Smart MD-Sampling Method for Interfacial Free Energy between Polymer-Grafted Substrate and Liquid

Masayuki Uranagase[1] and Shuji Ogata[1]

[1]Department of Physical Science and Engineering, Graduate School of Engineering, Nagoya Institute of Technology, Gokiso-cho, Nagoya, Aichi 466-8555, Japan

ABSTRACT

A novel and efficient scheme for evaluating the work of adhesion between a liquid and a polymer-grafted surface is proposed. A set of spherically symmetric potentials are gradually inserted at the interface to separate the liquid molecules from the surface according to its shape. This method is applied to the interface between the water and the gold substrate modified by poly(ethylene glycol). We find that the work of adhesion becomes maximum at the intermediate density of grafted poly(ethylene glycol). This is attributed to penetration of the water molecules into grafted poly(ethylene glycol) and hydrophilic interaction between them.

INTRODUCTION

Polymer modification of the solid surface is the important industrial technology to change surface properties such as friction, wettability, and biocompatibility from those of the original surface. When wettability of the liquid on the solid surface is considered, the interfacial free energy is a key quantity for quantitative evaluation of it. The interfacial free energy is also related to the adhesive property of two materials. The adhesive property is quantitatively evaluated via the work of adhesion, which is defined by subtracting the interfacial free energy from the sum of the surface free energies of two materials [1].

The interfacial free energy or the work of adhesion can be experimentally evaluated from the contact angle of the liquid droplet on the solid surface. The framework to estimate the interfacial free energy from the surface free energy is also established [1]. In addition to them, molecular simulations such as molecular dynamics simulation and Monte Carlo simulation are expected to be used for the accurate evaluation of the interfacial free energy. There are several sophisticated methods for the calculation of the free energy through molecular simulations. In particular, thermodynamic integration method is often used to calculate the interfacial free energy or the work of adhesion between the liquid and the solid surface [2,3].

In this paper, we propose the novel scheme for the evaluation of the work of adhesion efficient for polymer-grafted surface via thermodynamic integration and show

results obtained by applying the present method to the interface between the water and the gold substrate modified by poly(ethylene glycol) (PEG).

THEORY

When a system is dependent on a parameter λ, the free energy F of the system, which is a function of λ, is obtained as

$$F(\lambda) = \int_{\lambda_0}^{\lambda} \left(\frac{\partial F}{\partial \lambda}\right) d\lambda' + F(\lambda_0), \quad (1)$$

where λ_0 is the value of λ at the reference state. When the λ dependent potential $V(\lambda)$ is added to the system, that is, the Hamiltonian H of the system is given by $H = H_0 + V(\lambda)$, where H_0 is the Hamiltonian of the original system, the integrand in Eq. (1) is given by

$$\left(\frac{\partial F}{\partial \lambda}\right) = \left\langle \frac{\partial V}{\partial \lambda}\right\rangle, \quad (2)$$

where $\langle A \rangle$ denotes the ensemble average of A. Since the right-hand side in Eq. (2) can be evaluated via molecular simulations, the free energy is obtained by performing integration in Eq. (1) as the difference from the reference state.

The way to appropriately choose λ and $V(\lambda)$ depends on the problem. For the calculation of the work of adhesion between the liquid and the *flat* surface, λ associates with the distance from the solid surface and $V(\lambda)$ is the external potential with planar wall shape which exerts on the liquid molecules [2]. This potential separates the liquid molecules from the solid surface by gradually changing λ, that is, gradually shifting the position of the wall. This method works well when the solid surface is sufficiently flat. However, if this method is applied to the surface with complex structure such as a polymer-grafted surface, the external potential must be shifted over long distance in order to achieve sufficient separation of the liquid molecules from the surface. This may induce some inefficiency.

This inefficiency can be avoided by performing separation of the liquid molecules according to the shape of the solid surface. To do this, we introduce a set of spherically symmetric potentials around atoms selected in advance from the solid surface. Then, by gradually changing λ, the liquid molecules near the atoms selected as centers of potentials are separated from the surface.

In order to construct $V(r; \lambda)$, where r is the distance from the atom selected as the center of the potential, we impose several conditions for $V(r; \lambda)$. First, $V(r; \lambda)$ has both repulsive and attractive parts. Though separation of the liquid molecules is done by the repulsive part of the potential, sudden change in the surface shape of the liquid occurs after the separation if there is no attractive part, which should be avoided. Second, $V(r; \lambda)$ has a finite value for all r in order to uniformly converge to zero for all r in the limit $\lambda \to 0$. Third, $V(r; \lambda)$ is sufficiently smooth as a function of r. Taking these conditions into account, the form of $V(r; \lambda)$ is defined as

$$V(r; \lambda) = \begin{cases} [C_1 + C_2 \exp(-C_3 r)]^{-1} + C_4 & 0 \leq r \leq R_0 \sigma(\lambda) \\ V_{\mathrm{LJ}}(r; \lambda) - V'_{\mathrm{LJ}}(r; \lambda)(r - R_c\sigma(\lambda)) - 0.5 V''_{\mathrm{LJ}}(r; \lambda)(r - R_c\sigma(\lambda))^2 & \\ & R_0\sigma(\lambda) \leq r \leq R_c\sigma(\lambda) \end{cases}, (3)$$

where parameters R_0 and R_c are set to 1.01 and 1.6, respectively, in the present analysis, C ($i = 1, \cdots, 4$) are determined from the continuity condition of the potential at $r = R_0\sigma(\lambda)$ and the value of $V(r; \lambda)$ at $r = 0$, $V_{LJ}(r; \lambda) \equiv V_{LJ}(r; \varepsilon(\lambda), \sigma(\lambda)) = 4\varepsilon(\lambda)\{(\sigma(\lambda)/r)^{12} - (\sigma(\lambda)/r)^6\}$ is the Lennard-Jones potential and ε and σ are dependent on λ. Then, the right-hand side in Eq. (2) is evaluated as

$$\left(\frac{\partial V}{\partial \lambda}\right) = \left(\frac{\partial \varepsilon}{\partial \lambda}\frac{\partial V}{\partial \varepsilon} + \frac{\partial \sigma}{\partial \lambda}\frac{\partial V}{\partial \sigma}\right). \quad (4)$$

In order to separate the liquid molecules from the solid surface, following (P1) – (P4) are performed in order. (Schematic picture is shown in figure 1.)

(P1) Select atoms from the substrate and the polymers grafted onto the substrate as centers of the potentials.

(P2) Separation of the liquid molecules is performed by gradually increasing λ of a set of potentials. Here, σ linearly increase with λ, while ε is constant. The free energy difference between final and initial states in this process is denoted by ΔF_2.

(P3) When the liquid molecules sufficiently separated from the solid surface, the solid surface will rarely affect the liquid molecules. Then, the solid surface is decoupled from the liquid. That is, there is no interaction between the solid surface and the liquid molecules. The free energy difference through this process is expected to be extremely small compared to other processes because of sufficiently small interactions between the liquid and the solid surface due to the separation process (P2). Therefore, we neglect the free energy difference in this process.

(P4) Potentials gradually shrinks by decreasing λ. Here, ε as well as σ linearly decreases with λ. The free energy difference between final and initial states in this process is denoted by ΔF_4.
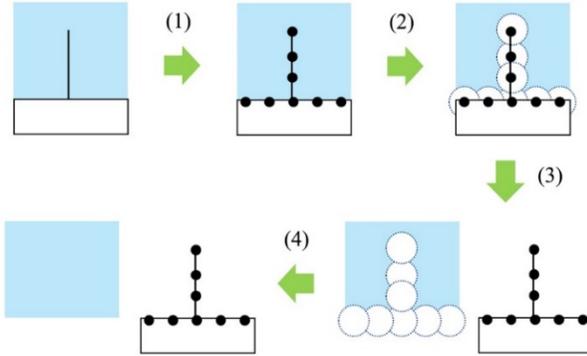
Figure 1. Schematic picture of the operation for separation of the liquid molecules from the solid surface. (1) Selection of atoms which become centers of potentials. (2) Separation of the liquid molecules near the atoms selected in (1). (3) Removal of the surface. (4) Recovery of the liquid with free surfaces.

Since the final state in (P4) corresponds to the state where the liquid and the solid surface independently exist, the work of adhesion is evaluated by the free energy difference between the final state in (P4) and the initial state in (P2). Therefore, the work of adhesion is obtained as the sum of ΔF_2 and ΔF_4. Note that the surface structure becomes natural for the initial state in (P2) and the final states in (P4) though the liquid surface is artificially deformed at the intermediate state by using a set of spherical potentials.

In this paper, we apply the present method to the interface between the water and the gold substrate modified by PEG. The dimensions of the gold substrate in $[\bar{1}10]$, $[\bar{1}\bar{1}2]$, and $[111]$ are 43 Å, 40 Å, and 14 Å, respectively. This surface gathers much attention in the field of biological engineering because it resists adsorption of proteins [4]. There are several works related to the interface between the water and this surface [5, 6] because hydrophilicity of the surface is partially related to the resistance of protein adsorption. The interface studied in this paper is modeled as follows. PEG whose formula is $CH_3(OCH_2CH_2)_6CH_2SH$ is grafted onto (111) surface of the gold substrate. If PEG is fully grafted onto the surface, the grafting points consist of $\left(\sqrt{3} \times \sqrt{3}\right)R30°$ lattice. Then, grafting points of PEG is randomly selected from this $\left(\sqrt{3} \times \sqrt{3}\right)R30°$ lattice in order to obtain the surface with desirable density of PEG. Below, the density of grafted PEG normalized by that when (111) surface is fully modified by PEG is denoted by ρ. 5400 water molecules are put on this surface. The TIP4P model is adopted for the water molecules. Periodic boundary condition is applied in all directions, but there is a slab between one of the water surface and the bottom of the substrate. Short range interaction among gold atoms is evaluated via the Lennard-Jones potential whose parameters are taken from Ref. [7]. Parameters related to short range interaction of PEG and interaction between PEG and a water molecule are taken from Ref. [8].

Velocity Verlet method is used to solve equations of motion. However, since the TIP4P model treats a water molecule as the rigid body, it is necessary to solve equations of motion for rotational degrees of freedom. Here, the scheme developed by Kajima *et al.* [9] is applied to solve them. Temperature keeps 300 K via the method by Bussi *et al.* [10]. We have confirmed that this thermostat works well throughout the processes (P2) and (P4).

DISCUSSION

Figure 2(a) shows $\partial F / \partial \lambda$ as a function of λ for $\rho = 0.6$ when λ increases from 0 according to (P2). Here, we set $\sigma = 7.2\ \lambda$ Å and $\varepsilon = 0.13$ eV. Oxygen and sulfur atoms in PEG are selected as centers of potentials. In addition, gold atoms in the surface layer which do not modified by PEG are also chosen as centers of potentials. At first, $\partial F / \partial \lambda$ decreases when λ exceeds 0.2. This corresponds to the attraction of the water molecules near oxygen, sulfur, or gold atoms due to the attractive part of the potentials. Decrease in $\partial F / \partial \lambda$ continues around $\lambda = 0.3$. Then, $\partial F / \partial \lambda$ increases because of the repulsion of the water molecules near oxygen, sulfur, or gold atoms due to repulsive part of potentials. $\partial F / \partial \lambda$ decreases again when λ exceeds 0.4. This is because the interactions between the water molecules and oxygen or sulfur atoms become week due to sufficient separation of the water molecules by the potentials and the attractive part of the potentials spreads. Another peak in $\partial F / \partial \lambda$ is appeared at $\lambda \simeq 0.55$, which corresponds to the separation of the water molecules near carbon or hydrogen atoms in PEG. When λ exceeds 0.6, $\partial F / \partial \lambda$ monotonically decreases. By numerically integrating this curve by the trapezoidal method, the difference ΔF_2 between the free energies at $\lambda = 1$ and $\lambda = 0$ is calculated as 15.42 eV.
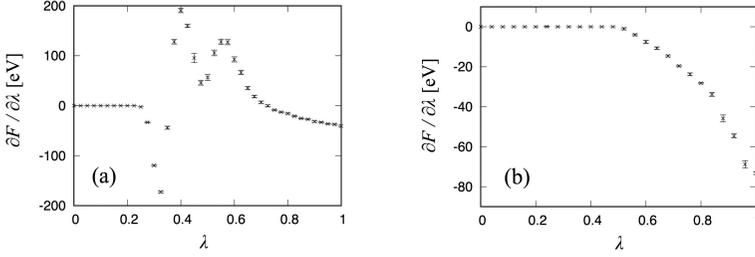
Figure 2. $\partial F/\partial \lambda$ as a function of λ for (P2) (a) and (P4) (b). Standard deviations are evaluated from 10 samples.

Figure 2(b) shows $\partial F/\partial \lambda$ as a function of λ for $\rho = 0.6$ when λ decreases from 1 according to (P4). Here, both σ and ε linearly change with λ as 7.2 λ Å and 0.13 λ eV, respectively. Unlike the case of (P2), $\partial F/\partial \lambda$ monotonously changes with λ. When λ is less than 0.5, $\partial F/\partial \lambda$ is approximately equal to 0. This results from the fact that the liquid surface becomes flat which is a natural state. The difference ΔF_4 between the free energies at $\lambda = 1$ and $\lambda = 0$ is evaluated as 14.18 eV from the numeric integration.

Next, we discuss the dependence of the free energy on the density ρ of grafted PEG. Figures 3(a) and (b) show the dependence of ΔF_2 and ΔF_4 on ρ. Note that the behavior of $\partial F/\partial \lambda$ is similar to figure 2 for every ρ except $\rho = 0$, where the second peak in the process (P2) disappears because there is no PEG grafted onto the gold substrate. ΔF_2 becomes relatively small at $\rho = 1$, while ΔF_4 becomes large at $\rho = 0.2$ and 0.4. The work of adhesion, which is obtained from the sum of ΔF_2 and ΔF_4 divided by the surface area of the gold substrate, is shown in figure 3(c). We can see that the work of adhesion has the maximum value at $\rho = 0.4$.
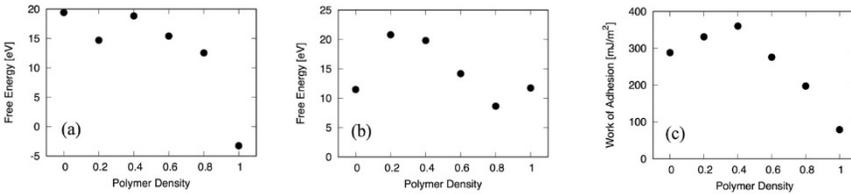
Figure 3. (a) The free energy difference obtained from (P2) as a function of the density of PEG. (b) The free energy difference obtained from (P4). (c) The dependence of the work of adhesion on the density of PEG

The reason why the work of adhesion represents the maximum value at intermediate ρ can be attributed to the interaction between the water molecules and PEG. Figures 4(a) and (b) show density profiles of the oxygen atoms in water molecules and in PEG for $\rho = 1$ and 0.4, respectively. For $\rho = 1$, the density profile of the oxygen atoms in PEG exhibits oscillatory behavior with decay, that is, PEG is arranged keeping a certain degree of regularity. We can see that few water molecules penetrate into grafted PEG. On the other hand, for $\rho = 0.4$, the ordered configuration of the oxygen atoms in PEG is disappeared and the water molecules can penetrate into grafted PEG. Since the water molecules strongly attract to the oxygen atoms in PEG via hydrogen bonding, the work of adhesion for $\rho = 0.4$ becomes large.
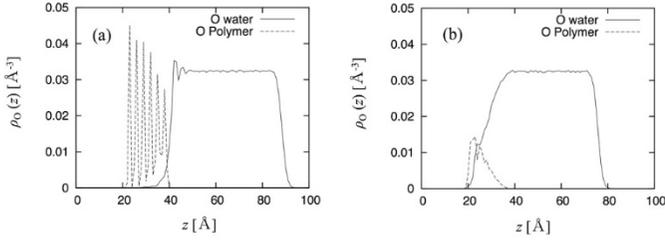
Figure 4. Density profile ρ_O of oxygen atoms in water molecule (solid curve) and PEG (dotted curve) as a function of the distance z from the bottom layer of the gold substrate for $\rho = 1$ (a) and 0.4 (b).

Finally, we compare our results with experimental observations. If θ is the contact angle of the liquid on the solid surface, the work of adhesion is given by $\gamma_L(1 + \cos\theta)$, where γ_L is the surface free energy of the liquid. Since $\gamma_L = 73\ \text{mJ}/\text{m}^2$ for the water, the contact angle for $\rho = 1$ is approximately obtained as $85°$. This value is intermediate between those for CH_3 terminated and OH terminated alkanethiols [11]. Our result is attributed to lowering of the hydrophilic nature of PEG due to terminated CH_3 in PEG. On the other hand, our calculation predicts that the surface is completely wet when $\rho = 0$. This is also consistent with the fact that the water on the clean gold surface spontaneously spreads [12].

CONCLUSIONS

In this paper, we have proposed a novel method for the efficient evaluation of the work of adhesion between the liquid and the polymer-grafted surface by introducing a set of spherically symmetric potentials around the selected atoms. The present method is applied to the interface between the water and the gold substrate modified by PEG in order to study the dependence of the work of adhesion on the density of PEG. Then, we have found that the work of adhesion has the maximum value at the intermediate density of PEG because, at the intermediate density, the water molecules penetrating into PEG strongly interact with the oxygen atoms in PEG via hydrogen bonding.

In the application of the present method, we have found relatively sharp variation in the free energy gradient as shown in figure 2(a). Generally, numerical integration of the function with sharp variation requires the values of the function at shorter interval. Therefore, the number of sampling points can be decreased if sharp variation in the free energy gradient is suppressed. Now, we address this issue by carefully choosing λ dependence of ε and σ. Results obtained through this effort will be reported elsewhere.

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