

FRICTIONAL PROPERTIES OF QUASI-TWO-DIMENSIONAL MATERIALS FROM THE PRANDTL-TOMLINSON MODEL

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Frictional properties of quasi-two-dimensional materials from the
Prandtl-Tomlinson Model

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September 2016

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in scope and in quality, as a thesis for the degree of Master of Science.

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ABSTRACT

FRICTIONAL PROPERTIES OF QUASI-TWO-DIMENSIONAL MATERIALS FROM THE PRANDTL-TOMLINSON MODEL

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Tribology, the study of friction, is both an old theoretical problem in physics and an area of great practical importance. The invention of experimental instruments such as Atomic Force Microscope (AFM) has lead to the emergence of the field of nanotribology, the exploration of friction phenomenon at the nanoscale. While more complete descriptions of friction make use of density functional theory (DFT) and molecular dynamics (MD) simulations, many essential features of frictional phenomena are accurately modeled by so called "reduced order models" such as the Prandtl-Tomlinson (PT) Model.

We illustrate the PT model in both one-dimensional and two-dimensional forms via application to various crystal lattice surfaces (cubic, planar hexagonal) and reproduce important results from the literature by solving the resulting Langevin equation within the PT model. We also discuss the parameter dependence in this model via relevant simulations.

We then generalize the PT model to a three-dimensional case and analyse quasi-two-dimensional systems. These systems thus exhibit a small amount of "buckling" - i.e. with out-of-plane basis atoms. The equations of motion of the Prandtl-Tomlinson model are solved numerically and the resulting friction force curves, tip path and lattice are analysed comparatively. The results agree with underlying theory and make testable predictions. We conclude that our generalized, three-dimensional PT model is a good approximation to the frictional dynamics at this scale for these systems and has the advantage of being computationally less intensive than full scale MD or DFT calculations.

Keywords: Friction, Nanotribology, 2D Systems, Silicene, Graphene, Prandtl-Tomlinson model, Stick-Slip motion.

ÖZET

PRANDTL-TOMLINSON MODELİNİ KULLANARAK İKİ BOYUTUMSU SİSTEMLERİN SÜRTÜNME ÖZELLİKLERİNİN İNCELENMESİ

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Triboloji, sürtünme kuvvetinin araştırması, hem teorik olarak önemli bir araştırma alanı hem de günlük hayatta en çok karşımıza çıkan pratik bir fiziksel problemdir. Atomik kuvvet mikroskopu gibi teknolojik yeni araçların bulunuşları ile birlikte, nano boyutlardaki sürtünmenin keşfedilmesi nanotriboloji alanının niteliksel olarak meydana çıkmasına öncülük etmiştir. Mikroskopik ölçekte temel sürtünme özellikleri, yoğunluk fonsiyoneli teorisi(YFT) ve moleküler dinamik benzetimleri gibi kapsamlı hesaplar ile tarif edilmektedir. Literatürde bunların yanı sıra, genel özellikleri doğru bir şekilde modelleyen Prandtl-Tomlinson(PT) modeli gibi indirgenmiş hiyerarşik modeller de bulunmaktadır.

Bu tezde bir ve iki boyutlu kristal ağ örgülerinde (kübik, üçgen yüzeyler gibi) PT modelin kapsayıcılığını gösterdik ve Langevin denklemini PT model çerçevesinde yeniden çözerek literatürdeki önemli sonuçları yeniledik. Ayrıca, bu sistemlerle ilgili modellerin literatürde tanımlanan parametrelere bağlı değişimi çalışılarak detaylı olarak tartışıldı.

Son yıllarda üzerinde oldukça yoğun olarak çalışılan Silisen yapısı, bazı Silisyum atomlarının burulmasından dolayı düzlemsel değilde yaklaşık iki boyutludur. Daha sonra, PT modelin üç boyutlu genelleştirmesi konusu özgün olarak yapıldı. Düzlemsel yüzey geometrisinin dışında üçüncü boyutta tanımlanan yeni birim hücre atomlarının sisteme eklenmesi aracılığıyla Silisen gibi iki boyutumsu yapıların sürtünme özellikleri PT modeli ile incelendi. Her bir durumda, Prandtl-Tomlinson modelinin zamana bağlı hareket denklemleri sayısal olarak çözüldü ve sonuçta elde edilen sürtünme kuvvetlerinin eğrileri, iğnenin katettiği yol ve ağ örgüsüne göre karşılaştırmalı olarak incelendi. Sonuçlar temel alınan teoriyle uyum göstermekte ve gözlemlenebilir sonuçlar vermektedir. Bizim genelleştirdiğimiz üç boyutlu PT modelinin sürtünme dinamiği için olayın fiziğini

kapsayıcı ve uygun bir model olduđu sonucuna vardık. MD ve YFT gibi hesaplamalara göre hesaplama bedeli olarak çok fazla avantajlıdır. Bunun yanı sıra elde edilen denklemler basit ve kapsayıcıdır.



Anahtar sözcükler: Sürtünme, Nanotriboloji, 2D Sistem, Silisen, Grafen, Prandl-Tomlinson modeli, Yapış-Kay hareketi.

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Chapter 1

Introduction:

1.1 Overview

The macroscopic or Antomon-Coulomb law of friction,

$$f_f = \mu N \tag{1.1}$$

which relates macroscopic frictional force to normal load via a friction coefficient μ has been known formally since the 18th century, and has been qualitatively described even earlier, by Leonardo Da Vinci [1]. However, there is no way to predict or derive μ from first principles. So far, a generally applicable method has not been devised to control or modify the coefficient of friction of a surface [2].

The rather slow development of the study of friction (tribology) has to do with the difficulties involved in conducting friction experiments. Any attempt to study the simplest case of friction, two dry bodies sliding against each other macroscopically, without any lubrication and without undergoing any bending, deformation or wear yields relatively little information, owing to the irremovable

presence of certain effects which may not be manifest at classical scales, but do matter at the atomic and other small size scales [3]. A full simulation of atomic scale friction uses methods like Molecular Dynamics (MD) to study friction which, while being quite an effective method at the small scale, has the disadvantage of being computationally very intensive [4].

Nanotribology, the study of the causes and behavior of frictional forces at the atomic and nano scales, is a relatively new branch of solid state physics. At its core, the rapid development of nanotribology in the last few decades was spurred by the development and use of vital tools for directly probing atomic-scale phenomena, Atomic Force Microscopes, etc. The friction force microscope or FFM is a modified atomic force microscope which records the lateral force experienced by a tip as it scans over a sample surface. A schematic of the basic operation of an FFM is shown in Figure 1.1. The system consists of a cantilever with a laser focused on it. Movement of the cantilever tip due to forces arising from its interactions with the sample surface are of two kinds. Deflection due to the effect of the normal force and a twisting motion due to friction. These forces are measured simultaneously using a four-quadrant photodiode.

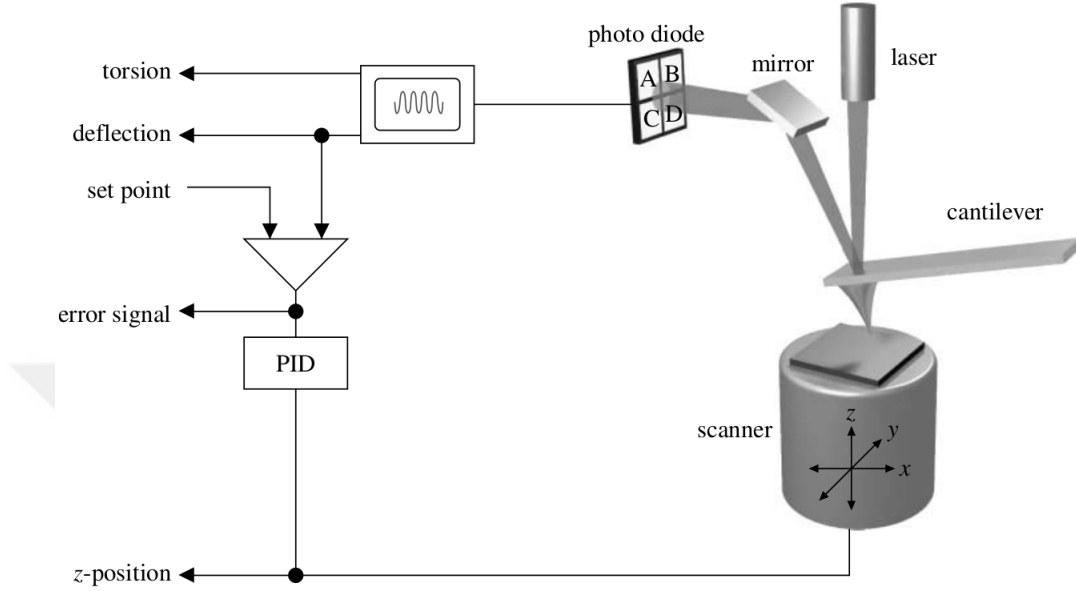


Figure 1.1: Schematic of a Friction Force Microscope. Reproduced from S. Krylov and J. Frenken, "The physics of atomic-scale friction: Basic considerations and open questions", Phys. Status Solidi B, vol. 251, no. 4, pp. 711-736, 2014.

The invention of the Friction Force Microscope (FFM) and its increased availability in recent years has allowed rapid progress in the field of nanotribology, making it possible to try and get close to the “ideal” investigation of friction, a single atom tip in contact with an individual atom at a time, with the assumption that if this basic problem was well understood, then macroscopic friction may emerge from a statistical consideration of this process.

This movement is computationally much easier to model, and allows the use of “reduced order models” [4] such as the Prandtl-Tomlinson (PT) model or the Frenkel-Kontorova-Tomlinson (FKT) model which do not include atomistic detail, but reduce the problem to modelling the movement of an FFM tip being dragged through a potential representing the substrate surface. The PT model has been extended in various ways, for different applications, e.g. the generalisation two dimensions to study friction at surfaces [5, 6, 7], to take into account thermal effects [8, 9, 10], and many others.

1.2 Outline of the Thesis

In Chapter 2, the relevant features of the PT model are introduced, showing how it is a reasonable approximation to model nanoscale friction. The method of solving the resultant equations to obtain the frictional force curves and to extract information about the FFM tip trajectory on the sample surface is also outlined.

In Chapter 3, this discussion is illustrated by applying the PT model to analyze tip motion on various different types of sample lattices, to demonstrate the wide variety of possible parameters, the lattices chosen are the Au(111) and Au(100) surfaces as well as Highly Oriented Pyrolytic Graphite (HOPG) ($\bar{1}2\bar{1}$), along the “zigzag” direction. The dependence of frictional force on temperature in the PT model as well as other miscellaneous results are also simulated and discussed in this section.

In Chapter 4, we propose an improvement to the PT model by extending it into three dimensions. It is then applied to a quasi 2D lattice, silicene. This material has the property that some of its basis atoms lie in a different vertical plane from the rest.

In Chapter 5, we discuss our results and conclude this thesis.

Chapter 2

Prandtl-Tomlinson model

2.1 Overview

The most general features of friction that are apparent even macroscopically must be included as a starting point in any good model of friction:

1. The existence of macroscopic motion should require that static friction be overcome, in other words, there must be some minimum force on the system below which there is no macroscopic motion.
2. There must be a macroscopic frictional force once sliding starts (i.e. kinetic friction must also be manifest).

We will see how the Prandtl-Tomlinson model, despite its simplicity, captures both of these features.

As a starting point, we consider the 1-Dimensional PT model. In this model, a mono-atomic FFM tip modeled as a point mass is dragged through a periodically varying potential and is damped proportional to its velocity. The tip is elastically coupled to a moving support via a spring of known elastic constant in the direction of motion. It is this support that moves with a constant velocity, with the probe

tip trailing along behind and below it. Figure 2.1 shows a support moving to the right with a constant velocity V through a corrugation potential U_0 arising from a surface with lattice constant a [11].

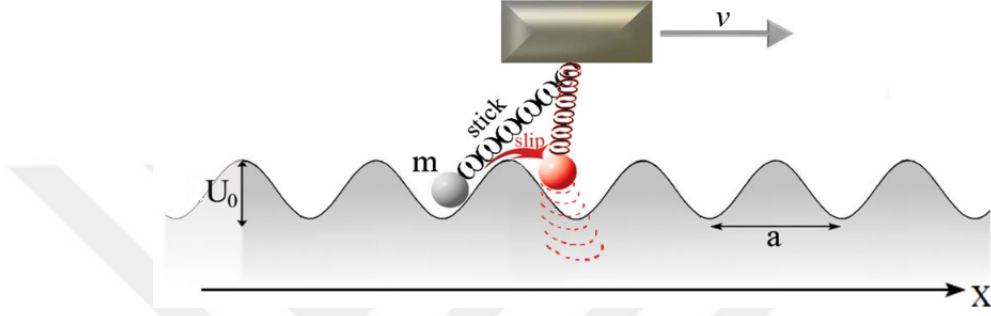


Figure 2.1: Schematic of Prandtl-Tomlinson Model. Reproduced from A. Vanossi, N. Manini, M. Urbakh, S. Zapperi and E. Tosatti, "Colloquium : Modeling friction: From nanoscale to mesoscale", Reviews of Modern Physics, vol. 85, no. 2, pp. 529-552, 2013.

This gives rise to an equation of motion for the tip:

$$m\ddot{x} = k_{eff}(Vt - x) - m\mu\dot{x} - \frac{dU(x)}{dx} \quad (2.1)$$

where the three terms on the right can be understood to be the spring force, damping and spatially varying tip-surface interaction. Analyzing the right hand side of this equation, assuming a simple sinusoidal potential $U_0\sin(kx/a)$ and looking at the case in the absence of damping, we see that if the tip is initially at rest and the spring force pulls it, then it will remain in an equilibrium position x . This holds only when the spring force has a smaller magnitude than $U_0\sin(kx/a)$. For a spring force higher than this, the tip would start to move. Thus in the absence of a damping term, the periodic force represented by the third term on the right hand side of Eq (2.1) can be seen to give rise to static friction. In order for the tip to still feel resistive forces once in motion, the damping term proportional to velocity is necessary [12]. Thus the PT model captures the two most basic and important features of friction in a very simple manner.

2.2 Stick-Slip Motion and the Langevin equation

The sort of set up described in the previous section must necessarily give rise to a stick-slip type of discontinuous motion whether in one or two dimensions as the support moves with a constant velocity, but the tip jumps discontinuously from atom to atom. Stick-slip motion is universal in that it is also observed on macroscopic scales (think of nails on a chalkboard!) and can be better understood if one considers the time evolution of the potential energy of the system. For the case mentioned above, let us consider the total potential energy of the system, as a sum of the tip-surface interaction (periodic) and the contribution of the deformed spring (parabolic):

$$U_{tot}(x, X) = \frac{U_0}{2} [1 - \cos(\frac{2\pi x}{a})] + \frac{k_{eff}}{2} (x - X)^2 \quad (2.2)$$

where $X = Vt$ is the instantaneous support position at time t .

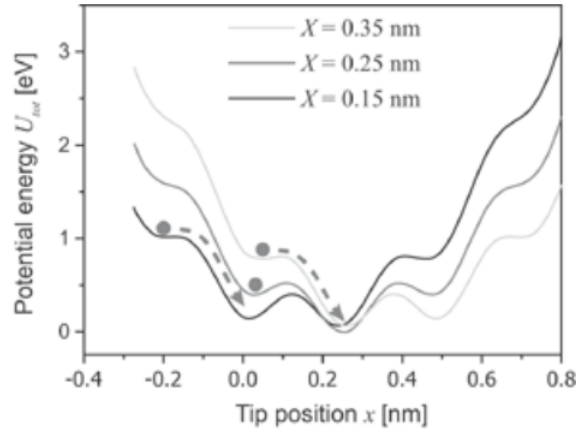


Figure 2.2: Reproduced from S. Krylov and J. Frenken, "The physics of atomic-scale friction: Basic considerations and open questions", Phys. Status Solidi B, vol. 251, no. 4, pp. 711-736, 2014.

The total potential energy is plotted in Figure 2.2 as a function of tip position,

for three different values of support position X , and hence at three different time steps. We can see that as time passes, the potential barrier seen by the tip reduces and eventually converts to a potential well instead. This, then is the origin of stick-slip motion, the tip jumps discontinuously to a minimum of the potential, then tends to stay there until another minimum becomes available, and so on. At each minimum, the tip is trapped in a well of height δE and only jumps to the next minimum when this barrier disappears as the cantilever moves across the surface and modifies the total energy landscape. Typically, these tip movements or jumps are much faster (tip velocity v_t) than the velocity with which the support moves across the surface (scan velocity (V)) and thus for $V \ll v_t$, we have nearly constant frictional force.

A slight modification can suggest a more realistic model. Noting that the previous discussion does not hold for finite temperature, and knowing there is an experimentally observed relationship between friction and temperature, the PT model has been extended to include temperature effects. There are multiple ways of doing this, for example, using a master equation that explicitly includes a probability for transition from one minimum to another. Another approach, the one used in this work, is to include a random noise term corresponding to thermal activation (i.e. increasing temperature making possible more transitions by pushing the tip over the δE barrier)

$$m\ddot{x} = k_{eff}(Vt - x) - m\mu\dot{x} - \frac{\partial U_{tot}(x, t)}{\partial x} + \xi(t) \quad (2.3)$$

where $\xi(t)$ is a term that describes the effect of temperature (i.e. thermal noise) and obeys the fluctuation dissipation relation: $\langle \xi(t)\xi(t') \rangle = 2m\mu k_b T \delta(t - t')$

To apply the PT model to a system, we will solve Equation 2.3, taking the potential U as the total potential energy of the system (corrugation plus spring), thereby obtaining the tip trajectory on the sample surface, using suitable parameters (listed in the next section). Then, the frictional or lateral force is calculated by the relation $F = k(Vt - x)$.

The obvious generalisation to a 2D surface is a two dimensional potential

$U(x, y)$ and equations of motion:

$$m\ddot{x} = -m\mu\dot{x} - \frac{\partial U_{tot}(x, y)}{\partial x} + \xi(t) \quad (2.4)$$

$$m\ddot{y} = -m\mu\dot{y} - \frac{\partial U_{tot}(x, y)}{\partial y} + \xi(t) \quad (2.5)$$

When these equations are solved $F_x = k_x(Vt - x)$ and $F_y = k_y(Vt - y)$ give the force exerted on tip in the x and y-directions respectively.

2.3 Numerical Method

Equation 2.3 above has the structure of a stochastic differential equation and cannot be solved analytically [4]. Various methods exist for solving this class of equations [13, 14, 15, 16, 17]. Regardless of the method, a wide range of parameter choices allow solutions which exhibit stick slip motion. Some typical parameter values are listed in Table 2.1. These parameters should be chosen carefully in each case to correspond to the physical system being simulated.

Variable	Typical Range
m - Tip Mass	10^{-12} kg
U - Potential Amplitude	~ 1 eV
v - Scan velocity	1 nm/s - 1 m/s
k - Effective spring stiffness	$0.1 - 50 \frac{N}{m}$
a - Lattice constant of substrate	0.3 nm
μ - Damping Coefficient	$2\sqrt{k/m}$
T - Temperature	0 - 1000 K

Table 2.1: Typical Parameter values for PT model simulation. Reproduced from Y. Dong, A. Vadakkepatt and A. Martini, "Analytical Models for Atomic Friction", Tribol Lett, vol. 44, no. 3, pp. 367-386, 2011.

We use the fourth order Runge-Kutta algorithm modified for this class of problems [18].

In brief, the method consists of:

1. Reducing the order: for both the x and y , 2nd order equations are reduced to two single order differential equations each.
2. Separating out the non-deterministic part: the system can be represented as the matrix equation $\dot{X} = F(X, t) + \epsilon(t)$ where X is the matrix of 1st order derivatives, $F(X, t)$ the right hand side of the two ODEs, and the noise components separated out into $\epsilon(t)$.
3. Modified Runge-Kutta iteration: for each equation, given initial values of position and velocity, the time evolution takes place in the usual way for Runge-Kutta fourth order methods, except there is an additional noise term, thus the Runge-Kutta slopes $k_1 \dots k_4$ become [18]:

$$k_1 = dtF(X_k, t_k) + dtD^{\frac{1}{2}}w_1$$

$$k_j = dtF(X_k + \sum a_{ji}k_i, t_k + \alpha_j t_k) + dt(Dq_j)^{\frac{1}{2}}w_j,$$

where dt denotes the time step (chosen depending on scan speed), $D = \frac{2m\mu k_B T}{dt}$, j runs from 2 to 4, and the w_j 's refer to a number chosen at random from a Gaussian distribution with a mean of zero and a variance of 1. The constants appearing in the above equations, $\alpha_i, \alpha_{ji}, q_j$ are coefficients calculated in [18] and are listed in Table 2.2.

The actual dynamical evolution at each time step (similar to ordinary Runge-Kutta, order four) is given by:

$$X_{k+1} = X_k + \alpha k_1 + \dots + \alpha k_n$$

Coefficient	Value
α_1	0.25001351164789
α_2	0.67428574806272
α_3	- 0.00831795169360
α_4	0.08401868181222
α_{21}	0.66667754298442
α_{31}	0.63493935027993
α_{32}	0.00342761715422
α_{41}	- 2.32428921184321
α_{42}	2.69723745129487
α_{43}	0.29093673271592
q_1	3.99956364361748
q_2	1.64524970733585
q_3	1.59330355118722
q_4	0.26330006501868

Table 2.2: 4th Order time varying RK coefficients. Reproduced from Kasdin, N., Runge-Kutta algorithm for the numerical integration of stochastic differential equations. J. Guid. Control Dyn. 18, 114 (1995)

Chapter 3

Some illustrative applications of the Prandtl-Tomlinson model:

3.1 Simulation Details

In this section, we apply the PT model to observe friction and the tip path across the surface for a variety of lattice types. Following the procedure in [4], the corrugation potential is calculated by the first term in the fourier series expansion of the primitive lattice vectors:

$$U(x, y) = U_0(\cos(\vec{b}_1 \cdot \vec{r}) + \cos(\vec{b}_2 \cdot \vec{r})), \quad (3.1)$$

where $\vec{b}_i$ s are the reciprocal vectors. Then, suitable physical parameters are chosen in each case. In reality, there are multiple sources of “stiffness” in the system and their detailed derivation is quite involved and there are also multiple experimental ways of determining their contributions [19, 20, 21]. We will be using an effective cantilever stiffness that is the same in both x and y direction. So that in all three cases below, $k_x = k_y$ for simplicity. Wherever important, results for both T=0K and T=300K are shown, though we focus on the (experimentally meaningful) 300K case more often.

Wherever the tip path is displayed, the procedure is as follows - the initial

y-coordinate is fixed ($y_0 = 0.0$), and the support is moved only in the x-direction. Then the y-value is changed and the simulation process is repeated. This allows us to draw multiple “scan lines” showing the tip trajectory on the surface. Note however that due to the structure of the Langevin equation (stochastic differential equation) the solution (tip movement) is no longer exactly determinable. Repeated simulations would thus yield a slightly different tip path as multiple paths are possible for the tip, weighed by different probabilities.

3.1.1 Au(100) Surface

We use the following parameters: a cantilever stiffness of $25\text{N}/m$, a tip mass of 10^{-8} kg , a scan speed of $400\text{ \AA}/s$ and the damping coefficient was taken to be $\mu = 2\sqrt{(k/m)}$. Finally, the lattice constant for the Au(100) surface was taken as $2.03\text{ \AA}$. To derive an expression for the corrugation potential of the surface, we note that the (100) face of Au has an FCC structure, displayed in Figure 3.1. In this figure, we also display a contour plot of the simulated interaction potential. Positive and negative values on the contour correspond to repulsive and attractive regions of potential respectively.

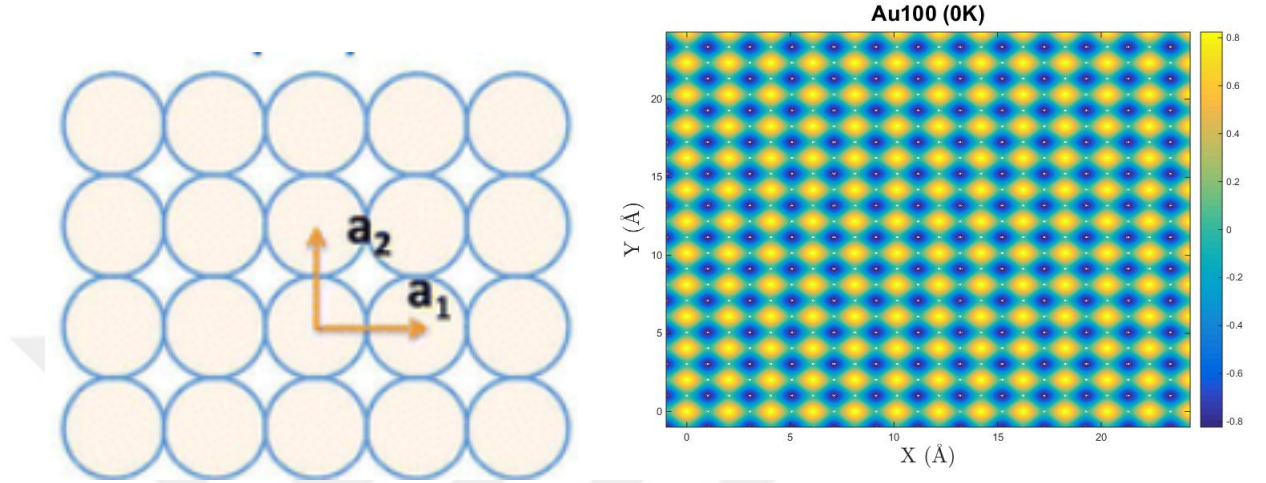


Figure 3.1: Arrangement of atoms in Au(100) surface showing primitive vectors. Reproduced from Y. Dong, A. Vadakkepatt and A. Martini, "Analytical Models for Atomic Friction", Tribol Lett, vol. 44, no.3, pp.367-386, 2011. Also shown: Plot of corrugation surface potential as obtained in text.

Taking $\vec{a}_1$ and $\vec{a}_2$ as the primitive lattice vectors, we construct the reciprocal lattice using $\vec{a}_i \cdot \vec{b}_j = 2\pi\delta_{ij}$.

The potential is then:

$$U(x, y) = U_0 \left[\cos\left(\frac{2\pi x}{a}\right) + \cos\left(\frac{2\pi y}{a}\right) \right] \quad (3.2)$$

The Langevin equation was solved for this potential with the parameters mentioned above and the results are shown below. Figure 3.2 displays the resulting friction force plotted as a function of the displacement of the support, at both 0K and 300K temperatures. The results clearly show oscillatory behavior as friction sharply falls off as the tip jumps discontinuously across the sample surface.

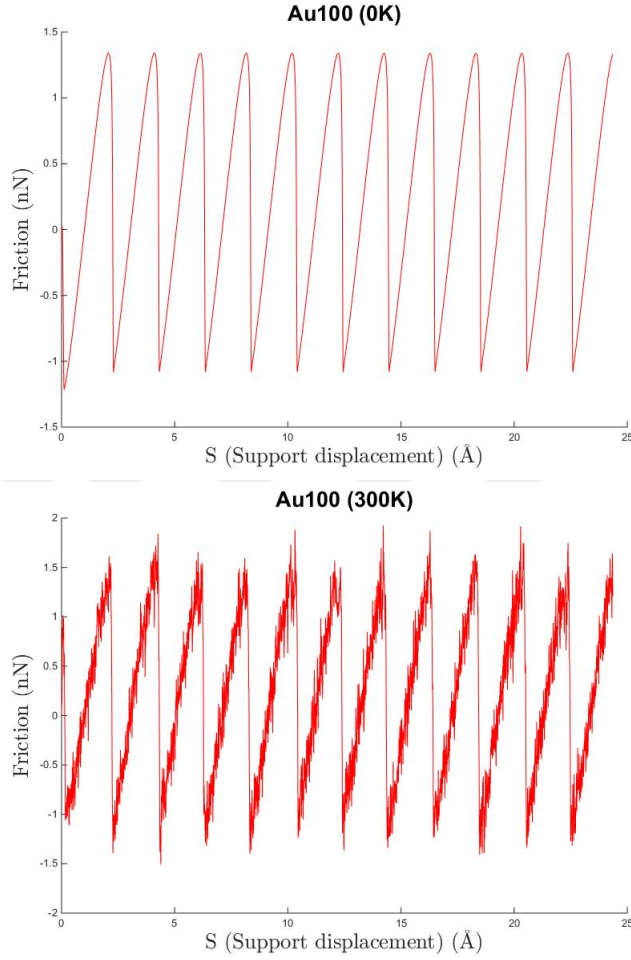


Figure 3.2: Simulated Friction forces on the Au(100) surface as a function of support displacement at $T=0\text{K}$ (Top) and at $T=300\text{K}$ (Bottom). The periodic nature of friction due to stick slip motion is clearly visible.

Figure 3.3 shows a contour plot of the corrugation potential, with the tip path plotted on top, at both $T=0\text{K}$ and at $T=300\text{K}$. We can see the stick slip nature of movement clearly as the tip oscillates rapidly at one minimum before jumping to the next at finite temperature. The absence of stick slip motion in the $T=0\text{K}$ case suggests that the choice of parameters is not a good fit for this system. Thus if the tip were to be sampled randomly at any instant in time, it would be likely to be found in a local minimum of the potential.

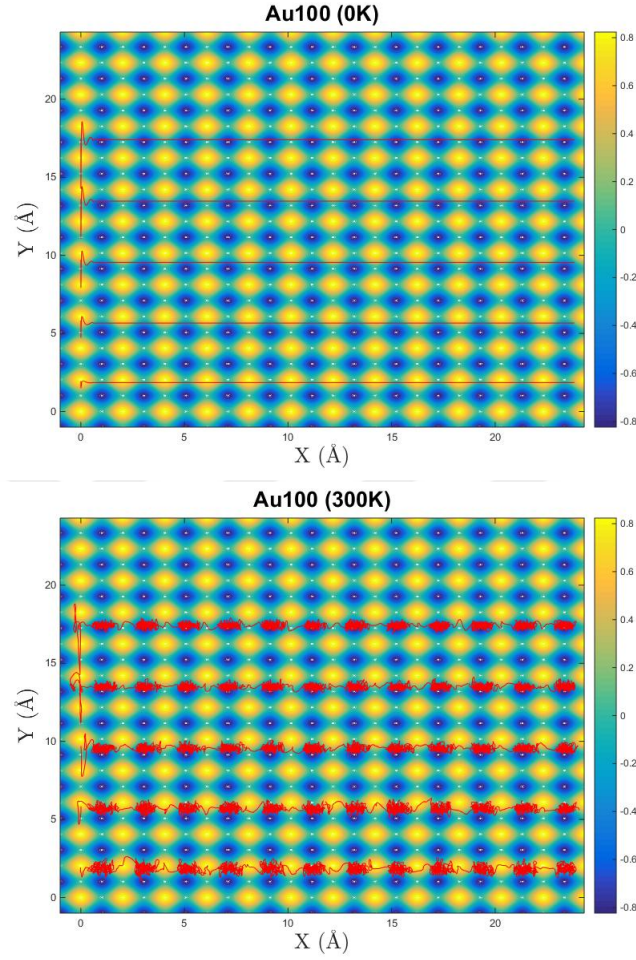


Figure 3.3: Tip path at Au(100) surface, at $T=0\text{K}$ (Top) vs at $T=300\text{K}$ (Bottom). Note the stick-slip nature of motion at finite temperature. The tip mostly stays in a local minimum of the potential.

3.1.2 Au(111) Surface

The procedure of the previous section was repeated for the Au(111) surface. A schematic, and the simulated potential are shown in Figure 3.4.

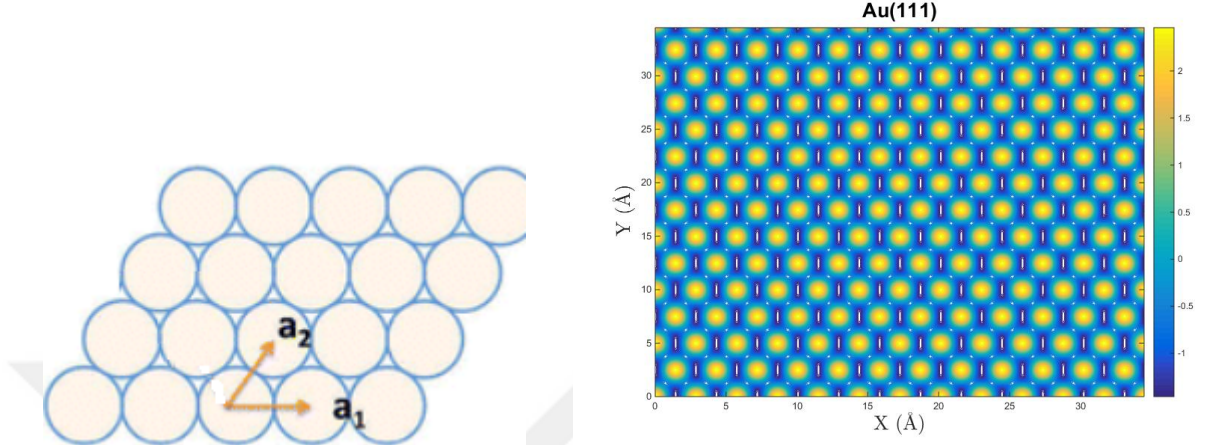


Figure 3.4: Arrangement of atoms in Au(111) surface showing primitive vectors. Reproduced from Y. Dong, A. Vadakkepatt and A. Martini, "Analytical Models for Atomic Friction", Tribol Lett, vol. 44, no. 3, pp. 367-386, 2011. Also shown: Plot of corrugation surface potential as obtained in text.

The corrugation potential was derived to be:

$$U = U_0 \left[2 \cos\left(\frac{2\pi x}{a}\right) \cos\left(\frac{2\pi y}{\sqrt{3}a}\right) + \cos\left(\frac{4\pi y}{\sqrt{3}a}\right) \right] \quad (3.3)$$

Here, the parameters used for simulation were as follows. The cantilver stiffness was chosen as 10 N/m , the tip mass as 10^{-12} kg , a sliding speed of 400 Å/s , and the damping coefficient was taken to be $\mu = 2\sqrt{(k/m)} \times 0.6$. Each time the support was moved in a straight line - what we refer to as the x direction, illustrated by the corresponding plots of tip paths. Finally, the lattice constant for the Au(111) surface was taken as 2.88 Å . This illustrates the very wide choice of parameters that could be used in the PT model. A good estimate of the real parameters corresponding to the actual physical system being studied is thus essential.

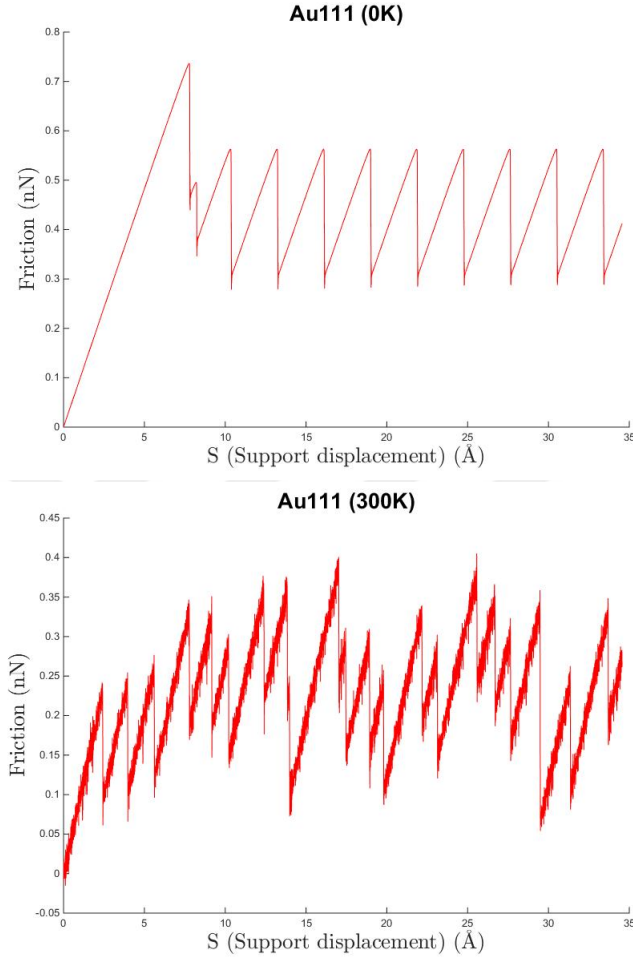


Figure 3.5: Friction vs Support displacement, Au(111) surface. $T=0\text{K}$ (Top) and $T=300\text{K}$ (Bottom).

Figure 3.5 shows the friction curves for this surface, and again oscillatory behavior of frictional forces can be discerned. Note that the length scale for oscillation of magnitude of periodic friction is again very close to the lattice constant a .

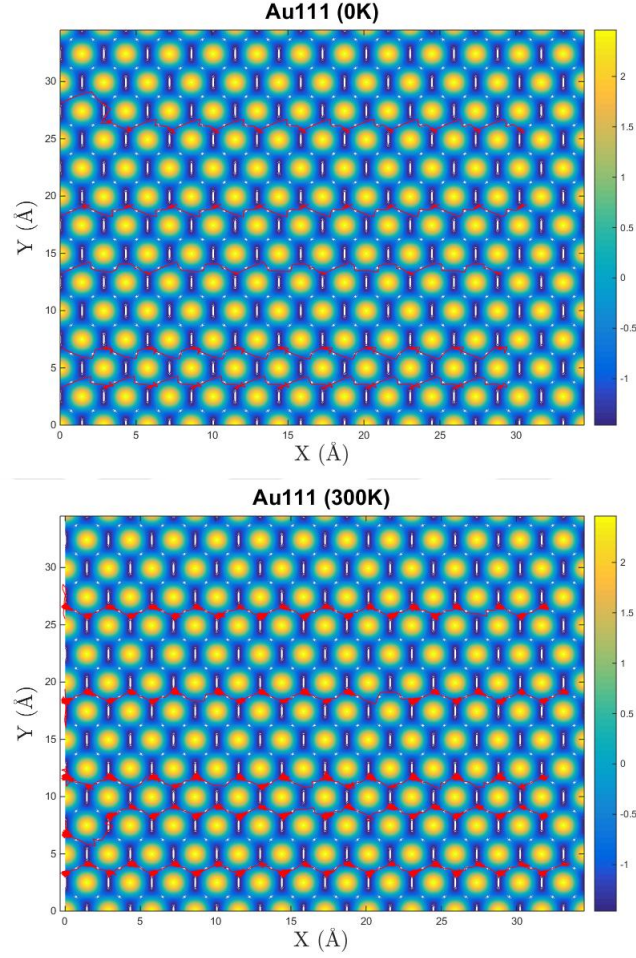


Figure 3.6: Tip path at Au(111) surface, at $T=0\text{K}$ (Top) vs at $T=300\text{K}$ (Bottom).

The tip path is plotted in Figure 3.6 and clearly demonstrates stick-slip regime motion for both $T=0\text{K}$ and $T=300\text{K}$. Note that the tip path is virtually the same in this case for both thermal regimes and that the $T=300\text{K}$ case seems mostly like a noisier version of the ultracold case. In the $T=300\text{K}$ case, due to thermal activation the tip jumps into a potential minimum. In the second scan line (from the bottom) we can see that the tip path significantly changes for the first few lattices scanned as we go from $T=0\text{K}$ to $T=300\text{K}$. Scan line number two shows how much cumulative difference to tip path can be made from thermal effects alone and why it's so important to consider them in the PT model.

3.1.3 Graphite (0001) surface:

For this case, the corrugation potential is the same as that for the Au(111) surface, except with an overall sign difference [4]. Physically, this means that the atomic locations (that were potential maxima) in Au(111) are now hollow positions (potential minima) for HOPG. Thus we have:

$$U(x, y) = -U_0[2\cos(\frac{2\pi x}{a})\cos(\frac{2\pi y}{\sqrt{3}a}) + \cos(\frac{4\pi y}{\sqrt{3}a})] \quad (3.4)$$

For simulating Graphite, the parameters were chosen as in [22]. Thus, we have a cantilever stiffness of 25 N/m , the corrugation potential amplitude is 0.5 eV and the tip mass is 10^{-8} kg. The damping constant was chosen as $\mu = 2\sqrt{(k/m)}$ and the scan velocity was 400 $\text{\AA}/s$. Figure 3.7 shows the resulting contour plot of the surface and the potential energy landscape of the surface of interest.

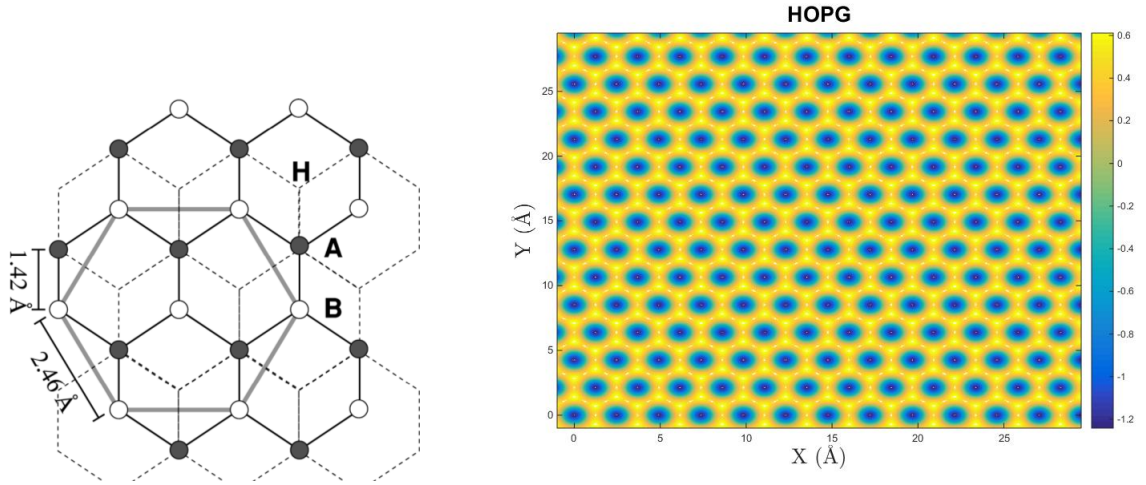


Figure 3.7: The surface of interest in HOPG. Reproduced from H. Hölscher, U. Schwarz, O. Zwörner and R. Wiesendanger, "Consequences of the stick-slip movement for the scanning force microscopy imaging of graphite", Phys. Rev. B, vol. 57, no. 4, pp. 2477-2481, 1998. Also shown is the surface corrugation potential of (0001) surface of graphene from our simulation

Figure 3.8 shows the simulated friction response curves at $T=0$ and $T=300\text{K}$. Clearly the friction minima occur every $2.46 \text{ \AA}$, matching the lattice constant.

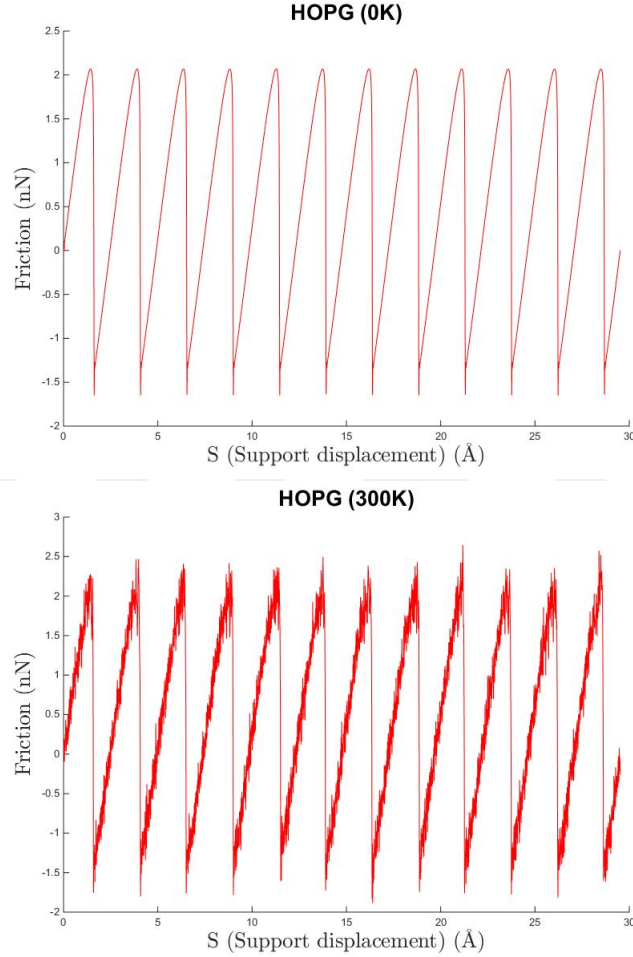


Figure 3.8: Friction vs Support displacement, HOPG(0001) surface. $T=0\text{K}$ (Top) and $T=300\text{K}$ (Bottom).

Figure 3.9 shows tip paths across the HOPG surface at both $T=0\text{K}$ and $T=300\text{K}$. With a very good choice of parameters here, we can extract more details and behaviors from the model. Note how the choice of starting 'y' coordinate actively changes the tip path. Here the starting y-coordinates were, from bottom to top: $0.00 \text{ \AA}$, $4.92 \text{ \AA}$, $9.84 \text{ \AA}$, $14.76 \text{ \AA}$, $19.68 \text{ \AA}$.

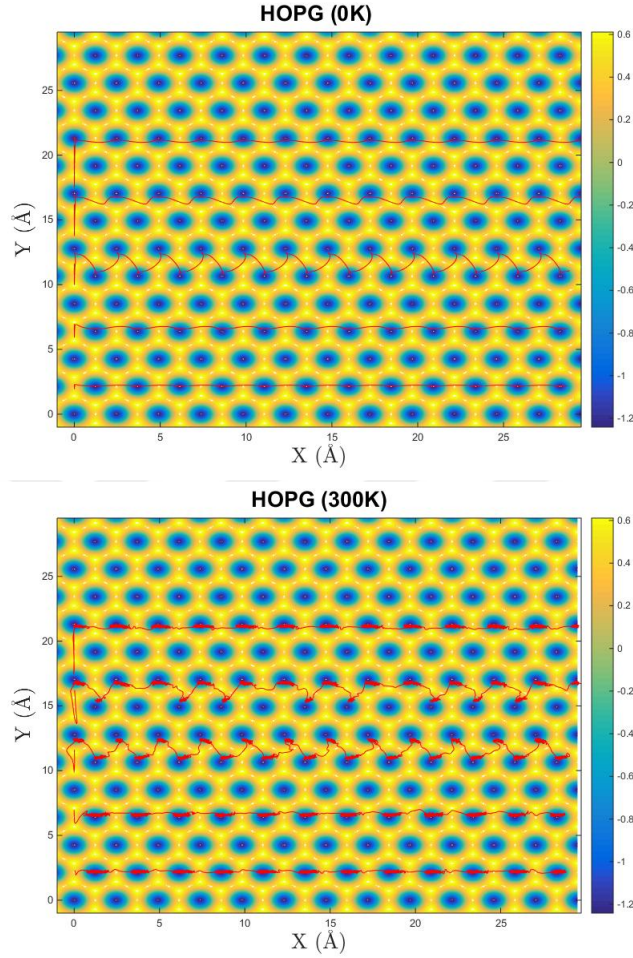


Figure 3.9: Tip path at HOPG surface, at $T=0K$ (Top) vs at $T=300K$ (Bottom).

If we “time-resolve” the motion of the tip across the potential energy surface, it becomes clear where the tip spends most of its time. The graphs in Figure 3.10 show such a time-resolved plot, where the points are plotted 1ms apart. The tip spends so much time in “hollow sites” (potential minima) that a topographic picture based on measuring friction alone would greatly over represent hollow sites and barely include filled atomic sites.

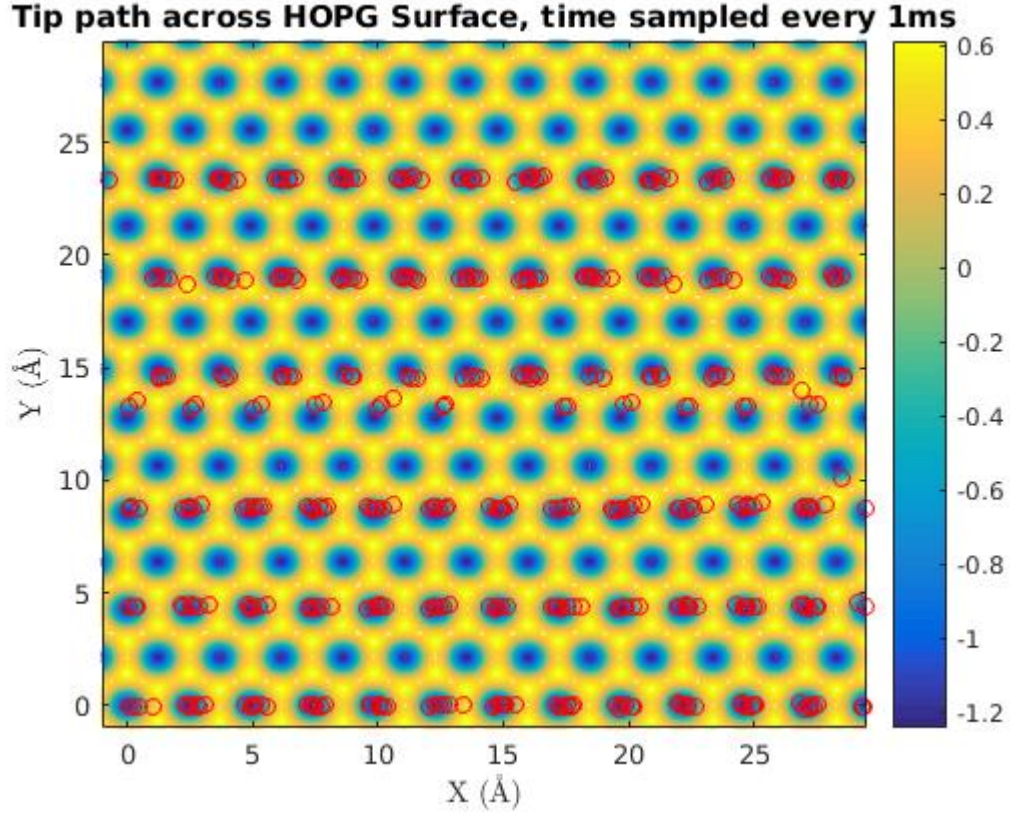


Figure 3.10: Tip path at HOPG surface, at $T=300\text{K}$, time resolved every 1 ms.

3.2 Parametric dependence in the PT model

The simulations reported in this section illustrate the dependence of frictional force on angle of scan as well as on temperature. All simulation parameters are the same as used in the case of HOPG.

3.2.1 Angular Dependence

Figure 3.11 shows three different scan lines, at different angles on the HOPG surface. In each case the tip spends most of its time in minima of the potential.

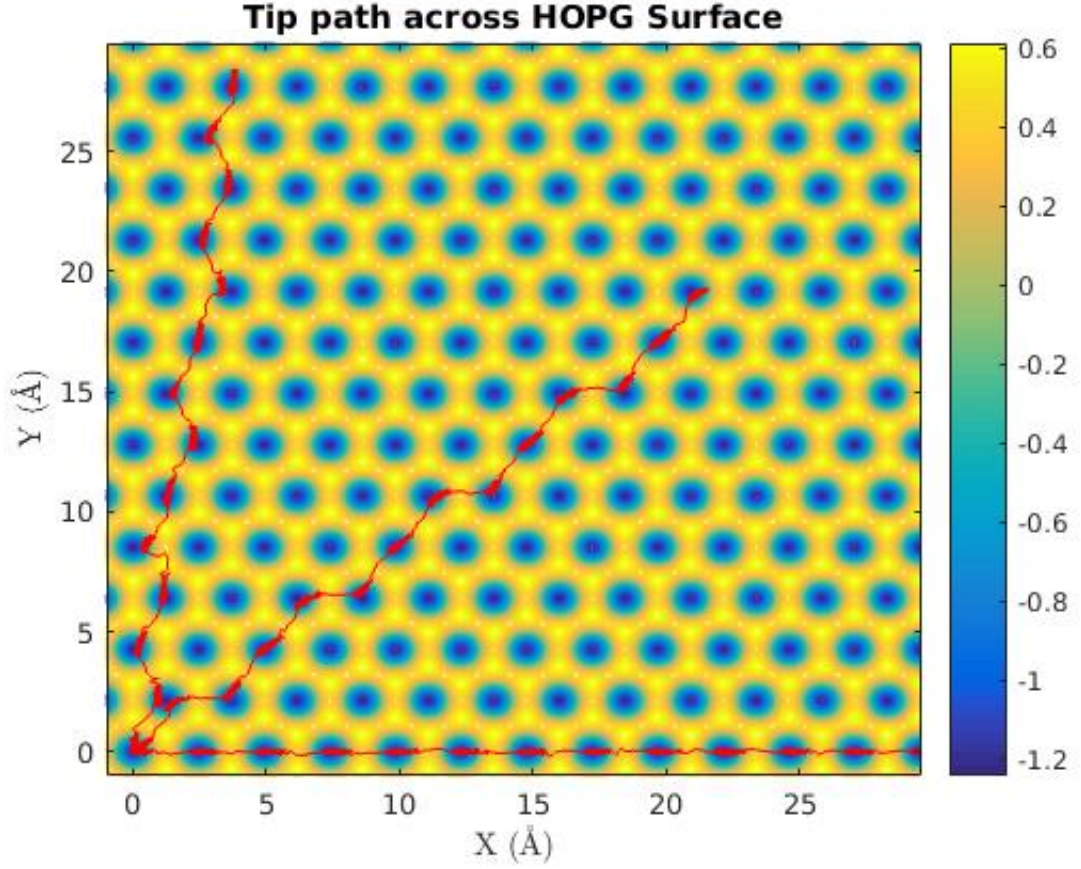


Figure 3.11: Tip path at HOPG surface, various scan angles, $T=300\text{K}$

However, the magnitude and periodicity of the observed frictional force changes as the tip moves across the lattice, for obvious reasons. The tip sees more atoms in some directions than others. Recent results indicate that friction force anisotropy may produce a frictional increase of upto 15% in graphene [23]. The anisotropic frictional response in various materials has been well studied [24, 25, 26, 27]. Figure 3.12 shows our simulated results for the scan angles 0 and 30 degrees as measured with respect to the $[1\bar{2}\bar{1}0]$ direction of the (0001) surface of HOPG. Along the 0 degree scan direction we see two kinds of alternating peaks, one slightly larger than the other. This difference is much greater in the 30 degree case.

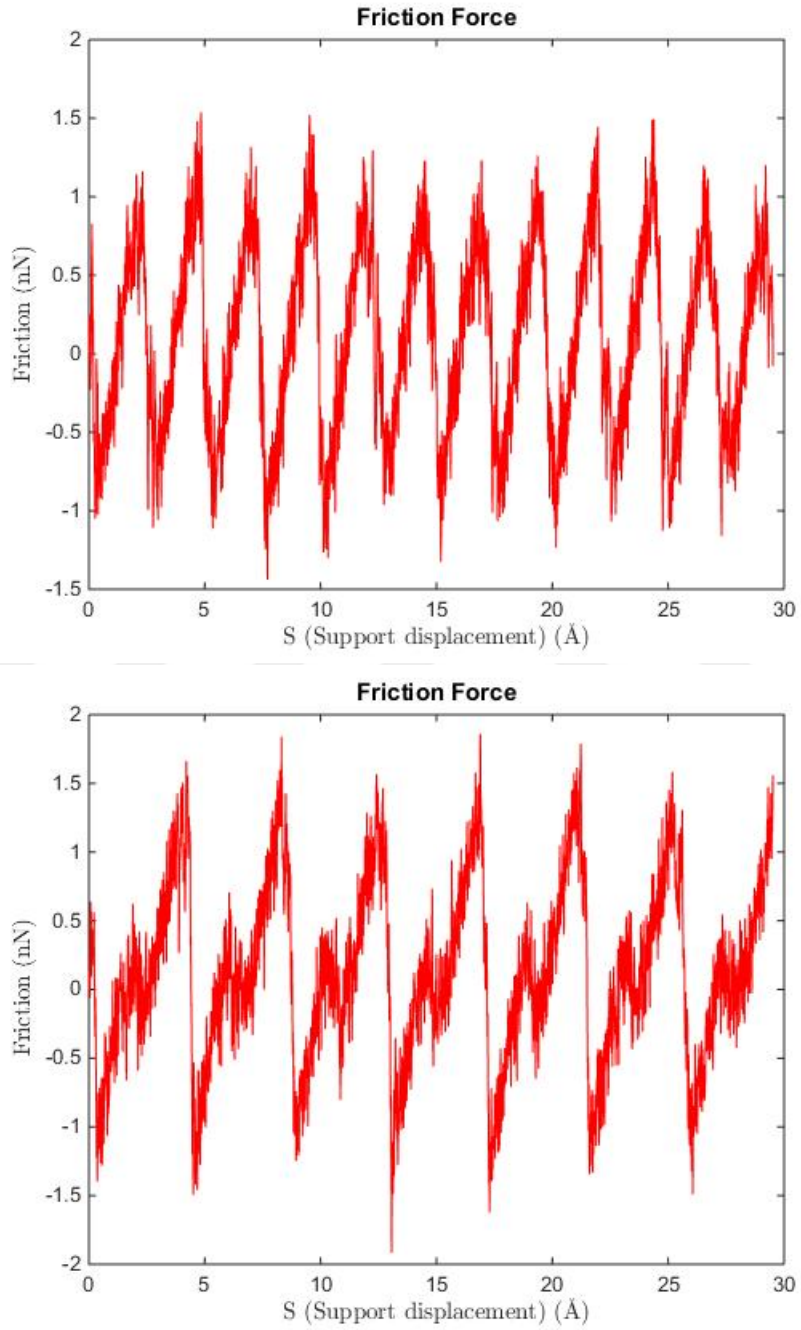


Figure 3.12: Simulated friction force curves at 0 degrees (Top) and 30 degrees (Bottom) with respect to the $[1\bar{2}\bar{1}0]$ direction of the (0001) surface of HOPG.

3.2.2 Temperature dependence

Figure 3.13 shows the effect of varying temperature upon the mean frictional force. This is another commonly studied dependence in nanotribology [28, 29]. The mean friction force is calculated by averaging the lateral force over the entire duration of the scan. Two regimes may be identified. At lower temperatures, ($T=300\text{K}$ in our plot) there is a rapid decrease in friction. This is the thermal activation regime, where mean frictional force is highly dependent on temperature. This regime is straightforward to explain with the PT model. As mentioned earlier, the AFM tip may be thought to reside in a potential well of height δE . At $T=0$, the tip jumps to the next minimum only when the potential well disappears at time t . At finite temperature ($k_b T$ comparable to δE) however, this jump to the next minimum can occur sooner.

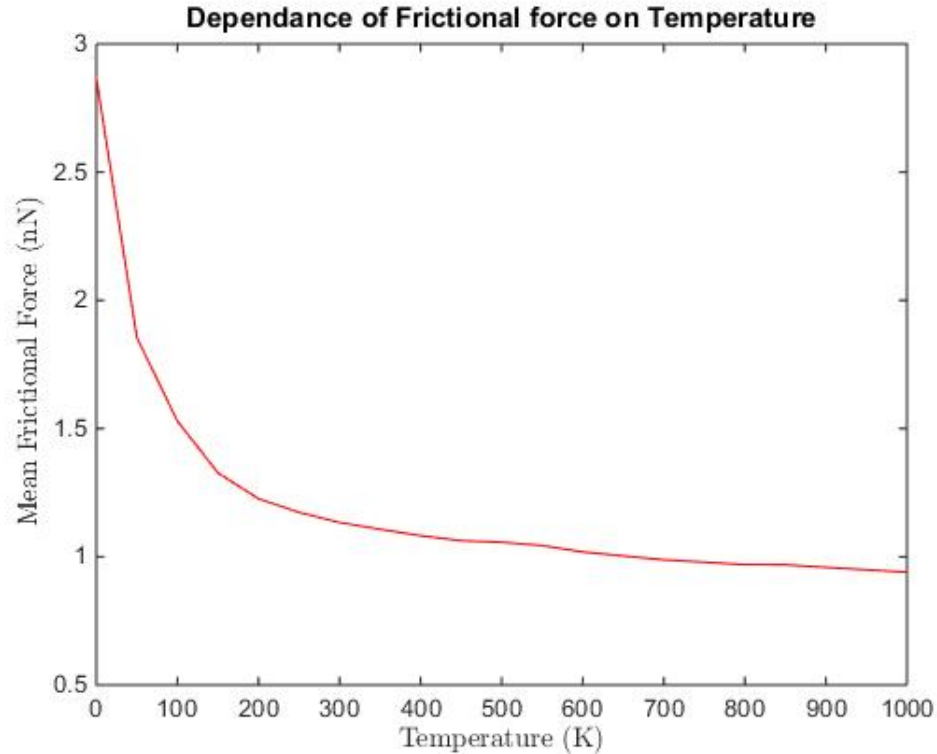


Figure 3.13: Temperature dependence of friction to illustrate thermal activation and thermal drift.

At higher temperatures however, ($T > 550$ K in our plot) we can observe the thermal drift regime which is characterized by small values of friction which do not dramatically change with further increases in temperature. For these temperatures, the effect of lowering the energy barrier δE extends in both directions-the tip may easily jump forwards (in the scan direction) or backwards (against the scan direction)[30].



Chapter 4

3D Generalization of PT Model

4.1 Overview

All the materials analyzed under the PT model so far have been represented as planar (atomically-flat) surfaces with an effective corrugation potential. This description works for these materials as they are planar structures where all the basis atoms lie in a single plane. However, to extend our analysis to materials where this isn't the case, (i.e. quasi-2D systems) we need to modify the PT model. Taking our lead from [31], we model the tip-interaction potential as a Lennard-Jones potential:

$$V(x, y, z) = \sum_{i=1}^N E_0 \left[\left(\frac{R_0}{r_i} \right)^{12} - 2 \left(\frac{R_0}{r_i} \right)^6 \right] \quad (4.1)$$

where R_0 represents an equilibrium position of the tip above the surface being scanned and r_i represents the distance to each lattice point. The amplitude E_0 of the potential represents the binding energy.

The equations of motion in this case are:

$$m\ddot{x} = k(V_x t - x) - \frac{\partial V(x, y, z)}{\partial x} - \gamma \dot{x} \quad (4.2)$$

$$m\ddot{y} = k(V_y t - y) - \frac{\partial V(x, y, z)}{\partial y} - \gamma \dot{y} \quad (4.3)$$

$$m\ddot{z} = -F_{load} - \frac{\partial V(x, y, z)}{\partial z} - \gamma\dot{z} \quad (4.4)$$

where F_{load} is a constant external loading force applied to the moving support (i.e. representing the AFM cantilever). γ is the damping coefficient, taken to be the same in all three directions. The effective tip mass in each direction is also explicitly allowed for in our model, though for simplicity we choose $m_x=m_y=m_z=m$. The methods discussed in the previous sections for the solution of the equations of motion still apply and generalize naturally to three dimensions. The number of coupled equations increases and with it so do the dimensions of the solution matrices.

The resulting plot of the lattice is shown in Figure 4.1. For buckled structures, different colored atoms lie in different vertical planes.

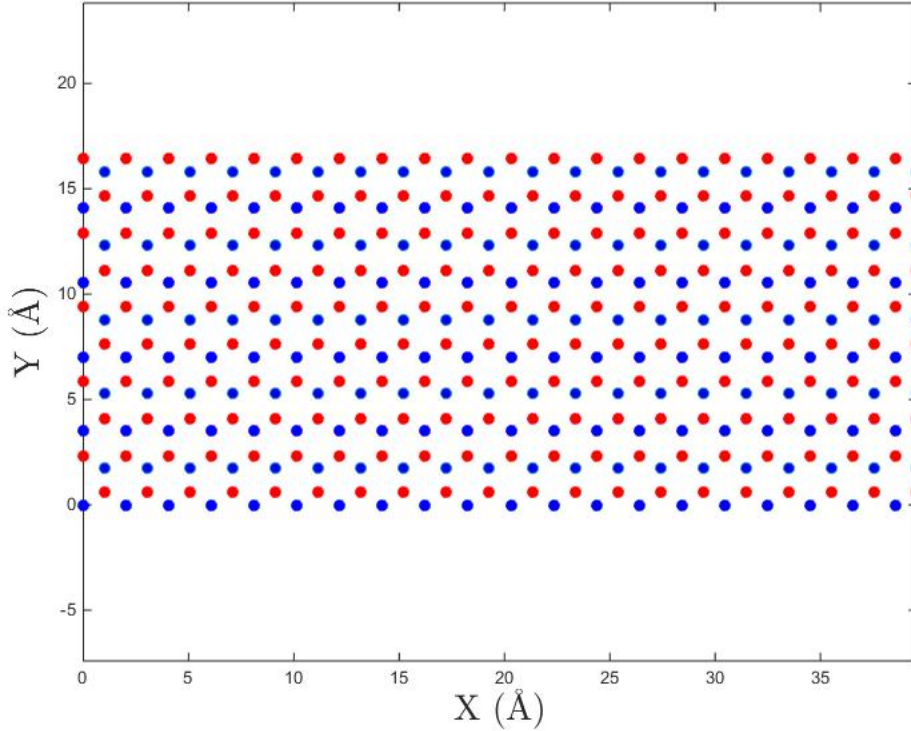


Figure 4.1: Hexagonal lattice structure, simulated using Lennard-Jones Potential

4.2 Application to Silicene and Germanene

The schematic structure of the silicene lattice is shown in Figure 4.2 and compared with that of graphene [32]. Silicene has an almost planar hexagonal lattice, very similar to graphene, except for a different lattice constant, at around $3.845 \text{ \AA}$ and atomic silicon as the building block instead of carbon. The more important structural difference is the quasi-2D nature of Silicene, there is a small buckling in the z-plane of $0.44 \text{ \AA}$ [33]. We are looking for a slightly different frictional profile to emerge due to this difference. Germanene is another material from the same family, a hexagonal lattice of Germanium atoms, with an in-plane lattice constant of $4.43 \text{ \AA}$ and a buckling parameter of $0.69 \text{ \AA}$.

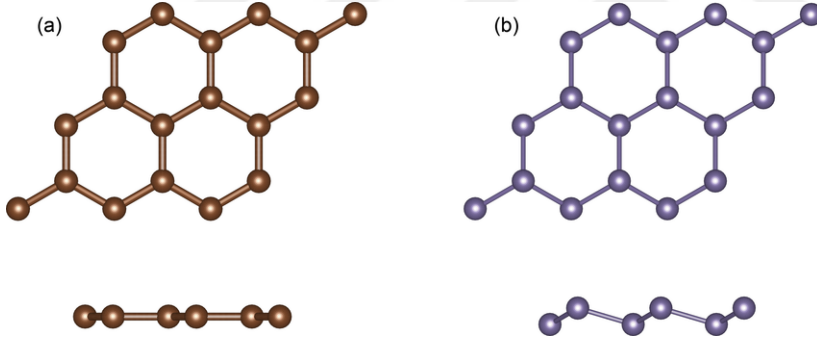


Figure 4.2: Structure of graphene lattice (left) shown both from above and from edge-on, compared with similar views of the Silicene lattice (right). Reproduced from: "Ab initio study of phonon-transport properties of two-dimensional group-IV materials". arXiv:1602.02266 [cond-mat.mes-hall]

Equations 4.2-4.4 were solved numerically for the tip-interaction potential arising from the silicene and germanene lattices and compared with those obtained from graphene at both $T=0\text{K}$ and at $T=300\text{K}$. In the rest of this chapter we will discuss and compare the results obtained from these simulations. Unless mentioned otherwise, the following parameters were used for all following simulations: a tip stiffness of 1N/m , a tip mass of 10^{-10}kg , an equilibrium position R_0 of $4.5 \text{ \AA}$ and a scan velocity of 1000nm/s in the absence of an external loading force, i.e. $F_{load}=0$.

Figure 4.3 shows the resulting friction force curves obtained as a function of support displacement for graphene at $T=0K$. Similar plots for silicene and germanene are shown in Figure 4.4. It is obvious that as we move from graphene to silicene to germanene, the maximum friction force rises and the three systems all exhibit stick-slip motion. The increase is more apparent in moving from graphene to silicene than from silicene to germanene.

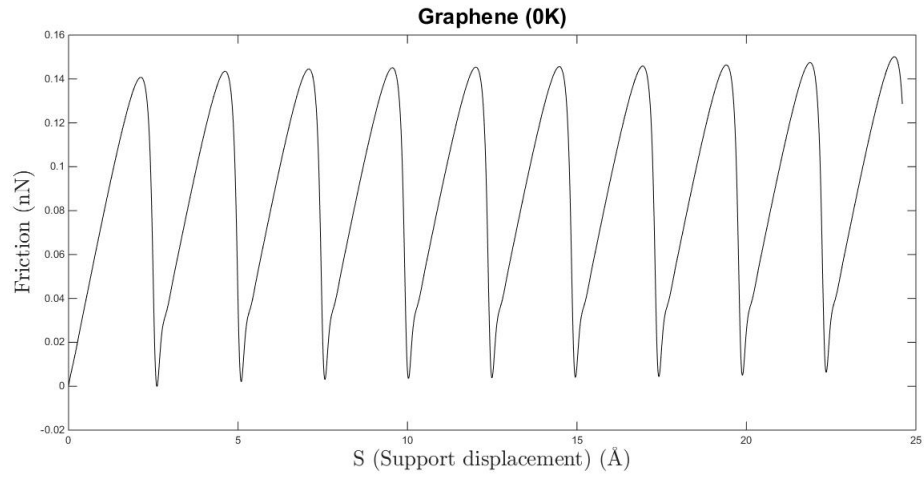


Figure 4.3: Zero temperature friction force curves for Graphene

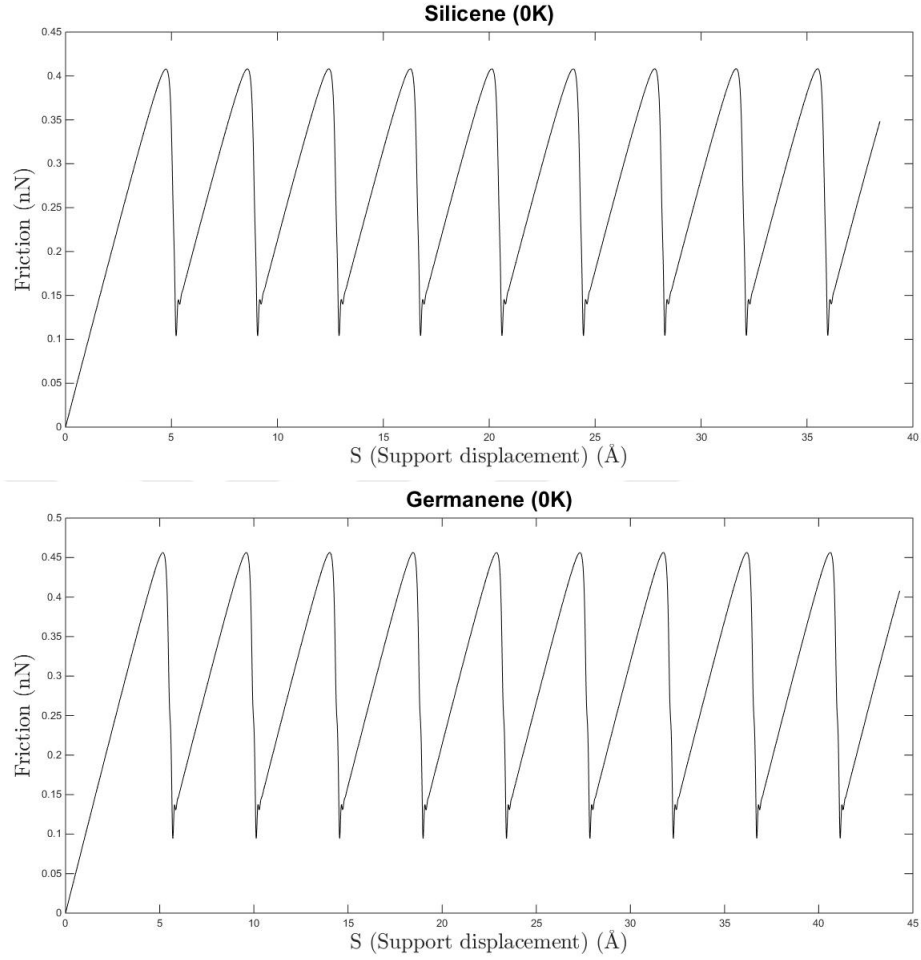


Figure 4.4: Zero temperature friction force curves for Silicene (Top) and Germanene (Bottom)

At $T=300\text{K}$ we again observed a smaller frictional force in Graphene (Figure 4.5) than in either Silicene or Germanene (Figure 4.6).

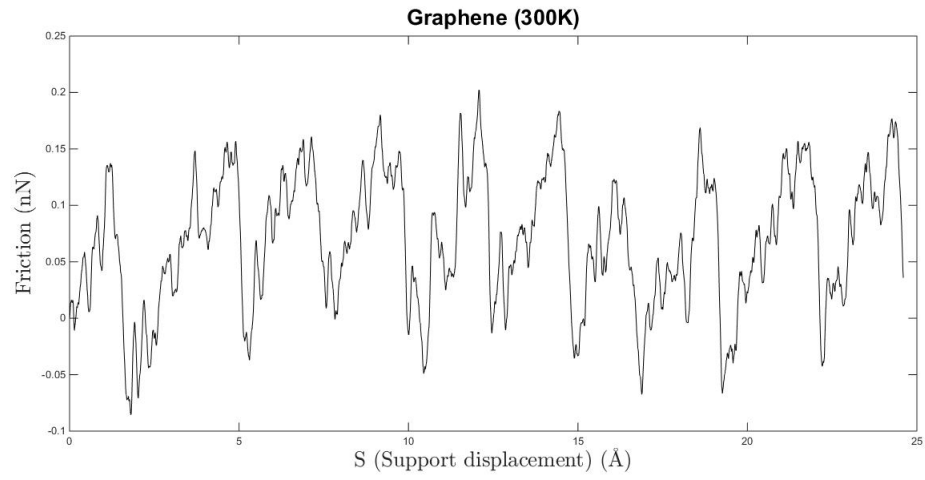


Figure 4.5: Finite temperature ($T=300\text{K}$) friction force curves for graphene

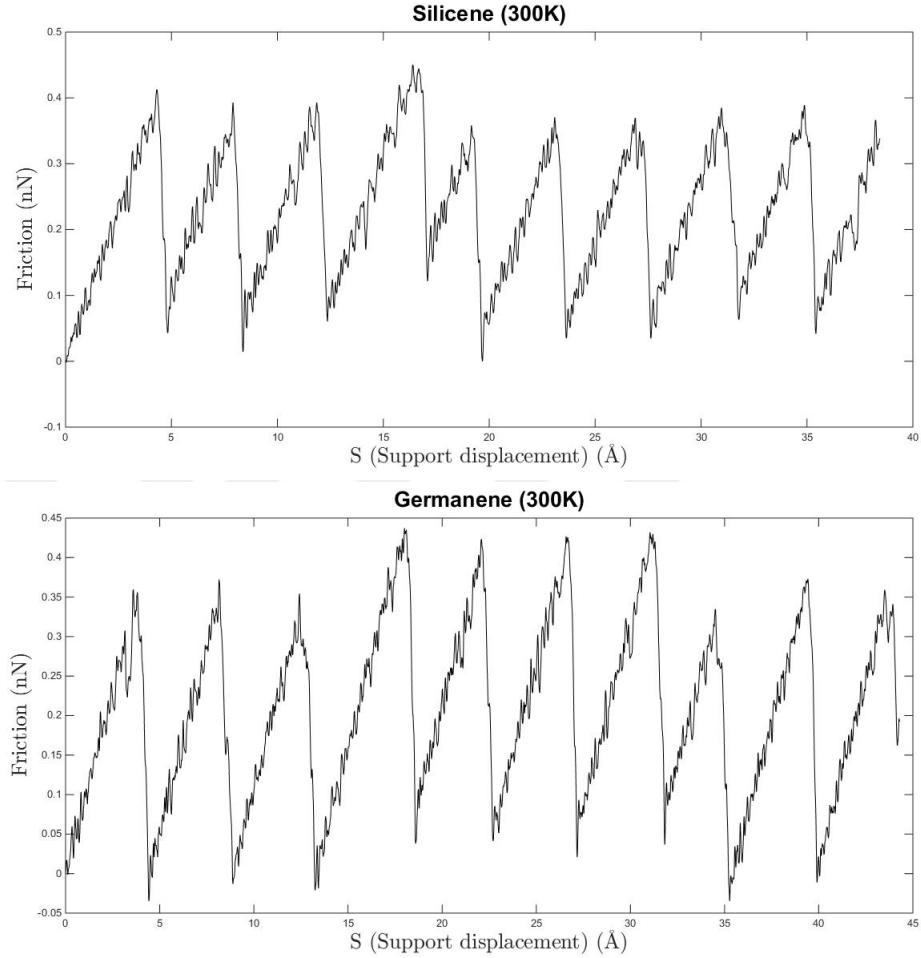


Figure 4.6: Finite temperature ($T=300\text{K}$) friction force curves for silicene (Top) and germanene (Bottom)

In Figure 4.7 we plot the atomic tip movement path across the lattice for graphene. In Figure 4.8 the path for silicene and germanene is shown. Surprisingly, silicene and germanene seem to exhibit the exact same path in the absence of thermal noise, i.e. at $T=0\text{K}$ with some slight oscillation. This is in marked contrast to graphene where the tip essentially proceeds in a straight line path, possibly due to the lower observed lateral (frictional) forces.

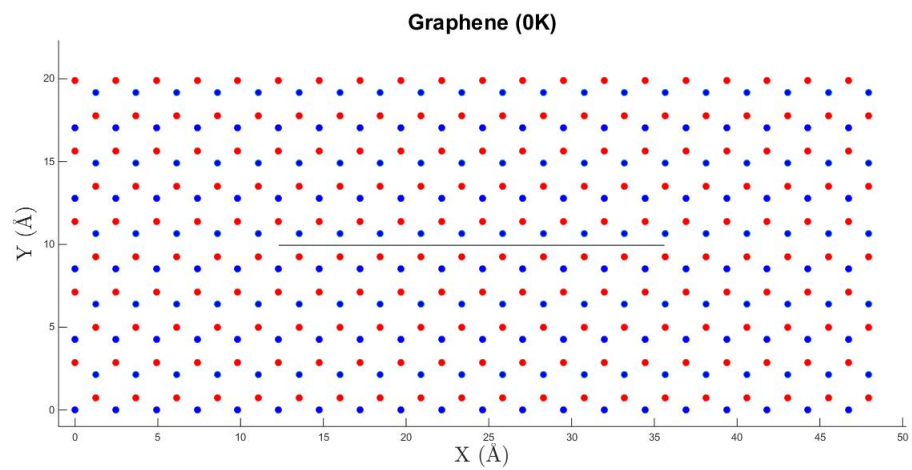


Figure 4.7: Tip Path at T=0K for the Graphene lattice.

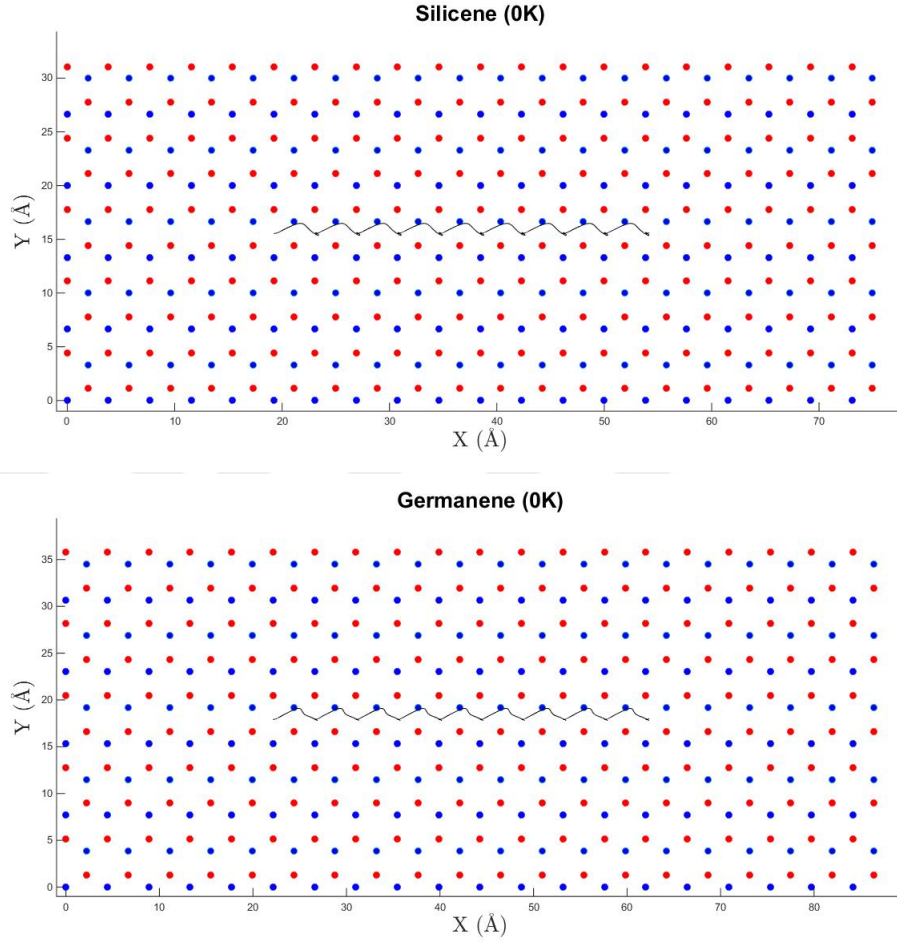


Figure 4.8: Tip Path at $T=0K$ for the silicene (Top) and germanene (Bottom) lattices.

At finite temperatures, the behavior again is quite interesting. At $T=300K$, the tip paths (shown for graphene in Figure 4.9 and for the other two systems in Figure 4.10) again show more similarity between silicene and germanene than as compared to the path in graphene. The tip path in graphene is much more convoluted, suggesting that at least in this limited comparison, FFM scanning over a planar structure is for some reason more susceptible to thermal noise effects than a quasi-2D material with slight buckling.

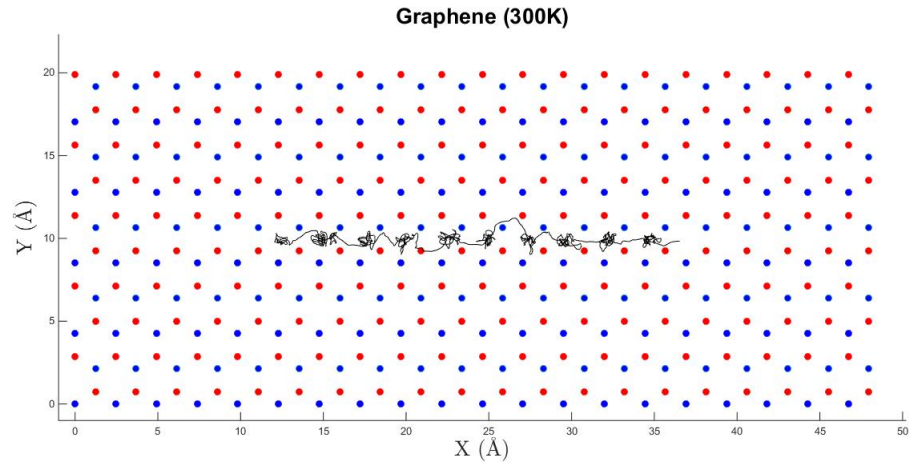


Figure 4.9: Tip Path at T=300K for Graphene.

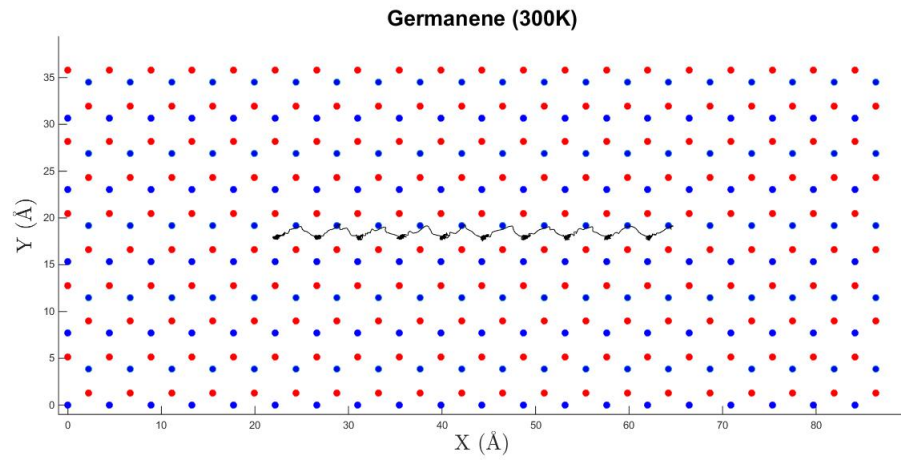
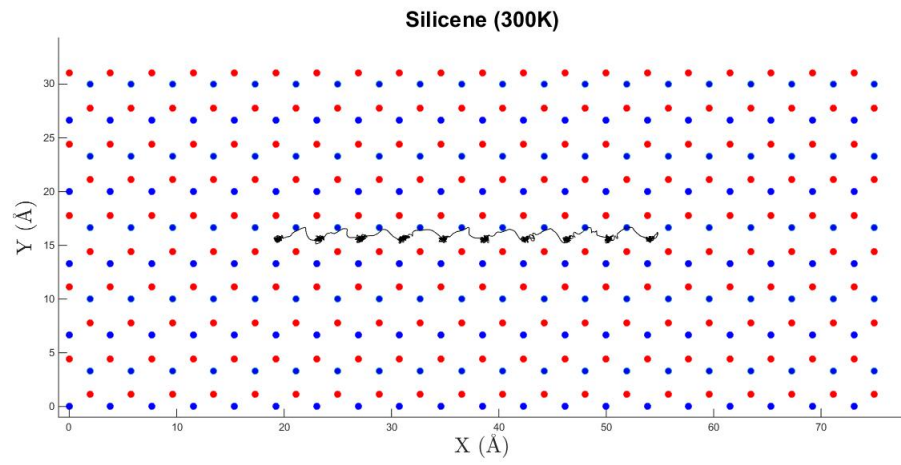


Figure 4.10: Tip Path at T=300K for Silicene (Top) and Germanene (Bottom).

In Figure 4.11 we display the simulated tip path in the Z-direction as the tip moves above the graphene surface. The corresponding plots for silicene and germanene are shown in Figure 4.12. In all cases, the tip periodically oscillates. The amplitude of these oscillations above the sample surface increases greatly as the buckling parameter changes from graphene ($0 \text{ \AA}$) through to silicene ($0.44 \text{ \AA}$) through to germanene ($0.69 \text{ \AA}$). Thus it appears that our model can distinguish between planar systems and buckled ones.

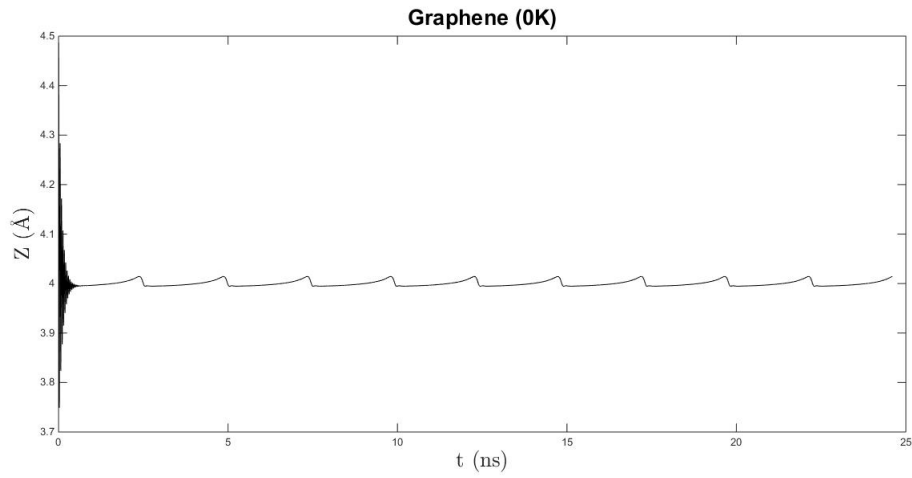


Figure 4.11: Vertical Tip Movement at $T=0K$ for graphene.

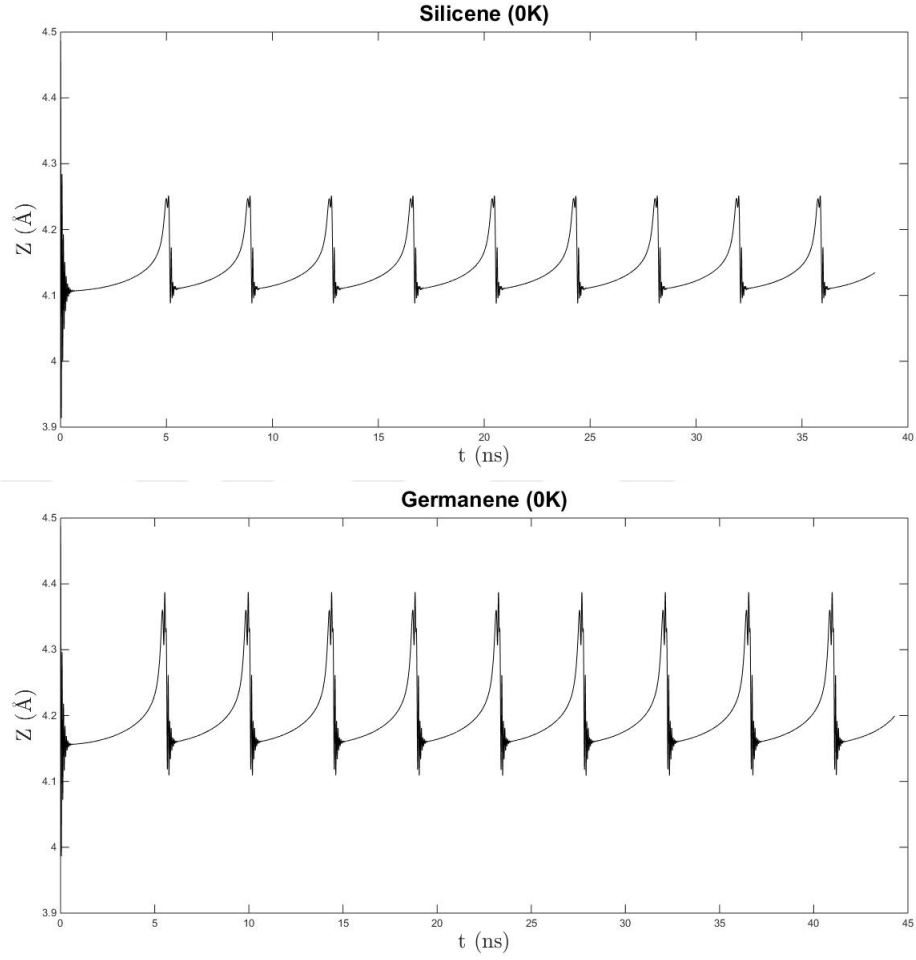


Figure 4.12: Vertical tip movement at $T=0K$ for silicene (Top) and germanene (Bottom).

This behavior extends through to the $T=300$ case, shown in Figure 4.13 (graphene) and Figure 4.14 (silicene and germanene). Again there is a marked increase in the vertical oscillation of the tip as it scans over a buckled system as compared to the planar hexagonal lattice of graphene.

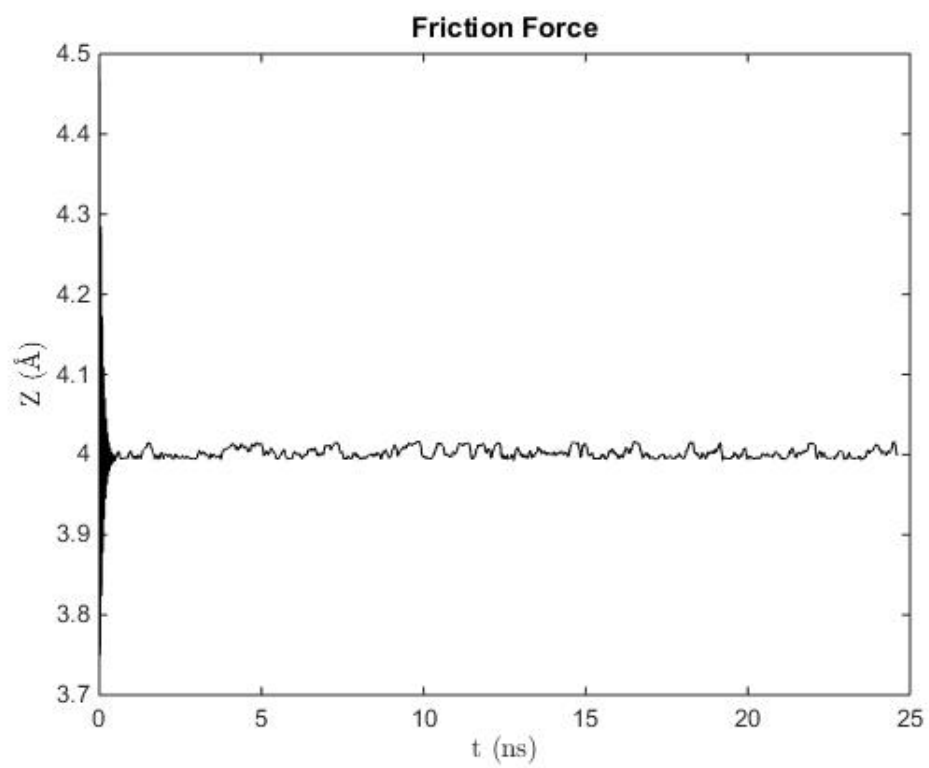


Figure 4.13: Vertical tip movement at $T=300\text{K}$ for the graphene lattice.

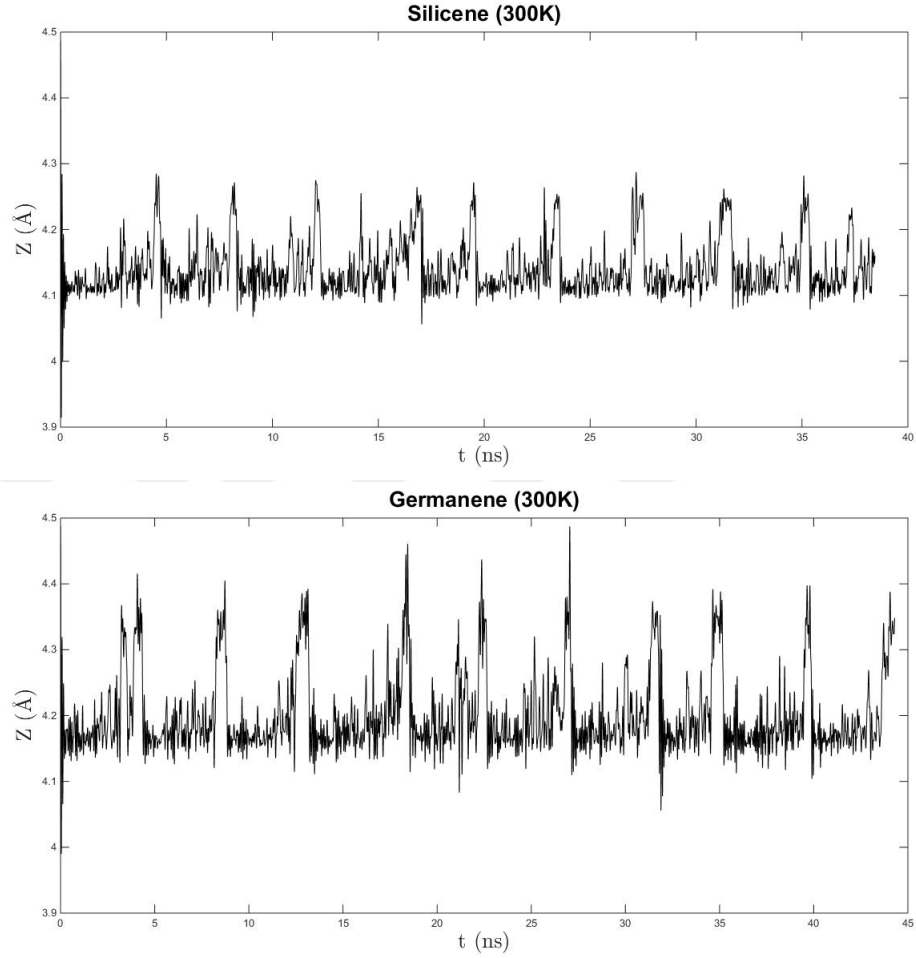


Figure 4.14: Vertical tip movement at $T=300\text{K}$ for silicene (Top) and germanene (Bottom).

4.3 Application to Phosphorene

In contrast to graphene, silicene and germanene, where the buckling was small compared to a single lattice constant, phosphorene has a highly buckled structure, with the edge on view displaying the very abrupt and sharp descent every other atom [34]. The structure of phosphorene is shown in Figure 4.15.

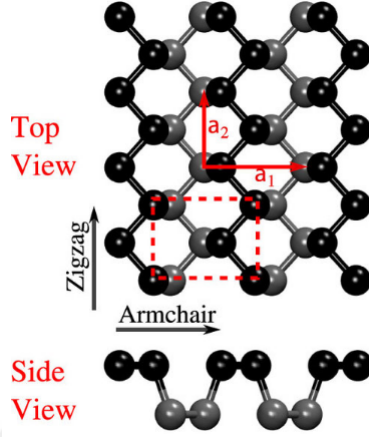


Figure 4.15: Structure of Phosphorene. Reproduced from A. Jain and A. McGaughey, "Strongly anisotropic in-plane thermal transport in single-layer black phosphorene", Sci. Rep., vol. 5, p. 8501, 2015.

The parameters used for simulation for phosphorene are the same as those in the previous section. The lattice constants were used as given in [35]. Thus $a_1 = 4.376$, $a_2 = 3.314$ and so on.

Figure 4.16 shows the friction force obtained as we scan at an angle of zero degrees near the middle of the lattice at $T=0K$. The corresponding plot for the $T=300K$ case is given in Figure 4.17. In both cases, we see that the peak frictional force seems to be close to the values obtained for silicene and germanene, again in sharp contrast to those obtained from the (totally planar) graphene.

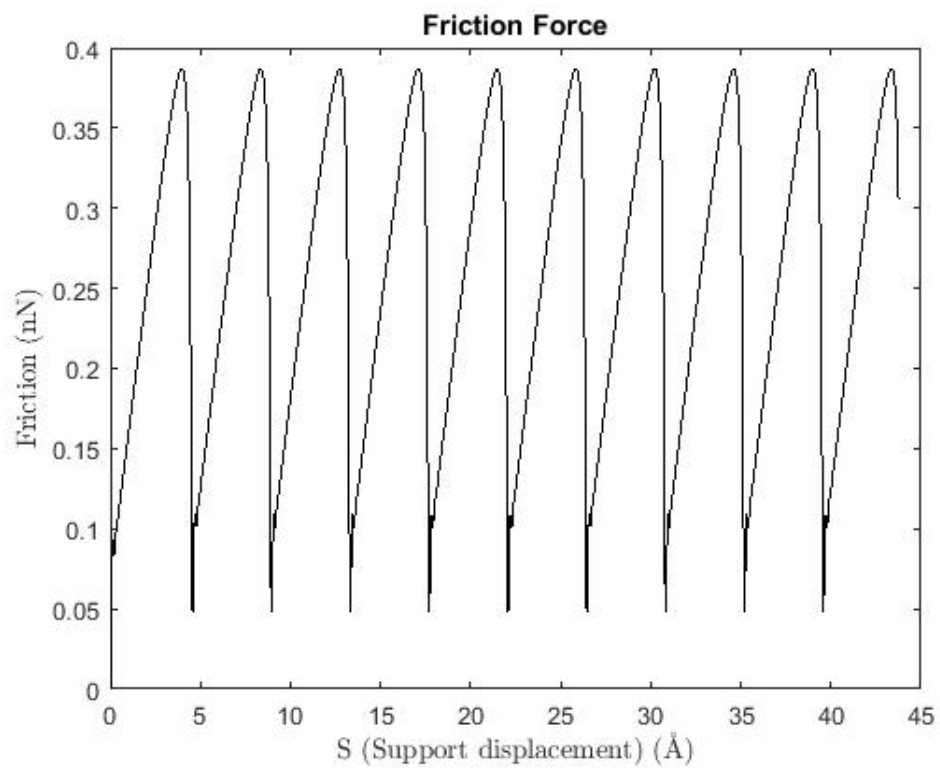


Figure 4.16: Friction force versus tip displacement for phosphorene at $T=0K$.

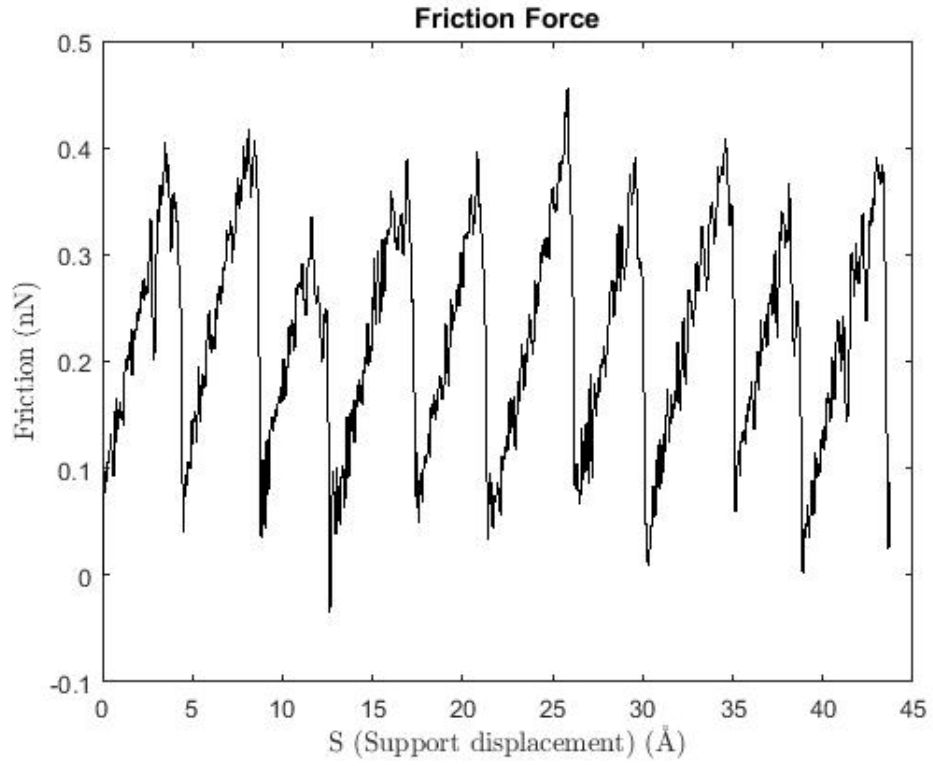


Figure 4.17: Friction force versus tip displacement for phosphorene at $T=300\text{K}$.

In Figures 4.18 and 4.19 we show the resulting tip path for Phosphorene at $T=0\text{K}$ and $T=300\text{K}$ respectively.

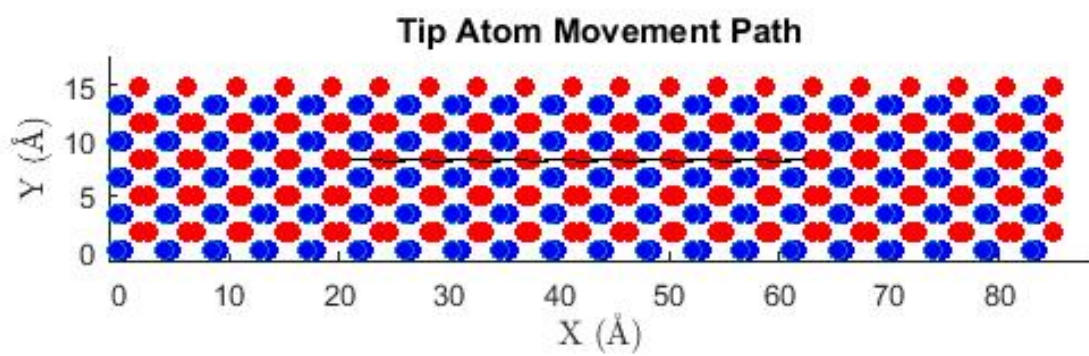


Figure 4.18: Tip path for phosphorene at $T=0\text{K}$.

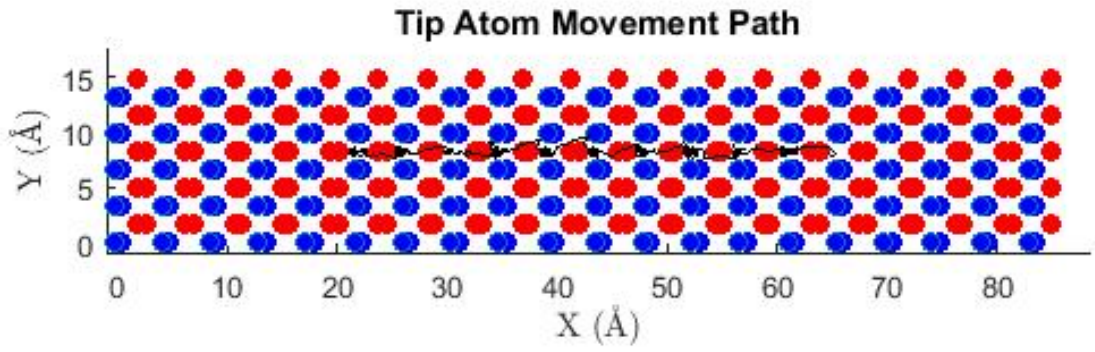


Figure 4.19: Tip path for phosphorene at $T=300\text{K}$.

Finally, the vertical displacements of the tip for both $T=0\text{K}$ and $T=300\text{K}$ case are shown in Figures 4.19 and 4.20 respectively. Note that the equilibrium Z position for the tip is significantly higher in phosphorene than it is for any of the other quasi-2D systems analysed.

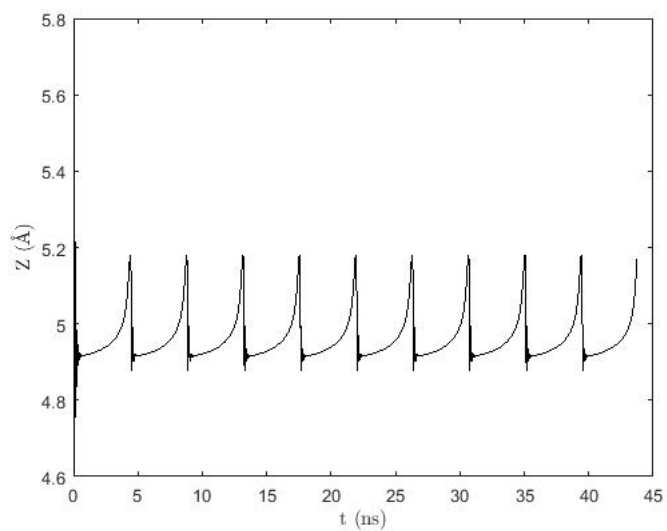


Figure 4.20: Vertical displacement of tip for phosphorene at $T=0K$.

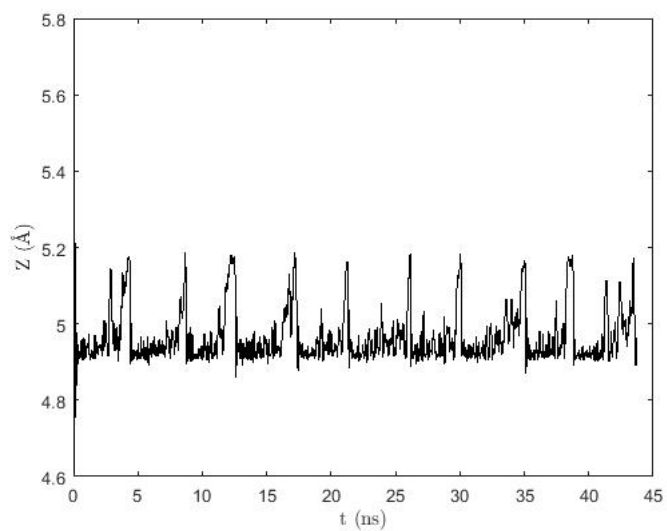


Figure 4.21: Vertical displacement of tip for phosphorene at $T=300K$.

4.4 Parametric Dependence in the 3D PT Model

4.4.1 Temperature Dependence

As noted in Chapter 3, the dependence of mean frictional force on temperature is well established. Thus, the correct parametric dependence in our extended model would provide valuable information. Figure 4.22 shows the variation of mean friction with increasing temperature for our model, which is in good agreement with the results obtained for the two-dimensional case (displayed previously in Figure 3.13).

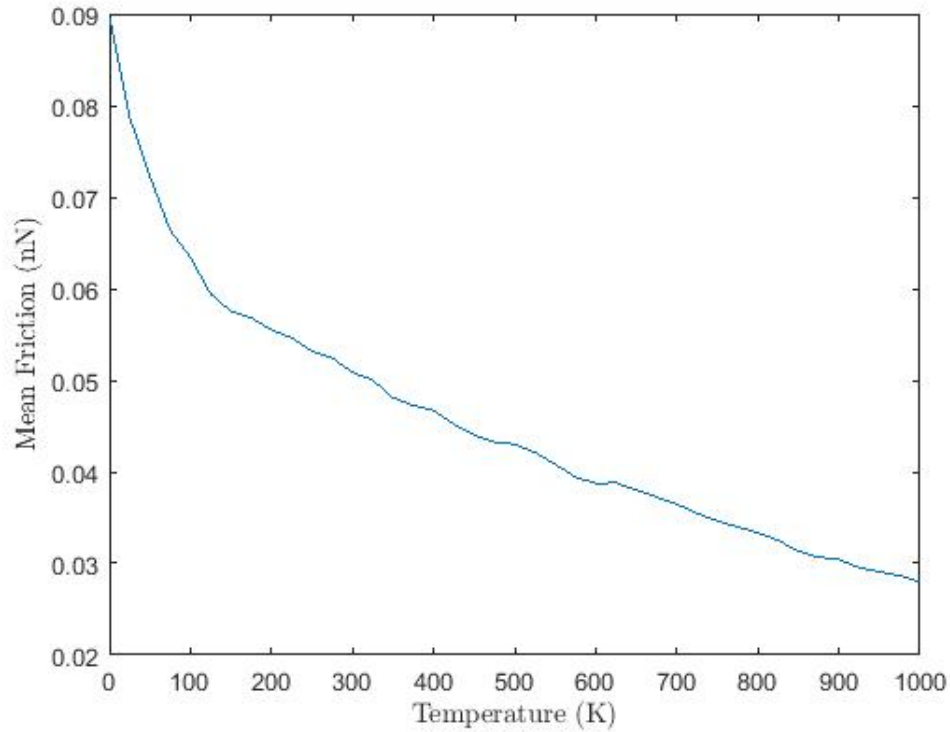


Figure 4.22: Temperature dependence of mean frictional force in the 3D PT model

4.4.2 Buckling Dependence

The introduction of the new "buckling" parameter in our analysis necessitates an analysis of how friction force varies with this new parameter. Figure 4.23 shows the trend of decrease in mean friction with an increase in the amount of buckling. To obtain this result, the parameters used in the rest of Chapter 4 were employed, with the lattice constant fixed at $2.46 \text{ \AA}$.

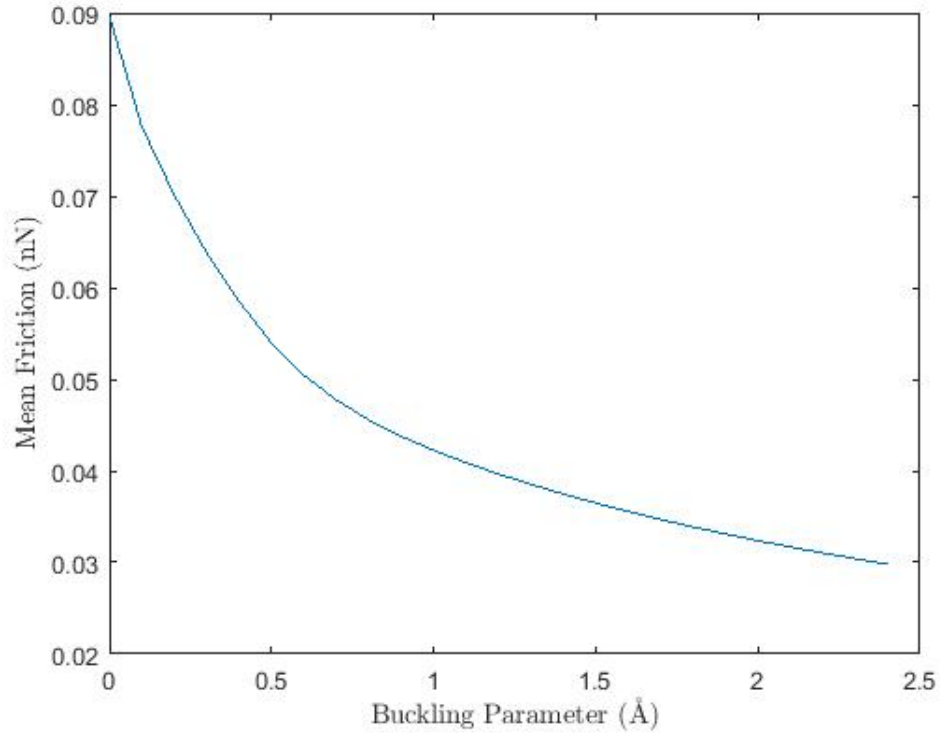


Figure 4.23: Buckling dependence of mean frictional force in the 3D PT model

4.4.3 Dependence on Lattice Constant

Similarly, the quasi-2D systems we analysed varied not only in the degree of buckling but also in the size of the lattice constant. Figure 4.24 shows the trend of increase in mean friction with an increase in the size of the lattice constant. Each curve represents a different value for the buckling parameter, and the mean

friction force is plotted as a function of the lattice constant, artificially extended to study the effect on mean friction. To obtain these results, the parameters used in the rest of Chapter 4 were employed.

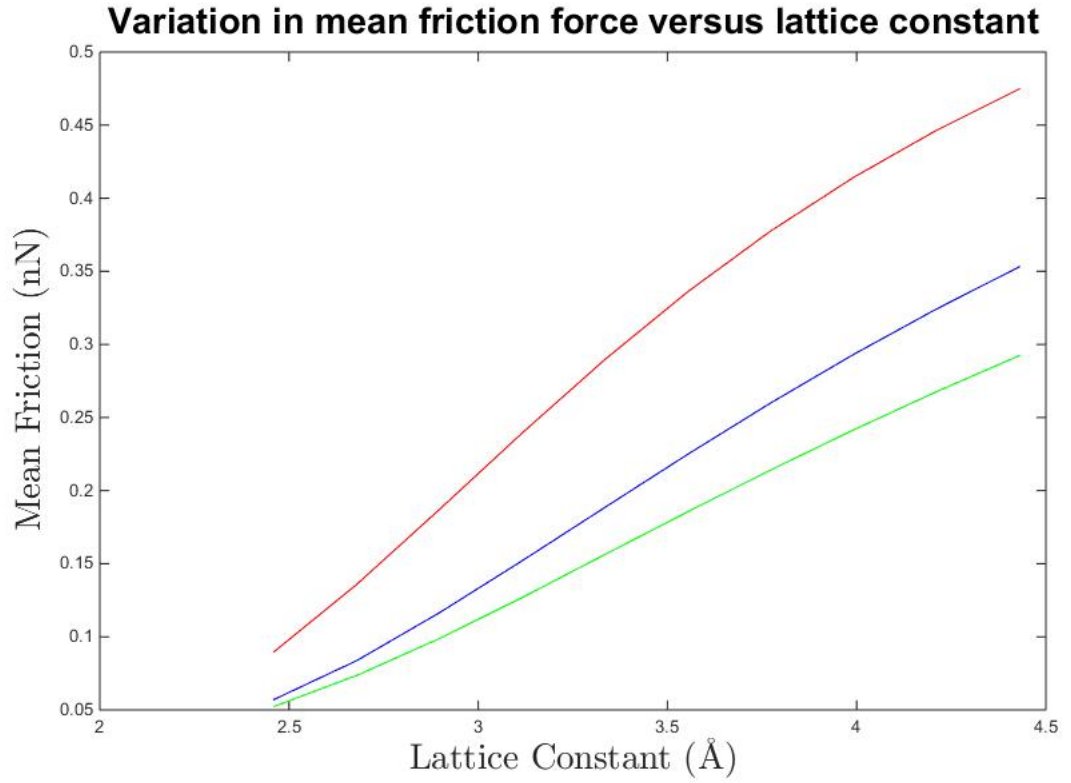


Figure 4.24: Lattice constant dependence of mean frictional force in the 3D PT model. The buckling parameter values are 0 Å (Red), 0.44 Å (Blue) and 0.69 Å (Green)

Chapter 5

Conclusion

In this work we have outlined the main features of the one and two dimensional Prandtl-Tomlinson model and solved it numerically for a wide variety of surfaces and parameters. The resulting force curves and tip displacement paths illustrate the suitability of the PT model for analyzing nanoscale frictional phenomena without needing the computing power required by more advanced methods such as Molecular Dynamics simulations.

However, the two dimensional models are inadequate to analyze systems which are not entirely planar. To explore friction for buckled structures, a model that takes into account tip motion in a vertical plane as it scans over the surface is needed.

In this work, we have extended existing PT models to accommodate quasi-2D systems. The extension of the PT model into three dimensions introduces two new parameters, the equilibrium position R_0 and the loading force F_{load} . This somewhat increases the complexity of the system as there are now more parameters to fine tune and optimize over. However, the benefit of such an approach is the ability to be able to detect smaller perturbations in frictional force curves arising due to buckling or other smaller variations across the sample surface. Further, the choice of a Lennard-Jones potential in principle allows for a more exact

determination of the surface potential than in the two dimensional case, where a corrugation potential was constructed using only the basic geometric features of the surface being analyzed. By contrast, in the Lennard-Jones potential employed, the entire lattice surface is mapped out, with the coordinates of each atom precisely defined.

Our model may be further refined by applying it to other quasi-2D systems and building up a library of good-fit parameters. The obvious choices are other quasi-2D materials widely used in nanoscience and nanotechnology, e.g. MoS_2 .

The results obtained showed that while friction varied as buckling constant and lattice constants increased, the effects of buckling were most pronounced when vertical tip motion was recorded. The closeness in periodicity of the friction force to the lattice constants of the systems being analyzed suggest that our parameter choices were suitable. In particular, the Z axis equilibrium position of the tip was significantly shifted in the case of phosphorene. The sharp Z-response to buckling suggests that a 3D PT model is a useful improvement over existing frictional models and likely to be very useful in analyzing other quasi-2D materials. However, the trends obtained when analyzing variation in mean friction as a function of the buckling parameters and the lattice constant are counter-intuitive and require further analysis.

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