LETTER

Reduced thermal conductivity of supported and encased monolayer and bilayer MoS$_2$

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Abstract

Electrical and thermal properties of atomically thin two-dimensional (2D) materials are affected by their environment, e.g. through remote phonon scattering or dielectric screening. However, while it is known that mobility and thermal conductivity (TC) of graphene are reduced on a substrate, these effects are much less explored in 2D semiconductors such as MoS$_2$. Here, we use molecular dynamics to understand TC changes in monolayer (1L) and bilayer (2L) MoS$_2$ by comparing suspended, supported, and encased structures. The TC of monolayer MoS$_2$ is reduced from ~117 W m$^{-1}$K$^{-1}$ when suspended, to ~31 W m$^{-1}$K$^{-1}$ when supported by SiO$_2$, at 300 K. Encasing 1L MoS$_2$ in SiO$_2$ further reduces its TC down to ~22 W m$^{-1}$K$^{-1}$. In contrast, the TC of 2L MoS$_2$ is not as drastically reduced, being >50% higher than 1L both when supported and encased. These effects are due to phonon scattering with remote vibrational modes of the substrate, which are partly screened in 2L MoS$_2$. We also examine the TC of 1L MoS$_2$ across a wide range of temperatures (300 K to 700 K) and defect densities (up to $5 \times 10^{13}$ cm$^{-2}$), finding that the substrate reduces the dependence of TC on these factors. Taken together, these are important findings for all applications which will use 2D semiconductors supported or encased by insulators, instead of freely suspended.

1. Introduction

Two-dimensional (2D) semiconducting MoS$_2$ is a promising material for technologies beyond silicon [1, 2], flexible and transparent electronics [3, 4], and thermoelectric applications [5, 6]. However, it is known that electrical and thermal conductivities in other atomically thin 2D materials, like graphene, degrade when in contact with a substrate due to scattering with substrate impurities or remote phonons [7–9]. This occurs because electron and phonon wavelengths are comparable to or larger than the 2D material thickness, especially in monolayers. In realistic applications, 2D materials will almost always be used in contact with a metal (for contacts) or an insulator (for gate dielectrics, substrates, or encapsulation layers), thus it is important to understand their thermal properties in this context. Moreover, it is already known that thermal bottlenecks limit nanoelectronics performance with traditional semiconductors [10, 11]. Therefore, such considerations must be included when evaluating future 2D material applications.

Thermal transport in 2D materials is fundamentally different than in bulk because transport is confined to two dimensions and 2D material interfaces are dominated by van der Waals (vdW) interactions, which present a bottleneck to heat removal from 2D devices [12, 13]. In fact, the MoS$_2$–SiO$_2$ vdW interface is known to have a large thermal resistance, equivalent to that of ~90 nm of SiO$_2$ [12]. To understand its effect in the context of a 2D device, we refer to figure 1. For a thermally ‘long’ 2D device (of length $L \gg 3L_{th}$, where $L_{th} \sim 0.1 \mu$m is the thermal heating length [14]), the temperature rise is mostly determined by this interfacial thermal resistance [14, 15]; however, for thermally ‘short’ devices ($L < 3L_{th}$) heat can be removed at the contacts and the temperature
rise strongly depends on the lateral, in-plane thermal conductivity of the 2D material [15]. Given that 2D devices have already been demonstrated with sub-100 nm dimensions [16–19], it is crucial to determine how the substrate limits the thermal conductivity of 2D materials like MoS₂.

Thermal measurements of geological, bulk MoS₂ samples have estimated an in-plane thermal conductivity [20–24] of 82 to 110 W m⁻¹ K⁻¹ and cross-plane thermal conductivity of ~5 W m⁻¹ K⁻¹ [25]. On the other hand, a vast majority of measurements of monolayer (1L) MoS₂ exist only for freely suspended samples, revealing a range of 13 to 97 W m⁻¹ K⁻¹ for the in-plane thermal conductivity, ostensibly due to sample-to-sample variation between mechanically exfoliated [26, 27] and chemically synthesized samples [28–32]. (Below, we will see that variation of defect densities could explain this measurement variation.) Simulation efforts also display large variations due to different techniques or inter-atomic potentials, and have only focused on bulk or suspended MoS₂. Interestingly, most simulations find the 1L in-plane thermal conductivity to fall in two distinct ranges at 300 K (excluding studies with extremely high or low values), i.e. between 19 to 38 W m⁻¹ K⁻¹ on the low end [26, 33–41] and between 82 to 178 W m⁻¹ K⁻¹ on the high end [30, 42–56], with no calculations falling between the two (as summarized in supplementary figure S1 (available online at stacks.iop.org/2DM/8/011001/mmedia)).

Despite these efforts, there are no simulation studies on the thermal conductivity of MoS₂ supported or encased by an insulator such as SiO₂, and only one recent experiment [57]. In contrast, several studies of substrate-supported [7, 8, 57–59] or encased [60] graphene have found its thermal conductivity reduced by 5–10× or 30–40×, respectively, compared to suspended graphene, agreeing well with simulations [8, 61]. Similarly, simulations of SiO₂-supported silicene [62] predict ~78% thermal conductivity degradation compared to suspended silicene. One reason for the lack of thermal measurements on other supported or encased 2D semiconductors is that their thermal conductivity is much lower than graphene. This makes it difficult to distinguish the heat flowing laterally in the ultrathin 2D material vs. the much thicker supporting or encasing insulator. Thus, this is an area where atomistic simulations can play an important role, not only to quantify the effects of the adjacent insulator on the thermal conductivity of a 2D semiconductor, but also to provide physical insight into why this occurs, opening the door for tuning such 2D material properties. This is the aim of the present study, with respect to 1L and 2L MoS₂, supported and encased by SiO₂.

2. Simulation methodology

The thermal conductivities of crystalline materials can be well described by the Peierls-Boltzmann transport equation paired with calculations from density functional theory [63]. However, when systems have broken symmetry, these methods struggle to reproduce experimental measurements [64]. Such is the case for supported 2D material systems (which include interfaces) and disordered materials (i.e. amorphous, defective), both breaking symmetry. Given that adequate material potentials exist, classical molecular dynamics (MD) can overcome these limitations and accurately model all anharmonicities and phonon-phonon interactions at relevant length and time scales [51]. Recently, a comparative study of empirical MD potentials has determined the optimal potential for thermal transport in MoS₂ [51], making MD a more attractive method. For these reasons, we choose to use MD for all simulations in this study.

All results in this study are calculated using the Graphics Processing Units Molecular Dynamics (GPUMD, here version 2.1) package [65–67]. For supported and encased MoS₂ calculations, we
modified the GPUMD package to isolate only the MoS$_2$ contributions to thermal conductivity. We use the LAMMPS package [68,69] to check for consistent forces between the different simulation packages. To model the atomic interactions in MoS$_2$, as well as between layers of MoS$_2$, we use the reactive empirical bond-order potential with a Lennard-Jones addition (REBO-LJ) [70, 71]. The REBO-LJ implementation in GPUMD has a modification introduced by Stewart and Spearot [72], and we use the LJ parameters designed for a 300 K crystal temperature [71]. We model the SiO$_2$ with the Tersoff potential [73] parameterized by Munetoh et al [74] and the MoS$_2$-SiO$_2$ van der Waals (vdW) interactions with the LJ potential using the Lorentz-Berthelot mixing rules. The mixing parameters are listed in table S1 of the supplement.

All simulations are based on three structures: suspended MoS$_2$, MoS$_2$ supported on amorphous SiO$_2$ (a-SiO$_2$), or MoS$_2$ encased (top and bottom) by a-SiO$_2$. We study both monolayer and bilayer MoS$_2$ in these scenarios. The simulation cell areas are 10 $\times$ 10 nm$^2$, the MoS$_2$ monolayer is 6.15 Å thick, consistent with experimental observations [75], and the a-SiO$_2$ substrate is 5.4 nm thick as shown in figure 1(c). We choose our simulation cell area to be the minimum size needed to reproduce the 1L MoS$_2$ thermal conductivity results from previous work [51] and find the MoS$_2$ thermal conductivity to be independent of a-SiO$_2$ thickness (see section 3 in the supplement). We use periodic in-plane boundary conditions (BCs) to model an infinite MoS$_2$ sheet and minimize finite-size effects on phonon mean free paths. In the out-of-plane direction, vacuum and free BCs are used. The a-SiO$_2$ is created by a simulated annealing, the details of which can be found in section 4 of the supplement.

To compute the thermal conductivity we use the homogeneous nonequilibrium MD (HNEMD) method [76]. This method is consistent with, but more efficient than, the commonly used equilibrium MD (EMD) and nonequilibrium MD (NEMD) methods [77], and it does not have boundary scattering because of periodic BCs in the transport direction. The HNEMD method requires an additional driving force parameter $F_e$ to calculate an applied external force [76]. Because MoS$_2$ has hexagonal symmetry, the intrinsic in-plane thermal conductivity is isotropic. As such, we apply the driving force parameter in only one direction, reducing it to a scalar. Here we choose $F_e = 0.2 \mu$m$^{-1}$, consistent with previous HNEMD simulations for MoS$_2$ [51]. The thermal conductivity $\kappa$, with a simplification due to isotropy, is then [51, 76]:

$$\kappa(t) = \frac{1}{T} \frac{1}{V} \frac{1}{t} \int_0^t \left( \langle J(\tau) \rangle_{\text{eff}} / TVF_e \right) d\tau$$

(1)

where $J$ is the heat current, $T$ is the temperature, and $V$ is the system volume. The integral represents a post-processed, running average of thermal conductivity over a simulation up to time $t$. The integrand is the direct thermal conductivity calculated by GPUMD. Using a time step of 0.5 fs, we output average heat current every 500 fs, and use equation (1) to compute the final value of thermal conductivity, which converges by 10 ns. (Additional simulation details are given in supplementary section 5.)

Due to the influence of the driving force parameter ($F_e$) on the heat flux and the direct calculation of thermal conductivity, the HNEMD method is able to compute the substrate-supported thermal conductivity, a situation where using the EMD method was shown to be challenging [62]. Furthermore, GPUMD decomposes the in-plane thermal conductivity into contributions from in-plane atomic motion (dominant in longitudinal and x-y transverse phonons) and out-of-plane atomic motion (dominant in flexural phonons) [52]. Schematics of phonons related to each type of motion are shown [78] in figure 1(d) and discussed further below. More details about the HNEMD thermal conductivity and the GPUMD heat flux formulation can be found in [76] and [79]. The final thermal conductivity of each simulation is taken to be $\kappa (t = 10 \text{ ns})$ using equation (1). Our reported values are averaged over $n = 10$ independent runs (i.e. simulations with different initial velocities) with a standard error of $\sigma / \sqrt{n}$, where $\sigma$ is the standard deviation of $\kappa (t = 10 \text{ ns})$ values over the $n$ independent runs.

3. Results and discussions

3.1. Monolayer MoS$_2$

We first calculate the in-plane thermal conductivity of suspended and SiO$_2$-supported monolayer MoS$_2$ in figures 2(a) and (b) respectively, including its decomposition into in-plane and out-of-plane atomic motion contributions. The suspended 1L MoS$_2$ thermal conductivity (converged at $t = 10$ ns and averaged over $n = 10$ independent runs) is $\kappa = 117.0 \pm 2.0 \text{ W m}^{-1} \text{ K}^{-1}$ (in agreement with measurements of bulk [20] MoS$_2$ and recent simulations [51]) with contributions from in-plane atomic motion of $85.9 \pm 2.1 \text{ W m}^{-1} \text{ K}^{-1}$ and out-of-plane motion of $31.1 \pm 1.6 \text{ W m}^{-1} \text{ K}^{-1}$. In contrast, we find the in-plane thermal conductivity of MoS$_2$ supported on a-SiO$_2$ to be $30.9 \pm 1.5 \text{ W m}^{-1} \text{ K}^{-1}$ (~74% decrease) with in-plane and out-of-plane contributions of $26.3 \pm 1.2 \text{ W m}^{-1} \text{ K}^{-1}$ (~69% decrease) and $4.6 \pm 0.7 \text{ W m}^{-1} \text{ K}^{-1}$ (~85% decrease), respectively. We note this result is smaller than the $63 \pm 22 \text{ W m}^{-1} \text{ K}^{-1}$ recently measured for SiO$_2$-supported MoS$_2$ [57]; however, a sputtered, 20 nm Ni capping layer may have affected these in-plane thermal conductivity measurements.

While our simulations show a greater proportion of the out-of-plane contribution is damped on...
Figure 2. Total thermal conductivity (green lines) of (a) suspended 1L MoS$_2$ and (b) SiO$_2$-supported 1L MoS$_2$ including contributions from in-plane (blue lines) and out-of-plane (red lines) atomic motion. Semi-transparent lines represent independent simulations, solid lines represent averages over all runs, and dotted lines show the standard error. The percent reduction in thermal conductivity from suspended to supported MoS$_2$ is labeled in (b). The elemental vibrational density of states (VDOS) for the suspended and supported MoS$_2$ systems are shown in (c) and (d), respectively, with the shaded regions highlighting the heat-carrying, acoustic phonons in MoS$_2$.

The reduction of the in-plane contribution drives the overall reduction in thermal conductivity. This contrasts the thermal conductivity reduction in supported graphene, which, experimentally and through simulation, has been shown to suffer an $\sim$80% to $\sim$90% degradation mostly from the damping of its out-of-plane motion (which directly corresponds to flexural phonons in graphene) [7, 8, 61]. The difference is due to the dominant mode of thermal transport in MoS$_2$ and graphene. Graphene follows a symmetry-based selection rule that restricts anharmonic phonon-phonon scattering of flexural modes [80] leading to an out-of-plane contribution that carries approximately $2 \times$ more heat than in-plane [81]. Monolayer MoS$_2$ is three atoms thick and does not follow this rule, leading to an in-plane contribution that carries more than $2 \times$ the heat of its out-of-plane contribution. Thus, our findings show that the suppression of the dominant mode of thermal transport (out-of-plane atomic motion for graphene, in-plane for MoS$_2$) drives the overall reduction of thermal conductivity in supported 2D materials, not only the damping of the out-of-plane motion.

To better understand thermal transport in supported MoS$_2$, we plot the vibrational density of states (VDOS) of both suspended and supported MoS$_2$ with a-SiO$_2$ in figures 2(c) and (d), respectively. From either VDOS plot, we can see that molybdenum contributions to the overall VDOS are much larger than sulfur below 8 THz. This is the frequency range of the acoustic modes which are the main heat carriers [56], meaning that much of the thermal transport is carried out by vibrations of molybdenum atoms. Because the acoustic modes of MoS$_2$ do not appear to be affected by the substrate, we conclude that additional scattering with the SiO$_2$ causes the reduction in thermal conductivity of supported MoS$_2$. This is confirmed by figure 2(d) which reveals a significant overlap of the a-SiO$_2$ and MoS$_2$ VDOS, especially at the lower frequencies of the heat-carrying acoustic modes. The supported MoS$_2$ phonons have substantially more modes (including substrate vibrations) to interact with, i.e. through anharmonic scattering or harmonic energy transfer [82], disrupting thermal transport in the MoS$_2$ and reducing its thermal conductivity. This phenomenon is similar to that of remote phonon scattering for the reduction of transistor mobility in ultrathin films or silicon inversion layers [83,84]. For additional details on the calculation of the VDOS, see supplementary section 7.

3.2 Temperature dependence

MoS$_2$ electronic devices will sometimes operate several hundred Kelvin above room temperature as seen already in self-heating field-effect transistors [13,85], and as desired for some thermoelectric applications...
Thus, we also investigate the thermal conductivity of both suspended and supported MoS₂ from 300 K to 700 K. This range is above the Debye temperature ($θ_D$) of MoS₂, ensuring the validity of these classical MD simulations without the need for quantum corrections [87]. For suspended 1L MoS₂, previous calculations [38] have placed the Debye temperature at $θ_D ≈ 262$ K, with bulk MoS₂ measured to be $θ_D ≈ 260–320$ K [88]. The simulation results for suspended 1L MoS₂ are shown in figure 3(a), revealing a steep temperature-related decline for both in-plane and out-of-plane atomic motion contributions. The overall reduction of thermal conductivity with temperature scales as $κ ∝ T^{-1.94}$ (solid black line) which implies a stronger contribution of four-phonon scattering [89] ($κ ∝ T^{-2}$; more common at high $T > θ_D$ which also plays a role at high temperature in Si and Ge) [90, 91] than of three-phonon Umklapp scattering ($κ ∝ T^{-4}$; dashed black line).

This temperature dependence appears stronger than in other suspended low-dimensional materials, such as carbon nanotubes and graphene (with natural concentrations of $^{13}$C isotopes), which experimentally show a $T^{-x}$ dependence, with $1.1 < x < 1.3$ [92, 93]. However, the carbon nanotube and graphene data do not probe temperatures above their $θ_D$, which is very high, $θ_D ≈ 2100$ K [94]. In addition, the temperature dependence of isotopically pure graphene (0.01% $^{13}$C) was found to be steeper than for natural graphene [93]. Since our modeled Mo and S masses are weighted averages over naturally occurring isotopes, we effectively have an isotopically pure system (i.e. one mass for each atom type), which may explain why the temperature dependence we find here for MoS₂ is more akin to that of isotopically pure graphene. Relevant details on the kinetic theory and fitting can be found in supplementary sections 8 and 9, respectively.

Figure 3(b) shows the temperature dependence of supported 1L MoS₂ is substantially different than the suspended 1L MoS₂. We note that, since the out-of-plane motion is already severely damped by the substrate, the in-plane contribution dominates the total thermal conductivity reduction with temperature. Comparing our calculations to kinetic theory again, we find the temperature decay scales as $~T^{-1.2}$, which suggests that three-phonon processes dominate the reduction of thermal conductivity with temperature. However, this is not necessarily an accurate characterization of the dominant phonon processes in MoS₂ because we cannot decouple its intrinsic scattering events from those involving the substrate vibrations. We do know that the four-phonon processes, which are influential in our suspended MoS₂, are overwhelmed by the effects of the substrate.

3.3. Defect dependence

It is known that the properties of 2D materials are degraded or altered by defects that are either naturally occurring or introduced during growth or layer transfer processes [95]. Here, we study the effects of the most common defect type, zero-dimensional sulfur vacancies [95–99], on the thermal conductivity of MoS₂. Previous experimental studies have reported sulfur vacancy densities from $n_v = 7 \times 10^{10}$ cm$^{-2}$ to $6.5 \times 10^{13}$ cm$^{-2}$ for exfoliated MoS₂ or MoS₂ grown by chemical vapor deposition (CVD) [97–101]. For this set of simulations, we randomly introduce sulfur vacancies such that their density ranges from $10^{12}$ cm$^{-2}$ to $5 \times 10^{13}$ cm$^{-2}$, which corresponds to 1 to 50 sulfur vacancies in the simulated $10 \times 10$ nm$^{2}$ MoS₂ sheet. Overall, there are no vacancy clusters and...
we expect similar trends for different single sulfur vacancy configurations [54].

The results for suspended MoS$_2$ are shown in figure 4(a), with vacancy-free calculations plotted left of the x-axis break for reference. Here we find that a small vacancy density of 10$^{12}$ cm$^{-2}$ already reduces the total thermal conductivity by ~19%. For the vacancy densities studied, the calculated thermal conductivity range is 94.4 ± 3.1 W m$^{-1}$ K$^{-1}$ to 30.7 ± 2.5 W m$^{-1}$ K$^{-1}$, which encompasses the experimental results of ~84 W m$^{-1}$ K$^{-1}$ for exfoliated 1L MoS$_2$ and ~30 W m$^{-1}$ K$^{-1}$ for CVD-grown 1L MoS$_2$ [27, 29]. This relationship between our calculations and experiment is not unexpected because CVD-grown MoS$_2$ could be more defective than exfoliated [97, 98], particularly at the time of the measurements referenced here. Recent Peierls-Boltzmann transport calculations have also pointed to defects when explaining the large range in reported experimental thermal conductivities [54].

We also find that the contribution from out-of-plane motion is less sensitive to defects than the in-plane contribution. This imbalance is most severe at our lowest defect density (10$^{12}$ cm$^{-2}$) as the out-of-plane contribution, when compared to our defect-free structure, is reduced by only ~7% compared to the ~24% reduction of the in-plane contribution. The dashed line in figure 4(a) plots the expected defect dependence trend based on kinetic theory ($\kappa \propto n_v^{-1}$) [89]. The suspended MoS$_2$ follows this trend with small deviations at extremes. More information on the relevant kinetic theory and fitting can be found in supplementary sections 8 and 9, respectively.

Compared to defective suspended MoS$_2$, defective supported MoS$_2$ has a thermal conductivity that is less sensitive to changes in vacancy density. Figure 4(b) reveals that the thermal conductivity only decreases by ~5.5% at a vacancy density of 10$^{12}$ cm$^{-2}$ compared to defect-free, supported MoS$_2$. At the highest vacancy density, the thermal conductivity has decreased by ~58% to 12.9 ± 1.2 W m$^{-1}$ K$^{-1}$, which comes from a ~62% decrease to 10.0 ± 1.0 W m$^{-1}$ K$^{-1}$ from the in-plane contribution and a ~36% decrease to 2.9 ± 0.6 W m$^{-1}$ K$^{-1}$ from the out-of-plane contribution, with respect to defect-free, supported MoS$_2$. We note that the out-of-plane contribution is not as sensitive to defects as the in-plane contribution. For supported MoS$_2$, vacancies are not the dominant dampening factor to the out-of-plane motion because the substrate effects are much stronger. As before, in figure 4(b) we also show the total thermal conductivity vs. vacancy density based on kinetic theory (dashed line). The trend agrees well with our simulations, suggesting that effects of the substrate and defects on thermal conductivity are not coupled. Overall, the thermal conductivity of supported MoS$_2$ is significantly lower than of suspended MoS$_2$ (for the same defect density), meaning the substrate always plays a substantial role in reducing the thermal conductivity of monolayer MoS$_2$.

3.4. Bilayer MoS$_2$

In addition to 1L MoS$_2$, we also investigate the thermal properties of the bilayer (2L) material, which is of interest for electronics because it has smaller band gap, lower contact resistance, and generally higher mobility [102, 103]. We repeat the previous simulation protocol but with a Bernal-stacked (ABA) 2L MoS$_2$. The resulting suspended bilayer thermal conductivity, seen in figure 5(a), is $\kappa_{2L} = 94.6 \pm 1.6$ W m$^{-1}$ K$^{-1}$ and is consistent with previous 2L MoS$_2$ simulations [51]. The
in-plane contribution is $73.0 \pm 2.1 \text{ W m}^{-1} \text{ K}^{-1}$ and out-of-plane atomic vibrations contribute $21.6 \pm 0.9 \text{ W m}^{-1} \text{ K}^{-1}$, representing a $\sim15\%$ and $\sim30\%$ decrease from suspended 1L MoS$_2$. For suspended 2L, we note out-of-plane motion contributes a smaller proportion of the thermal conductivity compared to 1L MoS$_2$. Previous studies attributed this to a change in the phonon dispersion as well as an increase in flexural phonon scattering rates [27, 52]. The drop in thermal conductivity from 1L to 2L is also consistent with experiment [27], although the measurement uncertainty does not yield a definitive trend.

Our supported 2L MoS$_2$ calculations, seen in figure 5(b), reveal a thermal conductivity of $46.8 \pm 1.8 \text{ W m}^{-1} \text{ K}^{-1}$ ($\sim50\%$ decrease vs. suspended 2L) with in-plane and out-of-plane contributions of $38.5 \pm 1.8 \text{ W m}^{-1} \text{ K}^{-1}$ ($\sim47\%$ decrease) and $8.3 \pm 0.3 \text{ W m}^{-1} \text{ K}^{-1}$ ($\sim61\%$ decrease), respectively. This thermal conductivity is $50\%$ larger than supported 1L MoS$_2$. Thus, given it has double the thickness, supported 2L MoS$_2$ can carry three times more heat than supported 1L MoS$_2$. The top layer of 2L MoS$_2$ is partly 'shielded' (screened) from remote phonon scattering with the a-SiO$_2$ better maintaining intrinsic behavior and yielding a higher thermal conductivity than supported 1L MoS$_2$. Again, we find the suppression of in-plane atomic motion drives the overall reduction in thermal conductivity. Experimentally, a larger thermal conductivity in supported 2L MoS$_2$ than 1L MoS$_2$ has also been observed [57].

These results have interesting implications for 2L-based electronic devices because, in addition to improved lateral heat flow (as seen here), previous work has also suggested that 2L MoS$_2$ has a lower thermal boundary resistance with SiO$_2$ than 1L MoS$_2$ [104], i.e. better cross-plane heat flow. In other words, heat removal from 2L-based MoS$_2$ devices is expected to be better than 1L devices all-around. Thus, 2L MoS$_2$ could be more attractive for flexible electronics and integrated circuit applications, where heat removal is more important, in addition to its electronic advantages mentioned earlier.

3.5. Encased monolayer and bilayer MoS$_2$

For technological reasons such as encapsulation, doping, or top-side gating, MoS$_2$ devices are often encased by a superstrate, such as an oxide [17, 103, 105, 106]. In order to simulate these circumstances, we duplicate the substrate and place it above MoS$_2$, creating the SiO$_2$-encased 1L and 2L MoS$_2$ structures shown in the insets of figure 6. In figure 6(a), we find the thermal conductivity of encased 1L MoS$_2$ is $22.1 \pm 1.8 \text{ W m}^{-1} \text{ K}^{-1}$, with in-plane and out-of-plane contributions of $18.3 \pm 1.4 \text{ W m}^{-1} \text{ K}^{-1}$ and $3.8 \pm 0.6 \text{ W m}^{-1} \text{ K}^{-1}$, respectively. Compared to supported 1L MoS$_2$, the thermal conductivity drops an additional $\sim28\%$. A similar degradation of the thermal conductivity of encased graphene was observed experimentally [60], but with a $\sim70\%$ decrease from supported [7] to encased [60]. However, we note that in the encased experiments [60] the graphene may have been damaged during the top SiO$_2$ layer deposition, partly causing the lower thermal conductivity.

Surprisingly, the 1L MoS$_2$ out-of-plane contribution only dropped by $\sim17\%$ from supported to encased structures, in stark contrast to the $\sim85\%$ drop from suspended to supported structures. This suggests a substrate already suppresses most out-of-plane motion and a superstrate cannot suppress it much further. Additionally, comparisons of the VDOS calculations (as in figure 2(d) but for encased MoS$_2$) reveal non-negligible changes in the out-of-plane VDOS for sulfur atoms ($\sim10\%$–$15\%$ reduction for superstrate structure) for frequencies above 10 THz. These frequencies are in the optical phonon range which do not contribute significantly to thermal conductivity in MoS$_2$ due to low phonon velocities. The main reduction factor is likely the large number of vibrational modes in a-SiO$_2$ (encased structure has...
twice as many as supported structure) that MoS$_2$ phonons can interact with.

We also examine encased 2L MoS$_2$ as shown in figure (b). We repeat the simulation protocol verbatim except we reduce the run time from 10 ns to 5 ns when the thermal conductivity appears sufficiently converged. The thermal conductivity of encased 2L MoS$_2$ is $36 \pm 0.2$ W m$^{-1}$ K$^{-1}$, a decrease of $\sim23\%$ from the supported 2L structure (and a decrease of $\sim62\%$ from suspended bilayer). However, this reduction is proportionally less than that experienced by the encased 1L MoS$_2$. Overall, encased 2L MoS$_2$ has a thermal conductivity $\sim63\%$ larger than and can carry over three times the heat of encased 1L MoS$_2$. Thus, 2L MoS$_2$ will have a higher thermal conductivity than the monolayer, both when interacting with a substrate and/or superstrate, making 2L MoS$_2$ more attractive for applications with larger heat removal requirements. An increase in thermal conductivity with number of layers was also measured in encased graphene around room temperature [60]. As it did in graphene, we expect the thermal conductivity of encased MoS$_2$ to increase with number of layers up to the bulk MoS$_2$ thermal conductivity value ($83 \pm 3$ W m$^{-1}$ K$^{-1}$ for MoS$_2$ using this potential [51]). Given that remote phonon scattering (with the substrate) only penetrates up to $\sim1$ nm into the MoS$_2$ (see section 3 of the supplement), we expect the thermal conductivity of encased MoS$_2$ to converge to the bulk value within a few layers. However, an extended study on the layer-dependent thermal conductivity for supported and encased MoS$_2$, up to bulk-like thickness, is left for follow-up work.

4. Summary and conclusions

We investigated the effects of an SiO$_2$ substrate and encapsulation on the in-plane thermal conductivity of MoS$_2$ using molecular dynamics simulations. Figure 7 summarizes the thermal conductivities of all structures considered. The thermal conductivity of 1L MoS$_2$ decreases from $\sim117$ W m$^{-1}$ K$^{-1}$ (suspended) to $\sim31$ W m$^{-1}$ K$^{-1}$ when supported by an a-SiO$_2$ substrate, a drop of $\sim74\%$ due to remote phonon scattering with a-SiO$_2$ vibrational modes. While out-of-plane atomic motion is more sensitive to substrate effects, we found the dominant mode of thermal transport drives the overall reduction in thermal conductivity of supported 2D materials; for MoS$_2$ it is the in-plane atomic motion, for graphene it is the out-of-plane atomic motion.

Our simulations suggest that a large range of defect concentrations could explain the range of thermal conductivities measured for suspended MoS$_2$ in the literature. However, the thermal conductivity of supported MoS$_2$ appears less sensitive to sulfur vacancy defects (up to $5 \times 10^{13}$ cm$^{-2}$) and temperature (up to 700 K) than suspended MoS$_2$. In both supported and encased structures we found 2L has $>50\%$ higher thermal conductivity than 1L.
MoS$_2$, thus it can carry over three times more heat. In other words, for certain applications (like integrated circuits) 2L (or slightly thicker) MoS$_2$ could be preferred from a purely thermal point of view because it suffers less from substrate or encapsulation effects than 1L MoS$_2$. However, thicker films could also have drawbacks from cross-plane heat transport [25], and ultimately applications must consider a combined electro-thermal design. Overall, our results will lead to more informed device or system designs with 2D materials from a thermal perspective.

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