Monte Carlo analysis of frequency domain thermoreflectance data for quantitative measurement of interfacial thermal conductance at solid-liquid interfaces modified with self-assembled monolayers

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Abstract. A Monte Carlo method, implemented for quantifying confidence bounds on thermoreflectance (TR) measurements of interfacial thermal conductance $G$ at solid-liquid interfaces modified with self-assembled monolayers (SAMs) is presented in this paper. Here we used 1-decanethiol (1DT) and $\text{H}_2\text{H}_2\text{H}_2\text{H}\text{-Perflurodecanethiol (PFDT)}$ SAMs to achieve two distinct work of adhesion. Using TR measurements in conjunction with Monte Carlo simulations, we determined $G$ values to be $51 \pm 7 \text{MWm}^{-2}\text{K}^{-1}$, $58 \pm 8 \text{MWm}^{-2}\text{K}^{-1}$, and $72 \pm 17 \text{MWm}^{-2}\text{K}^{-1}$ for Au-PFDT-H$_2$O, Au-1DT-H$_2$O, and Au-H$_2$O, respectively. Our results with the new confidence bounds position our experimental data on surfaces modified with SAMs comparable to literature. However, contrary to previous results shown in the literature, our data showed that a significant decrease in $G$ can be seen for DI water on bare Au that was exposed in ambient for extended period. Our results indicate that $G$ could be influenced by factors beyond a simple work of adhesion, an indication also seen from the work of Park et al. To solidify this finding, further investigation is necessary to better understand $G$ dependence on surface wettability.

1. Introduction

The need for well-controlled interface thermal transport characteristics has led to several investigations focused on improving thermal conductance at solid-liquid interfaces [1–5]. The use of self-assembled monolayers (SAMs) to tailor the interfacial thermal conductance $G$ through modification of the van der Waals interaction strength at solid-liquid interfaces has been demonstrated. Using time domain thermoreflectance (TDTR), Harikrishna et al. showed that interfacial thermal conductance $G$ is proportional to the thermodynamic work of adhesion between functionalized gold and water for a series of five alkane-thiol monolayers at the Au-H$_2$O interface [2]. They were able to achieve $G_{\text{Au-H}_2\text{O}}$ value of $190 \text{MWm}^{-2}\text{K}^{-1}$ for Au-H$_2$O with hydrophilic 11-mercapto-undecanoic acid (COOH) surface treatment. They also determined uncertainty values of $G_{\text{Au-H}_2\text{O}}$ as $\pm 30 \text{MWm}^{-2}\text{K}^{-1}$ by using a range of $G$ values that could fit the experimental data. This is a common method in quantifying the margin of error in $G$. This method assumes that the measuring technique is sensitive to $G$, which is not always the case. In this work we use frequency domain thermoreflectance (FDTR) to measure $G$ for Au-H$_2$O with and without selected SAMs. By using a Monte Carlo approach we extract a value for the interface thermal conductance and confidence intervals on this value [6]. In particular, we quantify the lower and upper
2σ or 95% confidence intervals of $G$ of Au-H$_2$O interfaces. We then compare the Au-H$_2$O interface conductance as a function of surface treatments. Our results for modified surfaces with SAMs are comparable to literature [1,4,5], while our result for bare Au is comparable to the lower trend of the molecular dynamics (MD) predictions by Acharya et al.. We note that the SAMs samples were submerged immediately in dilute solution with their respective thiol post Au deposition, while the sample with bare Au surface was exposed in ambient for a short period until the liquid cell is assembled. We also purposely left a bare Au sample with its surface exposed to ambient for four days, and we observe a $G$ value significantly lower compared to literature.

2. Method

This work involved sample fabrication, solving heat diffusion equation of a multilayer stack structure [7], thermoreflectance (TR) measurements [8] and modelling the data acquired from the measurements. The chemical synthesis and sample fabrication processes involved for this work can be found in [6]. Here we mainly focus on data acquired from FDTR [9,10] and results of the Monte Carlo analysis.

2.1. Thermoreflectance measurements

A ~100 nm layer of Au is deposited onto fused silica substrates which acts as a transducer. TR techniques such as FDTR utilize the transducer material’s change in reflectivity $R$ due to change in temperature $T$, and it is related to the TR coefficient $\kappa_{TR}$ of the material by:

$$\frac{\Delta R}{R} = \left(\frac{1}{R} \frac{\partial R}{\partial T}\right) \Delta T = \kappa_{TR} \Delta T$$

(1)

FDTR is typically set up to have a fixed optical path such that the probe beam records at a fixed time delay relative to the pump beam. In that case the phase lag at different pump frequencies can be used to extract thermal properties from the frequency response in the model. Our custom built FDTR setup uses two continuous wave lasers and we used this setup to measure $G_{\text{solid-liquid}}$ in this work [6].

2.2. Mathematical modelling

The $G$ values with their respective working fluid were extracted by fitting the phase lag by

$$\phi(\omega) = \tan^{-1}\left(\frac{\text{Im}[R(\omega)]}{\text{Re}[R(\omega)]}\right).$$

(2)

where the frequency response $R(\omega)$ which contains the thermal properties is given by [7]

$$R(\omega) = \frac{\pi a \kappa_{TR} w_1 w_2 P_1 P_2}{2} \int_0^\infty \frac{T}{q''} \exp\left(\frac{\pi^2 k^2 (w_1^2 + w_2^2)}{2}\right) k dk.$$

(3)

We attain $G$ by holding all other involving parameters constant when fitting to the experimental data. Those other parameters include material density, thermal conductivity $\kappa$ and volumetric heat capacity $C_v$ at each layer, and interfacial thermal conductance between layers except the interface of interest. Here we used measured thermal conductivity of the substrate and Au film by FDTR and four-point probe in conjunction with Wiedemann-Franz law, respectively. The remaining parameters were taken from literature.

2.3. Monte Carlo simulations

Confidence intervals at 2σ were determined by fitting the data 1000 times using normal distributed random values within the margin of error of $\kappa$ and $C_v$ for the Au transducer, substrate, working fluid, and the laser spot size used in the fitting process. We also applied a uniform random multipler between 0.1 and 10 to our best initial guess values to ensure that our best fit values correspond to a unique global minimum. The lower confidence interval $C_{L_{ub}}$ and upper confidence interval $C_{U_{ub}}$ were determined by applying lognormal fit to the $G$ distribution.
3. Results and Discussions
Figure 1 shows the results of $G$ distribution of H$_2$O paired with and without 1-decanethiol (1DT) and 1H,1H,2H,2H-Perfluorodecanethiol (PFDT) SAMs surface treatments on Au by Monte Carlo simulations (MCS). The $G$ distribution from MCS for H$_2$O are almost Gaussian and remained almost Gaussian regardless of the type of surface treatment. To be more precise, we used 2σ of lognormal distribution instead of Gaussian distribution, and determined $G_{PFDT} \sim 51 \pm 7$ MWm$^{-2}$K$^{-1}$, $G_{1DT} \sim 58 \pm 8$ MWm$^{-2}$K$^{-1}$, and $G_{bare\ Au} \sim 72 \pm 17$ MWm$^{-2}$K$^{-1}$.

![Figure 1](image1.png)

**Figure 1.** $G$ distribution of Au-PFDT-H$_2$O, Au-1DT-H$_2$O and Au-H$_2$O by MCS, where solid lines represent mean, while dashed and dotted lines represent, $CI_{ub}$ and $CI_{lb}$ at 2σ, respectively.

Figure 2 shows our measured $G$ for water as a function of the dimensionless work of adhesion, $1+\cos(\theta_a)$, in comparison to previous experimental and simulation studies in the literature. Our measured value of $G$ for 1DT at $1+\cos(\theta_a) \sim 0.76$ is consistent with the value found by Ge et al. for a similar hydrocarbon chain [1]. While our data for PFDT at $1+\cos(\theta_a) \sim 0.59$ is consistent with MD data [4,5]. The MCS also showed that our 95% confidence intervals is comparable to the margin of error from the work of Ge et al. Moreover, based on all previous results shown here, all three, simulations, experimental, and analytical; we expected $G$ to scale proportionally with work of adhesion, $G \propto 1+\cos(\theta_a)$. However, for our well-quantified measurements, we observe $G$ significantly below the trend when our bare Au surface has been exposed in our laser lab environment for four days before introducing H$_2$O to the surface. Simultaneously, our results indicate that $G$ is not purely dependent on work of adhesion and the experimental work of Park et al. [11] also indicates this. We believe further investigation is required to accurately characterize these modified interfaces.

![Figure 2](image2.png)

**Figure 2.** Interfacial thermal conductance $G$ of Au-H$_2$O as a function of the dimensionless work of adhesion for this work and from literature [1,2,4,5,12]. The lines represent analytical model, unfilled markers represent simulation data, and filled markers represent experimental data.
4. Conclusions
The research showed that Monte Carlo simulations can determine the margin of error for interfacial conductance comparable to the work of Ge et al. but larger than Harikrishna et al. This method provides dynamic lower and upper confidence intervals for asymmetric distributions which results in more realistic confidence bounds. Additionally, 99% confidence intervals can be obtained with 3σ. Our well-quantified Au-H$_2$O measurements indicate that there may be more complicated relationship between $G$ and surface wettability characteristics. Our preliminary results indicate additional resistances between bare Au and H$_2$O could be due to physisorbed layer formed on the surface from extended exposure to ambient environment. We intend to investigate the contribution of physisorbed layer in $G$ at solid-liquid interfaces by exposing Au surfaces with known comparable species that exhibits distinct surface wettability.

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