1. INTRODUCTION

Atomic force microscopy (AFM) which measures the force acting on the probe tip pressed against the surface has been extensively used to study the surface properties of polymers in nano-scale such as the change of the glass transition temperature at surfaces.\(^1\)\(^-\)\(^7\) Using AFM, we can measure the surface properties, such as the elastic modulus and the adhesive force at each point on the surface. This measurement has been used as an imaging technique of bio-related materials.\(^8\)\(^-\)\(^14\) Several groups have applied the technique to show the distribution of the elastic modulus or the adhesion force on the surface. For example, Jiao and Schaffer\(^12\) succeeded to construct clear images of human chromosome based on elastic modulus. Nukaga et al.\(^6\) have developed imaging technique of polymer surface, and applied it to various surfaces of soft materials.

Despite the extensive usage of the technique, not much study has been done to the physical interpretation of the force-distance curve obtained by the experiments. For example, it has been observed that when the probe is pulled off from the surface at low speed, a large long-standing adhesive force appears. The force has been conjectured to be caused by the polymer chains which bridge the tip and the sample, but the detail of the bridging polymer has not been studied. Other example is the friction experiment,\(^7\) which measures the frictional force when the probe pressed against the polymer surface is moved laterally. The frictional force is conjectured to be caused by the nano-scale scratch made by the probe on the polymer surface, but the actual process has not been seen.

To confirm such presumptions in the AFM experiments, we conducted a coarse-grained molecular dynamics (CGMD) simulations for nanorheology and nanotribology. We developed a convenient method to construct the model surface,\(^15\)\(^,\)\(^16\) and performed the simulations for the loading-unloading and the lateral motions of AFM tip. The simulation shows the dynamics of individual polymer chains taking place in these experiments.

2. SIMULATION MODEL

In our simulation, the polymer is represented by the bead spring model\(^7\), and the simulations are performed using COGNAC\(^18\) in OCTA.\(^19\) The AFM tip is represented by a big sphere which interacts with the beads of polymer via the Lennard-Jones potential. The interaction for bonding and nonbonding between the beads in the polymer is represented by the following potentials eq.(1) and eq.(3), respectively.

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\[ U^B(r) = U^{\text{FENE}}(r) + U^{\text{LJ}}(r) \]  
\[ U^{\text{FENE}}(r) = \begin{cases} \frac{1}{2} k R_0^2 \ln \left( 1 - \frac{r}{R_0} \right)^3, & (r \leq R_0) \\ \infty, & (r > R_0) \end{cases} \]  
\[ U^{\text{LJ}}(r) = \begin{cases} 4 \varepsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right] - \left( \frac{\sigma}{r^{\text{cut}}} \right)^{12}, & (r \leq r^{\text{cut}}) \\ 0, & (r > r^{\text{cut}}) \end{cases} \]  

where \( r \) is the distance between the beads, \( k \) is the spring constant, \( R_0 \) is the maximum extension of the spring, \( r^{\text{cut}} \) is the cut-off distance, \( \varepsilon \) is the strength of the interaction. They are chosen as \( k = 30.0 \varepsilon / \sigma^2 \), \( R_0 = 3.0 \sigma \), \( r^{\text{cut}} = 2.0 \sigma \). The interaction between the polymer and the AFM tip is also represented by the LJ potential (eq(3)) with the parameter \( \sigma_{\text{PT}} = 4.0 \sigma \), \( r^{\text{cut}}_{\text{PT}} = 6.0 \sigma \) and \( \varepsilon_{\text{PT}} = 1.5 \varepsilon \). We took \( m \), \( \sigma \) and \( \varepsilon \) as the unit of mass, length and energy respectively. The unit of time \( \tau \), and the unit of the temperature are \( T_0 \) are defined by

\[ \tau = \sigma (m / \varepsilon)^{1/2}, \quad T_0 = \varepsilon / k_B \]  

Figure 1(a) shows the snapshot of the initial structure for CGMD simulation. This structure is obtained by the density biased monte carlo method. The size of the simulation box is 26.3655 \( \times \) 26.3655 \( \times \) 32 \( \sigma \). In the simulation, periodic boundary conditions are used in \( x \) and \( y \) directions. In the boundary face normal to the \( z \) direction, staggered reflective boundary condition is used. (Therefore the film is actually the free-standing film which does not contact with the substrate wall.) This model film has been used in the study of the surface glass transition temperature, and its applicability has already proved.

The mapping between the bead spring model and the real polymer chain has been discussed by Kremer and Grest for the bulk system of polymer. If the same mapping is used, \( \sigma \) corresponds to 1.26 nm and \( r \) to 3.1 \( \times \) 10^{-10} second. Therefore the diameter of our tip is about 10 nm, which is the same order of the diameter of the real tip head (20-30 nm). The typical scanning rate \( (V_s) \) of the loading and the unloading process in our simulation is 0.01 \( \sigma / \tau \), which corresponds to 3.6 \( \times \) 10^7 nm/s.

In the typical experimental condition, the distance 1 \( \mu \)m is scanned with frequency 1 Hz, which gives the scanning rate 2.0 \( \times \) 10^7 nm/s. Therefore, the scanning rate in our simulation is about 100 times faster than the experimental one.

To convert the temperature, we use the correspondence for the bulk glass transition temperature. We performed the simulations for the bulk polymer system of 100 chains with 100 beads using the NPT ensemble (control of the pressure by Andersen and that of the temperature by Kremer and Grest). Figure 2 shows the temperature dependence of the density. From Fig. 2, we can observe a break at about \( T = 0.4 T_o \). On the other hand, the value of the glass transition temperature of the bulk of polystyrene at high molecular weight is about 373 K. Therefore our simulation of \( T = 0.4 T_o \) is done near the glass transition temperature. To study the temperature dependence, we performed the simulation for \( T = 0.3 T_o \), \( 0.4 T_o \), and \( 0.5 T_o \).

3. NANORHEOLOGY SIMULATIONS

3.1 Loading and Unloading Processes

To simulate the loading and the unloading processes of AFM tip, we place the tip above the surface and move down the tip with velocity \( V_s = 0.01 \sigma / \tau \) and then move up with the
same speed. Figures 3 and 4 show the results of the simulation for $T = 0.3 T_0$ and $0.5 T_0$. Figure (c) to (a) are the snapshots in the loading process and (d) to (f) the unloading process. The $z$ component of the force acting on the AFM tip is also plotted against the displacement $z$ in Fig. 3 and 4. (The force is taken to be negative if the tip is attracted by the surface.) This curve corresponds to the force-distance curve in the AFM experiments, but it must be noted that the experimental curve includes the spring effect of the cantilever.

In the case of $T = 0.3 T_0$ as the AFM tip approaches the polymer surface in the early process, a weak attractive force appears (see Figure 3). This is due to the van der Waals attraction between the AFM tip and the polymer surface. As the AFM tip is pushed into the polymer surface, the force becomes repulsive. The repulsive force increases as the tip is pushed further. In the unloading process in Fig. 3, the repulsive force decreases and then changes to attractive force. As the tip sphere is pulled further, it disengages from the polymer surface and the force becomes zero.

On the other hand, in the case of $T = 0.5 T_0$ shown in Figure 4, the curve and the snapshots are quite different. The large fluctuation in the force curve reflects the thermal noise of the polymer segments. The absolute value of the forces is much smaller than that at $T = 0.3 T_0$. Other characteristic difference is that the attractive force now persists over a long time in the unloading process. This long lasting attractive force is caused by the bridging polymer “fished up” from the bulk by the tip (see the snapshots (Figs. 4(e) and (f)). In Fig. 4, it is seen that the chains interacting with the tip form train conformation,\(^{15}\) which is similar to the adsorbed chain on a substrate wall.

The force acting on the tip is explained by the balance between the local interaction to the AFM tip and the relaxation of polymer chain. In the model of AFM tip, the interaction force between polymer bead and tip is decided only by the distance between each center, and there is no extra force for the polymer bead to slide around the tip. Due to this reason, in the indentation process, local beads attached with tip move sideways easily. On the other hand, the excluded volume effect surrounded polymers restricts the movement of the polymer bead near the tip. In the case of $T = 0.3 T_0$, the movement of polymer beads near the tip is limited near the local area and

\[\text{Fig. 3. Force-Distance curve obtained by CGMD simulation, and snapshots simulation in the loading-unloading process at } T = 0.3 T_0. \text{ Loading and unloading processes correspond to (c)- (a) and (d)-(e), respectively.} \]

\[\text{Fig. 4. The same as in Figure 4. The temperature is } T = 0.5 [T_0].\]
the polymer behaves like an elastic solid. This is the origin of the repulsive force in the case of $T = 0.3 \, T_0$. On the other hand, in the case of $T = 0.5 \, T_0$, the polymer chains relax and the polymers around the AFM tip move easily sideways. Due to the relaxation effect, the force becomes almost zero.

### 3.2 Temperature Dependence and Velocity Dependence

Figure 5 shows the temperature dependence of the force-distance curve. As the temperature increases, the absolute value of the force becomes smaller, and the attractive force persists longer.

Figure 6 shows how the force-distance curve changes when the tip speed $V$ is changed. The unloading curve depends strongly on the tip speed. As the unloading velocity decreases, the absolute value of the force becomes smaller, and the region where the attractive force is observed in force-distance curve becomes larger. This feature is the same as the results of the temperature dependence.

Figure 7 shows the magnified image of polymer chains near the tip in the unloading process. It is seen that the “fishing up” of the polymer chain takes place only at high temperature and low tip velocity.

### 3.3 Comparison with Experimental Results

Fig. 8 shows the results of real AFM experiment. Polystyrene film was prepared by casting a PS solution of toluene on the substrate. (The detail of the sample preparation and the

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**Fig. 5.** Temperature dependence of the force-distance curves of $T = 0.3$, 0.4, and 0.5 $T_0$.

**Fig. 6.** Scanning rate dependence of the force-distance curves in the unloading process at $T = 0.4 \, T_0$.

**Fig. 7.** Magnified snapshots near the AFM tip as a function of temperature and scanning velocity.

**Fig. 8.** Experimentally obtained force-distance curves of polystyrene surface.
experimental setup is written in ref. 7 and 1, respectively.) At low temperature, the polymer film behaves like an elastic material: the force-displacement curve in the loading process is linear, and the attractive force observed in the unloading process appears only in a small range of displacement. At high temperature, on the other hand, the curves in loading and unloading process overlap over a wide range, and the attractive force can be obtained in long distance. These characteristics are similar to what have been obtained by the simulation. Our simulation shows that the “fished up” polymers give the long lasting attractive force.

4. NANOTRIBOLOGY SIMULATIONS

4.1 Friction Loop Simulation

We also conducted the simulation of nanotribology. The tip pressed onto the polymer surface is moved in the lateral direction, and the force (or the force component in the scanning direction) acting on the tip is obtained by simulation. Since this simulation requires a large surface, we constructed polymer surface using 400 chains each consisting of 100 beads, and the size of the lateral direction was twice as large as the former loading simulations. The size of the simulation box is $52.7112 \times 52.7112 \times 32$ Å. AFM tip moves 40 Å along the diagonal line of the x-y square face.

In the simulation, we first load the tip onto the polymer film with the indentation depth of about 6 Å, and then start to move the tip in the lateral direction keeping its z position constant. We set the lateral velocity $V_{Fric} = 0.1$ Å/s. Figure 9 shows the friction force curve of $T = 0.3 T_0$. The force indicated in Fig. 9 is the force against the scan direction acting on the tip, and a positive and a negative signs of the force indicate the friction force against the positive and negative scanning direction, respectively. The starting point is at the right bottom (Distance is about 45 Å). First, the tip is moved to negative direction and then to the positive direction, and the cycle is repeated. Large frictional force is shown in the first negative scanning, but then frictional force approaches to a steady cycle which is called as “friction loop”. The steady frictional force is smaller than that in the first scanning process.

Figures 10 and 11 show the snapshots of chain conformation in the first scanning. Tip moves from right to left. In Fig. 11, a chain is expanded to lateral direction by AFM tip. The withdrawn chains are seen only in the first scanning process. This is the reason for the large friction force in the first scanning process.

4.2 Temperature Dependence of Friction Loop

Figure 12 shows the friction loop curves at $T = 0.3$, 0.4, and 0.5 $T_0$. In these simulations, the loading distance at the initial configuration is set to be equal to 6 Å. It is seen that the frictional force is largest at $T = 0.4 T_0$. The reason for this can be understood by looking at the configuration of the chains.

At low temperature $T = 0.3 T_0$, the groove made by the first scanning remains and the tip moves easily in the groove in the following cycles. At $T = 0.4 T_0$, the groove made by the first scanning becomes flatter due to the relaxation of polymers, and the friction force increases. At $T = 0.5 T_0$ (above the glass transition temperature) the relaxation of polymer occurs very fast, and the frictional force becomes smaller due to the slippage effect of tip explained at in section 3.1.

This result is in agreement with the experiment. Figure 13 shows the results of the friction loop of the blend of polystyrene/polyvinylmethylethel with changing the temperature. Our simulated curves correspond to the friction loop observed in the experiments qualitatively.

5. CONCLUSION

In this paper, we have shown the results of the molecular dynamics study of the nanorheology and nanotribology. We have shown that the withdrawn chain is quite important in interpreting the force-distance curve or the friction loop curves. In the nanorheology simulation, chains bridging the AFM tip and the sample surface in the unloading process have been observed. In the nanotribology simulation, the expanded polymer can be seen in the first scanning process.

In our simulation, we model the AFM tip by a sphere interacting with polymer segments via the Lennard-Jones
potential. This model does not account for the frictional force between the AFM tip and the polymer segment since the model allows the polymer chains to slide freely on the surface of the tip. Accordingly, our simulation probably underestimates the force. This problem can be resolved if we use a model of AFM tip which consists of many beads fixed on the surface. Such study is now being done, and the result will be published in future.

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![Fig. 10. Snapshot of the structures at the friction process in the CGMD simulation.](image)

![Fig. 11. Snapshot of the typical chain structures in the CGMD simulation.](image)

![Fig. 12. Friction loop curve obtained by CGMD simulation of T = 0.3, 0.4, and 0.5 T₀.](image)

![Fig. 13. Friction loop curve obtained by AFM experiments. Sample is the blend film of PS/PVME.](image)
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