ASSESSMENT OF VIBRATIONAL COUPLING AT SOLID-SAM JUNCTIONS

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ABSTRACT

Self-assembled monolayers (SAMs) have recently garnered much interest due to their unique electrical and chemical properties. The limited literature detailing SAM thermal properties has suggested that thermal boundary conductance (TBC) at solid-SAM junctions is not only low, but also insensitive to changes in SAM length as the number of methylene groups (-CH2-) along alkanedithiol chains is varied from 8 to 10. The present study investigates the vibrational spectra of alkanedithiol SAMs as a function of the number of methylene groups forming the molecule backbone via Hartree-Fock methods and the subsequent effects on TBC calculated using a diffuse scattering model. In particular, the vibrational overlap between the alkanedithiol and Au is studied. It is found that despite the addition of 9 new vibrational modes per added methylene group, only one of those modes is elastically accessible to Au. It is believed that this “vibrational inaccessibility” is the cause of the insensitivity of thermal conductance to molecule length.

INTRODUCTION

Self-assembled monolayers are of much interest in current literature due to their unique electrical properties and their ability to form relatively uniform molecular surfaces. A self-assembled monolayer (SAM) is a layer of molecules which organize themselves in an ordered array on a substrate surface. Typically SAMs are linear molecules, ranging from a few to tens of Angstroms long, with functional groups at either end to facilitate bonding to substrates or impose some other desired property, such as hydrophilicity [1]. Recent developments in SAMs and in nanoscale science and technology have led to the investigation of SAMs for use in such fields as thermoelectrics [2], organic electronics [3, 4] and thermal rectifiers [5, 6]. In each of these applications, the devices being developed require the creation of solid-SAM junctions, where the solid may be a metal or a semiconductor. While studies of the thermal...
properties of such junctions are limited, knowledge of thermal transport across these junctions is crucial to the successful implementation of SAMs in each of these applications.

The limited work that has been performed investigating the thermal properties of solid-alkanedithiol SAMs junctions suggests a TBC which is insensitive to molecular length as the number of methylene (-CH\(_2\)-) groups, \(N_M\), along the alkanedithiol (HS(CH\(_2\))\(_N\)SH) chain is varied [7–10]. Segal and Nitzan [7] developed a quantum mechanical model to investigate the molecular thermal conductance through molecular wires. Their investigation showed that the conductance of alkanes was independent of changes in length for SAMs greater than 5-6 methylene groups long, \(N_M=5-6\). Wang, Segalman and Majumdar [11] experimentally measured the thermal conductances of Au-alkanedithiol SAMs-GaAs junctions, with SAM lengths ranging from eight to ten methylene groups long using the 3\(\omega\) technique. They too report an insensitivity of junction conductance to chain length [11]. The chain length dependence of thermal transport was also studied by Wang et al. [8, 9] using sum-frequency generation (SFG). They also observed that the conductance of the junction is independent of SAM length [9]. Luo and Lloyd employed nonequilibrium [10] and equilibrium [12] molecular dynamics to investigate the thermal conductance of Au-SAM-Au junctions and report a weak dependence on alkane chain length [12].

References 7, 8, 11, and 12 investigated the effect of molecular length on thermal junction conductance, which is the conductance of the entire system considered and includes molecular conductance, crystalline conductance and TBC, and most have found that the smallest conductance channel is across the interface. This implies that the total observed junction conductance is controlled by the interface conductance or thermal boundary conductance (TBC), which is in turn a function of interface roughness, bond strength between the two materials that make up the interface, and overlap of the vibrational density of states. While each have investigated the effect of molecular length on TBC, none have thoroughly investigated the reason for TBC independence of chain length. The focus of this study is an investigation of the vibrational trends of the SAM molecules and subsequent development of an explanation for the observed TBC behavior. This work uses Hartree-Fock (HF) methods to first calculate the vibrational spectra of SAM molecules, then standard quantum theory to calculate heat capacity and molecular conductance, and finally a diffuse scattering model to calculate TBC at a SAM-Au interface. This physical description of the thermal transport, based on the vibrational properties of the SAMs and the interface, may allow for predictions of mechanisms that may yield improvements in the previously mentioned fields.

**THEORY AND CALCULATIONS**

**Vibrational Spectra**

This study begins with calculation of the vibrational spectra of linear alkanedithiol molecules ranging from 5 to 15 methylene groups long. All calculations were performed using the Gaussian 09W program package. First, a molecule was constructed using Gaussview5 with an estimated geometry. The rough molecule was then sent to the Gaussian program to be optimized into the lowest energy structure possible using Hartree-Fock methods with LANL2DZ [13–15] basis.

In computational chemistry, HF methods are used to approximate the ground state wave function and energies of quantum many body systems [16]. In order to solve the Schrödinger equation of a many body system, HF methods make several assumptions or approximations. The Born-Oppenheimer approximation and the non-relativistic assumption are inherently made. When calculating the ground state wave function, it is assumed to be a linear combination of a finite number of basis functions. These basis functions must be supplied as an input, and can be customized or they can be selected from the most successful basis sets in literature. In this work we have chosen the LANL2DZ basis due to its computational efficiency. The method also assumes that each energy eigenfunction can be described by a single Slater determinate. This is important to the method, but its detailed description is out of the scope of the work. The final approximation, the mean field approximation, simplifies all the interactions on one particle into one average interaction. It is similar to approximating the effect of the planets on the Earth’s rotation by taking the average effect of each planet on the Earth and summing them into an averaged total effect. Using these assumptions and approximations, the Hamiltonian describing the many body system is then solved iteratively until a minimum eigen-energy is found. The output of these calculations is thus the lowest energy geometry of the molecule.
including bond lengths, bond angles, polarizations, polarizabilities and atomic coordinates.

Once the optimized structure is calculated, the curvature of the potential surface near the minimum along each bond stretching and bending coordinate is calculated. Under the HF harmonic assumption, this curvature is the force constant of each stretch or bend. From the force constants and masses of each atom, the classical system of equations for the many-body system may be constructed and solved yielding the normal modes and frequencies.

**Thermodynamic Properties**

Both specific heat ($c_p$) and molecular conductance ($G$) were calculated using standard quantum mechanical expressions,

$$ c_p = \sum_i \frac{\hbar \omega_i}{m} \frac{\partial f(\omega_i, T)}{\partial T}, \quad (1) $$

and,

$$ G = \frac{1}{3} \sum_i \frac{\hbar \omega_i v(\omega_i)}{L_{SAM}} \frac{\partial f(\omega_i, T)}{\partial T}. \quad (2) $$

where $\omega_i$ is the angular frequency of the $i^{th}$ vibrational mode, $f(\omega_i, T)$ is the Bose-Einstein distribution at temperature $T$, $v(\omega_i)$ is the group velocity of the $i^{th}$ mode and $L_{SAM}$ is the length of the SAM molecule being considered.

**Diffuse Scattering Model**

Using a diffuse scattering model developed for use with an isotropic material and an anisotropic contact layer, TBC was calculated. The model used is similar to that of Duda et al. [17] for solid-graphite junctions, but has been extended for use in solid-SAM junctions and employs a quasi-elastic formulation of detailed balance(For details refer to Case 3 from Duda et al. [18]).

The model begins by describing the phononic flux at either side of the interface. When describing the flux on the Au side of the interface, the phononic properties are assumed to be isotropic. Since the SAM molecules of the system of interest are aligned on Au(111), the phonon dispersion in the [111] direction was used for the phonon dispersion in all directions when calculating the phononic flux in Au. However, rather than using an exact dispersion, computations were simplified by approximating the dispersion with a sine type dispersion. Using this dispersion, the phonon flux from Au to the SAM becomes,

$$ q_{Au-SAM}^{Au} = \frac{1}{8\pi^2} \sum_j \int \hbar \omega_j(k_j) k_j^2 \zeta_{Au-SAM} \left| \nu_j(k_j) \right| f dk_j, \quad (3) $$

with,

$$ \omega_j(k_j) = \omega_{j, \text{cutoff}} \sin \left( \frac{a}{2\pi} k_j \right), \quad (4) $$

and,

$$ \nu_j(k_j) = \frac{\partial \omega_j(k_j)}{\partial k_j} = \frac{a}{2\pi} \omega_{j, \text{cutoff}} \cos \left( \frac{a}{2\pi} k_j \right), \quad (5) $$

where $f$ is the Bose-Einstein distribution, $\omega$ is the phonon angular frequency, $\omega_{\text{cutoff}}$ is the cutoff frequency, $\zeta$ is the transmission probability, $k$ is the wavevector, $v$ is the phonon group velocity, $j$ is the phonon polarization, $a$ is the lattice parameter, and the integration is over the first Brillouin zone. The flux calculation on the SAM side is approached a little differently than for Au. Duda et al. [17] showed that due to the weak interactions between graphite layers, there is very little coupling between the graphite layers. Thus, the anisotropic phononic flux for graphite can be approximated as a superposition of the 2-D fluxes for the individual graphite layers normalized by the spacing between layers. This idea was then extended to 1-D molecular SAMs by assuming that there is very little coupling between the SAM molecules and normalizing by the effective coverage area of the SAM. Due to the discreteness of the vibrational frequencies in a molecule a summation over frequencies was used rather than an integral and group velocities were assumed to be $k$ independent and were taken from experiment, yielding,

$$ q_{\text{SAM} \rightarrow Au} = \frac{1}{AL} \sum_i \hbar \omega_i \zeta_{\text{SAM} \rightarrow Au} \nu_i \chi, \quad (6) $$

where $A$ is the effective coverage area per alkanedithiol and $L$ is the length of the molecule calculated from the optimized structure. The group velocity was assumed to be...
950 m s\(^{-1}\) for all frequencies, which is the “heat propagation velocity” experimentally determined in Refs. 8 and 9 and the coverage area was taken to be 21.6 Å\(^2\) from Ref. 19. The “heat propagation velocity” was used in Refs. 8 and 9 to describe the propagation of thermal energy by the range of frequencies observable by their SFG experiment. When calculating the flux from SAM to Au, the frequencies were only summed up to the cutoff frequency of Au. Limiting the sum to the cutoff frequency of gold is equivalent to assuming that phonons elastically scatter across the Au-SAM interface. This implies that a phonon of frequency \(\omega\) can only scatter across the interface if a vibrational frequency of \(\omega\) is below the cutoff frequency of the opposite side of the interface. This assumption is validated by the findings of Segal and Nitzan, which show that very little anharmonic behaviour exists in linear alkanes, thus elastic processes will dominate at the interface. The final unknown is the transmission probability, which can be determined with application of detail balance and the diffuse scattering assumption, \(\zeta_{\text{Au} \rightarrow \text{SAM}} = 1 - \zeta_{\text{SAM} \rightarrow \text{Au}}\), where the following formulation parallels that of Ref. 18.

Application of the principle of detailed balance requires that the interface is in a state of equilibrium between side 1, Au, and side 2, SAM, implying that Eq. 3 and Eq. 6 must be equal. We then make the assumption that phonon scattering events are completely diffuse, i.e. have no memory of their polarization and direction after scattering from Au to SAM or vice versa. This is explicitly written as \(\zeta_{\text{Au} \rightarrow \text{SAM}} = 1 - \zeta_{\text{SAM} \rightarrow \text{Au}}\), showing that the probability of a phonon scattering from Au to the SAM is equal to one minus the probability of scattering from the SAM to Au. At this point the transmission probability can be solved for in terms of the material properties by setting Eq. 3 and Eq. 6 equal to one another yielding,

\[
\zeta_{\text{Au} \rightarrow \text{SAM}} = \frac{B}{B + C} \tag{7}
\]

\[
\zeta_{\text{SAM} \rightarrow \text{Au}} = \frac{C}{B + C} \tag{8}
\]

where,

\[
B = \frac{1}{8\pi^2} \sum_{k_j} \int \hbar \omega_j(k_j) k_j^2 | v_j(k_j) | f dk_j \tag{9}
\]

and,

\[
C = \frac{1}{AL} \sum_i \hbar \omega_i f v \tag{10}
\]

Taking the temperature derivative of the internal energy, which is contained in Eq. 3, yields the equation for TBC at the Au-SAM interface as,

\[
h^{\text{Au-SAM}} = \frac{1}{8\pi^2} \sum_{k_j} \int \hbar \omega_j(k_j) k_j^2 \zeta_{\text{Au} \rightarrow \text{SAM}} | v_j(k_j) | \frac{\partial f}{\partial T} dk_j. \tag{11}
\]

Using this equation, we calculated TBC for Au-alkanedithiol SAM junction, where the molecular lengths varied from 5 to 15 methylene groups long.

**RESULTS AND DISCUSSION**

To confirm that the HF calculations of vibrational spectra are consistent with those found in literature, we first qualitatively compare the calculated vibrational spectra of an individual pentadecanethiol (HS(CH\(_2\))\(_{15}\)SH) molecule to the spectra of pentadecane (H\(_2\)C(CH\(_2\))\(_{15}\)CH\(_3\)) calculated by Segal [7] in Fig. 1. Pentadecanethiol is an alkanedithiol (HS(CH\(_2\))\(_{15}\)SH) that is compared to pentadecane because both are linear chains of 15 methylene groups, \(N_M=15\). The difference being the terminal thiol (S-H) groups on pentadecanethiol. The top spectrum in Fig. 1 is calculated by Segal and Nitzan in Ref. 9. The lower is a histogram of the vibrational spectra for SAM molecules with \(N_M=5\), 8 and 15, pentanethiol (HS(CH\(_2\))\(_8\)SH), octanethiol (HS(CH\(_2\))\(_8\)SH) and pentadecanethiol respectively. For each additional methylene group 9 vibrational modes are added to the spectrum, only one of which falls below the cutoff frequency of gold, 156 cm\(^{-1}\) [19], and thus is able to contribute to elastic thermal transport across the interface. Both spectra have three characteristic regions, a broad region of low frequencies, a primarily vacant region in the 1500-3000 cm\(^{-1}\) range, and a densely populated region around 3000 cm\(^{-1}\). The high frequency region is due to the asymmetric vibrational modes of the hydrogens attached to the backbone of the SAM molecule. The peak around 1450 cm\(^{-1}\) is primarily due to symmetric hydrogen modes and some asymmetric carbon modes. The main discrepancy between the two calculations is the frequencies of
the symmetric and asymmetric C-H stretching modes in the 1500 and 3300 cm$^{-1}$ range. These modes are experimentally observed to lie closer to 1450 and 3000 cm$^{-1}$ [20]. This is expected since HF methods tend to over predict vibrational frequencies by about 10% [21].

Figure 2 shows a comparison of specific heat calculated for octane (H$_3$C(CH$_2$)$_8$CH$_3$), $N_M$=8, from the calculated vibrational spectra to that of experimental crystalline polyethylene (H$_3$C(CH$_2$)$_{Large}$CH$_3$) data. The heat capacity data calculated from the HF vibrational spectra are used as a calibration of the subsequent properties based on calculated spectra. As can be seen from Fig. 2, the calculated octane specific heat data very closely matches experimental crystalline polyethylene data [22]. Octane was chosen because, like polyethylene, it is a linear saturated organic molecule that should have similar properties below the boiling point of octane. This calibration was used to gain an estimate of the accuracy of the following calculations. Figure 2 provides an illustration of the change of specific heat with chain length at a low temperature of 300 K and a high temperature of 1000 K. At 300 K, there is very little affect on specific heat with increasing chain length. However, at 1000 K, $\sim$1000 J kg$^{-1}$ K$^{-1}$ change in heat capacity is calculated for a 12.5 Å increase in molecular length corresponding to an increase from 5 to 15 methylene groups. This is because the Bose-Einstein statistics allow more of the higher frequency modes to participate in the specific heat at higher temperatures. Therefore, each additional methylene group contributes more to specific heat at higher temperatures. As previously mentioned,
the high frequency antisymmetric C-H vibrations do not affect the specific heat at these temperatures. This is again due to the Bose-Einstein distribution having very low expectation values for those modes at 1000 K.

During the thermal investigations of SAMs by Refs. 8 and 9, the “heat propagation velocity” was calculated to be 950 m s\(^{-1}\) based on time resolved observations of SFG. Assuming that all vibrations propagate at this group velocity and that the length of the SAM is not significantly changed by heating, the molecular conductance can be calculated from Eq. 2 and the HF spectra. Under these assumptions, the molecular conductance then becomes the heat capacity scaled by both the assumed group velocity, which is the heat propagation velocity, and the length of the molecule.

Figure 4 shows the molecular conductance of alkanedithiol plotted versus chain length at 300 K and 1000 K. Very little dependence on chain length is observed at either temperature. However, a mild disagreement seems to exist in the actual magnitude of the determined molecular conductances. At 1000 K, Wang et al. calculates \(\sim 50 \text{ pW K}^{-1}\) from experimental SFG measurements [8, 9]. Segal calculates \(\sim 95 \text{ pW K}^{-1}\) from theoretical quantum mechanical calculations [7]. This study yields values in the 200 pW K\(^{-1}\) range. This discrepancy is most likely due to the frequency independent group velocity assumption made previously, causing modes with low group velocities to over contribute to thermal transport. A more accurate calculation could be made using exact group velocities for each frequency, but the point of this work is an assessment of the TBC trends observed with respect to SAM molecular length.

Using the diffuse scattering model, the effect of SAM length on Au-SAM TBC was studied. Figure 5 shows the calculated TBC versus number of methylene groups at 300 K and 1000 K. Thermal boundary conductance is

![FIGURE 4. CALCULATED MOLECULAR CONDUCTANCE PLOTTED VERSUS NUMBER OF METHYLENE GROUPS IN ALKANEDITHIOL MOLECULES AT 300 K AND 1000 K.](image1)

![FIGURE 6. NUMBER OF MODES THAT FALL BELOW THE CUTOFF FREQUENCY OF GOLD VERSUS THE LENGTH OF INDIVIDUAL SAM MOLECULES.](image2)

![FIGURE 7. NUMBER OF MODES THAT FALL BELOW THE CUTOFF FREQUENCY OF GOLD PER UNIT LENGTH OF THE SAM MOLECULE.](image3)
weakly dependent on chain length. That is, TBC increases only 30% from the shortest SAM (\(N_M=5\)) to longest SAM (\(N_M=15\)) despite the factor of 150% increase in length. This is in general in good agreement with findings by Refs. 7-10. The question then becomes, why do we consistently observe an independence of TBC on chain length?

Figure 6 is a plot of the number of vibrational modes that fall below the cutoff frequency of gold versus \(N_M\). Comparing the SAM vibrational spectra to the density of states of gold as in Fig. 1, it is clear that very few vibrational frequencies fall below the cutoff frequency of Au (156 cm\(^{-1}\) [19]) as is seen in Fig. 6. This implies that there are very few modes that are elastically accessible for thermal transport and thus a low TBC is expected. As can also be seen, approximately one mode is added below the cutoff frequency of gold per methylene group, which means that there are very few additional elastic scattering channels added per methylene group, implying very little change in TBC. Figure 7 plots the number of modes that fall below the cutoff frequency of gold per unit length. This in essence can be taken to be the density of states overlap between Au and SAM. It can also be seen, there is a very small upward trend, but TBC is generally invariant with chain length. It has been shown that TBC is closely linked to vibrational overlap [23]. Thus, attempts to augment TBC of Au-alkanedithiol SAM junctions by variation of SAM molecular length will to a large extent be unsuccessful.

CONCLUSION

We have developed a diffuse scattering model specifically applicable to solid-SAM junctions. Using the SAM molecule vibrational spectra calculated by Hartree-Fock methods, we then calculated heat capacity, molecular conductance and then TBC of a gold alkanedithiol SAM junction. In general, the results were in good agreement with experiment and previous calculations, especially in trend.

Through investigations of the calculated vibrational spectra, it was determined that the insensitivity of TBC to molecular length is due to a limited change in volumetric density of states overlap. Because the overlap does not change significantly with increasing molecular length, the number of modes that are elastically accessible under the elastic scattering assumption is relatively constant. Therefore, for each additional methylene group, few modes are added that are able to elastically participate in thermal conductance, leading to an observed insensitivity of TBC to molecular length.

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