Benchmarking Potential Energy Models Against Bulk Properties for Simulations of Bismuth Clusters

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Abstract

A number of experiments have recently focused on melting transitions near room temperature of supported bismuth clusters, which is in marked contrast to the melting point of the bulk (544K). In order to understand the size dependence of the temperature effect, we are preparing to carry out Monte Carlo simulations of the caloric curves for large bismuth clusters. To this end, all of the relevant crystal lattices of solid bismuth were analyzed using several different potentials and potential forms. These potentials were gleaned from the literature and/or developed in our laboratory. Using converged lattice sums with periodic boundary conditions, the cell parameters of all relevant lattice types were varied so as to find the cell volume which minimized the lattice energy. Extensive comparisons to known experimental parameters are given.

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Introduction

Numerous computational and theoretical studies have been carried out on "melting transitions" in atomic clusters. These studies have shown that small atomic clusters can display significant mass-dependent effects on transition temperatures and caloric (heat capacity) curves. The features of the caloric curves reveal structural transitions which yield important information about enthalpic and entropic contributions to structure distributions. However, most theoretical studies have focused on neutral rare gas clusters. Experiments on melting transitions in supported bismuth clusters therefore provide an excellent opportunity for establishing an important connection with experimental data.

Bismuth is a relatively soft, slightly pink metal with unusually large magnetic susceptibility, a remarkably high specific gravity and a very low melting point (544K). Many of the high-temperature superconducting ceramics contain bismuth, and bismuth is also used to form a number of the III-V semiconductors such as MnBi (a very useful magnetic material which is relatively soft and malleable). However, in many respects bismuth is a unique element with a number of unusual physical properties whose origins are not fully understood at the atomic level. Most strikingly, bismuth expands by 3.32% as it solidifies into its rhombohedral form, so the solid phase floats on the liquid. This results in a melting curve with a strongly negative slope throughout the solid-liquid coexistence curve. The expansion property of bismuth, coupled with its low melting point, makes it useful for sharp castings of objects which can be damaged at higher temperatures. Its low melting point has also led to its use as an automatic heat-sensitive trigger in fire-extinguishing sprinkler systems. In addition, bismuth is polymorphic and exhibits a number of solid-solid phase transitions at elevated pressures and temperatures.

Like bismuth, water also expands as it freezes. The expansion of water upon freezing is due to the formation of a low-density cage structure, created by hydrogen bonds which link one water molecule to the next. As there are no hydrogen bonds between atoms of elemental bismuth we must look to a different explanation in this case. The most plausible explanation proposed thus far, based on resistance studies, is that liquid bismuth is highly structured and is composed of a liquid phase of high-density clusters, sort of a "cluster soup" of well-defined, long-lived structures (these may perhaps even be chemically distinguishable species). The "cluster soup" model is supported by the observation of a persistent resistance anomaly and the fact that liquid bismuth is a semiconductor even up to very high temperatures. Again, studies of bismuth clusters would seem to have some relevance.

The only direct experimental structural data we have to date for bismuth clusters is for surface-physisorbed clusters. Molecular beam and cluster beam deposition techniques were used to attach bismuth clusters onto a graphite surface, and then electron diffraction and dark-field TEM methods were used to look for signatures of crystalline structure. These clusters were studied over a range of coverages, including a low-thickness study of isolated clusters of sizes ranging from 2 to 10 nm. It was found that thin films of bismuth clusters are crystalline at low temperatures, with a pattern resembling that of bulk.
bismuth. It was also noted that the diffraction pattern was destroyed by warming the system up to room temperature (~300K). When we recall that the melting point of bulk bismuth is 544K, we realize that there is either a large finite-size effect on the melting temperature, or that the cluster-surface interaction is having a huge effect (or these effects are working in concert). Crystallinity only gradually returned as the film was cooled, consistent with the coexistence of liquid and crystalline clusters.

The existence of a size effect on the melting point of bismuth should be contrasted to the rapid approach to the bulk electron affinity of much smaller bismuth clusters. \(^5\) It is fairly typical for various cluster properties to converge at different cluster sizes. Experimental information about the melting temperatures of gas-phase bismuth clusters would be useful in sorting out the reason for the size-dependence of the melting point, but this information is not yet available. This motivates the present study. Of course, it would also be most interesting to model the surface-adsorbed cluster species in order to make direct comparison to these experiments. This is one of our long-term goals. However, there is still much to learn about the pure phases of bismuth. Consequently, our interests are currently focused on developing a potential energy model for use in studies of gas-phase bismuth clusters.

In order to establish the plausibility of a potential energy model for thermodynamic cluster simulations, we have first turned our attention to studies of the bulk. We have developed computer codes to carry out converged lattice sums with periodic boundary conditions for the numerous solid forms exhibited in the bismuth phase diagram as a function of the cell parameters. The lattice sums employed various effective pair potentials for bismuth that have been proposed in the literature, as well as forms we developed. The use of an effective pair potential is desirable for Monte Carlo work because of its high computational efficiency, as long as accuracy is not compromised. The reason for this is that millions of Monte Carlo samples may be required to completely converge caloric curves for even small atomic clusters, \(^1\) which can make the use of direct quantum-mechanical energy computations impractical. The approach can also be justified by the fact that a very simple effective pair potential has been shown to reproduce some features of the radial distribution function in liquid bismuth. \(^6\) Of course, there is no proof of the general applicability of such an approach. In particular, the electron density of atoms at the surface of a finite cluster may or may not be the same as that of atoms at the interior. Our view is that the present study is merely a "first pass" at the problem of characterizing the effective interaction potential, and it is to be hoped that improved methods will be used in the future.

Our work indicates that the use of an accurate effective pair potential that includes Friedel oscillations \(^7\) can yield reasonably good agreement with the experimental crystal structure. The details of the most successful pair potential constructed in the present work were obtained from a previous study of molten bismuth, in which pseudopotential-based interatomic forces were computed using a full relativistic treatment of the core states. \(^8\) The hope is that although many-body interactions are not explicitly included, their effect will be adequately taken into account in an implicit way through the pseudopotential treatment. Future work will assess the consequences of this assumption.
Theory

Bismuth is a particularly challenging element to handle in simulation work because of its large atomic number and semimetallic nature. Among the most exhaustive and accurate calculations of liquid bismuth to date appear to be those carried out by Hafner and Jank (HJ). In the context of pseudopotential theory, these authors found that the high degree of nonlocality in the pseudopotential (largely due to relativistic effects) necessitated the use of a fully relativistic treatment of the core states. They were able to compute highly accurate effective pair potentials using this technique, in an effort to implicitly (albeit approximately) include the effect of three-body and higher terms. These numerically constructed effective pair potentials were then used in microcanonical molecular dynamics (MD) simulations of liquid bismuth. $V$, the potential energy of a configuration of $N$ atoms characterized by $N(N-1)$ interparticle separations $r_{ij}$ between atoms $i$ and $j$, was given by

$$V = E(r) + \sum_{i>j} V_{HJ}(r_{ij})$$

where $V_{HJ}(r_{ij})$ is the HJ effective pair potential and $E(r)$ is a (density dependent) quantity representing the cohesive energy at a fixed absolute Cartesian configuration $r$. The second term determines which crystal structure is favored at a given density and also determines the shape of the radial distribution function. $E(r)$ must be explicitly calculated in addition to $V_{HJ}(r_{ij})$ in certain cases (for example, if one is interested in the effects of external fields on the system) but need not be explicitly computed for the applications considered here. This ansatz has been referred to as the "nearly free electron" model when a pseudopotential is used instead of an explicit calculation of the core states. The pair-correlation functions and static structure functions obtained by Hafner and Jank were in excellent agreement with experiment. It should be noted that as many as 2000 atoms were required for complete convergence of the molecular dynamics simulations, which is what necessitated their use of an effective pair potential. Encouraged by these results, we have made use of the published empirical pair potential by digitizing them and either using interpolation schemes and/or fitting an analytic function to them, as described in the Procedure section. The strategy of using bulk properties to parameterize potential energy surfaces is discussed by Allen and Tildesley.

The HJ pair potential exhibits long range oscillations, which are widely known as Friedel oscillations. These oscillations also appear in the electron charge density. They are said to appear due to the cutoff of electron energy which occurs at the Fermi surface. The resulting singularity in the density of states gives rise to interference between waves scattered by the ion cores. As will be seen in the Results section, we have found that the Friedel oscillations, when properly accounted for, are essential in correctly describing the rhombohedral phase of bismuth, which is the phase favored at the standard temperature and pressure.

We have also considered a number of analytic potentials gleaned from the literature. The first analytic potential model studied was developed by Katircioglu and Erkoc (KE) by
fitting various parameters of solid bismuth (such as the density) and the diatomic Bi$_2$ molecule to a model including two-body and three-body terms.\textsuperscript{15} Notably, this model does not exhibit Friedel oscillations. The KE model was intended to be useful for studies of atomic clusters. Minimum-energy structures for clusters with up to 7 atoms were determined by direct minimization from various starting geometries.\textsuperscript{15} However, we found that the KE model has asymptotic properties which make it inappropriate for Monte Carlo (MC) or MD simulation work. The three-body term causes the total energy of even a triatomic bismuth cluster to rapidly diverge to negative infinity if the three bodies come within a chemically relevant distance of one another. The problem is magnified as the number of atoms is increased, and reasonable attempts to correct the problem were unsuccessful. In the end, further work with this potential was deemed unwarranted. From this we see that the inclusion of three-body interaction terms in an empirical potential is not always desirable or appropriate, although it may be absolutely necessary in some cases to do so. Of course, this does not preclude the development of accurate potentials which include three-body terms, but the computational advantages of effective pair potentials are well known.\textsuperscript{10}

Another analytic pair potential considered in this study, mostly for purposes of testing our lattice codes, was the well-known Morse potential.\textsuperscript{16} The Morse potential has been extensively used to model bulk metals\textsuperscript{17} and metal clusters.\textsuperscript{18} Moreover, the KE potential used the Morse potential for Bi$_2$ as its starting point. The Morse potential is known to favor cubic structures in the bulk,\textsuperscript{19} and so we expect to see this reflected in our own computations of the bulk solid. As is well known, the Morse potential does not exhibit Friedel oscillations. The Morse potential may be written in the simple form

$$V_M(r_{ij}) = D\{1 - \exp[-\alpha (r_{ij} - r_e)]\}^2 - D$$

where $r_e$ is the diatomic equilibrium pair distance (2.6596 Å), $D$ is the diatomic well depth (2.04 eV), and $\alpha$ is a parameter controlling the curvature and range of the potential (1.676 Å$^{-1}$). In addition, an extended Morse (EM) potential was used which includes a 12-6 Lennard-Jones (LJ) term to take account of atom-atom dispersion forces.\textsuperscript{20, 21, 22} The attractive LJ term was parameterized using atomic polarizability and ionization energy data and the well-known London formula.\textsuperscript{23} The repulsive term was (arbitrarily) required to equal the square of the attractive term, which is a commonly used ansatz for estimating the repulsion parameter.\textsuperscript{10, 21, 23} Our EM potential then becomes

$$V_{EM}(r_{ij}) = V_M(r_{ij}) - C_6 / r^6 + C_{12} / r^{12}$$

where $C_6 = 132.985$ eV Å$^6$ and $C_{12} = 17685.0$ eV Å$^{12}$. The introduction of the 6-12 LJ terms has the effect of making the EM pair potential broader and somewhat deeper than the Morse potential. The Morse and extended Morse potentials, parameterized for bismuth, appear in Figure 1.

We also considered an effective pair potential which exhibits Friedel oscillations due to Cummings\textsuperscript{24} and Bretonnet.\textsuperscript{25} Cummings developed a functional form for liquid metals using an exact solution of the Ornstein-Zernike theory of fluids within the mean spherical
Bretonnet later developed parameters suited for liquid bismuth, fitting the model to either (a) the first peak of the experimentally determined structure factor, or (b) the entire structure factor. This model has no repulsive shoulder at short pair distances, so a hard sphere repulsion was introduced at $\sigma = 3.1 \, \text{Å}$. The Cummings potential has the form

$$V_C(r_{ij}) = \infty, \quad r_{ij} < \sigma;$$
$$V_C(r_{ij}) = -\left(\frac{1}{r_{ij}}\right) \exp\left[-z(r_{ij} - \sigma)\right] \left[\lambda_1 \cos \mu(r_{ij} - \sigma) + \lambda_2 \sin \mu(r_{ij} - \sigma)\right], \quad r_{ij} > \sigma$$

When fitted to the first peak of the structure factor, $z = 0.152877 \, \text{Å}^{-1}$, $\lambda_1 = 0$, $\lambda_2 = -0.042318$ eV, and $\mu = 3.168 \, \text{Å}^{-1}$ are appropriate. If the entire structure factor is fitted, the new parameters are $z = 0.7999 \, \text{Å}^{-1}$, $\lambda_1 = -0.045068431$ eV, $\lambda_2 = -0.051791$ eV, and $\mu = 3.168 \, \text{Å}^{-1}$. We note that other effective pair potentials have been developed which exhibit Friedel oscillations (for example, see Pettifor$^7$) but to our knowledge no other closed-form models in the literature have been parameterized specifically for elemental bismuth. The two different parameterized forms of the Cummings potential are shown in Figure 2.

Finally, we considered a modified version of the Cummings potential (MC), where the HJ potential was used as input to determine a new set of Cummings potential parameters. In addition, a repulsion function was introduced to create a piecewise continuous function. The MC potential has the form

$$V_{MC}(r_{ij}) = A (r_{ij} - B)^6, \quad r_{ij} < \sigma_1$$
$$V_{MC}(r_{ij}) = -\left(\frac{1}{r_{ij}}\right) \exp\left[-z(r_{ij} - \sigma_2)\right] \left[\lambda_1 \cos \mu(r_{ij} - \sigma_3) + \lambda_2 \sin \mu(r_{ij} - \sigma_3)\right], \quad r_{ij} > \sigma_1$$

with $A = 2.83714$ eV Å$^6$, $B = 1.86031$ Å, $\sigma_1 = 3.9$ Å, $\sigma_2 = 3.1$ Å, $\sigma_3 = 3.3$ Å, $z = 0.825$, $\lambda_1 = -0.0436992$ eV, $\lambda_2 = -0.339$ eV, and $\mu = 3.26767 \, \text{Å}^{-1}$. This modified Cummings potential is graphed alongside the digitized data from the HJ potential in Figure 3.

**Procedure**

Bismuth is polymorphic, i.e., it exists in a number of different lattice forms.$^8$ This work focused on the simple cubic (SC), body-centered cubic (BCC), face-centered cubic (FCC), diamond-type tetrahedral (DIA), hexagonal close-packed (HCP), and rhombohedral (RH) lattices. Each of these were modeled using FORTRAN code developed in our laboratory. The Cartesian coordinates of each atom in a lattice were determined by the chosen size of the cell length, the lattice type, and the number of atoms, with the RH lattice requiring the specification of a single rhombohedral angle as well. This method of basing lattice construction on a single value, or pair of values, made "expanding" the lattice particularly simple.

"Expanding" the lattice involved increasing the cell length (or some other cell parameter) in order to increase uniformly the dimensions of the lattice while maintaining the overall lattice structure. For example, a simple cubic lattice of unit cell sides 1.0 Å long was
expanded to one of unit cell sides 1.1 Å long, and so on. Expanding the lattice changes the lattice's total potential per atom, and thus the optimal cell parameter can be determined by this simple procedure. The RH lattice was expanded numerous times at uniformly increasing values of the rhombohedral angle. Illustrations of lattice expansions, as well as of the variation of the rhombohedral angle at a fixed cell parameter, may be viewed by consulting the Supplementary Materials section.

The total potential of a lattice was calculated by summing up all pairwise interactions and dividing the sum by the number of atoms used in the model. Of particular importance in such lattice sums is their ability to converge, so that one can be assured that the system used is large enough to accurately model the bulk phase. For a given potential, three considerations principally dictate the rate of convergence of the lattice sum: the nature of the application of periodic boundary conditions (PBC’s), the number of atoms used to construct the lattice, and the manner in which the lattice is constructed. If the lattice is constructed in such a way as to reflect the translational symmetry as much as is possible using a finite number of atoms, convergence is more rapid. Though no systematic attempt was made to assess this last aspect of convergence, every effort was made at the outset to construct lattices with this aspect of the situation in mind. After the lattices were constructed and expanded, PBC’s were implemented using a standard minimum-image convention. The effect of this convention is twofold: it limits the number of calculations required, and it dramatically reduces the size of lattice one must model to achieve convergence. For the cubic lattices (SC, BCC, FCC, and DIA), periodic boundary conditions were implemented within a cubic box. However, in the case of the HCP lattice a rectangular boundary box was used, and a rhombohedral boundary box was used in the case of the RH lattice.

Using the PBC’s as described above, lattice sums were implemented using lattices with relatively few atoms (about 100 atoms) to obtain preliminary lattice energy profiles. New lattices were then created by adding a unit cell to the models in each dimension, thereby increasing the number of atoms in each model, and lattice sums were taken again. This continued until the lattice sums, computed as the total potential per atom, converged to three decimal places. A converged lattice potential sum was found for each lattice, using each potential to be analyzed. The number of atoms used to generate the converged sum was then used throughout the rest of the procedure for that combination of lattice and potential. This method of determining the number of atoms to be used for each lattice/potential combination ensured that the number of atoms being used was the minimum acceptable for precision to three decimal places in all results.

Once convergence was reached, lattices of the convergence size or larger were used to generate profiles of total potential per atom versus the volume per atom. In the RH case, a three-dimensional surface of total potential versus volume per atom and rhombohedral angle was minimized.

Most of the potentials used were in closed functional form, so that finding potential as a function of interatomic distance was simply a matter of direct computation. However, the pseudopotential-based interatomic potential models were not given in a functional form,
as they were calculated from quantum molecular dynamics simulations of molten bismuth using a full relativistic treatment of core states. This potential was presented in graphical form, and so the graph itself was digitized and transformed into a matrix of potential values as a function of interatomic distance. To utilize this graph effectively, a substitute for direct computation of potentials was needed. A linear interpolation algorithm was implemented to take the place of the potential calculation, so that the interatomic potentials could be interpolated directly from the digitized data. The digitized data became an interpolation schedule from which the interpolation algorithm could read off and interpolate potential as a function of interatomic distance. A cutoff radius of 9.9 Å was imposed, beyond which the interaction energy was taken to be equal to zero.

When it was found that linear interpolation from the digitized data did not provide a smooth potential sum profile, however, it was necessary to find a method more accurate than straight-line interpolation. MATLAB was used to fit a smooth 20th-degree polynomial to the data, and to generate a new interpolation schedule with a much finer grid. This schedule was then used in place of the original digitized data, resulting in a significant reduction in the roughness of the profiles. Finally, a third interpolation schedule for this potential was created with an even finer grid in an effort to further smooth the resulting profiles. Analysis on the Morse potential, one of the steepest, and thus most likely to cause error when being interpolated, showed that at the grid sizes being used for interpolation schedules there was no error to at least three decimal places when comparing interpolated data to calculated data. Thus, interpolation was the preferred method of pair potential calculation for all potentials. Higher-order interpolation schemes could of course be implemented, but are not required for the purposes of the present study.

**Results and Discussion**

The converged lattice potential sum profiles for all six lattice types for the Morse potential are shown in Figure 4 and Figure 5. Note that all profiles for close-packed structures coincide with one another, and are the lowest in energy. One would expect that when using a non-oscillating potential the profiles would take forms similar to the pair potential itself. This is certainly the case for the Morse potential: the profiles are all Morse-type, and all have minima when most interatomic distances correspond to the minimum-energy radius of the pair potential.

The converged lattice potential sum profiles for all six lattice types for the Extended Morse potential are shown in Figure 6 and Figure 7. Adding the Lennard-Jones potential to the Morse potential yields a less symmetrical shape to the potential well, and an inverse power repulsive term. This gives the potential a harder scattering boundary than the exponential term of the Morse potential. Note that again all profiles tend to coincide over the entire range except for SC and DIA, which are not close-packed structures.

The converged lattice potential sum profiles for all six lattice types for the Cummings potential, with parameters fitted to the first peak of the structure factor, are given in Figure 8. It is apparent that this potential is unsuitable from both the erratic nature of the oscillations and the magnitude of the profiles, even at high volumes per atom (low
densities). It is apparent not only that a pair potential with a large degree of accuracy over a large range of interatomic distances is required, but that potentials for interatomic distances beyond the first minimum in the potential function contribute significantly to the total potential. Oscillating potentials can produce radically different potential sum profiles than a potential with a single minimum such as the Morse potential.

Figure 9 and Figure 10 show the potential profiles for the same Cummings potential, but this time with parameters fitted to the structure factor over the entire range. Figure 10 seems incomplete, in that the curves seem to stop in mid-oscillation as they approach smaller values of the volume per atom. This is due to the fact that the (infinite) hard-sphere repulsion potential is not accessed until the volume per atom becomes sufficiently small. Since the oscillations are so strongly negative before the radius for the hard sphere is attained, a more gradual repulsive term would need to be added before values at lower atomic potentials could yield qualitatively correct behavior.

Recall that the implementation of the pair potential by Hafner and Jank was first achieved by interpolating pair potentials from the original digitized data (cf. Procedure). The resulting profiles for this technique are presented in Figure 11 and Figure 12. These potentials took into account repulsive interactions, and so the curves tend toward infinity as the volume per atom approaches zero. This is noticeable in Figure 11, as is the tendency of the curves toward zero as atomic volume becomes large. Note that a full profile for the tetrahedral, diamond-type lattice (DIA) was not obtainable from the digitized data because the data did not cover a wide enough range of interatomic distances to model this densest lattice, and extrapolation of the potential would be unjustified. Also, rhombohedral angles of 55 and 65 degrees are plotted here because an accurate minimum angle could not be obtained from such rough data.

Figure 13 and Figure 14 show the results after the interpolation chart was generated using a finer grid. While there is still some local variation, one can now discern distinct minima. Figure 14 shows the minima of interest, which all lie very close together in volume per atom and in potential, except for DIA. In particular, HCP, FCC, and RH are very close to one another in both the total potential per atom and in the corresponding volume per atom at the minimum-energy positions. The correlation between these three lattice forms persists even away from the minimum, as they are all very close to one another across the entire range of values plotted. The SC and BCC lattice forms are somewhat different in minimum potential, and the SC lattice is shifted a bit in volume per atom, but they both exhibit minima very close to those of the other three lattices. Figure 13 and Figure 14 also exhibit noise that blurs the data somewhat. In an effort to reduce this noise, an interpolation schedule was derived from the same 20th-degree polynomial fit as before, but with a grid which was 90% smaller. The results are shown in Figure 15 and Figure 16. As can be seen, reducing the grid size produces virtually no reduction in the noise. Since the interpolation algorithm was shown to work with negligible error, the noise must be inherent to the generation of the interpolation schedule. The probable source of this noise is the slight errors involved in fitting a very high order polynomial curve to the raw data, and computer roundoff error in the representation of coefficients.
Finally, as described in the Theory sections, the Cummings potential was parameterized without regard to the structure factors, instead matching its functional form as closely as possible with the data digitized from the pair potentials computed by Hafner and Jank. Special care was taken to match the depth and shape of the largest, first potential well, but other wells were also matched in depth. The process resulted in a slight shifting of the position of the second potential well, but the rest of the potential form used matched the phase of the oscillations well (see Figure 3).

After the Cummings potential was fitted to the digitized pseudopotential-derived data, a repulsive term was added so as to somewhat mimic the behavior of the digitized data. The results obtained from this modified Cummings potential are presented in Figure 17 and Figure 18. The striking similarities to Figures 15 and 16 seem to justify the use of the modified Cummings potential form to model the pseudopotential-derived data. It is interesting to note that the first minima seen in Figure 18 are very similar to those in Figure 16, and that the FCC, HCP and RH lattice profiles still remain very close to one another throughout the range analyzed. Note also that the tetrahedral, diamond-type lattice (DIA) can now be evaluated to the point of locating desired potential minima. Beyond the first minima, however, this potential fails to truly represent the digitized data. This was to be expected, since the second minimum of the potential used to generate these profiles was shifted when the Cummings functional form was fitted.

Table I displays the near-complete coincidence of minima of the BCC, FCC, HCP, and RH lattices for the Morse, Extended Morse, and Cummings full-range parameter fit potentials. The fact that the coincidence occurs for the non-oscillating potentials as well as one of the oscillating potentials is notable. One reason for the coincidence of the BCC, FCC, HCP and RH lattices is the fact that in each of these lattices many negative potentials add constructively, since so many pairs of atoms in these lattices are the same distance apart. This would not be true for a rhombohedral lattice in general, but a rhombohedral lattice with an angle of approximately 60 degrees possesses a great amount of symmetry (a rhombus with a sixty-degree angle is equivalent to two equilateral triangles). In this context, we note that all three potentials that exhibit this pattern also predict a minimum-energy rhombohedral angle very close to 60 degrees. Thus, the symmetry provided by this rhombohedral angle lowers the overall potential, and it stands to reason that such symmetry could lower the potential in other lattice forms as well. This great degree of symmetry is not present in the SC lattice simply because it possesses fewer atoms in the same space, and thus less ability for negative potentials to add constructively.

It is also interesting to note that in the case of the oscillating potentials, the BCC lattice is slightly displaced from the other three practically coincidental lattices in potential and volume per atom. This effect is magnified in the two sets of profiles that approximate the effects of the pseudopotential-derived pair potential (Figure 15, Figure 16, Figure 17, Figure 18). The minima are still very close in volume per atom, but the BCC lattice is at a noticeably shallower potential. The other distinctive feature of the profiles generated by oscillating potentials is the HCP lattice minimum. For the profiles generated from the
Hafner-Jank pair potential, the HCP lattice is at a slightly lower potential than the RH or FCC potentials. For the profiles generated from the Cummings potential fit to the digitized pseudopotential data, the HCP lattice is at a slightly higher potential than the RH or FCC potentials.

The rhombohedral angle producing the minimum potential per atom also differed when using the pseudopotential-based potentials. The angles moved away from 60 degrees, closer to 57.26 degrees, the rhombohedral angle found in actual rhombohedral bismuth crystals. The effect of the symmetry of the lattice seems to be overshadowed slightly by another effect, just enough to pull the angle away from 60 degrees. The extra effect seems to be the detailed nature of the Friedel oscillations, i.e., their amplitude and location. However, the possible contribution of three-body and higher forces, as well as thermal fluctuation effects and zero-point energy, cannot be excluded.

All calculations are summarized in Table 1. In general, the volumes per atom at the minima, and the associated densities, are not accurate. The density of solid bismuth is 9.79 g/cm$^3$ at 25 degrees Celsius. The worst performance in this regard is obtained from the Morse potentials, which predict densities 2 to 3 times higher than experiment. Since bismuth exists as a diatomic gas with an intermolecular distance of 2.6596 Å, it might be expected that the solids would be predicted to be too dense. On the other hand, the oscillating potentials are derived from the properties of molten bismuth, which is known to be more dense overall than the solid (solid bismuth floats as it solidifies). Thus, it might also be expected that these oscillating potentials would predict solids that are slightly more dense than they should be. However, this is not the case.

The minima for the oscillating potentials show the relative pattern of the HCP, FCC and RH lattices being practically identical at the lowest potential per atom, followed by the BCC and SC lattices, and at the highest minimum potential, the DIA lattice. This pattern is interesting when looking at the phase diagram for solid bismuth. At lower temperatures and pressures, the rhombohedral lattice is favored. At slightly higher pressures, the tetrahedral (diamond-type) and simple cubic lattices are favored, and at much higher pressures the body-centered cubic lattice is favored. While this ordering cannot be directly deduced from the profiles generated, this ordering is certainly consistent with the results obtained here using the Cummings model fit to the Hafner and Jank pair potential.

**Conclusions / Future Research**

A number of different potential energy models developed for molten bismuth have been tested to see how well they describe the properties of solid bismuth. Several of the potentials evaluated in this study produced converged lattice sum profiles which were consistent with experimental data regarding bulk solid bismuth. The most important aspects of an effective bismuth pair potential appear to be the existence of Friedel oscillations, the period of the oscillations, and the nature of the repulsive term.
The modified Cummings potential,\textsuperscript{24} when parameterized using the pseudopotential-derived quantum effective pair potential computed by Hafner and Jank as input,\textsuperscript{8} seems promising enough to apply to more demanding studies. We are currently working on Monte Carlo simulations of liquid bismuth using this potential, so that data including radial distribution functions may be calculated and analyzed. If the radial function is in good agreement with experiment, we will know that the modified Cummings potential is an adequate representation of the interatomic forces at bulk liquid densities. The lack of good quantitative agreement with the solid densities remains to be better understood, and might be revealed by accurate quantum calculations of solid bismuth. We are investigating various alternatives for such calculations, including some recently developed semi-empirical extended-Hückel methods.\textsuperscript{30}

Our ultimate goal is to investigate the caloric curves of bismuth clusters in sizes ranging from a few atoms to over a hundred atoms. It should be noted that to our knowledge caloric curve calculations of atomic clusters with pair potentials which exhibit Freidel oscillations have not yet appeared in the literature. Such a study should provide an interesting contrast to previous studies of metal clusters in the literature which have not included this effect in the potential model.

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References

Table I: Summary of Global Potential Minima for Potentials and Lattice Types

<table>
<thead>
<tr>
<th>SC</th>
<th>BCC</th>
<th>FCC</th>
<th>DIA</th>
<th>HCP</th>
<th>RH</th>
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Note: Energies are given in eV, volumes in Å\(^3\), densities in gm/cm\(^3\), and angles in degrees.
**Figure 1.** Interatomic pair potentials for Morse and extended Morse potentials. Blue -- Morse potential; Magenta -- extended Morse potential.

**Figure 2.** Interatomic pair potentials for Cummings potentials, fit to the first minimum structure factor, and to the full range of structure factors. Blue -- Cummings potential fit to first minimum structure factor. Magenta -- Cummings potential fit to full range of structure factors.
**Figure 3.** Interatomic pair potentials for the digitized Hafner-Jank potential, and the Cummings potential fit to the digitized Hafner-Jank potential.

**Figure 4.** Converged lattice potential sum profiles for the Morse potential.
**Figure 5.** Converged lattice potential sum profiles for the Morse potential (close-up of Figure 4).

**Figure 6.** Converged lattice potential sum profiles for the extended Morse potential.
Figure 7. Converged lattice potential sum profiles for the extended Morse potential (close-up of Figure 6).

Figure 8. Converged lattice potential sum profiles for Cummings potential fit to structure factor at first minimum.
Figure 9. Converged lattice potential sum profiles for Cummings potential fit to the full range of structure factors.

Figure 10. Converged lattice potential sum profiles for Cummings potential fit to the full range of structure factors (close-up of Figure 9).
Figure 11. Converged lattice potential sum profiles for the digitized Hafner-Jank potential.

Figure 12. Converged lattice potential sum profiles for the digitized Hafner-Jank potential (close-up of Figure 11).
**Figure 13.** Converged lattice potential sum profiles for the interpolated 20th degree fit to the digitized Hafner-Jank potential.

**Figure 14.** Converged lattice potential sum profiles for the interpolated 20th degree fit to the digitized Hafner-Jank potential (close-up of Figure 13).
Figure 15. Converged lattice potential sum profiles for the interpolated 20th degree fit to the digitized Hafner-Jank potential, with a finer interpolation grid.

Figure 16. Converged lattice potential sum profiles for the interpolated 20th degree fit to the digitized Hafner-Jank potential, with a finer interpolation grid (close-up of Figure 15).
Figure 17. Converged lattice potential sum profiles for the modified Cummings potential.

Figure 18. Converged lattice potential sum profiles for the modified Cummings potential (close-up of Figure 17).
Supplementary Materials
(available separately)

The following files are movies in QuickTime format that show expansion of lattices:

1.) hcp.mov. This movie depicts the expansion of a hexagonal close-packed lattice by increasing the base interatomic distance.
2.) rh.mov. This movie depicts the variation of a rhombohedral lattice by increasing the rhombohedral angle from 45 to 90 degrees, keeping the base interatomic distance fixed.

The following files are models of various lattice expansions. They are all in the .XYZ Cartesian coordinate format, and can be viewed with many common molecular viewing programs.

scexp.xyz (simple cubic);
bccexp.xyz (body-centered cubic);
fccexp.xyz (face-centered cubic);
diaexp.xyz (diamond);
hcpexp.xyz (hexagonal close-packed);
rh60exp.xyz (rhombohedral expansion with 60 degree angle);
rhangexp.xyz (rhombohedral angle variation with fixed lattice constant).