Effect of the Chain Length and Temperature on the Adhesive Properties of Alkanethiol Self-Assembled Monolayers

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Supporting Information

ABSTRACT: Stable and hydrophobic self-assembled monolayers of alkanethiols are promising materials for use as lubricants in microdevices and nanodevices. We applied high-rate dynamic force spectroscopy measurements to study in detail the influence of the chain length and temperature on the adhesion between methyl-terminated thiol monolayers and a silicon nitride tip. We used the Johnson–Kendall–Roberts model to calculate the number of molecules in adhesive contact and then the Dudko–Hummer–Szabo model to extract the information about the position and the height of the activation barrier per single molecule. Both parameters were determined and analyzed in the temperature range from 25 to 65 °C for three thiols: 1-decanethiol (measured previously), 1-tetradecanethiol, and 1-hexadecanethiol. We associate the increase of the activation barrier parameters versus the chain length with lower stiffness of longer molecules and higher effectiveness of adhesive bond formation. However, we relate the thermal changes of the parameters rather to rearrangements of molecules than to the direct influence of temperature on the adhesive bonds.

INTRODUCTION

Alkanethiols are known to form self-assembled monolayers (SAMs) on gold (111) surfaces. If they are sufficiently hydrophobic and stable, they can serve as lubricants in microdevices and nanodevices, because the adhesion between a hydrophobic SAM and a nano-object remains low as compared to liquid lubricants.1,2 Termination of alkanethiols with a methyl group guarantees hydrophobicity of the layer. The research for an optimal chain length of alkanethiols, however, requires taking into account not only the structural stability of SAMs but also the independence of their adhesive properties of temperature changes in a typical operating range. Temperature can influence the nanoadhesion of SAMs either directly by affecting the adhesive interactions or indirectly, through reorganization of the SAM structure. In this paper, we perform systematic experimental studies to characterize the adhesive interaction potential as a function of temperature and we discuss both of the kinds of influence.

Because standard experimental studies of temperature-dependent adhesion or friction, which are limited to the measurement and analysis of force (normal or lateral) versus temperature,3,4 cannot give a deep insight into the kinetics and energetics of adhesive processes, we extended the studies by using the so-called dynamic force spectroscopy. It is a measurement of adhesion force as a function of separation rate performed usually with an optical tweezers or an atomic force microscope (AFM).5 In our experiments, we have used a modified AFM to expand the accessible range of separation rates to over 10^6 nm s^-1. By applying theoretical models of mechanical adhesive contact (the Johnson–Kendall–Roberts (JKR) model)6 and thermally activated unbinding (the Dudko–Hummer–Szabo (DHS) model7), we could determine parameters of the interaction potential such as the energy and the position of the activation barrier per single thiol molecule. Finally, we discuss the dependence of the parameters on temperature, suggesting possible reasons for their non-

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THEORY

There are several theoretical models interpreting the dynamic force spectroscopy data. One of the most commonly used is the so-called Bell–Evans (BE) model, which predicts a logarithmic dependence of the mean adhesion force \( F_{ad} \) on the loading rate \( \nu \) \(^{11,12,13} \)

\[
F_{ad} = \frac{k_B T}{x_p} \ln \left( \frac{x_p}{k_B T x_p F_{off}} \right)
\]

(1)

Here, \( k_B \) is the Boltzmann constant, \( T \) is the absolute temperature, \( x_p \) is the distance between the bound state and an activation barrier on the free-energy potential in the absence of external forces, and \( k_B^0 \) is the kinetic off-rate constant. The BE model fitted to experimental data allows researchers to extract the values of \( x_p \) and \( k_B^0 \) from the slope and intercept of an \( F_{ad} - \ln(\nu) \) line. Therefore, it has been widely applied to study specific interactions between or within biomolecules. \(^{14-17} \)

Because the model does not introduce any restrictions to narrow its applicability exclusively to specific interactions, it has been applied also to study nanoadhesion between an AFM tip and the SAMs of silanes \(^{18} \) and thiols. \(^{19,20} \) However, the applicability of the BE model is generally limited, because it lumps all the information about the potential shape into one parameter—\( x_p \). In addition, it does not take rebinding processes into account (Figure 1).

Figure 1. Interaction potential (energy profile) of an adhesion bond loaded by a harmonic potential (solid curve) and the load-free potential (dashed line).

Friddle et al. \(^{21} \) proposed a model which considers the contribution of rebinding and can be applied to a multibond. It is based on the BE model but an additional parameter is defined—the equilibrium unbinding force—which together with \( x_p \) and \( k_B^0 \) describes an adhesive bond. In addition, Friddle et al. showed that there exists a critical loading rate \( \nu_0 \) given by a simple relation

\[
\nu_0 = \frac{k_B T}{x_p}
\)

(2)

above which the behavior of real adhesive bonds deviates from the BE model predictions sufficiently to apply a more precise model. Here, \( \nu_0 \) is the attempt frequency, which is the reciprocal of the characteristic time, \( t_\alpha = (1/\nu_0) / k_B T \), where \( l_s \) is the length representing the thermal spread in the bound state, \( l_a \) is the length representing the thermal spread in the transition state, and \( \gamma \) is the molecular damping coefficient. \(^{15} \)

One of such significantly detailed models is the DHS model formulated by assuming a stochastic character of the escape process from a potential well \(^{22} \) and specifying the free-energy potential shape. The prediction of this model for the mean rupture force versus the loading rate is

\[
\langle F \rangle \equiv \frac{\Delta G_p}{\nu x_p} \left\{ 1 - \frac{k_B T}{\Delta G_p} \ln \left( \frac{x_p}{k_B T x_p F_{off}} \exp \left( \frac{\Delta G_p}{k_B T} + \gamma \right) \right) \right\}^{1/\nu}
\]

(3)

where \( \Delta G_p \) is the free energy of activation in the absence of external forces, \( \gamma = 0.577 \) is the Euler–Mascheroni constant, and the parameter \( \nu \) corresponds to the shape of the free-energy potential. As suggested by the authors, the universal value for \( \nu \) is \( 2/3 \). Then, the DHS model can precisely characterize unbinding processes in the case of real interatomic or intermolecular interactions (described by van der Waals or Morse potentials, for instance). Additionally, the DHS model enables us to extract not only \( k_B^0 \) and \( x_p \)—like the BE model—but also \( \Delta G_p \). Equation 3 reduces to eq 1 of the BE model for \( \nu = 1 \) and \( \Delta G_p \gg k_B T \); however, these conditions are normally not fulfilled in force spectroscopy experiments.

There are also alternate theoretical approaches, for instance, by Li and Ji. \(^{23} \) They combined a model developed by them for ultralow loading rates, with the DHS model for the loading rates higher than a threshold value, which is below the lower limit of the experimental data qualified by us to quantitative analysis (Figure 2, region 2).

EXPERIMENTAL SECTION

Preparation of Self-Assembled Monolayers and Their Characterization. Two types of SAM samples were prepared by chemisorption of 1-tetradecanethiol (Sigma-Aldrich) and 1-hexadecanethiol (Alfa Aesar) on Au(111) substrates. Au(111) substrates were immersed in 1 mM thiol solution in ethanol. After 24 h self-assembly, samples were rinsed with ethanol, dried under nitrogen, and used immediately. The quality of the Au(111) substrates was controlled with X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and scanning tunneling microscopy (STM) measurements. The SAM samples were characterized at nanoscale (STM imaging) and macroscale (contact angle measurements, XPS). For details, see the Supporting Information.

AFM Modification, Calibration, and Measurements. A commercial AFM (Bruker, EnviroScope with the NanoScope IIIa controller), modified and thereafter calibrated to perform dynamic
force spectroscopy measurements at a high surface separation rate and a high temperature. Details on the setup used can be found elsewhere. Briefly, an additional low-mass and high-frequency piezo-actuator (PI Ceramic, model PLO55 PICMA) was mounted on a heating plate using thermal glue. The investigated samples adhered to the piezo-actuator were located in a hermetic chamber with slow nitrogen flow. The piezo-actuator was driven by a function generator (Agilent, model 33220A) combined with a custom-made voltage amplifier. This additional piezo-actuator allowed us to expand the range of fast loading rates by about 3 orders of magnitude. Force spectroscopy data, the existence of two activation barriers related to the tip wear and SAM disorder under load.

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The adhesion force between a silicon nitride tip and the layer of methyl-terminated thiols increases monotonically with an increase in the loading rate for both SAMs: 1-tetradecanethiol and 1-hexadecanethiol, and for different temperatures from 25 to 65 °C (Figure 2). For the 1-hexadecanethiol SAM, the highest temperature was limited to 55 °C; above this temperature, changes occur in the ordering of the molecular layer, which affects the results leading to high measurement uncertainty. We will discuss the changes in response to temperature later in this section. The determined relationship between the adhesion force and the loading rate resemble that measured for 1-decanethiol SAM. It shows two regions, of weak and strong dependence, with the threshold loading rate about 10^5 nN/s for the 1-tetradecanethiol SAM (Figure 2a), and 4 × 10^5 nN/s for the 1-hexadecanethiol SAM (Figure 2b). Because both the thiol SAMs are hydrophobic and the experiments were performed in an N2 atmosphere at low relative humidity, the influence of capillary forces as well as fluid viscosity can be neglected.

In the standard interpretation for the occurrence of two distinct regions with different slopes in the dynamic force spectroscopy data, the existence of two activation barriers within the interaction potential of nanoadhesion is needed: (1) the outer barrier, which determines the dependence at low loading rates and (2) the inner one, which determines the dependence at larger loading rates when the outer barrier is already strongly lowered by an external force at the moment of force-induced unbinding. This interpretation cannot be applied to the results of our experiments as the studied nonspecific interactions between a silicon nitride tip and methyl-terminated thiols, which come mainly from the van der Waals forces, are characterized by a barrier-free, Lennard-Jones type of potential. Instead, we assume an effective rebinding of single adhesive bonds (van der Waals interactions per single molecules terminated with a methyl group) as a reason for the weak dependence at low loading rates. A rupture of a single adhesive bond does not lead to the rupture of the whole adhesion contact between the AFM tip and a SAM, because each broken bond can easily rebind as long as the adjacent bonds still exist. Only a rupture of a significant fraction of adhesive bonds can lead to full detachment. Therefore, the adhesion force at lower loading rates (region 1) will be strongly influenced by rebinding and does not weaken with decreasing loading rate as steeply as it does at higher loading rates (region 2), where rebinding becomes more and more unlikely. Because the models of thermal activation escape from the potential well, which describe unbinding (e.g., the DHS model), not taking into account the re-binding processes, only region 2 should be considered for further analysis.

![Figure 2. Adhesion force vs loading rate for nanoadhesion between a silicon nitride tip and a SAM of (a) 1-tetradecanethiol and (b) 1-hexadecanethiol for different temperatures. 1, region of weak dependence and 2, region of strong dependence. The error bars were calculated as a standard deviation.](image-url)
In region 2, single adhesive bonds behave independently during rupture and hence the force distributed per single bond can be given as

$$ F_i = \frac{F_{ad}}{N} + \frac{k_B T}{x_{fi}} \ln \left( \frac{x_{fi} F_{ad}}{k_B T} \right) $$

where $F_{ad}$ is the resultant adhesion force (measured with the AFM), $N$ is the number of single independent bonds in parallel, $k_B$ is the Boltzmann constant, $T$ is the absolute temperature, and $x_{fi}$ is the distance between the bound state and the activation barrier on the effective free-energy potential.\(^{2,28}\) Because $F_{ad}$ is measured and $T$ is controlled in our experiments, two parameters: $x_{fi}$ and $N$ have to be determined to calculate a precise value of the unbinding force per molecule. $x_{fi}$ was obtained with the DHS model fitted to region 2. We decided to apply this model because we exceeded the threshold value of the loading rate (eq 2) given by Friddle et al.\(^{21}\) Substituting $x_{fi}$ from our results (Table S1 in the Supporting Information) and $\nu_0 = 10^9$ s\(^{-1}\) provided by Friddle et al., a value of $F_{ad} \approx 10^6$ nN/s was obtained. Although this is around 2 orders of magnitude beyond the present standard experimental range, we exceeded this threshold using our modified AFM system with an additional Z-piezo-actuator and performing the experiments in air instead of liquid.

An example result of the fitting for the adhesion between a silicon nitride tip and a 1-tetradecanethiol SAM on Au(111) measured at 35 °C is shown in Figure 3 (red solid curve).

![Figure 3](image-url)

Figure 3. Adhesion force vs loading rate for nanoadhesion between a silicon nitride tip and a 1-tetradecanethiol SAM on Au(111) at $T = 35$ °C. The error bars were calculated as a standard deviation. The red solid line is a result of the fitting with the DHS model.

Fittings for a narrower range of loading rates within region 2, that is, for 7, 6, or 5 highest loading rates, give similar results, which indicates independence from the rebinding within region 2.

The number of bonds in the adhesion contact ($N$) was estimated using the JKR model.\(^{7}\) The JKR model considers the contribution of adhesion within a mechanical contact between a homogeneous, elastic planar surface and a sphere. The radius of the contact area between an AFM tip and an elastic monolayer at the moment of rupture can be given as

$$ a_i = \left( \frac{RF_{ad}}{E_i} \right)^{1/3} $$

where $R$ is the radius of the tip curvature and $E_i$ is the elastic modulus of the monolayer, assuming that the elastic moduli of the tip material and the gold substrate are much higher. Although different values of $E_i$ can be found in the literature depending on the measurement method and configuration of the sample,\(^{29-32}\) we decided to use the value calculated from AFM measurements by DelRio et al.\(^{33}\) for a thiol SAM alone (without the influence of the substrate), that is, (0.86 ± 0.14) GPa. Most of the literature values were obtained from experiments or simulations with compression of the monolayer under load and, therefore, the contributions of the underlying substrate as well as the steric repulsion in squeezed molecules were significant. In our experiment, however, the rupture of adhesion contact occurs at a small negative (stretching) load, when the molecules straighten up to a vertical position\(^{34}\) and are slightly stretched rather than compressed. Therefore, the effects of the substrate and steric repulsion do not occur.

CH\(_3\)_terminated alkanethiols are found to adopt ($\sqrt{3} \times \sqrt{3}$)R30° ordering on the Au(111) substrate, which leads to an area of 0.216 nm\(^2\) per molecule.\(^{8,11}\) The radii of the AFM tips were determined from the SEM images as (59 ± 6) nm for the experiments with the 1-tetradecanethiol SAM, which results in 1600–2150 contacting molecules (depending on the temperature), and (50 ± 5) nm for the experiments with the 1-hexadecanethiol SAM, which results in 940–1350 contacting molecules. Detailed values of the contact area at rupture and the number of contacting molecules are presented in Table S2 (Supporting Information).

Inserting $x_{fi}$ and $N$ into eq 4, the adhesion force per single molecule could be calculated. In this manner, the total adhesion force dependences (an example in Figure 3, region 2) were recalculated into the adhesion force per single molecule versus the loading rate (an example in Figure 4). After this, the DHS model was applied to region 2 of these new plots to extract parameters describing the shape of the interaction potential between an individual methyl group and the silicon nitride tip, namely $x_{fi}$ and $\Delta G^\alpha_{gi}$ (Table S3).

In the case of the van der Waals potential, which does not exhibit any activation barrier until it is subjected to an external force (Figure 4), $x_{fi}$ can be defined as the distance between the bound state and an apparent activation barrier, and $\Delta G^\alpha_{gi}$ as the height of the apparent activation barrier. These quantities are defined by the first and third derivative of the interaction potential, $U_0(s)$, at the inflection point, $x_{inf}$ respectively:

$$ x_{fi}^\alpha = \frac{2[U^\prime_0(x_{inf})]^{3/2}}{[-U_0''(x_{inf})]^{1/2}} $$

$$ \Delta G^\alpha_{gi} = \frac{2[2U^\prime_0(x_{inf})]^{3/2}}{[-U_0'''(x_{inf})]^{1/2}} $$

The values of parameter $x_{fi}$ which were used in further calculations, determined for all measured temperatures for the SAMs of 1-tetradecanethiol and 1-hexadecanethiol, are given in Table S1 (Supporting Information). Because they were obtained for the nanoadhesion treated as a single effective bond, we needed to recalculate them per individual adhesive bond to discuss their physical meaning.
The parameters describe the shape of a load-free interaction potential. When the adhesive bond is subjected to an external force (for instance, by AFM cantilevers in our experiments), an energy barrier and a second minimum are created as a result of the added harmonic potential (Figure 1).\textsuperscript{21,26}

The dependences of $\Delta G^*_{\beta}$ versus temperature and $x^*_{\beta}$ versus temperature for three thiols, 1-decanethiol,\textsuperscript{8} 1-tetradecanethiol, and 1-hexadecanethiol, are plotted in Figures 5 and 6, respectively. The general observation is that longer molecules have higher values of $\Delta G^*_{\beta}$ and $x^*_{\beta}$. This can be explained by lower stiffness of longer molecules and hence longer stretching distances before the unbinding occurs, resulting in lower probability for transition over the energy barrier (Figure 1).

Another explanation is that longer molecules can create more effectively adhesive bonds with a rough surface of the AFM tip, which was not assumed in our methodology. Therefore, the average values of the interaction potential parameters per molecule, in particular, $\Delta G^*_{\beta}$, are overestimated for longer molecules in comparison to shorter ones.

The value of $\Delta G^*_{\beta}$ appears stable and independent of temperature for 1-decanethiol and 1-tetradecanethiol SAMs. For 1-hexadecanethiol, an increase is observed while the temperature rises from 25 to 35 °C (Figure 5). A similar increase between 25 and 35 °C occurs, in the case of $x^*_{\beta}$ for all three thiols: 1-decanethiol, 1-tetradecanethiol, and 1-hexadecanethiol (Figure 6). Above 35 °C, no abrupt changes are observed for both $\Delta G^*_{\beta}$ and $x^*_{\beta}$.

We assume that the relative changes in the temperature are too low to directly influence the van der Waals forces which, in the case of our experiments, constitute the main contribution to adhesive interactions. However, temperature can influence the interaction potential indirectly, through processes not considered by the model of thermal activation, for example, some reorganization of the molecules in the SAM during the unbinding.

The energy of the activation barrier can be separated into enthalpic and entropic contributions\textsuperscript{35}

$$\Delta G^*_{\beta} = \Delta H^*_{\beta} - T \Delta S$$

The enthalpic component to the bond strength ($\Delta H^*_{\beta}$) is temperature-independent, but the entropic component ($T \Delta S$) depends on temperature and can be negative or positive. Its sign and value depends on the changes in the arrangement of molecular groups in the adhesion contact zone during the unbinding process. Therefore, some changes of $\Delta G^*_{\beta}$ can occur even in a narrow range of temperature change.

Another possible mechanism affecting the parameters, particularly $x^*_{\beta}$, can be related to the thermal change of the angle between the longitudinal axis of the thiol molecules and the normal to the substrate.\textsuperscript{36} The tilt angle decreases with temperature, which leads to a reduction in the tip–sample distance necessary to rupture the adhesive contact. As a result, a slight change of $x^*_{\beta}$ in the interaction potential could be observed.

Also, an interplay between unbinding and rebinding (Figure 1) can influence the interaction potential parameters. The rates
of unbinding and rebinding processes are determined basically by the heights of the corresponding energy barriers in relation to \( k_BT \). If the probability of rebinding increases faster with the temperature up to 35 °C than that of unbinding, then an increase in \( \Delta G^\beta \) can be observed. A similar effect has been observed for friction between a silicon AFM tip and some substrates, for example, a silicon wafer. However, in the case of our results, extraction of the interaction potential parameters was performed for the region of high loading rates, where rebinding processes are negligible. Thus, the thermal rearrangements (but without decomposition or desorption) of the molecules rather than rebinding processes are responsible for the observed changes of \( \Delta G^\beta \) and \( x^\beta \) versus temperature. Over 65 °C, the two-dimensional melting of the SAMs occurs (Ramin and Jabbarzadeh report about 60 °C for 1-dodecanethiol (15)), which leads to significant changes in the adhesion force; hence, we limited our analysis to 65 °C.

## SUMMARY AND CONCLUSIONS

We applied high-rate dynamic force spectroscopy measurements to study in detail the influences of the chain length and temperature on the adhesion between the methyl-terminated thiol monolayers and a silicon nitride tip. We used the JKR model to calculate the number of molecules in adhesive contact and then applied the DHS model to extract the information about the interaction potential per single molecule. We have decided to apply the DHS model for two reasons: (i) it describes the behavior of adhesive bonds at high loading rates better than other considered models of thermal activation escape from the potential well and (ii) it delivers information about the height of the activation barrier (\( \Delta G^\beta \)) additionally to its position (\( x^\beta \)).

Finally, we were able to determine the dependence of \( \Delta G^\beta \) and \( x^\beta \) versus temperature for two thiols: 1-tetradecanethiol and 1-hexadecanethiol. We compared the results with previously obtained data for 1-decanethiol. We associate the increase of \( \Delta G^\beta \) and \( x^\beta \) versus the chain length with lower stiffness of longer molecules which facilitates the adhesive bond formation. However, we relate the thermal changes of the parameters rather to rearrangements of molecules than to the direct influence of temperature on the adhesive bonds. Because the higher limit of adjusted temperatures is below the melting point, the rearrangements can be due to the thermal changes of the tilt angle of molecules in the layer. The demonstrated measurements and calculations enabled us to deepen the knowledge about adhesive bonds and their temperature dependence at the single-molecule level.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.langmuir.7b01921.

Structure–property relationships of 1-tetradecanethiol and 1-hexadecanethiol SAMs on Au(111) at various temperatures; description of the sample preparation; characterization of Au(111) substrates with XRD (Figure S1a), STM (Figure S1b), and XPS (Figures S3 and S4); characterization of the thiol SAMs with STM (Figure S2) and XPS (Figures S3 and S4); and intermediate (Tables S1 and S2) and complete, final (Table S3) results (PDF)

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### Notes

The authors declare no competing financial interest.

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### REFERENCES


