Inverse calculation of three-dimensional solvation structure on an arbitrary surface from a force distribution measured by liquid AFM

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Abstract. Recent frequency-modulated atomic force microscopy (FM-AFM) can measure the three-dimensional force distribution between a probe and a sample surface in liquid. The force distribution is currently regarded to approximate the solvation structure on the surface, because shapes of the force distribution and the solvation structure are somewhat similar to each other. However, the force distribution is never the solvation structure. Therefore, we propose a method that converts the force distribution to the solvation structure. (This conversion is an example of inverse calculations.) A new benefit of the method is that it can perform the inverse calculation without any simplifications of the shape and the solvation affinity of the actual probe tip in a three-dimensional system.

1. Introduction
Recent frequency-modulated atomic force microscopy (FM-AFM) can measure the three-dimensional force distribution between a probe and a sample surface in liquid [1]. The force distribution is currently regarded to approximate the solvation structure on the surface (local liquid’s density), because shapes of the force distribution and the solvation structure are somewhat similar to each other. However, the force distribution is never the solvation structure. When we wish to obtain the solvation structure by using the liquid AFM, a method for converting the force distribution into the solvation structure is necessary. Therefore, in this paper, we briefly show a converting method. We call this method an inverse calculation, because in a general calculation process the solvation structure is first obtained and the force distribution is obtained next.

There have already been two conversion methods in the researches of the inverse calculation problem. Amano et al. [2,3] and Watkins and Reischl [4] independently constructed a relational expression between the force and the solvation structure. The relational expression can be used for converting the force into the solvation structure. However, in the theory, the probe tip is approximated to be one solvent particle and the other parts of the probe are completely ignored. The model probe is called an ideal probe. Although the introduction of the ideal probe enables us to perform the inverse calculation very easily, the approximation is considered to be not small. To reduce the character of approximation, Amano [5] proposed another conversion method. In the method, the probe is modeled as a sphere with an arbitrary size and its solvation affinity is also arbitrary. However, the sample surface is modeled as a spherical shell and the calculation system is limited to a one-dimensional system in order to finalize the calculation within a practical time length. Furthermore, this method uses...
an empirically optimized trial function. Since the above two methods contain these problems, another efficient solution has to be developed.

The solution for the inverse problem proposed here is clearly different from the above two previous methods. In the new method, the probe tip with an arbitrary shape is employed in the theory. Furthermore, the model probe can take various surface properties. Of course, the conversion can be performed for three-dimensional systems. These improvements are realized by the completely new approach as explained in the next chapter.

2. Inverse calculation of three-dimensional solvation structure

In what follows, we explain the method for converting the force distribution measured by the liquid AFM to the three-dimensional solvation structure. As mentioned above, the system considered here is three-dimensional and the shape and solvation affinity of the probe tip are arbitrary. The shape and solvation affinity of the sample surface are also arbitrary. A solid plate which is fixed at a given position represents the surface sample. Here, we consider the probe and the solid plate in a simple liquid, i.e. an ensemble of small spheres where the two-body potential between the spheres is rigid, square-well, or Lennard-Jones, etc. In this situation, “mean force between the probe and the solid plate in the solvent” minus “two-body force between them in vacuum”, which we call the solvation force acting on the probe \( f_{DP} \), can be expressed as:

\[
\begin{align*}
\mathcal{f}_! & = \rho_! g_{DP} \left( \frac{\partial u_{PS}}{\partial \mathbf{r}} \right) d\mathbf{r}.
\end{align*}
\]

where the subscripts D and P represent the solid plate and the probe, respectively, and the integral represents a volume integral. The solvation force is assumed to be a conservative one in this theory. \( \mathbf{r}_D \) and \( \mathbf{r}_P \) are the position vectors of the solid plate and the probe, respectively. \( \rho(\mathbf{r}; \mathbf{r}_D, \mathbf{r}_P) \) is the number density of the solvent at \( \mathbf{r} \), the solid plate and the probe being positioned at \( \mathbf{r}_D \) and \( \mathbf{r}_P \), respectively. \( u_{PS} \) is the two-body potential between the probe and the solvent particle, where the subscript S represents the solvent particle. The partial differentiation of vector \( \mathbf{r} \) is denoted as \( \partial / \partial \mathbf{r} = (\partial / \partial x) \mathbf{e}_x + (\partial / \partial y) \mathbf{e}_y + (\partial / \partial z) \mathbf{e}_z \), where \( \mathbf{e}_i \) (i = x, y, or z) is the unit vector along i-axis. Eq. (1) derived by considering an infinitesimal movement of the probe in the system is an exact one in classical statistical mechanics of liquid. This equation is strictly consistent with the contact theorem [6-9]. (The contact theorem explains the pressure on a wall, the derivation of which is performed by an infinitesimal change of the system or solute volume.) In experiments of the liquid AFM, the sample surface is fixed whereas the position of the probe is artificially changed, and they obviously do not change their own orientations. In such a case, there is no need to consider orientational (rotational) factors in Eq. (1). To connect the solvation force \( f_{DP} \) and the solvation structure on the solid plate \( g_{DS} \), we take advantage of Kirkwood superposition approximation [10] and express \( g \) as \( \rho_0 g_{DS} g_{PS} \) [11,12] where \( \rho_0 \) is the bulk number density of the solvent (which is constant) and \( g_{ij} \) is the pair correlation function between i and j. Here, setting the position of the solid plate at the origin \( (\mathbf{r}_D = 0) \), \( f_{DP} \) is rewritten as:

\[
\begin{align*}
f_{DP}(\mathbf{r}_P) &= \rho_0 \int g_{DS}(\mathbf{r}) g_{PS}(\mathbf{r} - \mathbf{r}_P) \frac{\partial u_{PS}(\mathbf{r} - \mathbf{r}_P)}{\partial \mathbf{r}} d\mathbf{r}.
\end{align*}
\]

Then, we introduce a function \( q_{PS} \) which is defined as:

\[
q_{PS}(\mathbf{r} - \mathbf{r}_P) = g_{PS}(\mathbf{r} - \mathbf{r}_P) \frac{\partial u_{PS}(\mathbf{r} - \mathbf{r}_P)}{\partial \mathbf{r}}.
\]

Thus, \( f_{DP} \) is expressed as:
\[ f_{DP}(r_P) = \rho_0 \int g_{DS}(r) q_{PS}(r - r_P) dr. \]  

Noticing that both sides in Eq. (4) are three-dimensional vectors, it can be rewritten as:

\[
\begin{align*}
    f_{DPx}(r_P)e_x + f_{DPy}(r_P)e_y + f_{DPz}(r_P)e_z \\
    &= \rho_0 \int g_{DS}(r) \left[ q_{PSx}(r - r_P)e_x + q_{PSy}(r - r_P)e_y + q_{PSz}(r - r_P)e_z \right] dr.
\end{align*}
\]  

Thus, the distribution of the solvation force along the z-axis (which can be measured by the liquid AFM) is simply expressed as:

\[
\begin{align*}
    f_{DPz}(r_P) &= \rho_0 \int g_{DS}(r) q_{PSz}(r - r_P) dr = \rho_0 \int h_{DS}(r) q_{PSz}(r - r_P) dr + \rho_0 \int q_{PSz}(r - r_P) dr, \\
    &= \rho_0 h_{DS}(r) q_{PSz}(r - r_P) + \rho_0 q_{PSz}(r - r_P).
\end{align*}
\]  

where \( h_{DS} = g_{DS} - 1 \), which is a so-called total correlation function. The introduction of \( h_{DS} \) enables us to perform the Fourier transforms, because \( h_{DS}(\infty) = 0 \) whereas \( g_{DS}(\infty) = 1 \). The second integral of the right-hand side in Eq. (6) becomes zero, because the integral represents the solvation force acting on the probe in the bulk solvent, i.e., when the probe is infinitely separated from the solid plate, the force acting on the probe is zero. (The second integral corresponds to the z-component of the solvation force of Eq. (2) with \( g_{DS} = 1 \).) Next, we apply the forward Fourier transform to Eq. (6). This operation simplifies the form of Eq. (6):

\[
\begin{align*}
    f_{DPz}(k) &= \rho_0 h_{DS}(k) q_{PSz}(k),
\end{align*}
\]  

where the symbol ‘\( \sim \)’ represents the forward Fourier transform. This equation can be rewritten as

\[
\begin{align*}
    h_{DS}(k) &= \frac{f_{DPz}(k)}{\rho_0 q_{PSz}(k)}.
\end{align*}
\]  

Finally, the object of this derivation \( g_{DS} \) can be obtained as follows:

\[
\begin{align*}
    g_{DS}(r) &= \mathcal{F}^{-1} \left[ \frac{f_{DPz}(k)}{\rho_0 q_{PSz}(k)} \right] + 1,
\end{align*}
\]  

where \( \mathcal{F}^{-1} \) represents the backward Fourier transform. This is the solution for the inverse problem in the liquid AFM. This simple equation explains how to get the three-dimensional solvation structure from the three-dimensional distribution of solvation force.

### 3. Conclusions

The method for converting the force distribution along the z-axis measured by the liquid AFM to the solvation structure (local liquid’s density) on the sample surface was derived based on the statistical mechanics of liquid where we take advantage of the contact theorem and Kirkwood superposition approximation. The input of the solvation force was assumed to be conservative. This inverse calculation requires \( u_{PS} \) and \( g_{PS} \) as inputs. An improved point against the previous conversion methods is that it can calculate the three-dimensional solvation structure without any changes of the actual shape and solvation affinity of the probe tip (i.e., the shape and solvation affinity of the probe tip are not simplified to solve the inverse calculation problem).
A concern about the new method is the inclusion of Kirkwood superposition approximation. This approximation cannot treat the phase transition occurring between the surfaces of the solid plate and the probe. Therefore, if there is a possibility of the phase transition, the conversion method should not be used. Fortunately, however, in some simple liquids, the approximation has been verified to be useful [11,12]. That is, the approximation can capture the confined solvation structure in the simple liquids. In the near future, we improve the approximation from both theoretical and empirical standpoints to increase accuracy of the conversion method.

X-ray and neutron scatterings can measure solvation structures. However, their experimental conditions are limited to the crystal surface, because they require periodicity on their samples. In contrast, the liquid AFM does not require such periodicity. Hence, the solvation structure on the amorphous plate can be obtained by using both the liquid AFM and the conversion method proposed here, if measurement accuracy of the liquid AFM is very high. The solvation structure on a biomolecule that is adsorbed on a plate is also of interest as an application of this conversion method.

Our new method contains significant progresses in the field of the liquid AFM, because the shape and solvation affinity of the probe tip need not be changed in the inverse calculation. In the near future, we will write a calculation program for the inverse calculation and show how the new conversion method works.

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