Toward Understanding Low Surface Friction on Quasiperiodic Surfaces

by

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<td>BCC</td>
<td>Body-Centered Cubic</td>
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<td>D-ALCONI</td>
<td>Decagonal Aluminum Cobalt Nickel</td>
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<td>DoS</td>
<td>Degrees of Freedom</td>
</tr>
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<td>DMT</td>
<td>Derjaguin-Muller-Toporov</td>
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<td>FCC</td>
<td>Face-Centered Cubic</td>
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<tr>
<td>GCC</td>
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TOWARD UNDERSTANDING LOW SURFACE FRICTION ON QUASIPERIODIC SURFACES

Keith McLaughlin

ABSTRACT

In a 2005 article in Science [45], Park et al. measured in vacuum the friction between a coated atomic-force-microscope tip and the clean two-fold surface of an AlNiCo quasicrystal. Because the two-fold surface is periodic in one direction and aperiodic (with a quasiperiodicity related to the Fibonacci sequence) in the perpendicular direction, frictional anisotropy is not unexpected; however, the magnitude of that anisotropy in the Park experiment, a factor of eight, is unprecedented. By eliminating chemistry as a variable, the experiment also demonstrated that the low friction of quasicrystals must be tied in some way to their quasiperiodicity. Through various models, we investigate generic geometric mechanisms that might give rise to this anisotropy.
CHAPTER 1

INTRODUCTION

Discovered in 1982 [59], quasicrystals (QCs) exhibit spectacular properties and have been the focus of countless theoretical and experimental investigations. Nearly defect-free QCs once piqued the interest of thermoelectrics researchers due to their remarkably low thermal conductivities [18]. Titanium-based QCs have been found to adsorb hydrogen particularly well, making these an interesting prospect in hydrogen-storage technology [18, 32]. Their low-friction surfaces, resistance to corrosion and abrasion, and non-stick properties make application as cookware and surgical blades possible [18, 48, 63]. Other developments include thermal barriers [10] and quasicrystalline reinforced metal-matrix composites [67]. Moreover, QCs are immensely exciting for the challenges they’ve presented to theory. The classification of symmetry groups in QCs has initiated further consideration of Ewald and Bienenstock’s Fourier-space crystallography [3, 56], superspace approaches involving projection from higher-dimensional spaces [5, 30], and more recently, application of group cohomology [14, 15, 50, 52], which provided a simplified explanation of symmetry-induced band-sticking [34, 35], as well as a novel effect that is not yet understood [13, 16, 50]. Models using Fibonacci chains have been developed to investigate spectral, electronic, and phononic effects in QCs [4, 12, 47], while the development of lattice-gas models [41], application of tiling theory [51], and adaptation of low-energy electron diffraction techniques [8] have been essential to making progress towards the determination of QC atomic structure.

Although only a few of the properties that make QCs special are well understood, it has been especially difficult to pinpoint the physical mechanisms that are fundamentally responsible for low friction on QC surfaces. For some time, low friction was believed to primarily result from hardness or surface chemistry [18, 64]. However, a 2003 experi-

\(^1\)Though quasicrystals were discovered in 1982, Shechtman did not publish his findings until 1984.
ment found a two-fold difference in friction coefficients between an icosahedral-AlPdMn quasicrystal and a nearby crystalline approximant [37], perhaps suggesting that the quasiperiodicity of a system may also play some role in friction, while serving to eliminate surface chemistry as a major contributor. Then, in 2005, Park et al. measured an eight-fold frictional anisotropy along the surface of decagonal-AlCoNi which possessed coexisting periodic and aperiodic axes [44–46]. This result, along with the notion that symmetry may lead to significant consequences in the phononic and electronic spectra of solids [4, 12, 16, 26, 34, 35, 47, 50], seems to implicate quasiperiodicity as being largely responsible for the low friction observed in these systems.

By modeling the AlCoNi system used by Park et al., our goal was to investigate the importance of the role played by quasiperiodicity as it relates to this huge frictional anisotropy, and low-friction QC surfaces in general. To this end, we performed numerical calculations on a model stochastic differential equation and ran molecular-dynamics simulations on two model sets of quasicrystalline systems: a replica of AlCoNi approximants and a simple-cubic system with quasiperiodicity imposed by modulating atomic masses.

Before going into further detail, we will use the rest of chapter one to review the experiment performed by Park et al. and briefly overview our proposed models. To follow, chapter two will review some concepts of quasicrystals and quasicrystallography, including Fourier-space crystallography, classification of space groups, the Fibonacci sequence, and an example space-group calculation.

In chapter three, we will examine a stochastic ordinary differential equation used by Tshiprut et al. to model the temperature dependence of stick-slip friction on a periodic surface [68]. We have reproduced these results and will elaborate on the algorithm used before applying this model to an aperiodic surface. Chapters four and five will pertain to molecular-dynamics simulations on two separate sets of models. Finally, in chapter six, we will draw conclusions from the sum of our three models and discuss future work.
1.1 Park’s experiment

Although symmetry was known to be intimately tied to properties such as heat and electronic transport, prior to the 2005 publication in Science by Park et al., symmetry\(^2\) was not strongly implicated as being responsible for low friction on QC surfaces. Rather, many researchers focused on incommensurability between interfaces and hardness [18, 37], in particular the latter’s effect on surface-to-surface contact area. Though these properties may play a role, Park’s experiment, which compared the friction coefficient measured along a periodic and an aperiodic axis of decagonal-AlCoNi, provided strong evidence to suggest that symmetry was the true culprit [44–46].

In the experiment, a single-grain Al\(_{72}\)Ni\(_{11}\)Co\(_{17}\) QC was cut to produce a sample with dimensions 1 cm × 1 cm × 1.5 mm, and such that the largest surface possessed two-fold symmetry with a periodic axis (parallel to a ten-fold axis) and an aperiodic axis (parallel to the two-fold axis); see figure 1.1. The tip was coated with 50 nm of TiN, which was then passivated with C\(_{16}\) alkanethiol; the final product measured 30-50 nm prior to contact and possessed a spring constant of 2.5 N/m. The sample and tip were both prepared, and the experiment was performed, in an ultra-high-vacuum (UHV) chamber at 1.0 × 10\(^{-10}\) Torr.

The cantilever was scanned at some angle \(\theta\), where \(\theta = 45^\circ(-45^\circ)\) corresponded to the aperiodic (periodic) axis, see figure 1.1,\(^4\) and the torsional and deflection response were measured. Using the assumption that the frictional force was a function of separable variables, scanning direction and applied load, the relationship between torsional response and frictional force was derived and used to determine the friction for applied loads from –130 to 70nN and sliding velocities from 20 to 2000 nm/s. Frictional anisotropy with a value \(\beta = \mu_{\text{periodic}}/\mu_{\text{aperiodic}} = 8.2 \pm 0.4\) was found with no significant dependence on load or velocity, where \(\mu_a\) is the coefficient of friction for sliding along direction \(a\); see figures 1.2 and 1.3. The measured shear stresses of 690 (85 MPa) for the periodic (aperiodic) directions applied to the Derjaguin-Muller-Toporov

\(^2\)Specifically, the difference between translational symmetry and quasiperiodicity.
\(^3\)The chemical composition was verified by energy-dispersive x-ray analysis.
\(^4\)Symmetric angles were used to eliminate possible differences in cantilever deformation and buckling.
Figure 1.1. (A) Illustration of single grain d-AlCoNi. Friction measurements were performed on the two-fold surface, along the two-fold and ten-fold axes. (B) Friction is measured by moving the cantilever at some scanning angle, and recording the torsional and deflection response. Originally printed in Science 309. Reprinted with permission from Miguel Salmeron.

(DMT) model [7] yielded the solid lines shown in figure 1.2 in good agreement with the measured friction.

Park et al. explained that because the contact area was found to be unaffected by sliding angle, hardness was eliminated as an explanation for this huge frictional anisotropy, at least in this case. Slip planes were also eliminated since there was no observed plastic deformation of the sample. Because the TiN tip was structurally different from d-AlCoNi, and possibly amorphous, arguments involving commensurability are not well founded.⁵

1.2 Proposed models

Though we initially sought to investigate a d-AlCoNi approximant using MD, unexpected results led us to formulate two additional models: a S-ODE approach and our Fibonaccium model.

We were optimistic that performing MD simulations on d-AlCoNi would yield some anisotropy in agreement with Park et al. From there, we would focus on investigating

⁵Though such arguments may still be useful to understand other experiments.
the exact mechanism of the anisotropy by modeling phonon participation ratios and differences in stick-slip along each axis. After tweaking the potentials, using different approximants and different surface terminations, and exploring several points in the parameter space, we were unable to measure anisotropy in agreement with Park’s experiment.

Aside from the exclusion of electronic degrees of freedom, we found two major deficiencies in our d-AlCoNi model were its poor stability even at 0 Kelvin and our inability to use realistic sliding velocities. The correction of these two failures were the focus of our two alternative models. First, we used a S-ODE model, developed by Tshiprut et. al [68]. With this approach we lose atomicity, and thus any notion of phonon propagation. The silver lining is that velocities as low as a picometer/second can be explored. Second, we performed MD simulations on a series of fictitious solids with cubic symmetry, but with masses perturbed according to the Fibonacci sequence, such that in the limit, our sample has a surface possessing a periodic axis and a quasiperiodic axis. The strength here is that we have access to a very large number of stable approximants of increasing quasiperiodicity. The strength of this model is that we can
focus on the coexistence of quasiperiodic and periodic axes while essentially ignoring any other variables.

Finally, we investigated the possibility of using a linear-response approach [1] but found that this would not adequately describe the stick-slip behavior that we observe in our MD trials. This is discussed in more detail in appendix A.
CHAPTER 2
WHAT IS A QUASICRYSTAL?

We’ve discussed quasicrystals for the length of this paper without yet discussing in
detail what exactly is meant by quasicrystal. The International Union of Crystallography states that a QC is “any solid having an essentially discrete diffraction pattern” [43]. That might not be very helpful, so we’ll come back to it later.

Foremost, quasicrystal is short for quasiperiodic crystal. Clearly, this implies the
lack of true translational symmetry, a feature that is the defining characteristic of any
conventional crystal. QCs, however, exhibit an approximate translational symmetry:
taking any finite patch of size \( S \) from a QC, one can find an exact copy at some distance
\( L \). Because \( \lim_{S \to \infty} L = \infty \), there is no true periodicity in a QC; we cannot translate an
infinite quasicrystal and bring it back into exact coincidence with itself. On the other
hand, this approximate symmetry implies that there is long-range ordering. In fact, if
we lift the requirement for identity under translation or other symmetry operation and
replace it with \textit{indistinguishability}, we may restore the notion of symmetry in QCs.

Next, consider that a discrete periodic lattice can only exhibit 1,2,3,4, and 6-fold
symmetry.

\textbf{Proof} 1 Consider the two-dimensional case. Suppose we can generate a discrete lattice
with \( n \)-fold rotational symmetry, with \( n = 5 \) or \( n > 6 \), \( n \in \mathbb{N} \). Take one generating
vector of the lattice to be \( \mathbf{a}_1 = [a_x, 0] \in \mathbb{R}^2 \). 2 Apply the rotation matrix

\[ R(\theta) = \begin{pmatrix} \cos \theta & -\sin \theta \\ \sin \theta & \cos \theta \end{pmatrix}, \quad (2.1) \]

\footnote{Although this result is well-known, this proof is original.}
\footnote{We are free to choose our coordinate system in such a way to make one component of \( \mathbf{a}_1 = 0 \).}
where $\theta = \frac{2\pi}{n}$ for an $n$-fold rotation. Applying the rotation gives two linearly independent vectors, $\mathbf{a}_1$ and $\mathbf{a}_2 = R(\frac{2\pi}{n})\mathbf{a}$. We require that $\mathbf{a}_2$ be in the lattice, since it is symmetry-equivalent to $\mathbf{a}_1$. Since $n \neq 1$ or 2, $\mathbf{a}_1$ and $\mathbf{a}_2$ are not co-linear; they are sufficient to generate the lattice. Applying the inverse rotation on $\mathbf{a}_1$ yields $\mathbf{a}_3 = R(-\frac{2\pi}{n})\mathbf{a}$. Since the lattice is discrete, and no two of $\mathbf{a}_1$, $\mathbf{a}_2$ and $\mathbf{a}_3$ are co-linear, we require that $\mathbf{a}_1$ be an integral linear combination of $\mathbf{a}_2$ and $\mathbf{a}_3$,

$$R(-\theta)\mathbf{a}_1 = m_1\mathbf{a}_1 + m_2 R(\theta)\mathbf{a}_1.$$ (2.2)

Taking the $x$ components,

$$a_x = (m_1 a_x \cos \frac{2\pi}{n} + m_2 a_x \cos \frac{2\pi}{n})$$ (2.3)

$$\cos(\frac{2\pi}{n}) = \frac{1}{m_1 + m_2},$$ (2.4)

$$\frac{1}{\cos(\frac{2\pi}{n})} \in \mathbb{Z},$$ (2.5)

but this is not the case for $n = 5$ or $n > 6$; thus we reach a contradiction.4

This is a very important result, for it implies that periodic decagonal, octagonal, and pentagonal crystals cannot exist. However this restriction does not hold for quasicrystals. In fact, diffraction patterns with eight-fold and ten-fold symmetry have been observed. Unlike their periodic siblings, the diffraction patterns of quasicrystals are dense. However, if we choose some minimum intensity $\epsilon$ and only consider Bragg peaks with intensity $> \epsilon$, then we are left with an “essentially discrete” pattern; see fig. 2.1.

2.1 An example: the Fibonacci sequence

The Fibonacci sequence is an ordered list of character strings whose limit demonstrates quasiperiodicity. It is constructed by starting with the string $S$, and then applying the transformation rule $S \rightarrow L$, $L \rightarrow LS$; see table 2.1. The Fibonacci sequence has an intimate relationship with both the Fibonacci numbers and the golden mean

---

3This is true since we have excluded $n = 1, 2, 4$.

4$\cos \frac{2\pi}{n}$ for $n \geq 6$ is monotonically decreasing in the interval $(\cos \frac{2\pi}{n}, \lim_{n \to \infty} \cos \frac{2\pi}{n}) = (2, 1)$; therefore $(1/\cos \frac{2\pi}{n}, \lim_{n \to \infty} 1/\cos \frac{2\pi}{n}) = (\frac{1}{2}, 1)$. 
\[ \tau = \frac{1 + \sqrt{5}}{2}. \] In particular, the length of each term \( N_i(L) + N_i(S) \) corresponds to the \( i \)th Fibonacci number, and the ratio \( \frac{N_i(L) + N_i(S)}{N_i(L)} = \frac{N_{i-1}(L)}{N_{i-1}(S)} \) yields the continued-fraction approximations to the golden mean.

<table>
<thead>
<tr>
<th>Order</th>
<th>Length</th>
<th>Sequence</th>
<th>( \frac{N(L)+N(S)}{N(L)} )</th>
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<tr>
<td>1</td>
<td>1</td>
<td>S</td>
<td>( \infty )</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>L</td>
<td>1</td>
</tr>
<tr>
<td>3</td>
<td>2</td>
<td>LS</td>
<td>2</td>
</tr>
<tr>
<td>4</td>
<td>3</td>
<td>LSL</td>
<td>1.5</td>
</tr>
<tr>
<td>5</td>
<td>5</td>
<td>LSLLS</td>
<td>1.667</td>
</tr>
<tr>
<td>6</td>
<td>8</td>
<td>LSLLSLSL</td>
<td>1.6</td>
</tr>
<tr>
<td>7</td>
<td>13</td>
<td>LSLLSLLSLLSLLS</td>
<td>1.625</td>
</tr>
<tr>
<td>8</td>
<td>21</td>
<td>LSLLSLLSLLSLLSLLSLLSLLS</td>
<td>1.615</td>
</tr>
<tr>
<td>9</td>
<td>34</td>
<td>LSLLSLLSLLSLLSLLSLLSLLSLLSLLSLLSLLSLLSLSLLS</td>
<td>1.619</td>
</tr>
<tr>
<td>( \infty )</td>
<td>( \infty )</td>
<td>( \ldots )LSLLSLLSLLSLLSLLSLLSLLSLLS</td>
<td>( \tau )</td>
</tr>
</tbody>
</table>

Table 2.1. The first nine terms of the Fibonacci sequence. The lengths of the terms correspond to Fibonacci numbers, and the ratio \( \frac{N(L)+N(S)}{N(L)} \) converges to the golden mean \( \tau \). The limiting term is an example of a quasiperiodic sequence. Each preceding term is the unit cell for a quasiperiodic approximant.

Imposing periodic boundary conditions,\(^5\) one finds that each finite term displays translational symmetry.\(^6\) The limiting term, however, is quasiperiodic: one can take

\(^5\)So \( LSL \) becomes \( \ldots LSLLSLLSLLSLLSLLS \ldots \).

\(^6\)These are examples of quasiperiodic approximants.
any finite substring of size \( l \), and translate it a distance \( d \), finding an identical substring.

Of course, in any finite term this property can also be observed if \( l \) is sufficiently small. For instance, taking the term of length 13, we can choose the first occurrence of \( LSL \) as our substring. Translating to the right by three characters we find an identical substring. However, if we choose \( LSLLSL \) instead, we must translate by five characters.

Physically, we can investigate generic properties of quasiperiodic structures and model the effects of phason flips [31] by constructing a system with the symmetry of a term from the Fibonacci sequence. Examples include two early 90’s publications where calculations of the electronic and vibrational densities of state and heat capacities were performed for the Fibonacci chain and compared to its periodic counterpart [4, 47]. More recently, Engel et al. performed MD simulations of a Fibonacci chain using a double-well potential to allow for phason flips, finding a relationship between anharmonicity and the opening of band gaps in the vibrational density of states.

### 2.2 Fourier-space crystallography

Though we may observe the symmetries of quasicrystals simply by observing their diffraction patterns, we may use Rokhsar, Wright and Mermin’s Fourier-space crystallography [3, 9, 50] to classify these symmetry groups with mathematical rigor. Usually, we define the point group of a direct lattice\(^7\) to be the set of all isometries about a fixed point that leave the direct lattice invariant. Instead, we replace the criterion of complete coincidence with the notion of \textit{indistinguishability}. That is, instead of leaving the direct lattice invariant, we require that all \( n \)-body correlation functions of the density\(^8\) be left invariant.

\[
\frac{1}{V^n} \int \rho(r - r_1) \cdot \rho(r - r_n) \, dr = \frac{1}{V^n} \int \rho'(r - r_1) \cdot \rho'(r - r_n) \, dr, \quad (2.6)
\]

\(^7\)In this section, we refer to the real-space lattice as the “direct lattice,” and the Fourier-space lattice as simply “the lattice.”

\(^8\)This density may be mass, nuclear, electronic, etc.
where $\rho(\mathbf{r})$ is the density and $\rho'(\mathbf{r})$ is that same density under some transformation. By taking the Fourier transform of each side, we arrive at the following relation:

$$
\sum_{i=0}^{n} \mathbf{k}_i = 0 \Rightarrow \rho(\mathbf{k}_1) \cdots \rho(\mathbf{k}_n) = \rho'(\mathbf{k}_1) \cdots \rho'(\mathbf{k}_n), \quad \forall n \in \mathbb{Z},
$$

(2.7)

from which it follows that two densities are indistinguishable if there exists a gauge function $\chi(k)$, linear on the lattice $\mathcal{L}$, such that

$$
\rho'(k) = \rho(k) e^{2\pi i \chi(k)}.
$$

(2.8)

It follows immediately that for all point-group operations on the lattice, $g \in G$, we have

$$
\rho(g \mathbf{k}) = \rho(\mathbf{k}) e^{2\pi i \Phi(g)(\mathbf{k})},
$$

(2.9)

where we call $\Phi(g)(\mathbf{k})$ the phase function, which is defined modulo unity and is required to be linear on the lattice $\mathcal{L}$. If the value of the phase function is zero for all $\mathbf{k} \in \mathcal{L}$ then we know that the operation is in the real-space point group. If it is non-zero for some $\mathbf{k}$ then it is possible that the operation must be combined with some translation to recover indistinguishability. We can show by the associativity of the group elements that

$$
\Phi_{gh}(\mathbf{k}) \equiv \Phi_g(h \mathbf{k}) + \Phi_h(\mathbf{k}),
$$

(2.10)

where $\equiv$ is equality modulo unity. We call this the group-compatibility condition (GCC). Finally, we have an additional freedom to choose a gauge, as two phase functions related by

$$
\Phi_g(\mathbf{k}) - \Phi'_g(\mathbf{k}) \equiv \chi(g \mathbf{k} - \mathbf{k})
$$

(2.11)

describe the same symmetry. Given a particular density function, we can use gauge-invariant linear combinations of the form $\sum_i \Phi_{g_i}(\mathbf{k}_i)$, where $g_i \mathbf{k}_i - \mathbf{k}_i = 0$, to uniquely determine the space-group [50]. The space group is *symmorphic* if and only if all gauge-invariants are equal to zero. We normally specify a space-group operation by $\{R(g), t_g\}$.

---

9 For a periodic crystal, the phase function is simply $\Phi_g = -\frac{\mathbf{t}_g \cdot \mathbf{k}}{2\pi}$, where $\mathbf{t}_g$ corresponds to the symmetry operation $\{g, \mathbf{t}_g\}$.  
10 One can show that a translation in real-space changes $\rho(\mathbf{k})$ only by a phase.
where \( R(g) \) is a rotation, reflection or inversion, and \( t_g \) is a corresponding translation. A symmorphic space group is one where, with the correct choice of origin, all space-group operations are of the form \( \{ R(g), 0 \} \). If a space group is not symmorphic, we say that it is nonsymmmorphic. For an example of an operation that would make a space group nonsymmorphic, see fig 2.2.

2.3 Gauge-invariant quantities

The simplest type of gauge-invariant takes the form \( \Phi_g(k), gk = k \). \( gk = k \) implies that \( \rho(gk) = \rho(k) \), but there are cases where \( \Phi_g(k) \neq 0 \). In such a case, symmetry requires that \( \rho(k) = 0 \) to satisfy equation (2.9). This gauge-invariant of the first kind is called a systematic extinction and results in missing Bragg peaks in diffraction patterns.

Of the 230 crystallographic space groups, only two, \( I2_12_12_1 \) and \( I2_13 \), possess gauge-invariants of the second kind [50].\(^{11}\) Here we consider a Fourier-space vector \( q \), which may or may not be an element of \( L \), and the group of symmetry options \( g \in G_q \subseteq G \) such that \( q - gq = k_g \in L \). If we take two elements \( g, h \) in the little group \( G_q \) we find that the quantity \( \Phi_g(k_h) - \Phi_h(k_g) \) is gauge-invariant. It can be shown that a non-zero

\(^{11}\)Although there are 157 non-symorphic space groups, only these two contain invariants that cannot be reduced to first-order.
value for this gauge-invariant requires all electronic energy levels to cross the Bloch wave vector $q$ in pairs [34, 35].

The third known gauge-invariant quantity falls out of group cohomology [16, 52] and only appears in quasicrystallographic space groups. In an unpublished paper by Fisher and Rabson [13], such a space group is constructed from the point group $D_4$ with the lattice generated by $b_1 = e^{i\theta}, b_2 = e^{-i\theta}$ and $b_3 = \hat{z} + \frac{1+i}{2}(b_1 - b_2)$. Although there has been some headway in understanding the physical implications of the third invariant [26], this topic has not been explored in great detail.

2.4 Calculation of space groups

d-AlCoNi is an example of an axial quasicrystal [24, 40] consisting of five-fold planes such that each plane is rotated $36^\circ$ with respect to its neighbor [6]. Clearly in an analogous crystallographic system this would give rise to a screw-axis symmetry, and we will show that in the quasicrystallographic case this is no different.

We start with a simple model for each of the three five-fold plane groups: $p\overline{5}, p\overline{5}m1, p\overline{5}1m$. We will choose a small number of wave-vectors in Fourier-space and assign $\rho(k)$ on these points such that we achieve the desired symmetry and the real-space density is real. This is known as a density-wave pattern. Unlike in a tiling model, we truncate the number of wave-vectors with non-zero weight and therefore lose atomicity in real-space.

To start, we take the following two-dimensional densities:

\begin{align*}
\sigma_{p\overline{5}}(k_s) &= c\delta(k_s) + c\sum_{l=0}^{9} i(-1)^l \left( \delta(k_s - k_l) + \delta(k_s - k_l - k_{l+1}) \right); \\
\sigma_{p\overline{5}m1}(k_s) &= c\delta(k_s) + c\sum_{l=0}^{9} i(-1)^l \delta(k_s - k_l) + \delta(k_s - k_l - k_{l+1}); \\
\sigma_{p\overline{5}1m}(k_s) &= c\delta(k_s) + c\sum_{l=0}^{9} \left( \delta(k_s - k_l) + i(-1)^l \delta(k_s - k_l - k_{l+1}) \right);
\end{align*}

\footnote{12 For instance, a crystal with hexagonal planes with $30^\circ$ rotations.}
\footnote{13 $\rho(k) = 0$ elsewhere.}
\footnote{14 As opposed to complex. This requires $\rho(k) = \rho^*(\mathbf{-k})$.}
\footnote{15 By defining our densities in such a way we are implicitly choosing a gauge, For $p\overline{5}m1$ this choice is $\chi(k) = \Phi, (\frac{1+i}{\mathbf{k}_1})$.}
where $k_l$ is a ten-fold star on the unit circle, such that $k_{2l}$ and $k_{2l+1}$ are disjoint five-fold stars and $k_l = -k_{l+5}$, $l \in \mathbb{Z}_{10}$, and $c$ is a constant with units of inverse area;\textsuperscript{16} see figure 2.3.

A ten-fold rotation on these densities would require $\Phi_{10}(k_l) \equiv \frac{1}{2}$ to satisfy equation (2.9), but such a phase would violate linearity as $0 \equiv \Phi_{10}(0) \equiv \Phi_{10}(\sum_l k_l) \neq \sum_l \Phi_{10}(k_l) \equiv \frac{1}{2}$. On the other hand, $\Phi_5(k_s) \equiv 0$ works fine for five-fold rotations.

Take the Fourier transform $\sigma(s) = \int \sigma(k_s)e^{i\mathbf{s} \cdot \mathbf{k}_s}d^2\mathbf{s}$ for each of (2.12)-(2.14) to obtain the following 2D real-space densities:

$$\sigma_{p5}(s) = c\left(1 + \sum_{l=0}^{9} i(-1)^l(e^{is\cdot k_l} + e^{is\cdot (k_l+k_{l+1})})\right); \quad (2.15)$$

$$\sigma_{p5m1}(s) = c\left(1 + \sum_{l=0}^{9} i(-1)^l e^{is\cdot k_l} + e^{is\cdot (k_l+k_{l+1})}\right); \quad (2.16)$$

$$\sigma_{p5m1}(s) = c\left(1 + \sum_{l=0}^{9} e^{is\cdot k_l} + i(-1)^l e^{is\cdot (k_l+k_{l+1})}\right); \quad (2.17)$$

see figure 2.4.

Next, we obtain the desired axial quasicrystal by choosing one of the real-space densities in equations (2.15)–(2.17) and forming an ABAB stacking with interlayer

\textsuperscript{16}This makes $\sigma(k_s)$ unitless and gives $\sigma(s)$ units of inverse area.
Figure 2.4. Density waves in real space for $\sigma_{p5m1}(s)$, $\sigma_{p51m}(s)$ and $\sigma_{p5}(s)$ density wave models (left to right). Mirror symmetry can be found in $p5m1$ and $p51m$.

spacing $a$ with each adjacent layer rotated by $180^\circ$.\(^{17}\) By this method we find

$$\rho(r) = \rho(s, z) = \sum_{m \in \mathbb{Z}} \left( \sigma(s)\delta(z-2ma) + \sigma(-s)\delta(z-(2m-1)a) \right). \quad (2.18)$$

where we use $s$ as a vector in the plane with $z$ along the perpendicular axis. Now, to determine the space group of these axial stackings, we must obtain the 3D Fourier-space density by means of Fourier transform:

$$\rho(k) = \rho(k_s, k_z) = \frac{1}{8\pi^3} \int \rho(r)e^{-ikr}d^3r = \frac{1}{8\pi^3} \int \rho(k)e^{-i(k_s \cdot s + k_z z)}d^2sdz. \quad (2.19)$$

Plugging in (2.18) along with some simplification, we find

$$\rho(k) = \frac{1}{8\pi^3} \int \left( \sigma(s) + e^{ik_z z} \sigma(-s) \right) e^{-i k_s \cdot s} d^2s \sum_{m \in \mathbb{Z}} e^{2ik_z ma}. \quad (2.20)$$

Invoking the identity $\sum_m e^{imx} = \sum_n \delta(x-2n\pi)$ leads to

$$\rho(k) = \frac{1}{8\pi^3} \sum_{n \in \mathbb{Z}} \delta(k_z - \frac{n\pi}{a}) \left( \int \sigma(s) + (-1)^n \sigma(-s) e^{ik_s \cdot s} d^2s \right). \quad (2.21)$$

We can apply this result to equation (2.15), while using $k_l = -k_{l+5}$. Upon rearrangement of the sum and simplification we find

$$\rho_{p5m1}(k) = \ldots$$

\(^{17}\)This is symmetry equivalent to a $36^\circ$ rotation.
Thus, we find the $p5m1$ stacking has inner-star ($k_s = k_l$) extinctions on even layers, while $k_s = 0$ and the outer-star ($k_s = k_l + k_{l+1}$) are both extinct on the odds. Similarly, we find

$$
\rho_{p51m}(k) = \frac{c}{\pi} \sum_{n \in \mathbb{Z}} \left( \delta_{n,\text{even}}(k_s) + \sum_{l=0}^{9} (i(-1)^l \delta_{n,\text{odd}}(k_s - k_l) + \delta_{n,\text{even}}(k_s - k_l - k_{l+1}) \right)
$$

(2.23)

$$
\rho_{p5}(k) = \frac{c}{\pi} \sum_{n \in \mathbb{Z}} \left( \delta_{n,\text{even}}(k_s) + i \sum_{l=0}^{9} (-1)^l \left[ \delta(k_s - k_l) + \delta(k_s - k_l - k_{l+1}) \right] \right)
$$

(2.24)

We can look again to figure 2.3, but this time, for each symmetry, the squares represent extinctions on odd layers, while the crosses and circles are extinct on even layers. Additionally, figure 2.5 depicts a few layers of $\rho_{p51m}(k)$. We can use equations (2.22) – (2.24) to determine the phase functions and the values of the gauge invariants for our model quasicrystals.

Let $h$ denote a mirror in the $xy$-plane. It is easy to convince oneself that $h \in G$ our three densities, but formally, we must solve for the phase function $\Phi_h(k)$. We take $\rho(hk) = \rho(h(k_s + k_z))$. Since $k_s$ lies in the plane of the mirror, $hk_s = k_s$, while $hk_z = -k_z$, and we have $\rho(h(k_s + k_z)) = \rho(k_s - k_z) = \rho(k_s + k_z) e^{2\pi i \Phi_h(k_s+k_z)}$. Substituting any of equations (2.22) – (2.24) gives the following result

$$
\Phi_h(k) = 0 \quad \forall k \in \mathcal{L}.
$$

(2.25)

By confirming $h \in G$ we rule out any space-groups that do not contain $h$. Still, we must consider other possible space-group operations such as those generated by $r$ and $m$, where $r_k l \rightarrow k_{l+1}$, corresponding to a 36° rotation, and $m$ is a vertical mirror leaving
Figure 2.5. A few layers of the Fourier-space density $\rho_{p\overline{5}1m}(k)$. The solid layers are even, checkered are odd. Wave-vectors with non-zero weight are marked as blue spheres. Red stars indicate extinct wave-vectors.

$k_l$ and $k_{l+5}$ invariant for some $l \in \mathbb{Z}_{10}$. Starting with $p\overline{5}m1$, we will need to determine the values of the gauge-invariant quantity $\Phi_g(\frac{\pi\hat{z}}{a})$.\(^{18}\) With this information, we can uniquely determine each space group using tables from reference [53].

Consider $\rho_{p\overline{5}m1}(r k)$.

\[
\rho(r(k_l + k_{l+1})) = \rho(k_{l+1} + k_{l+2}) = \rho(k_l + k_{l+1})e^0,
\]
\[
\therefore \Phi_r(k_l + k_{l+1}) \equiv 0;
\]
\[\tag{2.26}
\]
\[
\rho(r(k_l + \pi\hat{z}/a)) = \rho(k_{l+1} + \pi\hat{z}/a) = \rho(k_l + \pi\hat{z}/a)e^{i\pi},
\]
\[
\therefore \Phi_r(k_l + \pi\hat{z}/a) \equiv 1/2.
\]
\[\tag{2.28}
\]

Now we apply linearity and the fact that $l$ is arbitrary,

\[
1/2 \equiv 5/2 \equiv \sum_{l \in \mathbb{Z}_{10}^{nht}} \Phi_r(k_l + \pi\hat{z}/a) \equiv 5\Phi_r(\pi\hat{z}/a),
\]
\[\tag{2.30}
\]

\(^{18}\)We choose this quantity because it is invariant for both $g = r$ and $g = m$. 

17
where \(\mathbb{Z}_{10}^{\text{odd}} = \mathbb{Z}_{10} \cap \{\text{Odds}\}\). Thus we find \(\Phi_{r}(\pi \hat{z}/a) \equiv \frac{1}{2}\).

Next, we consider \(\rho_{p5m1}(mk)\).

\[
\rho(m(k_l + k_{l+1})) = \rho(k_{l'} + k_{l'-1}) = \rho(k_l + k_{l+1})e^0, \quad (2.31)
\]
\[
\therefore \Phi_{m}(k_l + k_{l+1}) \equiv 0; \quad (2.32)
\]
\[
\rho(m(k_l + \pi \hat{z}/a)) = \rho(k_{l'} + \pi \hat{z}/a) = \rho(k_l + \pi \hat{z}/a)e^0, \quad (2.33)
\]
\[
\therefore \Phi_{m}(k_l + \pi \hat{z}/a) \equiv 0 \quad (2.34)
\]

where \(l\) and \(l'\) have the same parity. Again employing linearity,

\[
0 \equiv \sum_{l \in \mathbb{Z}_{10}^{\text{odd}}} \Phi_{r}(k_l + \pi \hat{z}/a) \equiv 5\Phi(\pi \hat{z}/a), \quad (2.35)
\]

and we have \(\Phi_{m}(\pi \hat{z}/a) \equiv 0\), and finally find that the space group for \(\rho_{p5m1}(k)\) is \(V(r^{1/2}, h, m)\) or using International notation \(P_{10} \frac{2}{m} \frac{2}{m} \frac{2}{m}\).

Next, we tackle the p51m. Starting from \(\rho_{p51m}(rk)\),

\[
\rho(r(k_l + k_{l+1} + \pi \hat{z}/a)) = \rho(k_{l+1} + k_{l+2} + \pi \hat{z}/a) = \rho(k_l + k_{l+1} + \pi \hat{z}/a)e^{i\pi}, \quad (2.36)
\]
\[
\therefore \Phi_{r}(k_l + k_{l+1} + \pi \hat{z}/a) \equiv 1/2; \quad (2.37)
\]
\[
\rho(r(k_l)) = \rho(k_{l+1}) = \rho(k_l)e^0, \quad (2.38)
\]
\[
\therefore \Phi_{r}(k_l) \equiv 0. \quad (2.39)
\]

Linearity gives

\[
\Phi_{r}(k_l + k_{l+1} + \pi \hat{z}/a) \equiv \Phi_{r}(k_l) + \Phi_{r}(k_{l+1}) + \Phi_{r}(\pi \hat{z}/a) \equiv 0 + 0 + \Phi_{r}(\pi \hat{z}/a) \equiv \Phi_{r}(\pi \hat{z}/a) \equiv 1/2. \quad (2.40)
\]

\[\text{19} \]

Since \(\pi \hat{z}/a\) is invariant under \(r\), this gauge-invariant explains the systematic extinction at wave-vectors of the form \(k = (2n - 1)\pi \hat{z}/a\).

\[\text{20} \]

In the language of reference [53].

\[\text{21} \]

It is simple to check that these phase functions satisfy the group-compatibility condition (2.10).
For we \( \rho_{p51m}(mk) \) we have

\[
\rho(m(k_l + k_{l+1} + \pi \hat{z}/a)) = \rho(k_l + k_{l-1} + \pi \hat{z}/a) = \rho(k_l + k_{l+1} + \pi \hat{z}/a)e^{i\pi},
\]

\[
\therefore \Phi_m(k_l + k_{l+1} + \pi \hat{z}/a) \equiv 1/2; \quad (2.42)
\]

\[
\rho(mk_l) = \rho(k_{l+1}) = \rho(k_l)e^{i0},
\]

\[
\therefore \Phi_m(k_l) \equiv 0; \quad (2.44)
\]

\[
\Phi_m(k_l + k_{l+1} + \pi \hat{z}/a) \equiv 0 + 0 + \Phi_m(\pi \hat{z}/a).
\]

We obtain \( \Phi_r(\pi \hat{z}/a) \equiv 1/2 \) and \( \Phi_m(\pi \hat{z}/a) \equiv 1/2 \) and thus the space group \( V(r^{1/2}, h, m^{1/2}) \) or \( P\frac{105}{m} \).

Finally, consider the p5-generated density, \( \rho_{p5}(k) \),

\[
\rho(r(k_l + \pi \hat{z}/a)) = \rho(k_{l+1} + \pi \hat{z}/a) = \rho(k_l + \pi \hat{z}/a)e^{i\pi},
\]

\[
\therefore \Phi_r(k_l + \pi \hat{z}/a) \equiv 1/2; \quad (2.47)
\]

\[
0 \equiv \Phi_r(k_l + k_{l+1} + \pi \hat{z}/a) - \Phi_r(k_l + \pi \hat{z}/a) \equiv \Phi_r(k_{l+1}).
\]

Thus, \( \Phi_r(\pi \hat{z}/a) \equiv 1/2 \). Meanwhile, we assume that \( m \) is a valid group operation and find

\[
\rho(m(k_l + \pi \hat{z}/a)) = \rho(k_{l'} + \pi \hat{z}/a) = \rho(k_l + \pi \hat{z}/a)e^{i0},
\]

\[
\therefore \Phi_m(k_l + \pi \hat{z}/a) \equiv 0; \quad (2.52)
\]

\[
\rho(m(k_l + k_{l+1} + \pi \hat{z}/a)) = \rho(k_{l'} + k + \pi \hat{z}/a) = \rho(k_l + k_{l+1} + \pi \hat{z}/a)e^{i\pi},
\]

\[
\therefore \Phi_m(k_l + k_{l+1} + \pi \hat{z}/a) \equiv 1/2. \quad (2.55)
\]
Combining equations (2.52) and (2.54), we find $\Phi_m(k_l) \equiv 1/2$, but this leads to a contradiction as

$$0 \equiv \Phi_m(0) \equiv \Phi_m\left(\sum_{l \in \mathbb{Z}_{10}^{odd}} k_l\right) \neq \sum_{l \in \mathbb{Z}_{10}^{odd}} \Phi_m(k_l) \equiv 1/2. \quad (2.56)$$

We have deduced that $m$, in fact, does not belong to the point group for our stacked p5 model. The space group must then be $V(r^{1/2}, h)$ or $P^{10h}_{m}$.

Because each stacking of five-fold planes results in a ten-fold screw axis, we conclude that the system in question, d-AlCoNi, should also exhibit this ten-fold symmetry.
CHAPTER 3
STOCHASTIC-ODE METHOD

Molecular-dynamics simulations are computationally expensive and have many limiting factors. Although simulations can be performed with several millions of atoms, this may only correspond to micrometer length scales and picosecond time scales. Although this does not make MD simulation of friction impossible, many shortcuts must be taken. For instance, in the AlCoNi simulations we will discuss in the following chapter, a sliding velocity of 5 m/s is used. This is roughly six orders of magnitude larger than those velocities used in experiment [44]. In addition, large approximant unit cells must be avoided, else we incur even more computational cost.

For this reason, appealing to a simpler model can be extremely beneficial. One model in particular was developed by Prandtl and Tomlinson [2, 17, 38, 66] in the 1920’s and with the use of modern computational power has resulted in several publications [11, 19, 23, 25, 55, 57, 68]. The model is described by an ordinary-differential equation

\[ m\ddot{x} + \frac{d}{dx}U_0 \cos\left(\frac{2\pi x}{a}\right) + k(x - v_{\text{slide}}t) = 0, \]

(3.1)

where \( U_0 \) is the amplitude of the surface corrugation, \( a \) is the unit cell size, and \( k \) is a spring constant for the coupling between the particle and the sliding body; see figure 3.1.

More recently, studies have introduced two additional terms in order to include the effects of thermal fluctuations [11, 57, 68]. A Markovian-noise term \( R(t) \) and a dissipative viscosity-like term \( m\gamma\dot{x} \) are included in the model, and our ODE becomes a

\[ m\ddot{x} + \frac{d}{dx}U_0 \cos\left(\frac{2\pi x}{a}\right) + k(x - v_{\text{slide}}t) + m\gamma\dot{x} + R(t) = 0, \]

where \( U_0 \) is the amplitude of the surface corrugation, \( a \) is the unit cell size, and \( k \) is a spring constant for the coupling between the particle and the sliding body; see figure 3.1.\(^3\)

\(^1\)Partial-differential equation in the 2-D case.
\(^2\)Perhaps the tip and base of an AFM cantilever, respectively.
\(^3\)We will later replace the periodic potential with one that is quasiperiodic.
Figure 3.1. Tomlinson’s model describing atomic-scale friction. The classical particle is subject to a coupling force and surface corrugation. Figure obtained from reference [23].

Stochastic-ODE of the form

\[
m\ddot{x} + \frac{\partial}{\partial x} U_0 \cos \left( \frac{2\pi x}{a} \right) + k(x - v_{\text{slide}} t) + m\gamma \dot{x} + R(t) = 0,
\]

(3.2)

where \( R(t) \) obeys the fluctuation-dissipation relation, \(^5\)

\[
\langle R(t)R(t') \rangle = 2m\gamma k_B T \delta(t - t').
\]

(3.3)

This is called the generalized Prandtl-Tomlinson model and has been used to model the cantilever and tip used in FFM measurements [11, 55, 57, 68].

In a 2009 Physical Review Letter [68], Tshiprut et al. implemented this S-ODE approach, finding an intriguing temperature dependence of kinetic friction, including non-monotonicity for certain choices of parameters. A second quantity, slip length \( \langle L \rangle \) — the average displacement during a single stick-slip event — proved worthy of notice. For a particular choice of parameters, \(^6\) \( \langle L \rangle \) is found to belong in one of several regimes. For the lowest temperatures, the dynamics were characterized by triple-slips, \( \langle L \rangle \sim 3a \). Increasing to 15\( K \), a mixture of triple- and double-slips was found. As the temperature

---

\(^4\)S-ODE’s of this form are also known as Langevin equations.

\(^5\)The notation \( \langle \ldots \rangle \) always denotes a time average unless otherwise noted.

\(^6\)\( U_0 = 0.26 \) eV, \( a = 0.3 \) nm, \( k = 1.5 \) N/m, \( m = 5 \times 10^{-11} \) kg, \( \gamma = 1 \times 10^5 \) s\(^{-1} \), and \( v_{\text{slide}} = 10 \) nm/s.
Friction tends to decrease as temperature is increased, but changes in slip regime may lead to local maxima and plateaus. Figure obtained from reference [68].

continued to be increased, transitions to double-slips, a mix of double- and single-slips, and finally, with $T \sim 300K$, single-slips were observed, $\langle L \rangle \sim a$.

The importance of this stick-slip characterizing quantity is revealed in figure 3.2. With each transition to decreasing slip-lengths, one may find either an increase or plateau in the temperature dependence in particular, the peak in the temperature dependence of the friction coincides well with the transition from the triple-double-slip to the double-slip regime.

Tshiprut et al. conclude that two competing effects characterize the temperature dependence at constant sliding velocity. First, slip-length aside, the friction tends to decrease as the temperature increases as described by Sang et al. [57], $F \propto \text{const} - T^{2/3} \ln T^{2/3}$. However, with rising temperature, slip-length also decreases, which has the reverse effect on friction.

Investigations of the Prandtl-Tomlinson model and similar models typically include a periodic surface-corrugation potential term. Our goal in this chapter is to investigate the effect of replacing this periodic potential with that of a quasiperiodic approximant.
Before proceding in this fashion, we shall first discuss the S-ODE solving algorithm used, and we’ll review some tests we performed on simpler models — Brownian motion and linear transport. We will then reproduce some of Tshiprut’s results. Finally, we will perform calculations using our quasiperiodic approximant potentials and discuss our results.

### 3.1 Van Gunsteren and Berendsen’s Algorithm

To find a solution to the differential equation in question, we must perform integration of a random variable. We may use traditional methods only in the limit $\Delta t \ll \gamma^{-1}$; otherwise we violate fluctuation-dissipation, equation (3.3) [61, 70]. In Tshiprut’s problem, the sliding velocity for the cantilever $v_{\text{slide}} = 10 \text{ nm/s}$. Because the period of our surface is 0.3 nm, and it wouldn’t be unreasonable to have resolution over 1000 points per period, we need $\Delta t \leq 3 \times 10^{-5} \text{s} \ll \gamma^{-1}$. However, in this problem $\gamma^{-1} = 10^{-5} \text{s}$. Moreover, the slip events which dominate the behavior of the tip also occur on the microsecond scale, reinforcing the need to move to smaller time steps. To do so, we must employ an alternative technique.

Following the steps of van Gunsteren and Berendsen in their 1982 publication [70], we begin with the equation,

$$m\ddot{x} = -m\gamma \dot{x} + F(x) + R(t), \quad (3.4)$$

with mass $m$, viscosity coefficient $\gamma$, Markovian noise $R(t)$, and an external force with no explicit time dependence $F(x)$. In addition, we impose the following constraints on $R(t)$:

$$\langle R(t)R(t') \rangle = 2m\gamma k_B T \delta(t - t'), \quad (3.5)$$

$$W[R(t)] = [2\pi\langle R^2 \rangle]^{-1/2} \exp\left\{\frac{R^2}{2\langle R^2 \rangle}\right\}, \quad (3.6)$$

$$\langle \dot{x}(0)R(t) \rangle = 0, \quad t \geq 0, \quad (3.7)$$

$$\langle F(0)R(t) \rangle = 0, \quad t \geq 0, \quad (3.8)$$

---

7Such as the Euler or Verlet algorithms.
where angled brackets denote equilibrium ensemble averages and \( W[R(t)] \) is the Gaussian probability distribution of the stochastic term \( R(t) \).

By writing \( v = \dot{x} \) in equation (3.4), we obtain

\[
v(t) = e^{-\gamma(t-t_n)} \left( v(t_n) + \frac{1}{m} \int_{t_n}^{t} e^{-\gamma(t'-t_n)} \left( F(t') + R(t') \right) dt' \right). \tag{3.9}
\]

At this point, many algorithms restrict the time step \( \Delta t \) to satisfy fluctuation-dissipation, which allows \( R(t) \) to be treated as a constant for each individual time step [61, 65]. Instead, we will directly integrate the stochastic force with respect to \( t \). We expand \( F(t) \) into its Taylor series

\[
F(t) = F(t_n) + \dot{F}(t_n) \Delta t + O[(t-t_n)^2]
\]

then integrate to find

\[
x(t_{n+\Delta t}) = x(t_n) + \int_{t_n}^{t_{n+\Delta t}} v(t)dt \tag{3.10}
\]

\[
= x(t_n) + \frac{v(t_n)}{\gamma} (1 - e^{-\gamma \Delta t}) + \frac{F(t_n)}{m \gamma} \left( \gamma \Delta t - 1 + e^{-\gamma \Delta t} \right) \]

\[
+ \frac{\dot{F}(t_n)}{m \gamma} \left( \frac{1}{2} (\gamma \Delta t)^2 - \gamma \Delta t + 1 - e^{-\gamma \Delta t} \right) \]

\[
+ \frac{1}{m \gamma} \int_{t_n}^{t_{n+\Delta t}} \left( 1 - e^{-\gamma(t_{n+\Delta t}-t)} \right) R(t)dt \]

\[
+ O[(\Delta t)^4]. \tag{3.11}
\]

Using the definition,

\[
X_n(\Delta t) \equiv (m \gamma)^{-1} \int_{t_n}^{t_{n+\Delta t}} e^{\gamma t - \gamma \Delta t} R(t)dt, \tag{3.12}
\]

and adding (3.11) to itself but with the replacement \( \Delta t \rightarrow -\Delta t \), we find,

\[
x(t_{n+\Delta t}) = x(t_n)(1 + e^{-\gamma \Delta t}) - x(t_n - \Delta t)e^{-\gamma \Delta t} + \frac{F(t_n)\Delta t}{m \gamma} (1 - e^{-\gamma \Delta t}) \]

\[
+ \frac{\dot{F}(t_n)\Delta t}{m \gamma^2} \left( \frac{\gamma \Delta t}{2} (1 + e^{-\gamma \Delta t}) - (1 - e^{-\gamma \Delta t}) + X_n(\Delta t) + e^{-\gamma \Delta t} X_n(-\Delta t) \right) \]

\[
+ O[(\Delta t)^4], \tag{3.13}
\]
which reduces to the Verlet algorithm in the small $\gamma$ limit. By calculating the values $\langle X^2(\Delta t) \rangle$, $\langle X^2(-\Delta t) \rangle$ and $\langle X(\Delta t)X(-\Delta t) \rangle$, we find a bivariate distribution,\(^8\)
\[
W(X_{n-1}, \bar{X}_n) = \left(4\pi (X_{n-1}^2)^2 (\bar{X}_n^2)^2 (1 - r^2) \right)^{1/2} \times \exp \left( - \frac{\langle \bar{X}_n^2 \rangle^2 X_{n-1}^2 - 2\langle X_{n-1}^2 \rangle \langle X_{n+1} \rangle \bar{X}_n + \langle X_{n-1}^2 \rangle^2 \bar{X}_n^2}{2\langle X_{n-1}^2 \rangle^2 (\bar{X}_n^2)^2 (1 - r^2)} \right),
\]
(3.14)

where $\bar{X}(\Delta t) = X(-\Delta t)$.

Now the task is simple. At some timestep $t_{n+1}$, we assume $x(t_n)$, $x(t_{n-1})$, $X_{n-1}(\Delta t)$ and $F(t_{n-1})$ are known. $F(t_n)$ can be evaluated from the potential and $\dot{F}(t_n)$ can be evaluated through differencing. Next, we sample $X_n(\Delta t)$ from the bivariate distribution and calculate $X_n(-\Delta t)$ from a gaussian distribution. Equation (3.13) then supplies $x(t_{n+1})$. Combining (3.11) with itself, in a manner similar to the Verlet algorithm, yields an expression for velocity.

The code we’ve implemented can be found in appendix B.

3.2 Testing the algorithm

A necessary step when implementing any algorithm is to subject it to various tests. The obvious reason for this is to work out any bugs in the code or implementation and check for mistakes in the derivations. Moreover, we must be sure that the code still works for very small $\gamma\Delta t$, and find when the code breaks down for large $\gamma\Delta t$. In our case, we found the code failed for very small $\gamma\Delta t$ due to numerical underflow. We were required to expand several operations into their power series.\(^9\)

We don’t wish to bore our audience with details of each minor test. Rather, we will present details of the three primary benchmarks: agreement with known results from Brownian motion, linear transport and Tshiprut et al.’s model.

In Brownian motion, we are interested in the diffusion of a particle in a solvent. The particle is repeatedly kicked by solvent particles in random directions, while undergoing

\(^8\)The distribution is bivariate because $X(\Delta t)$ and $X(-\Delta t)$ are integrals of $R(t)$ over the same time intervals.

\(^9\)The expansions used can be found in the appendix of reference [70].
an a resistive force due to viscosity. In 1D, we have the differential equation,

\[ m\ddot{x} + m\gamma \dot{x} - R(t) = 0. \]  

(3.15)

Multiplying both sides by \( x \) and using the identity \( \frac{d}{dt}(x\dot{x}) \equiv x^2 + x\ddot{x} \) leads to

\[ m \frac{d}{dt}(x\dot{x}) = m\dot{x}^2 - m\gamma x\dot{x} + xR(t). \]  

(3.16)

Now, taking the expectation values of each side and invoking equipartition,

\[ m \frac{d}{dt}(x\dot{x}) = k_B T - m\gamma \langle x\dot{x} \rangle. \]  

(3.17)

Substituting \( u = \langle x\dot{x} \rangle - \frac{k_B T}{m\gamma} \) we have,

\[ \dot{u} = -\gamma u, \]  

(3.18)

whose solution is \( u = -\frac{k_B T}{m\gamma} e^{-\gamma t} \). This yields \( \langle x\dot{x} \rangle = \frac{k_B T}{m\gamma} (1 - e^{-\gamma t}) \). Substituting \( \frac{d}{dt}\langle x^2 \rangle = 2\langle \dot{x}x \rangle \) and integrating gives

\[ \langle x(t)^2 \rangle = \frac{2k_B T}{m\gamma} (t + \frac{1}{\gamma} e^{-\gamma t}), \]  

(3.19)

which is the desired result.\(^\text{10}\)

Using \( \gamma = 1 \times 10^{-7} \) ps\(^{-1} \), \( T = 300 \)K and \( 5 \times 10^{11} \) kg, we ran 1000 trials with our code, and found \( \langle x^2 \rangle \) in good agreement with theory, see figure 3.3.

Next, we added a constant force to our differential equation to observe linear transport. Starting with the DE,

\[ m\ddot{x} + m\gamma \dot{x} - F - R(t) = 0, \]  

(3.20)

we take the expectation value of each side, and set \( \ddot{x} = 0 \), to find the terminal velocity,

\[ \langle v(t) \rangle = \frac{F}{m\gamma}. \]  

(3.21)

\(^\text{10}\)This leads to the familiar \( \langle x^2 \rangle = 2Dt \) in the long-time limit.
Figure 3.3. 1000 trials of our S-ODE code found the mean-squared displacement for a Brownian particle (dotted) in good agreement with theory (solid).

Plotting the average of 1000 trials with $F = 0.001 \text{ ev/Å}$, we also find good agreement with this theoretical trajectory; see figure 3.4.

Finally, we wished to reproduce the results presented by Tshiprut et al. We replaced the constant potential with one that was periodic, and introduced an interaction with a second particle. We call the original particle the “tip” and the second particle the “bob.” The bob has the same initial position as the tip, but holds a constant velocity $v_{\text{slide}} = v_{\text{bob}}$. The bob and tip interact via a spring with force constant $k$. The equation of motion for the bob is

$$m\ddot{x}_{\text{bob}} = k(x_{\text{tip}} - v_{\text{bob}}t) + F_{\text{app}}, \quad (3.22)$$

where $-F_{\text{app}} = F_{\text{friction}} \equiv f$ is the force applied to keep $\dot{x}_{\text{bob}} = v_{\text{bob}}$ constant. The tip’s motion is governed by

$$m\ddot{x}_{\text{tip}} = -m\gamma x_{\text{tip}} - \frac{\partial}{\partial x_{\text{tip}}} U_0 \cos \left( \frac{2\pi x_{\text{tip}}}{a} \right) - k(x_{\text{tip}} - v_{\text{bob}}t) + R(t), \quad (3.23)$$

all variables having their usual meanings.
Figure 3.4. Comparison of 1000 trials of our S-ODE code (dotted) versus the theoretical curve $\langle x \rangle = \frac{F}{m \gamma} t$ (solid) for Brownian motion with a constant external force.

Since we are interested in the energy lost to friction\(^{11}\) we wish to calculate the spatial-averaged quantity $\langle f \rangle_{x_{bob}}$. Using the chain rule,

$$
\langle f \rangle_{x_{bob}} = \frac{1}{L} \int_0^L f(x_{tip}, t) \, dx_{bob}
$$

(3.24)

$$
= \frac{1}{L} \int_0^{T_f} f(x_{tip}, t) \, \frac{\partial x_{bob}}{\partial t} \, dt
$$

(3.25)

$$
= \frac{1}{L} v_{bob} \int_0^{T_f} f(x_{tip}, t) \, dt,
$$

(3.26)

$$
= \frac{1}{T_f} \int_0^{T_f} f(x_{tip}, t) \, dt = \langle f \rangle_t \equiv \langle f \rangle,
$$

(3.27)

where $T_f$ is the total time, and $L = v_{bob} T_f$.

Now, using the fact that the left hand side of equation (3.22) is identically zero,

$$
\langle f \rangle = \frac{\langle x_{tip} - v_{bob} t \rangle}{T_f},
$$

$$
= \frac{\langle x_{tip} \rangle - v_{bob} T_f}{2}.
$$

(3.28)

\(^{11}\)Energy loss implies work. $U_{loss} = \int f(x) dx = (x_f - x_0) \langle f \rangle_x$. 

29
Figure 3.5. Using our code, we reproduced results in good agreement with Tshiprut et al. The peak in the average friction force (dashed) coincides with a sudden decrease in slip length (solid) at $T \sim 40$K. A straightforward algorithm for calculating slip length is given in appendix B.

Thus we find that for this model, we have a very simple and elegant way of calculating the average frictional force — simply by calculating $x(t)$.

Applying the DE, equation (3.23), to our code and calculating $\langle f \rangle$ as given by equation (3.28), we found results in agreement with Tshiprut et al.: compare figures 3.5 and 3.2.

### 3.3 Quasiperiodic S-ODE

Because the generalized Prandtl-Tomlinson model was effective at predicting some interesting friction phenomena, we believed that it should also be effective at modeling friction in the quasiperiodic case. Though clearly the model lacks some physics — e.g., phonons — the reduction in computational cost relative to three-dimensional molecular dynamics is enormous. Moreover, regardless of the outcome, the results of these simulations may help determine whether certain properties are responsible for lowering the friction, while ruling out others.
To generate our approximant quasiperiodic surfaces we replace our periodic potential $U = U_0 \left( \frac{2\pi x_{\text{tip}}}{a} \right)$ with

$$U = U_1 \cos \left( \frac{2\pi x_{\text{tip}}}{b} \right) + U_2 \cos \left( \frac{2\pi x_{\text{tip}}}{b'} \right). \quad (3.29)$$

By setting $b/b'$ equal to the quotient of two consecutive Fibonacci numbers $\text{Fib}_{n+1}/\text{Fib}_n$ we find a series of quasiperiodic potential approximants; see figure 3.6. Of course, in the limit $n \to \infty$ we have $b/b' = \tau$, the golden mean, which yields a perfectly quasiperiodic potential.

We will use two different methods to investigate the role of quasiperiodicity in determining friction for this model. First, we can set $U_1 = U_0$ and run simulations over various values of $b/b'$, while searching for any trends as our potential tends to
Figure 3.7. Temperature dependence for select quasiperiodic approximants within in the generalized Prandtl-Tomlinson model. We observe very little difference between all approximants of third-order \( b/b' = 5/3 \) — not shown) and higher.

quasiperiodicity. Second, we can let \( b/b' = \tau \) and vary \( U_1 \) and \( U_2 \), thereby introducing quasiperiodicity perturbatively. In all cases we will impose constant power \( P = \lim_{x \to \infty} \frac{1}{x} \int_{-x}^{x} U(x')^2 \, dx' \).

Setting our parameters to be the same as those used by Tshiprut et al., with \( b = a = 0.3\text{nm} \) and \( P = 0.676 \text{eV}^2 \), we allow \( b/b' \) to take values \( 1/1, 2/1, 3/2, 5/3, 8/5, ... \). For each choice of this ratio, we performed calculations for temperatures \( T \in \{0, 395\} \text{K} \); see figure 3.7. Though we find that there is some deviation between the lowest order approximant and the others, this behavior settles and converges by \( b/b' = 3/2 \) for high temperatures, and for all temperatures by \( b/b' = 8/5 \). The traces for \( b/b' = 8/5 \) and all higher-order approximants are virtually indistinguishable. For example position time-series, see figure 3.8.

Using our second approach, we see much more interesting behavior. Here, we impose constant power in our potential while varying \( U_1 \) and \( U_2 \) with \( b/b' = \tau \); see figure 3.9. We find that for an unmixed high-frequency potential, \( U_1 = 0 \text{eV}, U_2 = 0.26 \) and fixed
Figure 3.8. Position time-series data for $b/b' = 3/2$ (left) and $b/b' = 8/5$ (right), at 395K. Both cases clearly demonstrate stick-slip behavior, with the former having fewer slips as well as larger average magnitude.

$T$, there is an absolute minimum in average frictional force. Strangely, we also find a local minimum at some temperature-dependent mixture of the potentials. At 0K, the minimum occurs when $U_2 = 0.11$ eV, but this “optimal” value for $U_2$ increases as the temperature increases, reaching $U_2 = 0.21$ eV for $T = 200$K, before being completely smeared out at 300K.

As compelling as this result may appear, we find that this effect is not only duplicated, but also magnified, when we choose commensurate potentials, $b/b' = 3/2$; see figure 3.10. Although it is difficult to deduce in the incommensurate case, here the position time-series clearly indicated a phase transition occurring at the local minimum. At 0K in the time-series for $U_2 \geq 0.04$ eV, we find the typical stair pattern, corresponding to 7.5 Å slips. However, lowering $U_2$ just below this critical value, we find that each slip-event splits into a 3.5 and a 4.0 Å slip; see figure 3.11. The consequence of this doubling of slip events is a huge increase in friction. Of further interest is that we see no similar phase transition as $U_2$ becomes large (as $U_1$ becomes small). Although we are cautiously excited about this effect, it does nothing to help us understand low-friction surfaces in quasicrystals.

Perhaps another comparison worth making is that at low temperature, we find that the friction measured with commensurate potentials is greater than what’s measured in the incommensurate case, except near the phase boundary. Unfortunately, this effect becomes completely washed out at $T = 100$K and above.
Despite any strong indication that quasiperiodicity leads to lower friction within this model, it is important to note that this is not a purely negative result. As we mentioned previously in this chapter, this S-ODE model leaves a lot of physics out of the equation. We’ve yet to consider either electronic or phononic effects. It isn’t particularly clear how to implement such physics in a model which lacks atomicity. In the following chapter, we will try to make up for these deficiencies by implementing an MD model.
Figure 3.10. Friction measured while varying the coefficients $U_1$ and $U_2$ of two commensurate potentials. The local minimum for small, non-zero $U_2$ is much more exaggerated than in the incommensurate case, and much easier to understand in terms of the position time-series.

Figure 3.11. The position time-series for commensurate potentials $b/b' = 3/2$, for $U_2 = 0.039$ (solid) and 0.042 (dotted) eV. We find that all values of $U_2 \leq 0.039$ look qualitatively like the solid trace, while those $U_2 \geq 0.042$ are qualitatively similar to the dotted trace.
CHAPTER 4
MD SIMULATIONS OF D-ALCONI APPROXIMANTS

Moving towards a more serious model of friction on quasiperiodic surfaces, we sought to qualitatively reproduce the frictional anisotropy through molecular-dynamics (MD) simulations. Unfortunately, MD simulations are not perfect replicas of the physical world. We’ve already mentioned that performing such simulations sets very restrictive limits on the size of our samples and sliding velocities. The former further restricts us to relatively small unit-cell approximants. MD simulations also completely ignore electronic degrees of freedom, which may play an important role in this phenomenon [64]. Moreover, the dynamics produced in MD simulations are only as precise as the potentials used. While we are grateful to Marek Mihalkovič for providing pair potentials [41], by definition, pair potentials do not include any many-body interactions, which are extremely important in describing interactions in most solids.

On the other hand, MD simulations have been used extensively throughout the literature to model tribology of periodic systems [21,22,29,33,60,62], due to their ability to accurately reproduce some complicated dynamical effects, particularly in cases that may be otherwise inaccessible to theory or other computation methods, such as Monte Carlo. With this in mind, we believe extending such simulations to the quasiperiodic case provides a well-understood, atomistic approach to examine the dynamics of such systems.

In this chapter, we will be building on the work of Heather M. Harper [20], who gained much experience performing and trying to perfect MD simulations on a 25-atom unit cell (H1) d-AlCoNi approximant [49]. We will first discuss her simulation details and results before discussing our experiences with the 343-atom T11 approximant.
4.1 Harper’s work

Harper performed 34770-atom simulations of sliding friction between a crystalline tip and the two-fold face of a d-AlCoNi approximant. The sample was built from 25-atom unit cells of the H1 approximant phase supplied by Mike Widom. Widom-Moriarty potentials were employed [42, 72, 73]. In the experiment conducted by Park et al., a thiol-passivated titanium-nitride tip was used to reduce adhesion with the sample. Rather than include the complicated interactions of the organic molecules, Harper used a nearly rigid “adamant” FCC tip, whose interaction with the sample was purely repulsive.

Both the tip and the sample were divided into three sections by planes parallel to the interacting surfaces. The sections of the tip and sample that were in direct contact obeyed the usual NVE dynamics. A Langevin thermostat was coupled to the middle section in the two directions orthogonal to sliding. Finally, the two sections farthest from contact were held completely rigid; see figure 4.1.

The simulations were performed using between one and two million timesteps of 4 femtoseconds at 0K. The tip was lowered by imparting a velocity on the rigid layer.
Figure 4.2. The average frictional force as a function of load force for aperiodic (dashed) and periodic (solid) sliding directions. Data for this figure adapted from reference [20].

until the desired load was achieved. The system was coupled to a thermostat until the system equilibrated at 0 K. Next, a transverse velocity of 2 m/s was assigned to the rigid layer of the tip. The force required to maintain this velocity is equal and opposite to the frictional force, and was recorded at fixed intervals.

Using five sliding velocities $v_{\text{slide}} \in [0.04, 0.12] \, \AA/\text{ps}$ and loads $F_{\text{load}} \in (0, 100) \, \text{nN}$, Harper found time-averaged frictional forces on the order of piconewtons, four orders of magnitude lower than experiment [46]. For each sliding velocity, the friction coefficient was found to be lower for the aperiodic case, though only by an average of 8%; see figure 4.2.

### 4.2 Beyond Harper

Although Harper’s results had some degree of qualitative agreement with experiment, quantitatively there was much to be desired. In an attempt to correct this, we

\[ v = 0.12 \, \AA/\text{ps} \]

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carried out two significant changes — the first to increase the anisotropy, and the next to increase the friction coefficient.

Experiment has found that the friction measured on quasicrystals is lower than on nearby approximant phases [37]. Extending this idea to our situation, if we switch to a larger unit-cell approximant, we may find greater frictional anisotropy between the two sliding directions. To this end, we replaced Harper’s 25-atom H1 approximant unit cell with a 343-atom T11 unit cell.\textsuperscript{2}

Next, comparing Harper’s simulation with the generalized Tomlinson-Prandtl model from the previous chapter reveals a significant difference. In the latter, the AFM cantilever is simulated by considering an interacting body attached by a spring to a non-interacting body moving at a constant velocity.\textsuperscript{3} The spring constant is a free parameter that can be set to a value determined by experiment. In Harper’s work, one replaces this two-body system with a single tip that is rigid and in constant motion on one end, and free and interacting on the other. The disadvantage here is that the spring constant is no longer directly adjustable — it is a function of the cohesive potential and geometry of the tip. Moreover, because the adamantine potential is rather steep, we can expect this spring constant to be rather large.

From experiment, it is known that a smaller spring constant allows for a more sensitive measurement of the frictional force [46]. In fact, a molecular-dynamics investigation by Shimizu et al. [60] found that the components of the spring constant in the sliding and load directions both play a vital role in determining the onset of stick-slip and the coefficient of friction: a reduction in the sliding-direction spring constant by a factor of four nearly doubles the measured friction coefficient.

With this in mind, we chose to replace Harper’s adamant tip with a tip-and-“bob” combination. The tip was constructed from an aluminum unit cell but made completely rigid. Each tip atom would interact with the sample via a Lennard-Jones potential. Meanwhile, the center of mass of the tip would be coupled to the bob by a spring with constant $k$; see figure 4.3.

\textsuperscript{2}Courtesy of Mike Widom.

\textsuperscript{3}The tip and base of the cantilever, respectively.
Figure 4.3. In our simulations with the T11 approximant, we replaced Harper’s tip with a tip and “bob” combination. This allows the spring constant to be set to values typical of experiment. The sample is still divided into rigid, thermostat, and free regions.

Because we switched to a larger approximant, we were faced with the additional complication of determining the correct surface termination. We selected two candidate surface terminations, which we will call T11(a) and T11(b), that were consistent with the description given in reference [44]; see figure 4.4. Some notable features include pentagons with a single vertex exposed to the surface, distorted pentagons with two vertices on the surface, only aluminum atoms exposed, and the Fibonacci sequence with lengths $L = 4.9 \pm 0.3$ Å and $S = 2.8 \pm 0.2$ Å parallel to the surface, all of which were absent from the surface termination used in Harper’s work.

We performed the bulk of our simulations on a small 2744-atom T11 sample with a 340-atom BCC tip but also performed a series of runs on a larger 49392-atom sample with a 1600-atom tip. Using 0.002 femtosecond timesteps, with $\sim 10^7 - 10^8$ total steps, the bob was lowered a distance $x_0$, and the tip and sample were equilibrated at a temperature $T$. A constant velocity $v_{\text{slide}}$ in the sliding direction was then assigned to the rigid layer of the sample, while the bob was fixed in space.\footnote{This is preferred over fixing the sample and sliding the “bob” because of a LAMMPS bug.} The spring force between
the tip and spring were recorded every 10 timesteps. The components of this force in the compression and sliding directions were the load and frictional force, respectively.

4.3 Results

Simulations were run for several choices in the parameter space, which are tabulated in table 4.1. Typical values for the load forces used were $F_{\text{load}} \in (0, 48)\text{nN}$, corresponding to pressures $P \in [0, 10.8] \text{ GPa}$.\textsuperscript{5} See appendix C for a sample input file and submission script.

Performing time averages of the forces on the bob was not a simple matter, especially in determining the frictional force, since the fluctuations due to stick-slip were of much larger magnitude than the average friction; see figure 4.5. Performing peak-to-peak averages was very difficult to automate, and picking out these “peaks” is not exceedingly

\textsuperscript{5}Compare these pressures to those used in experiment $P_{\text{exp}} \in [-1.13, 0.87]$. 

Figure 4.4. (Top) Surface structure taken from [44]. The blue atoms are aluminum, and pink are transition metals. Darker atoms are in the nearer of the two layers. Both, the T11(a) (middle) and T11(b) (bottom) surface terminations have several feature in common with Park’s sample. Here the blue atoms are aluminum, while red and green are the transition metals, cobalt and nickel, respectively. The asterisks denote atoms that were removed due to instability.
Table 4.1. The parameters used in molecular-dynamics simulations performed on the T11 approximant with two surface terminations (a) and (b). Friction was not found to be lower in the quasiperiodic sliding direction for any choice of parameters listed.

<table>
<thead>
<tr>
<th>Series</th>
<th>Sample</th>
<th>Atoms</th>
<th>T (K)</th>
<th>( k ) (eV/Å²)</th>
<th>( v_{\text{slide}} ) (Å/ps)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1)</td>
<td>T11(a)</td>
<td>3094</td>
<td>0</td>
<td>1</td>
<td>0.05</td>
</tr>
<tr>
<td>(2)</td>
<td>T11(a)</td>
<td>3094</td>
<td>0</td>
<td>1</td>
<td>0.075</td>
</tr>
<tr>
<td>(3)</td>
<td>T11(a)</td>
<td>3094</td>
<td>0</td>
<td>0.5</td>
<td>0.05</td>
</tr>
<tr>
<td>(4)</td>
<td>T11(a)</td>
<td>3094</td>
<td>0</td>
<td>1</td>
<td>0.033</td>
</tr>
<tr>
<td>(5)</td>
<td>T11(b)</td>
<td>3094</td>
<td>0</td>
<td>1</td>
<td>0.075</td>
</tr>
<tr>
<td>(6)</td>
<td>T11(b)</td>
<td>3094</td>
<td>0</td>
<td>0.5</td>
<td>0.075</td>
</tr>
<tr>
<td>(7)</td>
<td>T11(b)</td>
<td>3094</td>
<td>0</td>
<td>1</td>
<td>0.05</td>
</tr>
<tr>
<td>(8)</td>
<td>T11(b)</td>
<td>3094</td>
<td>300</td>
<td>1</td>
<td>0.05</td>
</tr>
<tr>
<td>(9)</td>
<td>T11(b)</td>
<td>50993</td>
<td>300</td>
<td>1</td>
<td>0.01</td>
</tr>
<tr>
<td>(10)</td>
<td>T11(b)</td>
<td>50993</td>
<td>0</td>
<td>1</td>
<td>0.01</td>
</tr>
</tbody>
</table>

Figure 4.5. The force time-series from series (1) in table 4.1 along the quasiperiodic sliding direction, with \( F_{\text{load}} = 3.12 \text{ eV/Å} \).

straightforward since there are two distinct frequencies contributing to the oscillations in the friction force: one characterized by the unit-cell length and the other due to stick-slip and largely dependent on the normal force and spring constant. After experimenting with some fitting routines, we decided to simply use the time-averaged values with error-bars calculated by taking the standard deviation of the cumulative average.

The runs using the T11(a) surface terminations turned out to be particularly troublesome, as several atoms dissociated from the surface, and in some cases, were completely ejected from the simulation box. This surface featured an approximately two-fold frictional anisotropy, but with the periodic sliding direction having lower friction, contrary
Figure 4.6. (Left) Friction as a function of load force for series (1) in table 4.1. We find a clear anisotropy, but with the periodic (dotted) sliding direction being lower than the quasiperiodic (solid) direction by a factor of $\sim 2.0$. (Right) Friction plotted against the load force for series (7) in table 4.1. Here we found some promise, as the anisotropy between the periodic (dotted) and quasiperiodic (solid) sliding directions increased with large load.

to the experimental results. We decided to remove the problematic atoms from the simulation entirely, but this had little effect on the results; see figure 4.6.

The T11(b) surface termination proved to be more stable, but in this case we found little to no frictional anisotropy whatsoever. When the 3094-atom T11(b) run with $v_{\text{slide}} = 0.05 \, \text{Å/ps}$ finally gave us a result with lower friction on the aperiodic sliding direction for large loads, we decided to probe even larger load forces; see figure 4.6. To do so, without plastic deformation, we were required to increase the size of the tip and sample, thereby increasing the contact area and decreasing the pressure. Also, because this effect was only seen in runs with lower sliding velocities, we chose to lower this velocity by another factor of five, to 0.1 Å/ps. At this time, only results from runs with $T = 300$ K are available, and unfortunately the frictional anisotropy was not reproduced here.

Although these results do not do much to improve on the work done by Harper, much of parameter space has yet to be explored. Specifically, we have not performed any runs with velocities anywhere near those used in experiment. Though it would be impossible to lower our sliding velocity to the order of micrometers per second, velocities of several centimeters per second are within reach. Moreover, it is unclear whether the stick-slip
mechanism played a role in the experimental results: the tip was passivated and the contact area was larger by nearly an order of magnitude. It may be worth exploring more points in the parameter space using a more repulsive tip-surface interaction or with $k \to \infty$.

On the other hand, it is possible that there is simply nothing to find here. Between this work and Harper’s, there have been glimpses of anisotropy favoring the quasiperiodic sliding direction, but only with a factor of $1.1 - 1.2$, far from the experimentally observed eight-fold anisotropy. Clearly, small changes in the parameters will not suffice. Rather, it is more likely that we need to move beyond pair-potentials, perhaps even including electronic degrees of freedom. Another alternative is to develop a model which emphasizes the quasiperiodicity of the system in a controlled manner. This is exactly what is done in the following chapter.
Although we failed to reproduce the experimental results of Park et al. in our MD simulations of d-AlCoNi approximants, the true failure was our inability to determine why. Why were we unable to reproduce the eight-fold anisotropy, or for that matter, any anisotropy whatsoever? We could continue in the fashion of chapter four, continuing to make tweaks and investigate a larger sample of parameter space, but without a significant breakthrough, it is doubtful whether a clear understanding will be achieved. On the other hand, we could develop a new model with this question in mind. Rather than generically trying to reproduce the frictional anisotropy, we can construct a model that isolates the feature of our primary interest: quasiperiodicity.

The Fibonacci sequence has been used in various works as a model of quasiperiodicity [4, 12, 36, 47] and in some cases has been expanded to the two-dimensional case [28, 69]. Here, we will use approximants from the Fibonacci sequence to generate three-dimensional solids with varying orders of quasiperiodicity. With this, we may directly probe the role of quasiperiodicity while minimizing interference from other unrelated mechanisms.

5.1 Constructing Fibonaccium

As discussed in section 2.1, the Fibonacci sequence can be useful for reproducing some physics of quasiperiodic structures. As with d-AlCoNi, we wanted to construct our model with two quasiperiodic and one periodic axes. We started by taking an existing cubic lattice and tried to perturb the interatomic distances according to the Fibonacci sequence. As we began to develop potentials for such a system, it became clear that perturbing spring constants or, almost equivalently, masses would not only simplify the
Figure 5.1. 5th-order Fibonaccium built from iron (BCC) unit cells. In simulations with this structure, we employ the embedded-atom method (EAM) potential from reference [39]. Key: \( m_{\text{blue}} = m_{LL} \), \( m_{\text{green}} = m_{LS} = m_{SL} \), \( m_{\text{red}} = m_{SS} \).

model a great deal, but also allow us to skip potential development altogether since we could simply plug in the potentials from the unperturbed system.

Ignoring the periodic axis for a moment, we took a two-dimensional grid and labeled each column — either L or S — according to some finite Fibonacci sequence approximant, then repeated for each row. At that point, each grid cell had a two-character label: LL, LS, SL, or SS. We then constructed a two-dimensional surface with two quasiperiodic directions by converting each grid cell into a cubic unit cell (FCC, BCC or SC) containing atoms with atomic masses corresponding to that cell’s label. For instance, all cells labeled SS would have atoms with mass \( m_{SS} = 50 \) amu, while LS and SL cells contained atoms with mass \( m_{LS} = m_{SL} = 100 \) amu and LL cells contained those with mass \( m_{LL} = 200 \) amu. Finally, we completed our construction of “Fibonaccium” by repeating this structure periodically in the third direction; see figure 5.1. The code used to generate the Fibonaccium sample is supplied in appendix D.

Using this recipe, we constructed two series of Fibonaccium approximants. The first series had samples built from body-centered cubic (BCC) unit cells, with lattice constant
Figure 5.2. Isotropic pair potentials developed by Rechtsman et al. were implemented for simulations of SC Fibonacci [54]. The potential takes the form $V_{sc}(r) = 48572 r^{-12} - 0.25142 \exp(-10.761(r - 3\sqrt{2})^2)$. The minimum is at the second nearest neighbor distance to avoid the formation of closed-packed structures.

We chose this structure, as a many-body embedded-atom-method (EAM) potential was readily available [39]. The second series was constructed from simple-cubic (SC) unit cells ($a = 3.0 \text{ Å}$) to minimize the number of atoms required for higher-order approximants. For this structure, we used isotropic pair potentials developed by Rechtsman et al. [54]; see figure 5.2. This potential is tailored to stabilize the simple-cubic structure by placing the minimum at the second-nearest-neighbor distance and is scaled to give the desired lattice constant and a cohesive energy comparable to that of our d-AlCoNi T11 approximant: 0.53 eV/atom. In each case, the tip was constructed with cubic symmetry and lattice constant incommensurate to the sample to avoid registry.

We also had two different ways of controlling the degree of quasiperiodicity in our sample. First, we can choose a single approximant and set $m_{LL} = m_{SS}$, thereby retaining a completely periodic structure.\footnote{We will always use $m_{LS} = m_{SL} = \frac{m_{LL} m_{SS}}{2}$.} Now, by increasing $m_{LL}$ while keeping $m_{SS}$ fixed, quasiperiodicity could be introduced to the system in a controlled and contin-
uous manner. Second, we can choose $m_{LL} \neq m_{SS}$ and instead control the degree of quasiperiodicity by the order of the approximant used.

### 5.2 Fixed order, variable mass

The first set of simulations were all performed on a 1024-atom sixth-order BCC Fibonaccium sample, corresponding to the Fibonacci sequence of length 8. The light mass was kept fixed and equal to the atomic mass of iron, $m_{SS} = 55.845$ amu, while the heavy mass was varied, taking one of six possible values: $m_{LL} \in [55.85, 1406.25]$ amu. The medium masses were set to the average of the light and heavy masses: $m_{LS} = m_{SL} = \frac{m_{SS} m_{LL}}{2}$. The simulations were performed using the same procedure as that used on the d-AlCoNi approximants, which is outlined in chapter 4, with 26 different load forces $F_{\text{load}} \in [-3.3, 5.8]$ eV/Å for each choice of $m_{LL}$ and sliding direction. The spring constant was set to 1 eV/Å$^2$, and the tip was dragged along the quasiperiodic/periodic surface for a total of 3.6 nanoseconds at 0.05 Å/ps at $T = 0$K. A sample input file is given in appendix C.

The results were not particularly interesting. For individual choices of mass, the average frictional force was a bit noisy as a function of load force, but the coefficients of friction extracted via linear regression had errors of only 4%. We performed the linear fits for both sliding directions and calculated the total frictional anisotropy $\beta = \frac{\mu_{\text{periodic}}}{\mu_{\text{quasi}}} \pm \frac{\mu_{\text{periodic}}}{\mu_{\text{quasi}}} \sqrt{\left( \frac{\delta \mu_{\text{periodic}}}{\mu_{\text{periodic}}} \right)^2 + \left( \frac{\delta \mu_{\text{quasi}}}{\mu_{\text{quasi}}} \right)^2}$, for each choice of mass. Unfortunately, we found no evidence that the anisotropy has any dependence on the mass ratio for fixed-order approximants; see figure 5.3.

Because these results weren’t very encouraging, we chose to forgo further calculations with larger samples and instead focus on our second approach.

### 5.3 Fixed mass, variable order

Rather than fixing approximant order, we performed simulations for fixed masses on SC and BCC Fibonaccium approximants of up to tenth-order; see figure 5.4. Because

---

2The loads correspond to pressures $P \in [-5.55, 9.76]$ GPa.

3Corresponding to the Fibonacci sequence of length 55.
Figure 5.3. (Left) Frictional anisotropy as a function of mass ratio. (Right) The average frictional force as a function of load for $m_{LL}/m_{SS} = 25$. Even for such a large mass ratio, we find no evidence of frictional anisotropy.

<table>
<thead>
<tr>
<th>Series</th>
<th>BCC/SC</th>
<th>Atoms (approx.)</th>
<th>$T$ (K)</th>
<th>$k$ (eV/Å$^2$)</th>
<th>$v_{slide}$ (Å/ps)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1)</td>
<td>BCC</td>
<td>12000</td>
<td>0</td>
<td>10</td>
<td>0.05</td>
</tr>
<tr>
<td>(2)</td>
<td>BCC</td>
<td>12000</td>
<td>0</td>
<td>1</td>
<td>0.05</td>
</tr>
<tr>
<td>(3)</td>
<td>BCC</td>
<td>12000</td>
<td>150</td>
<td>1</td>
<td>0.05</td>
</tr>
<tr>
<td>(4)</td>
<td>SC</td>
<td>31000</td>
<td>300</td>
<td>1</td>
<td>0.05</td>
</tr>
<tr>
<td>(5)</td>
<td>SC</td>
<td>31000</td>
<td>300</td>
<td>1</td>
<td>0.005</td>
</tr>
<tr>
<td>(6)</td>
<td>SC</td>
<td>31000</td>
<td>300</td>
<td>0.1</td>
<td>0.05</td>
</tr>
<tr>
<td>(7)</td>
<td>SC</td>
<td>31000</td>
<td>300</td>
<td>0.1</td>
<td>0.005</td>
</tr>
<tr>
<td>(8)</td>
<td>SC</td>
<td>31000</td>
<td>100</td>
<td>0.1</td>
<td>0.005</td>
</tr>
<tr>
<td>(9)</td>
<td>SC</td>
<td>31000</td>
<td>300</td>
<td>0.1</td>
<td>0.0005</td>
</tr>
</tbody>
</table>

Table 5.1. These parameters were used in the molecular-dynamics simulations on Fibonaccium. In all cases $m_{SS} = 50$ and $m_{LL} = 200$ were used. The number of atoms in each case is approximate because it varies depending on the approximant.

The results from these sets of runs did not show much promise either. Take series (7), for instance. We ran calculations for thirteen choices of compressions $F_{load} \in [0.45, 17.5]$ eV/Å — corresponding to pressures $P \in [0.06, 2.43] GPa$ — for Fibonaccium approximants of order four, seven, and ten. Here, we observed no significant difference in the the approximant unit cells are of varying sizes, smaller approximants were repeated in the simulation box so particle number (and volume) could be roughly constant for each sample. The simulations were performed in the usual way, with runs at both $T = 300K$ and absolute zero, and varying spring constants and sliding velocities. Choices for the experimental parameters for each series of runs are are listed in table 5.1.

The results from these sets of runs did not show much promise either. Take series (7), for instance. We ran calculations for thirteen choices of compressions $F_{load} \in [0.45, 17.5]$ eV/Å — corresponding to pressures $P \in [0.06, 2.43] GPa$ — for Fibonaccium approximants of order four, seven, and ten. Here, we observed no significant difference in the
Figure 5.4. Simple-cubic Fibonaccium of order 55. The different colors represent different atomic masses: dark blue = LL, light blue = LS = SL, green = SS. The tip is shown in yellow. The periodic and quasiperiodic sliding directions are to the upper-left and upper-right, respectively. Image rendered using rasmol [58].

Figure 5.5. The frictional force (versus load) for series (7) with simple-cubic Fibonaccium sample of order 3 and 55, (left) and (right) respectively. Despite a very significant difference in the unit-cell periodicity, we do not observe any significant differences in the frictional response.

Frictional behavior between the two sliding directions, and, if anything, the anisotropy dropped from $\beta = 1.05 \pm 0.12$ for fourth-order to $\beta = 0.90 \pm 0.08$ for tenth-order; see figure 5.5. We will not attempt to argue that larger-order approximants increasingly favor the periodic sliding direction since the anisotropies have overlapping error-bars, but certainly there is no evidence here to link quasiperiodicity to low friction.
CHAPTER 6
CONCLUSIONS AND FUTURE WORK

In this work, we have implemented three techniques in an attempt to understand the low-friction phenomenon on quasicrystals and how it relates to quasiperiodicity. We modeled friction on a 1-D quasiperiodic system using a stochastic differential equation and performed molecular-dynamics simulations on d-AlCoNi approximants and our own toy model, Fibonaccium. In no cases did we find a lowering of friction due to quasiperiodicity. These findings lead to two potential conclusions. Either there is a shortcoming (or shortcomings) in our models, or there is simply no effect to be observed. First, we shall assume the former.

In our S-ODE approach, there are several aspects that deserve scrutiny, but the most obvious is the lack of atomicity. Without atoms there cannot be neither phonons nor electrons but rather a viscosity-like mechanism for energy diffusion. Though it seems reasonable to model the transfer of energy away from the surface of our sample via the diffusion of energy,\(^1\) this eliminates the possibility of interference between different electronic and phononic modes and completely ignores the existence of extended or algebraically-decaying states. A second, possibly related, deficiency becomes evident when one considers the time scales involved in the model. Because of the very low sliding velocity, the time between each stick-slip event is typically on the order of ten milliseconds. On the other hand, the time scale for damping is \(\frac{1}{\gamma} = \frac{1}{10^{-7} \text{ps}} = \text{ten microseconds}\). Since the main dynamical variable related to friction in this problem, the velocity \(\dot{x}\), is so quickly damped out, we lack coupling between adjacent stick-slip events.

\(^1\)In the form of heat.
One possible remedy for these deficiencies is to add a memory term to the differential equation, one that couples stick-slip events emulating the effect of phonons. However, the correct way of doing this is not clear.

Next, let us consider our molecular-dynamics simulations. The most obvious weakness here, as mentioned in previous chapters, is the large sliding velocity. In the experiment conducted by Park et al. on d-AlCoNi, the sliding velocity never exceeded $10^{-6}$ Å/ps. Even when we push our computational limits, we can only reduce our velocity down to $5 \times 10^{-4}$ Å/ps — still two orders of magnitude too fast. It is possible that this large velocity simply washes out the effects that produce the frictional anisotropy. On the other hand, we would expect the anisotropy to grow as the velocity approaches the experimental magnitude, but we do not observe any such trends in the frictional response between $v_{\text{slide}} = 0.0005$ and $v_{\text{slide}} = 0.5$ Å/ps. Moreover, it is unclear whether a further reduction of velocity should alter the physics in any appreciable way, as we are already well below the characteristic speeds for our system: the lattice constant time spring frequency $a \sqrt{\frac{k}{m_{\text{bob}}}} = 660$ m/s, and the speed of sound in Fibonaccium, which we estimate to be on the order of $10^5$ m/s.

A second major deficiency is our lack of long-range potentials. The Rechtsman potential decays to zero quickly after the local minima at the second nearest-neighbor distance $3\sqrt{2}$ Å [54], the Widom-Moriarty potentials used are truncated at 7 Å to enhance stability [71], and the EAM potentials are cut off at 5.3 Å. Clearly long-range interactions are responsible for the stability of real-life quasicrystals, and such interactions may also enhance the effects of (approximate) quasiperiodicity as each atom will “see” a larger portion of the unit cell.

Third, the MD calculations lack electronic and accessible phason degrees of freedom. The electronic states may play a particularly important role, since d-AlCoNi and other quasicrystals are semi-metals. Moreover, quasiperiodicity affects electronic structure in a peculiar way, introducing a fractal-like structure riddled with Van Hove singularities [4]; see figure 6.1. Perhaps this or some other electronic effect is the true culprit behind the low friction.
Despite these deficiencies, it is still possible that we are doing all the right things, and there is simply no anisotropy here to find. This would seem to explain the failure of the Fibonaccium model, but without making accusations of Park’s experiment being “wrong,” it does little to explain the failure of our simulations of the d-AlCoNi approximants. Whatever the case, it is still possible that quasiperiodicity is not at all responsible for these low-friction surfaces; however there is no other mechanism to which we can really attribute this responsibility. As discussed in chapter 1, there are instances where arguments such as hardness, adhesion, or registry make sense, but none of these mechanisms can single-handedly explain all occurrences of low-friction quasicrystalline surfaces.

6.1 Future work

As we have not drawn any strong conclusions from this work, it is clear that more calculations are required. The obvious next step is to explore more points in the parameter space of our MD simulations. In particular, we would like to perform more
simulations with low velocities, larger samples, higher-order approximants, tips with increased surface area to allow for large load forces, and large spring constants to decrease the frictional contribution from stick-slip. Additionally, we would like to perform calculations of the phonon spectrum, phonon participation ratios, and thermal conductivity along the two sliding directions for both the d-AlCoNi approximants and Fibonaccium.

Next, we are interested in performing 2-D simulations of friction between a single-atom tip and a Fibonacci chain. We can impose periodicity on this Fibonacci chain in the same manner as used for Fibonaccium — by perturbing the atomic masses. Using an anharmonic potential, and referring to reference [12], we can choose atomic masses that open gaps in the phonon spectrum at certain frequencies; see figure 6.3. By measuring friction using sliding velocities corresponding to these frequencies and comparing to calculations with unperturbed masses, we believe we may uncover some interesting behavior. Furthermore, performing simulations on such a computationally lightweight model, as was the case with the S-ODE model, also opens up the possibility of exploring very small sliding velocities.

On another note, unrelated to quasiperiodicity, we uncovered some interesting features while experimenting with our S-ODE model. First, as we discussed in chapter 3 for the potential,

\[ U = U_1 \cos \left( \frac{2\pi x_{\text{tip}}}{b} \right) + U_2 \cos \left( \frac{2\pi x_{\text{tip}}}{b'} \right), \]  

(6.1)

taking \( b'/b \in \mathbb{Q} \), we found two distinct regimes of frictional response, separated by a deep minimum for low temperature; see figure 3.10. Starting from the left of the minimum, the frictional response is characterized by 7.5 Å stick-slip events. Upon crossing, these slip events suddenly split into a two separate events of length 3.5 and 4.0 Å; see figure 3.11. As we moved towards irrational values for \( b'/b \) this effect began to vanish; see figure 3.9. The next step in understanding this phenomenon is to perform more calculations and try to narrow the transition boundary to as small a region as possible. From there, we hope to uncover some clues by performing Fourier analysis of the potential against the time-series.

Finally, we performed S-ODE calculations with a periodic potential \( U_2 = 0 \), but with variable unit-cell length \( b \). Plotting the average frictional force against \( b \), we found
Figure 6.2. Friction versus the lattice constant calculated using the S-ODE method from chapter 3. On average, we find that friction decreases at large lattice constant, we find two jump discontinuities where the friction abruptly increases by several hundred piconewtons.

two jump discontinuities; see figure 6.2. At first sight, one would assume that these discontinuities likely correspond to some resonance between the sliding velocity and the spring frequency. It turns out that this is not the case, as $v_{\text{slide}}/b$ is different from $\sqrt{k/m}$ by several orders of magnitude. The next step is to perform calculations for lattice constants not covered by the interval [3, 6] Å. At that point, we may be able to find more clues in the position time-series data.
Figure 6.3. (Top) The phononic density of states for the harmonic (dotted) and anharmonic (solid) Fibonacci chains. (Bottom) The coherent structure factor for the anharmonic case. Image obtained from reference [12].
REFERENCES


[38] C.M. Mate, Tribology on the small scale: a bottom up approach to friction, lubrication and wear, 2008, Oxford.


APPENDICES
Appendix A Linear response

Given a Langevin equation, one may use linear-response theory to derive an expression based on equilibrium correlation functions. From the equation for a Brownian particle \( m\frac{dv}{dt} = -\gamma v + R(t) \), one finds the time-averaged force (friction) on the particle is proportional to the velocity, \( \langle F \rangle = -\gamma \langle v \rangle \). With some manipulation we may find
\[
\gamma = \frac{1}{2k_B T} \int_{-\infty}^{\infty} \langle R(0)R(t) \rangle dt \quad [1],
\]
where \( R(t) \) is the stochastic force in an equilibrium ensemble.

Now suppose, rather than Brownian motion, we are using the Tomlinson-Prandtl model to calculate the friction between a surface and a sliding AFM tip; see equation (3.1). Here we shall find that while this method may still be effective for a calculation of \( \gamma \), \( \gamma \) is no longer the dominant term in the frictional force. Because of this, we are no longer able to calculate friction based on equilibrium ensemble averages, but rather, we must perform dynamic simulations.

In the Tomlinson-Prandtl model, the AFM tip is connected to a “bob” via a spring with constant \( k \). The bob slides at a constant velocity, while the tip is subject to a periodic surface potential and thermal fluctuations.

The equation of motion for the bob is
\[
m \ddot{x}_{bob} = k(x_{tip} - v_{bob} t) + F_{app} = 0,
\]
where \( k \) is the spring constant and \(-F_{app} = F_{friction} \equiv f \) is the force applied force to keep \( \dot{x}_{bob} = v_{bob} \) constant.\(^1\) The tip’s motion is governed by
\[
m \ddot{x}_{tip} = -\gamma x_{tip} - \frac{\partial U(x_{tip})}{\partial x_{tip}} - k(x_{tip} - v_{bob} t) + R(t),
\]
where \( U(x) \) is a periodic potential which describes the surface corrugation of the sample, and \( R(t) \) is a Markovian noise term obeying \( \langle R \rangle = 0 \) and \( \langle R(t)R(t') \rangle = 2m\gamma k_B T \delta(t-t') \).

\(^1\)Hereafter, when we say “friction” we mean the magnitude of friction.
Since we are interested in the energy lost to friction\(^2\) we are interested in calculating the spatial-averaged quantity, \(\langle f \rangle_{x_{bob}}\). Using the chain rule,

\[
\langle f \rangle_{x_{bob}} = \frac{1}{L} \int_0^L f(x_{tip}, t) \, dx_{bob} = \frac{1}{L} \int_0^{T_f} f(x_{tip}, t) \frac{dx_{bob}}{dt} \, dt \quad \text{(A.3)}
\]

\[
= \frac{1}{L} v_{bob} \int_0^{T_f} f(x_{tip}, t) \, dt \quad \text{(A.4)}
\]

\[
= \frac{1}{T_f} \int_0^{T_f} f(x_{tip}, t) \, dt = \langle f \rangle_t, \quad \text{(A.5)}
\]

where \(T_f\) is the total time, and \(L = v_{bob} T_f\).

Using the fact that the left-hand side of equation (A.1) is identically zero,

\[
\langle f \rangle_t = -k (x_{tip} - v_{bob} t). \quad \text{(A.6)}
\]

Invoking equation (A.2),

\[
\langle f \rangle_t = \left\langle m \ddot{x}_{tip} + \gamma x_{tip} + \frac{\partial U(x_{tip})}{\partial x_{tip}} - R(t) \right\rangle_t = \left\langle \gamma x_{tip} + \frac{\partial U(x_{tip})}{\partial x_{tip}} \right\rangle_t,
\]

\[
= \gamma v_{bob} + \left\langle \frac{\partial U(x_{tip})}{\partial x_{tip}} \right\rangle_t \quad \text{(A.7)}
\]

where we have used the fact that the potential is periodic, and that in the long-time limit we have \(\langle \dot{x}_{tip} \rangle_t \to 0\) and \(\langle \ddot{x}_{tip} \rangle_t = \langle \ddot{x}_{bob} \rangle_t\).

We find that the first term contributes linearly to the friction as expected; however the second term contributes in cases when the tip does not move at a constant velocity, in particular, when stick-slip occurs. One may expect that at high temperatures, the stick-slip behavior might vanish; however this is not the case even at the highest temperatures explored by Tshiprut et al. in reference [68]. That is, using \(\gamma = 5 \times 10^{-6} \text{ kg/s}\), \(U(x) = U_0 \sin(2\pi x/a)\), \(U_0 = 0.26 \text{ eV}\), \(a = 0.3 \text{ nm}\) and \(v_{bob} = 10 \text{ nm/s}\), at 400K we find that second term is larger by a factor of 4000.

\[^2\text{Energy loss implies work. } U_{loss} = \int f(x) \, dx = (x_f - x_0)(f)_x.\]
Appendix B S-ODE solver

We discussed Van Gunsteren and Berendsen’s algorithm [70] for solving Langevin-type stochastic ordinary differential equations in section 3.1. This is our implementation in the C programming language.

```c
/* quasi-tsh.c
* Keith McLaughlin
* 2009 JUNE 23
*/

#include <stdio.h>
#include <stdlib.h>
#include <math.h>
#include <sys/time.h>

struct constants
{
    /*reciprocal mass*/
    double rm;
    /*relaxation time*/
    double eta;
    /*temperature in energy units*/
    double kT;
    /*sliding velocity*/
    double Vtip;
    /*average potential*/
    double Uzero1;
    double Uzero2;
    /*spring constant*/
    double Kspring;
    /*lattice constant*/
    double a;
    /*golden ratio approximation*/
    double tau;
};

/* from separate source file */
double gaussd ( double mean, double std );

void usage ( char * this )
{
    fprintf(stderr,"usage: %s dt Tmax Temp num(phi) den(phi) U_0_1 U_0_2\n", this);
    fprintf(stderr,"or\n");
    fprintf(stderr,"usage: %s help\n", this);
    exit(-1);
}

void printhelp ()
```

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Appendix B (Continued)

```
{ 
  fprintf(stderr,"quasi-tsh.c\n");
  fprintf(stderr,"Keith McLaughlin\n");
  fprintf(stderr,"2009 JUNE 23\n");
  fprintf(stderr,\"\n\n\nThis program is free software: you can redistribute it and/or modify
it under the terms of the GNU General Public License as published by
the Free Software Foundation, either version 3 of the License, or
(at your option) any later version.\n
This program is distributed in the hope that it will be useful,
but WITHOUT ANY WARRANTY; without even the implied warranty of
MERCHANTABILITY or FITNESS FOR A PARTICULAR PURPOSE. See the\nGNU General Public License for more details.\n
I'll solve the Langevin equation for 1-d friction on a quasiperiodic
surface, using a model similar to Tshiprut et al. in PRL 102 136102\n
m*dv/dt = -m*eta*v + R(t) - dU'(x)/dx - K*(x-V*t)
where R(t) is a stochastic force and K is a spring constant
Rather than using U ~ U_0*sin(2Pix/a), we will use
U' ~ U_0_1*sin(2Pix/a) + U_0_2*sin(2Pix/b), where b=phi*a, where phi is
a rational approximation to the golden ratio.\n
Solution is via Gunsteren and Berendsen, Mol. Phys. 1982 45 (637)\n
return;
}
```

/* get microsecond precision seed - needed since we will be using gaussd */
int initrnd()
{
  int rval=0;
  struct timeval thetime;
  if ( ( rval=gettimeofday(&thetime,(struct timezone *)0)) != 0 )
    fprintf(stderr,"gettimeofday returned an error.\n");
  srand( thetime.tv_usec);
  return rval;
}

/*calculate the systematic force*/
double ev_force( double x, double t, struct constants * c )
{
  double TwoPiOverA = 2*M_PI/c->a;
  double TwoPiOverB = 2*M_PI/(c->tau*c->a);
  return -(c->Kspring)*(x-(c->Vtip)*t) + /*spring force*/
        -(c->Uzero1)*cos(TwoPiOverA*x)*TwoPiOverA + /*atomic pot1*/
        -(c->Uzero2)*cos(TwoPiOverB*x)*c->Pi2; /*atomic pot2*/
}

void setconstants(double * A, double * EoverCpls, double * GoverCpls, double * Cpls,
  66
double * fA4, double * fA5, double * fA8, struct constants * c, double dt)
{
    int i;
    /*used to store various powers of c->eta*dt.
     emphasis on readability of power series expansions*/
    A[0]=1;
    for ( i=1; i<=9; i++ ) A[i]=A[i-1]*c->eta*dt;

    /*Power series expansions*/ /*good for c->eta*dt << 1*/
    235009./193536000.*A[9];
    1./120.*A[5]; /*eq A4*/
    1./360.*A[6]; /*eq A5*/
    1./120.*A[5]; /*eq A8*/
    return;
}

void printdetails(double dt, struct constants * c, double T)
{
    fprintf(stderr,"Running %d steps with:
", (int)(dt/T) );
    fprintf(stderr,"\tdt = %10lf m = %10lf
", dt, 1/c->rm);
    fprintf(stderr,"kT = %10lf eta = %10lf
", c->kT, c->eta);
    fprintf(stderr,"t x
");
    return;
}

void printcomplete(double t, struct constants * c, double xsum, int count, double dt, double T)
{
    fprintf(stderr,"<f>= %lf (eV/A)
", -c->Kspring*(xsum/count-(c->Vtip*t/2)));
    fprintf(stderr,"<f>= %lf (pN)
", -1602.17646*c->Kspring*(xsum/count-(c->Vtip*t/2)));
    fprintf(stderr,"dt tmax temp <f> nphi dphi U1 U2
" , t, c->kT / 8.6173423e-5,
    -1602.17646*c->Kspring*(xsum/count-(c->Vtip*t/2)));
    return;
}

int intloop ( double dt, double T, struct constants * c)
{
    67
Appendix B (Continued)

```c
/*used for calculation of \langle f \rangle*/
int count=0;
double xsum=0;

/*dynamic variables (and init)*/
double x[3], f[2], v, df, t;

/*random variables (and init)*/
double Xpls[2], Xneg[2];
Xneg[0]=Xneg[1]=Xpls[0]=Xpls[1]=0;

/*set some constants*/
double A[9], EoverCpls, GoverCpl, Cpl, fA4,
fA5, fA8, sig215, sig212;
setconstants(A, &EoverCpl, &GoverCpl, &Cpl, &fA4,
    &fA5, &fA8, c, dt);

/* useful identity */
double eneg=exp(-A[1]);

/*output run details*/
printdetails(dt, c, T);

/*calculate the first position - we assume x(0)=0, v(0)=0*/
/*highest index is the most current*/
f[1]=ev_force(x[2],t,c); /*f(0,0,c)*/
Xpls[1]=gaussd(0.,sig212);
x[2]=c->rm*f[1]/(c->eta*c->eta)*(fA8)+Xpls[1]; /*eq 2.26*/

/*iterate*/
for ( t=0; t < T; t+=dt )
{
    /*push variables*/
    Xpls[0]=Xpls[1]; Xneg[0]=Xneg[1];
    x[0]=x[1]; x[1]=x[2]; f[0]=f[1];

    /*step 2*/
    f[1]=ev_force(x[2],t,c);
    /*step 3*/
    df=(f[1]-f[0]); /*(this is df/dt)*/
    /*step 4*/
    Xneg[1]=Xpls[0]*GoverCpl+gaussd(0.,sig215); /*eq 2.25*/
    Xpls[1]=gaussd(0.,sig212);
    /*eq 2.6*/
    x[2]=x[1]*(1.+eneg)-x[0]*eneg+c->rm*f[1]*dt/c->eta*(fA4)
       +c->rm*df/(c->eta*c->eta)*(fA5)
       +Xpls[1]+eneg*Xneg[1]; /*use eq 2.6*/
    printf("%lf %lf\n", t, x[2]);

    /*used to calculate \langle f \rangle*/
    xsum+=x[2];
}
```

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Appendix B (Continued)

```c
    count++; 
}

/*dump some stuff to file*/
printcomplete(t, c, xsum, count, dt, T);

fprintf(stderr,"<f>= %lf (eV/A)\n",
-c->Kspring*(xsum/count-(c->Vtip*t/2)));
fprintf(stderr,"<f>= %lf (pN)\n",
-1602.17646*c->Kspring*(xsum/count-(c->Vtip*t/2)));
fprintf(stderr,"dt tmax temp <f> nphi dphi U1 U2\n";
fprintf(stderr,"%lf %lf %lf %lf ", dt, T, c->kT / 8.6173423e-5,
-1602.17646*c->Kspring*(xsum/count-(c->Vtip*t/2)));
return 0;
}

/* Receives: dt, T */
int main( int argv, char ** argc )
{
    double dt, T; /*ps*/
    struct constants c;
    int nphi,dphi;

    /*initialize constants*/
    c.rm = 3.2e-13; /*(eV*ps^2/A^2)^-1*/
    c.eta = 1e-7; /*ps^-1*/
    c.Kspring = 0.0936226462; /*eV/A^2*/
    c.a = 3.; /*lattice constant in A*/
    c.Vtip = 1e-10; /*A/ps*/

    /*print help message*/
    if ( ((argv-1)> 0) && (argc[1][0]=='h') )
    {
        printhelp();
        usage(argc[0]);
    }

    /*some error checks*/
    if ( (argv-1) != 7 ) usage(argc[0]);

    /*set timestep*/
    if ( ( sscanf(argc[1],"%lf", &dt) ) <= 0 ) usage(argc[0]);
    /*set total time*/
    if ( ( sscanf(argc[2],"%lf", &T) ) <= 0 ) usage(argc[0]);
    /*set temperature*/
    if ( ( sscanf(argc[3],"%lf", &(c.kT) ) <= 0 ) ) usage(argc[0]);
    c.kT = c.kT * 8.6173423e-5; /*convert from kelvin to eV*/

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Appendix B (Continued)

/*golden ratio approximation*/
if ( (sscanf(argc[4],"%d", &nphi) <= 0) ) usage(argc[0]);
if ( (sscanf(argc[5],"%d", &dphi) <= 0) ) usage(argc[0]);
c.tau=(double)nphi/(double)dphi;

/*Uzero amplitudes*/
if ( (sscanf(argc[6],"%lf", &c.Uzero1) <= 0) ) usage(argc[0]);
if ( (sscanf(argc[7],"%lf", &c.Uzero2) <= 0) ) usage(argc[0]);

/*initialize the random number generator*/
if ( initrnd() != 0 )
    fprintf(stderr,"initrand returned an error.\n");

/*iterate and output*/
if ( intloop(dt, T, &c) != 0 )
    fprintf(stderr,"intloop returned an error.\n");

fprintf(stderr, "%d %d %lf %lf\n", nphi, dphi, c.Uzero1, c.Uzero2);
return 0;
}

quasi-tsh.c requires random numbers selected from a normal distribution. gaussd.c supplies this.

/* gaussd.c
 * David A. Rabson
 */

#include <math.h>
#include <stdlib.h>

/* uniform deviate on the interval [0,1) -- called by gaussd() below */
static double uniform()
    return (double)random()/(double)((unsigned long)0x80000000);

/* Get two Gaussian deviates of zero mean and unit std., then get desired */
double gaussd(double mean, double std)
{
    static int notstored=1; /* 0 if there's a value stored in y2 */
double w1, w2, uni=0;
    static double y2;    /* see Num. Rec. p 289 */

    if( (notstored = !notstored) )
        return std*y2+mean;    /* return the stored value */
while ( uni==0 ) uni=uniform();
w1 = sqrt(-2.*log(uni)); /*see Num. Rec. eqn. 7.2.10 (2nd C ed)*/
uni=0;

while ( uni==0 ) uni=uniform();
w2 = 2.*M_PI*uni;
y2 = w1*cos(w2);
return std*w1*sin(w2)+mean;
}

Once each calculation is completed we can count the number of stick-slip events using \textit{counts}ips.c. This is performed as separately from the calculation itself, because it involves tweaking two tolerances, \texttt{xtol} and \texttt{ttol}, both used to prevent the double counting of events.

```c
#include <stdio.h>
#include <stdlib.h>
#include <string.h>
#define BUFFSIZE 300

/* countslips.c
 * University of South Florida
 * Solid-State Theory
 * Keith McLaughlin
 * 22 Jun 2009 */

/* Used with tshiprut.c or similar programs to calculate the average
 * slip length and the total number of slips. */

tint isnum ( char * string )
{
double dummy;
if ( sscanf(string,”%lf”, &dummy) == 0 ) return 1;
return 0;
}

tint isfile ( char * filename )
{
FILE * filetest;
if ( (filetest=fopen(filename,”r“)) == NULL ) return 1;
fclose(filetest);
return 0;
}
```
int errmsg( int errcode, char * string )
{
    if ( errcode == 0 )
    {
        fprintf(stderr,"Improper syntax.\n");
        fprintf(stderr,"Usage: \n");
        fprintf(stderr, "%s inputfile t x\n", string);
        fprintf(stderr,"OR\n");
        fprintf(stderr, "%s t x < inputfile\n", string);
        fprintf(stderr,"Where x and t are tolerences,\n");
        fprintf(stderr,"and the inputfile contains t and x.\n");
        exit(1);
    }
    if ( errcode == 1 )
    {
        fprintf(stderr,"%s is not a file.\n", string);
        exit(1);
    }
    if ( errcode == 2 )
    {
        fprintf(stderr,"Couldn't allocate temporary file.\n");
        exit(1);
    }
    if ( errcode == 3 )
    {
        fprintf(stderr,"Couldn't open temporary file.\n");
        exit(1);
    }
    if ( errcode == 4 )
    {
        fprintf(stderr,"Cannot open %s.\n", string);
        exit(1);
    }
    if ( errcode == 5 )
    {
        fprintf(stderr,"Did not properly read in command line args.\n");
        exit(1);
    }
    return 1;
}

struct filestruct
{
    FILE * ptr;
    char name[BUFFSIZE];
    /*if deletefile=1, we delete the file when we are done with it*/
Appendix B (Continued)

```c
int deleteme;

int readfromstdin( struct filestruct * input )
{
    int c;
    /*set the tmpfile name*/
    sprintf(input->name, "%s/tmp-XXXXXX", P_tmpdir);

    /*create a temporary file*/
    int fd = mkstemp(input->name);
    if ( fd == -1 ) errormsg(2,NULL);

    /*open for reading and writing*/
    input->ptr=fdopen(fd,"r+"神通);
    if ( input->ptr == NULL ) errormsg(3,NULL);
    rewind(input->ptr);

    /*read stdin into the tempfile*/
    while ( ( c=getc(stdin) ) != EOF )
        putc(c,input->ptr);

    /*in case we forget to later*/
    rewind(input->ptr);

    /*set the flag for deletion when we're done*/
    input->deleteme=1;

    return 0;
}
```

```c
int countslips ( double xtol, double ttol, struct filestruct * input )
{
    /*in our codes x(0)=0, and t(step=0)=0*/
    double xlast=0, tlast=0;
    double xread,tread;
    int count=0;
    char buffer[BUFFSIZE];

    /* Read in the values for x and t in the file. If Dx > xtol then we MIGHT have a jump. We don't want to count a single jump multiple times though, so we make sure that a certain amount of time has passed since the last jump. If that hasn't happened then we decide that we were double counting. */
    while ( NULL != fgets(buffer, BUFFSIZE, input->ptr) )
```
Appendix B (Continued)

```c
{    
    sscanf(buffer,"%lf %lf", &tread, &xread);
    if ( xread > xlast+xtol )
    {
        xlast=xread;
        if ( ( tread > tlast+ttol ) )
        {
            tlast=tread;
            count++;
        }
    }
}

/*need to print count and avg slip length*/
fprintf(stderr, "total slips\tavg slip\n");
printf("%d\t%lf\n", count, xlast/count);
return 0;
}

int main ( int argc, char ** argv )
{
    struct filestruct input;
    input.deleteme=0;

    double ttol, xtol; /*tolerances*/

    /*we will either read from stdin or from file*/
    switch (argc-1)
    {
        case 2:
            if ( isnum(argv[1]) == 1) errmsg(0,argv[1]);
            if ( isnum(argv[2]) == 1) errmsg(0,argv[1]);
            sscanf(argv[2], "%lf", &xtol);
            sscanf(argv[1], "%lf", &ttol);
            readfromstdin(&input);
            break;
        case 3:
            if ( isnum(argv[2]) == 1) errmsg(0,argv[1]);
            if ( isnum(argv[3]) == 1) errmsg(0,argv[1]);
            sscanf(argv[3], "%lf", &xtol);
            sscanf(argv[2], "%lf", &ttol);
            if ( isfile(argv[1]) == 1 ) errmsg(1, argv[1]);
```

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Appendix B (Continued)

    input.ptr=fopen(argv[1],"r");
    break;
    default:
      errormsg(0,argv[0]);
    }

    /*main program*/
    countsips(xtol,ttol,&input);

    /*we're done with this*/
    if ( input.delete == 1 ) remove(input.name);
    return 0;
  }

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Appendix C LAMMPS input files

This is a sample input file used in our molecular-dynamics simulations. Each input file is modified by `submit.sh` to replace text enclosed by angled brackets “⟨⟩” and submitted to the Sun Grid Engine. Text enclosed by curly brackets “{}” is to be edited manually by the user.

```plaintext
### template.in
### Fibonacci Friction Simulations
## Keith McLaughlin
## Solid State Theory
## Department of Physics
## University of South Florida

dimension 3
boundary s p p ## two periodic boundaries
## Metal units: Angstroms, eV, picoseconds, proton mass
units metal
timestep 0.002
## They're atoms! (no rotational DoF)
atom_style atomic
## Atomic coordinates
read_data {PATH_TO_SAMPLE}/<SAMPLE>
## Types of pots used
pair_style hybrid table linear 10000 lj/cut 6
## 1-3 interact with 4 via LJ
pair_coeff 1*3 4 lj/cut 0.05 2.672696154
## 1-3 interact with each other via table
pair_coeff 1*3 1*3 table {SC-POT-LOCATION} SC
## some stuff doesn't interact
pair_coeff 1*3 5 none
pair_coeff 4*5 4*5 none
## Define regions
## xlo xhi ylo yhi zlo zhi
## Using INF doesn't work properly, so I use +/- 300 instead.
region QC_rigid_region block -300 -24.00001 -300 300 -300 300 units box
region QC_tstat_region block -24 -18.00001 -300 300 -300 30 units box
region QC_free_region block -18 0.00001 -300 300 -300 300 units box
region DUMP_region block -18 10 -300 300 -300 300 units box
## Define groups
## xlo xhi ylo yhi zlo zhi
## Using INF doesn't work properly, so I use +/- 300 instead.
group QC type <= 3
group TIP type = 4
group BOB type = 5
## We don't use nve on rigid bodies.
group nve_group union QC BOB
```

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Appendix C (Continued)

## Used for dumping atoms. we only dump regions that are interesting

```
group DUMP_group region DUMP_region
```

## Define based on atoms *INITIALLY* in specified regions.

```
## It doesn't matter if they later move out.
group QC_rigid region QC_rigid_region
group QC_tstat region QC_tstat_region
group QC_free region QC_free_region
```

## NVE ensemble. We will control T via thermostating.

```
fix fix_nve nve_group nve
```

## Make the TIP rigid

```
fix TIP_rigid TIP rigid single torque * off off off
```

## Tether the TIP to the BOB; $k=1$

```
fix TIP_tether TIP spring couple BOB 1 0 0 0 0
```

## Set forces on the BOB to zero

```
fix BOB_force BOB setforce 0 0 0
```

## Set forces on the base of the QC to zero

```
fix QC_rigid_force QC_rigid setforce 0 0 0
```

## Calculate temperature of the dynamic region of the QC

```
compute temp_QC_free QC_free temp
```

## Output Options - for compression and relaxation steps

```
thermo 20
thermo_style custom step etotal c_temp_QC_free
```

## COMPRESSION #####################################################################

```
## thermostat the entire qc; relaxation time = 0.002 timesteps
fix tstat_qc_all QC langevin 0 0 0.002 109232
## Lower the tip. 10000 timesteps per 1A.
velocity BOB set -0.05 0 0 units box sum no
run <LOWER>
```

## FULL RELAXATION ####################################################################

```
## stop lowering the tip.
velocity all set 0 0 0 units box sum no
## relax the entire QC and TIP for a while.
unfix tstat_qc_all
fix tstat_all all langevin 0 0 1 98463
## Run!
run 10000
```

## HEAT THE SYSTEM ####################################################################

```
## Remove the thermostat from the bob and rigid layers.
```
unfix tstat_all
## Heat up the thermostat and free layers
fix QC_0_T_tstat QC_tstat langevin 0 {T_final} 1 31222
fix QC_0_T_free QC_free langevin 0 {T_final} 1 31222
## Run!
run 10000
## PREPARE FOR SLIDING ########################################
## Now that we are at T_final
unfix QC_0_T_tstat
unfix QC_0_T_free
fix QC_T_T_tstat QC_tstat langevin 300 300 200 398128
## We only want to consider perpendicular motion in the thermostat application
## DIRECTION can either be "0 1" or "1 0"
compute temp_QC_tstat_part QC_tstat temp/partial 1 <DIRECTION>
fix_modify QC_T_T_tstat temp temp_QC_tstat_part
## sliding velocity
velocity QC_rigid set 0 <velocities> sum no units box
## Run!
run 20000
## SLIDE ####################################################################
## dump atom coordinates
dump dump_xyz DUMP_group custom 10000 1.dmp id x y z type
## modify the output. we want to output the forces on the BOB
## Move the tip through the unit cell
run 2000000

Because such a large number of runs need to be performed to determine the friction coefficients, we automate the submission process for several different compressions using a pair of BASH shell scripts, submit.sh and mpi_sub.sh. submit.sh prepares the input file by making the necessary modifications to template.in and sets up the working directory.

#!/bin/bash
## submit.sh
## SUBMISSION SCRIPT FOR LAMMPS RUNS
SERIES=RUNS
Appendix C (Continued)

## Here we give a list of the approximants used
## the file name for each approximant should
## be $APPROX.struct
APPROXS="big-t11-A big-t11-B big-t11-C"
SLIDING_VELOCITY=0.01

## For each approximant
for sample in $APPROXS; do
    ## set the file name for the struct file
    struct=$sample.struct
    ## create a subdirectory for this approximant
    mkdir $sample
    cd $sample
    ## we will be sliding in the y and z directions
    for direction in y z; do
        if [ "$direction" = "y" ]; then
            ## Set the sliding velocity
            ## and turn the thermostat off along
            ## the y-axis
            vel="$SLIDING_VELOCITY 0"
            therm="0 1"
        fi
        if [ "$direction" = "z" ]; then
            vel="0 0.01"
            therm="1 0"
        fi
    done
    ## For each compression (in timesteps)
    for compression in 20000 40000 60000 80000 100000; do
        if [ -d $direction\_$compression ]; then
            continue
            echo $direction\_$compression skipped
        fi
        ## if it does not, make a directory for the
        ## sliding direction and compression
        mkdir $direction\_$compression
        cd $direction\_$compression
        ## prepare the input file by replacing
        ## angle bracketed variables
        sed -e "s|<DIRECTION>|$therm|"
        -e "s|<velocities>|$vel|"
        -e "s|<SAMPLE>|$struct|"
        -e "s|<LOWER>|$compression|"
        < $CWD/template.in > run.in
        ## submit to the grid engine via mpi_sub.sh
        echo -e "$direction\_$compression
4
lmp<run.in
200
" | mpi_sub.sh
        cd ..
    done
fi
```
Finally, `submit.sh` calls `mpi_sub.sh` which handles the actual submission process.

```bash
#!/bin/bash
## mpi_sub.sh
## generates and submits submission scripts for Grid Engine

EMAIL={EMAIL ADDRESS}
SHELL=/bin/bash
LOG=sub.log

## Is qstat in the path?
which qstat 2> /dev/null > /dev/null
if [ ! $? -eq 0 ]; then
  echo "error: qstat not found" 1>&2
  exit 1
fi

## Check command line arguments
if [ $# -eq 4 ]; then
  JOBNAME=$1
  NUMPROC=$2
  EXECUTE=$3
  HOWLONG=$4
else
  echo "JOBNAME?"
  read JOBNAME
  echo "Number of Processors?"
  read NUMPROC
  echo "Which Binary?"
  read EXECUTE
  echo "How long? (int) (hours)"
  read HOWLONG
fi

## create the input file
tmp=$( mktemp )
cat > $tmp << EOF
#!/bin/bash
#$ -N $JOBNAME
#$ -cwd
### Do merge stderr with stout
#$ -j y
EOF

```
### Send me mail
#$ -M $EMAIL
#$ -notify
#$ -m abe

### Which shell?
#$ -S $SHELL

#$ -o out.$JOBNAME.$JOB_ID
#$ -pe ompi* $NUMPROC
#$ -l h_rt=$HOWLONG:00:00

export DEBUG_MPI=true
sge_mpirun $EXECUTE

EOF

## Submit to grid
qsub < $tmp

## Write the a log in pwd
echo -ne 'date"":"$JOBNAME:"' >> $LOG
tail -n 1 $tmp >> $LOG

## Move the temp file to pwd
mv $tmp .
Appendix D Generating Fibonaccium

Although the recipe for constructing Fibonaccium given in given in section 5.1 is rather straight-forward, generating the structure file for LAMMPS is no trivial task. We’ve supplied the source code used to create these structure files for the simple-cubic case. The code expects the user to supply the Fibonacci sequence used, e.g. “LSLLS”.

```c
#include <math.h>
#include <stdio.h>
#include <stdlib.h>
#include <string.h>
#define buffsize 300

#include "error.h"

/* create_fibs_sc.c
 * University of South Florida
 * Solid-State Theory
 * Keith McLaughlin
 * 15 JUL 2009
 */

/* Creates a lammps input structure for a BCC samples whose masses are modulated according to the fibonacci sequence along two axes, and is periodic in the third. */

/*Handles all errors*/
void errmsg( int errcode, char * string )
{
    if ( errcode == 0 )
    {
        fprintf(stderr,
            "error: usage: %s small_mass L/S_ratio lattice_constant sequence\n",
            string);
        fprintf(stderr,
            "error: sequence is given as a string of L's and S's. Ex. \"LSLLS\"\n");
        if ( errcode == 1 )
        fprintf(stderr,"error: L/S_ratio must be greater than 1.\n", string);
        if ( errcode == 2 )
        {
            fprintf(stderr,"error: sequence must consist of only L's and S's.\n");
            fprintf(stderr,"error: you supplied: %s.\n", string);
        }
        exit(1);
    }
}
```

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Appendix D (Continued)

/* print header*/
int printheader( char * sequence, double * doubles, int natoms, double cellsize )
{
    printf("Fib Square\" BCC Lattice %s, S=%lf, L/S=%lf,
    Lattice Const.=%lf/n", sequence, doubles[0], doubles[1], doubles[2]);
    printf("\n");
    printf("%d atoms\n", natoms);
    printf("\n");
    printf("3 atom types\n");
    printf("\n");
    printf("%lf 0 xlo xhi\n", -cellsize);
    printf("%lf 0 ylo yhi\n", -cellsize);
    printf("%lf 0 zlo zhi\n", -doubles[2]);
    printf("\n");
    printf("Masses\n");
    printf("\n");
    printf("1 %lf\n", doubles[0]*doubles[0]); /*S^2*/
    printf("2 %lf\n", doubles[0]*doubles[0]*doubles[1]); /*S*L*/
    printf("3 %lf\n", doubles[0]*doubles[1]*doubles[0]*doubles[1]); /*L*L*/
    printf("\n");
    printf("Atoms\n");
    printf("\n");
    return 0;
}

/*generates the header for the output struct file*/
int genheader ( double * doubles, char * sequence )
{
    char * sequence0 = sequence;
    int natoms=0;
    double cellsize;

    /*Calc. the length of the unit cell in the aperiodic direction*/
    while ( *sequence0 != '\0' )
    {
        natoms++;
        sequence0++;
    }

    cellsize = natoms*doubles[2];
    natoms= natoms*natoms; /*natoms in x & y, and two layers in z*/

    printheader(sequence, doubles, natoms, cellsize);
    return 0;
}

/*generate and print the atoms for the output struct*/
int genstruct ( double * doubles, char * sequence )
{
    int xflag, yflag;
    double x=0; /*coordinates x and y*/
    double y=0;
    char * xseq = sequence;
    char * yseq = sequence;
    int natom=1;
    int atomtype;

    double s=doubles[0]; /*small mass*/
    double l=doubles[0]*doubles[1]; /*large mass*/
    double a=doubles[2]; /*lattice const.*/

    while ( *xseq != '\0' )
    /*loop through the sequence with 2-variables -> 2 dimensions*/
    /*place atoms in the lattice with mass dependent on the sequence*/
    {
        switch ( *xseq )
        {
            case 'L':
            case 'l':
                xflag=1;
                break;

            case 'S':
            case 's':
                xflag=0;
                break;

            default:
                errormsg(2,sequence);
        }
    } /*nested loop*/
    while ( *yseq != '\0' )
    {
        switch ( *yseq )
        {
            case 'L':
            case 'l':
                /*xflag+yflag+1 = atom type, ex. l+s+1=type 2, l+l+1=type 3*/
                yflag=1;
                break;

            case 'S':
            case 's':
                yflag=0;
                break;
        }
    }
}
Appendix D (Continued)

break;

default:
    errmsg(2,sequence);
}

/* add two atoms (bcc) */
atomtype=xflag+yflag+1;
printf("%d %d %lf %lf %d\n", natom, atomtype, x, y, 0);
natom++;

/*increment y by the lattice constant, for the next atom*/
y+=a;
/*move to the next char in the sequence*/
yseq++;
}

y=0; /*reset y=0, for the new value of x.*/
x+=a;
yseq=sequence;
xseq++;
}
return 0;
}

int main ( int argc, char * argv[] )
{
    double mass;
    double massratio;
    double length;
    double doubles[3];
    char sequence[bufsize];

    if ( (argc-1) != 4 ) errmsg(0, argv[0]);
    if ( isnum(argv[1]) == 1 ) errmsg(0, argv[0]);
    if ( isnum(argv[2]) == 1 ) errmsg(0, argv[0]);
    if ( isnum(argv[3]) == 1 ) errmsg(0, argv[0]);
    mass= strtod(argv[1], NULL);
    massratio= strtod(argv[2], NULL);
    length = strtod(argv[3], NULL);

    /* to simplify the passing of variables*/
    doubles[0]=sqrt(mass);
    doubles[1]=massratio;
    doubles[2]=length;

    /* Make sure Long > Short */
    if ( massratio < 1 ) errmsg(1, NULL);
Appendix D (Continued)

    sprintf(sequence, "%s", argv[4] );
    genheader( doubles, sequence );
    genstruct( doubles, sequence );
    return 0;