solvation structure on the solid plate. In the method [10,11], the probe is approximated as a solvent sphere (we call it the ideal probe). This method works well when a solvent sphere or a very similar particle is located on the apex of the probe. Therefore, it has been concluded that a nearly-ideal probe should be used in the real experiment in order to obtain the solvation structure. There have been proposed the simple transform method for AFM to obtain the solvation structure, although the transform method for SFA has not been proposed. This is also the motivation for derivation of the transform methods of SFA. (J.P. Cleveland et al. [14] has also proposed a similar equation in AFM study. However, the proposed one is relation between “the potential the AFM probe experiences” and “the position probability of the AFM probe”.)

In the present theory, SFA measurement is simply modeled as shown in Fig. 1. The two cylindrical solids are immersed in the solvent an ensemble of small spheres. (*In theory*, the two solids do not need to be the same, and triangular, rectangular, pentagonal prisms, and so on can be applied instead of the cylindrical solids.) The solvent species is limited to only one component and two-body potential between solvent spheres is *arbitrary*. However, two-body potential between the SFA probe and the solvent is restricted to rigid potential. A point that should be notified before the derivation of the transform methods is that evaporation and solidification (phase transitions in a local space sandwiched between the two surfaces) are neglected. That is, if the evaporation or solidification occurs in the measurement of the force curve, the force curve must not be used for calculation of the solvation structure.

In the present paper, we particularly explain the derivation process of the transform method 1 (in which Kirkwood superposition approximation is applied) and briefly explain that of the transform method 2 (in which a linear superposition approximation is applied). We obtain the two transform methods starting from a basic equation connecting the solvation force and the solvation structure. (The derivation process of the basic equation is written in the [Appendix](#).) In order to verify the transform methods, simple tests are performed in computer. The tests are conducted in both hard sphere fluid and LJ fluid with hard core potential. In the hard sphere fluid the number density is varied as a parameter, while in the LJ fluid the two-body potential between the SFA probe and the solvent is varied (solvation affinity of the cylindrical solid is varied). As a result, it is found that the transform methods can calculate the rough image of the solvation structure from the solvation force. The accuracies of the transformations are not so high, the reasons of which are originated from introductions of the Kirkwood and linear superposition approximations. However, it is found that the transform method 1 generally reproduces better results in comparison with the transform method 2 (the detailed results of the tests are shown in Chapter 3). In our opinion, the transform method 1 has a potential to become a fundamental method for SFA to obtain the solvation structure. (Recently, some liquid theories [15–18] can calculate the solvation structure very accurately. Thus, one might think that the transform methods here are not valuable methods compared to the liquid theories [15–18]. However, it is not appropriate picture. A different point of the liquid theories and the present transform methods is that the latter can calculate the solvation structure *from* the solvation force obtained by the SFA experiment. That is, the latter is the measurement theory for SFA. Therefore, the former and latter should not be compared directly.)

## 2. Theory

### 2.1. Derivations of the transform methods

In this chapter, derivation processes of the transform methods are written. To start the explanation, we introduce following conditions.

- (I) The solvent considered here is a simple liquid, an ensemble of the small spheres. Two-body potential between the solvent spheres is arbitrary.

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