

Thermal Ripples in Model Molybdenum Disulfide Monolayers

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Dedicated to Professor Anthony K. Cheetham on the Occasion of his 70th Birthday

Abstract. Molybdenum disulfide (MoS₂) monolayers have the potential to revolutionize nanotechnology. To reach this potential, it will be necessary to understand the behavior of this two-dimensional (2D) material on large length scales and under thermal conditions. Herein, we use molecular dynamics (MD) simulations to investigate the nature of the rippling induced by thermal fluctuations in monolayers of the

2H and 1T phases of MoS₂. The 1T phase is found to be more rigid than the 2H phase. Both monolayer phases are predicted to follow long wavelength scaling behavior typical of systems with anharmonic coupling between vibrational modes as predicted by classic theories of membrane-like systems.

Introduction

Recent years have seen renewed interest in layered van der Waals (vdW) materials in part because of the possibility to create novel monolayers and other few-layer nanostructures. This movement was initially driven by interest in carbon-based monolayers, such as graphene,^[1,2] and now inorganic structures have become the focus of much attention.^[1–6] One such class of 2D materials is the transition metal dichalcogenides (TMDCs). Monolayer TMDCs, created through exfoliation^[1] or unzipping^[7] of nanotubes,^[8] for example, display a wide array of unique and technologically advantageous properties. In particular, MoS₂ has been found to be a direct bandgap semiconductor as a monolayer – it has an indirect gap when layered – and has shown promise in nanoscale electronics, spintronics, energy devices, and catalysis.^[2,3]

Despite the immense promise shown by TMDCs, and MoS₂ in particular, the vast majority of theoretical studies involve small systems at 0 K using density functional theory calculations, for example. Real devices, on the other hand, operate at room temperature. At finite temperatures, 2D materials display intrinsic rippling due to thermal fluctuations.^[9–13] These fluctuations can alter the electronic properties of the material^[14,15] and present additional subtleties that need to be considered when designing nanoscale devices. In the context of flexible

devices, strain can lead to out of plane deformations in MoS₂ monolayers,^[16] and understanding ripples in the absence of strain could shed light on these deformations.

In this Short Communication, we quantify thermal rippling in a model of MoS₂ monolayers as a step toward understanding these important systems under typical device operating conditions. We exploit a peculiarity of the model – 2H and 1T phases of MoS₂ have the same energy – to isolate the influence of monolayer structure on the nature of the ripples. The height-height correlations that characterize monolayer fluctuations are found to scale in accord with previously developed theories for polymerized membranes^[17,18] and simulations of graphene.^[19,20] Our results suggest that such statistical mechanical theories can be used to predict the thermal behavior of TMDCs on length scales characteristic of those in nanoscale devices.

Results and Discussion

MoS₂ monolayers are modeled using the Stillinger-Weber (SW) parameterization of Jiang et al.^[21] This model includes two- and three-body interactions and was parameterized to reproduce the experimentally determined phonon spectrum of the 2H phase of monolayer MoS₂. Due to the ability of the model to describe phonons in this material, we expect it to describe longer wavelength thermal fluctuations with similar accuracy.

Despite the accuracy of the model for the 2H phase of MoS₂, it does not energetically distinguish between it and the 1T phase. This is schematically depicted in Figure 1, where we show the trigonal prismatic coordination of Mo in the 2H phase (a) and the octahedral coordination structure in the 1T phase (b). The SW MoS₂ model is independent of S–Mo–S angles, and all other triplet angles are equivalent in the two coordination structures. Thus, the 2H and 1T phases are equivalent energetically in this model, while the 2H has been shown to be lower in energy with density functional theory calculations.^[22] Moreover, while MoS₂ can support three phases – 2H, 1T, and 1T' – even simultaneously,^[23] the model does

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not support a 1T' phase, to which the less stable 1T typically converts; we do not consider 1T' herein. Despite these deficiencies, this model nevertheless predicts that the 2H phase is lower in free energy than 1T due to larger (entropic) fluctuations, as detailed below. Furthermore, the energy difference between the 1T' and 1T phases is much smaller in magnitude than that between the 2H and 1T phases.^[22] Hence, our analysis is useful as a comparison of the two phases. The model additionally allows us to isolate the influence of Mo coordination structure on thermal fluctuations.

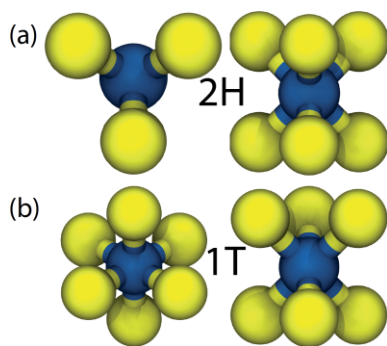


Figure 1. Top and side views of the coordination structure of Mo in the (a) 2H and (b) 1T phases, which are energetically equivalent in the model used herein.

We first quantify the thermal rippling of MoS₂ monolayers through the probability distribution of the deviation of the monolayer height from its mean value at any point in the (x, y) plane, $\delta h(x, y) = h(x, y) - \langle h(x, y) \rangle$, where $\langle h(x, y) \rangle$ is the average position of the monolayer and $h(x, y)$ is the instantaneous value of this height at the point (x, y) as measured by the positions of the Mo atoms and schematically illustrated in Figure 2a. Distributions of δh , shown in Figure 2b, illustrate that the 2H phase exhibits larger fluctuations than the

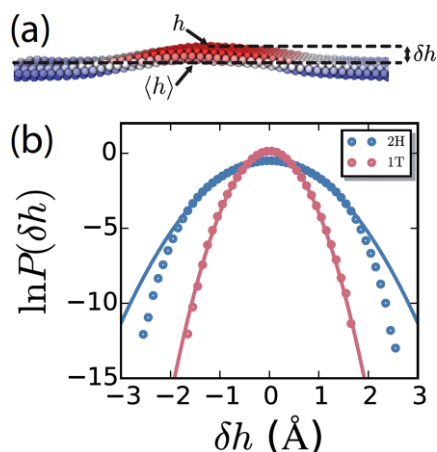


Figure 2. (a) Schematic definition of the monolayer height fluctuations δh from the mean position of the monolayer, $\langle h(x, y) \rangle$. The MoS₂ atoms are colored according to their relative height, with red indicating large positive values, blue corresponds to large negative values, and atoms near zero are colored white. (b) Probability distributions of δh for the 2H and 1T phases. Solid lines are Gaussian distributions with the same mean and variance. Representative results are shown for $L_x = 95 \text{ \AA}$, $L_y = 82 \text{ \AA}$.

1T phase. The order of magnitude of the height fluctuations are consistent with experimental measurements, which observe ripples on the order of 6–10 Å in height.^[12] Note, however, that the height fluctuations are anticipated to diverge^[9,17,18] as $\langle \delta h^2 \rangle \sim CL^{2-\eta}$, where η is the scaling exponent discussed below and L is the side length of a square monolayer.

Of particular importance are the correlations between fluctuations, especially at large distances. The Fourier transform of h quantifies these correlations through the height-height correlation function $H(k) = \langle |h(k)|^2 \rangle$. Harmonic theories of membrane fluctuations^[9] predict that this function behaves as $H(k) \sim k^{-4}$ as $k \rightarrow 0$. This theory assumes that the bending modes in and out of plane are not coupled. If anharmonic coupling between bending and stretching modes are present, the long wavelength correlations will be damped, and the height-height correlation function in the $k \rightarrow 0$ limit will scale as:^[9,17,18]

$$H(k) \sim N k_B T / \kappa S_0 k^{4-\eta} \quad (1)$$

where N is the number of atoms in the system, k_B is the Boltzmann constant, T is the temperature, κ is the bending rigidity of the monolayer, S_0 is the surface area per atom ($L_x L_y / N$), and η is a universal scaling exponent.

Figure 3 illustrates that both phases exhibit similar scaling behavior. At large k , short-range, atomic-scale correlations lead to deviations from the expected scaling behavior. As k is reduced, the height-height correlations are long-ranged and first scale harmonically, before deviating from harmonicity at lower k -values, as found previously for a different model of MoS₂ monolayers.^[24] Our results suggest that this lower k regime follows the scaling embodied by Equation (1), albeit with different bending rigidities between the two phases, illustrating the importance of anharmonic coupling between modes. Moreover, our fits predict that the bending rigidity of the 1T phase should be roughly 2 times larger than that of the 2H phase, consistent with the results in Figure 2. Experiments^[25] and simulations^[26,27] have estimated the bending rigidity of the 2H phase in the range of approximately 7–13 eV. Thus, the SW model of MoS₂ predicts that the 1T phase would have a rigidity of roughly 14–24 eV, with additional contributions from energetics that are not captured in the SW model. However, we are unaware of any available experimental measurements of the bending rigidity of the monolayer in the 1T phase to confirm this estimate.

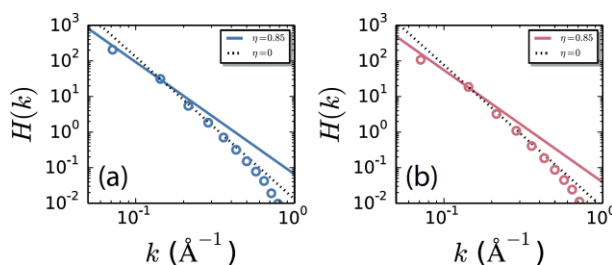


Figure 3. The height-height correlation function for (a) 2H and (b) 1T monolayers. Also shown are fits to Equation (1) with $\eta = 0.85$ (solid line) and $\eta = 0$ (dotted line).

In summary, we have used molecular dynamics simulations to study thermal rippling in 2H and 1T monolayers of MoS₂. While the model we use does not capture the energetic differences between the two phases,^[21] it predicts that 1T monolayers should be more rigid than 2H monolayers by a factor of approximately two. Both types of monolayers are consistent with the long-wavelength scaling predicted by continuum theories of polymerized membranes,^[9,17,18] with a scaling exponent of $\eta \approx 0.85$, as predicted by nonperturbative renormalization group estimates^[18] (0.849) and simulations of graphene membranes^[19,20] (0.85). Thus, continuum membrane theories may be able to accurately predict the rippling behavior of MoS₂ monolayers on large length scales. Future work will validate and extend our findings here to larger monolayers using advanced sampling techniques^[19] necessary to accurately probe significantly smaller k values. Our findings further the understanding of the thermal behavior of MoS₂ monolayers in nanotechnology applications.

Experimental Section

MoS₂ monolayers with x and y dimensions of $L_x = 95 \text{ \AA}$, $L_y = 82 \text{ \AA}$ were modeled using the Stillinger-Weber empirical potential developed previously.^[21] All simulations were performed using the LAMMPS software package^[28] in the isobaric-isothermal ensemble (fixed particle number, pressure, and temperature). A fixed temperature of 300 K and pressure of 0 bar were maintained by Nosé-Hoover thermostats and barostats, respectively, in all simulations.^[29–31] Averages were obtained over 20 ns trajectories, following an equilibration period greater than 5 ns. Height fluctuations and height-height correlation functions were determined using the z -coordinate of the Mo atoms as h .

Supporting Information (see footnote on the first page of this article): LAMMPS data files containing the starting coordinates for the 2H and 1T MoS₂ monolayers.

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