Simulation of Metallic Structure in an Electric Field

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Abstract

We explore a question about how the structure and strength of a metal is affected by an electric field. Specifically: "Is the metal weakened in the presence of an electric field?" Using a computer simulation we calculate the positions of metal ions based on some initial conditions. The simulation is set up to calculate this in two ways: a Coulomb force calculation and a Monte Carlo method. In electromagnetic theory, we treat the valence electrons in a metal as free particles within a conducting-material ion lattice. The metal is held together by interactions between these ions and electrons. When an electric field is put into place, the electrons can move relatively freely due to the force from the electric field. If a strong enough electric field were applied, we would have an under-abundance of electrons in one area of the metal and an over-abundance elsewhere. Since the structure of the metal relies on the electron-ion interactions, if we change the ratio of ions to electrons in a given area, we expect it to affect the strength of the metal's structure near the surface as well as a small increase in separation between the ions along the direction of the field. We tested this hypothesis via computer simulation.[1]

1 Introduction

With the growing interest in nanotechnology, there is a need to understand the specific aspects of materials on the molecular level. The purpose of this research is to examine the surface properties of single-element metals. As with most modern conceptions of metallic structure, we regard a metal as a "gas" or "sea" of approximately free valence electrons scattered throughout a lattice of positively charged ions [1]. It is the electromagnetic interaction of these positive and negative charges that bind the atoms of the metal together. Since we

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regard the valence electrons as a collection of relatively free charges, they can be influenced by an electric field and travel within the confines of the metal lattice. If we were to apply an external static electric field, the electrons should rapidly reorient themselves such that the magnitude of the electric field in the interior of the metal is zero, as predicted from electrostatic theory [2]. It is this static condition we wish to look at in further detail. Because the static electric field must be zero inside the metal, we expect a build-up of electrons on the surface of the metal near where the electric field lines enter the metal, and a deficiency of electrons on the surface of the metal where the field lines exit, as seen in Figure 1:
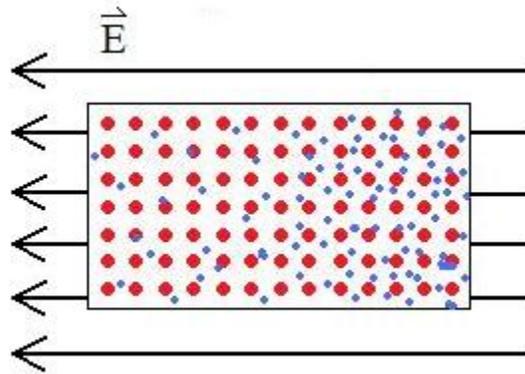

Figure 1: The red dots represent ions, and the blue represent electrons. The electron density on the right-hand side where the electric field lines enter is much greater than that of the left.

The electron-deficient metallic surface is the focus of this research. Because of the lower density of negative charge, there are fewer attractive interactions between oppositely charged ions and electrons, thereby allowing a stronger repulsive interaction between ions. With this increased repulsion, we expect to observe a separation of ions in the surface of the metal near this electron deficiency. We calculate the average separation between neighboring ions at the vertices of each metallic unit cell, along directions parallel and perpendicular to the surface of the metal. The results are reported as the average percent change of all such distance separations.

For our situation, we have created a computer program that calculates the position and movement of the electrons and ions for various elemental metals. The program uses two common simulation methods to perform these calculations: a particle dynamics (PD) simulation and a Monte Carlo (MC) simulation. The program allows the user to change the type of metal by changing the properties used in the calculations of particle movement. These properties are: the ionic charge, the ionic radius, the lattice constant[2], the ionic mass, the crystal structure of the metal, the work function of the metal, and the temperature. All the tests conducted in this research used ^{63}Cu (copper) as the metal, with a temperature of 273 K.

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[2]The lattice constants are the edge lengths of a single unit cell in a crystal structure. Because all the metals in this project have cubic structure, the edge lengths are all the same; thus, only one lattice constant is needed. In other words, the lattice constant is the distance between nearest neighbor ions.

The user can also change the initial dimensions of the lattice and the electron density[3]. The program collects data after a certain user-defined number of simulation iterations, recording the average change in ion separation parallel and perpendicular to the surface. For testing, the program can automatically change the electron density at a user-defined time as well, simulating the activation of an external electric field.

Both simulation types are initialized in the same manner: the program generates a lattice of ions using the given properties of the metal, then fills the lattice volume with a number of randomly positioned electrons such that the situation is electrically neutral (We decrease the electron density to simulate the application of an electric field later). The particles start with velocities in random directions, with magnitudes equal to the average speed of a particle given by the kinetic theory of matter [1]:

$$v = \sqrt{\frac{3k_bT}{m}}, \tag{1}$$

where k_b is the Boltzmann constant, T is the absolute temperature, and m is the mass of the particle. From these initial conditions, the program then executes either a PD or MC simulation to calculate the movement and position of each particle. In both simulations, all particles (both the ions and electrons) are free to move under the influence of all the other particles and their movement restricted only by their own mass.

Because the scale of the simulation is limited by the processing power of the computer, we employ slab boundary conditions (SBC), a special case of periodic boundary conditions (PBC), to simulate the seemingly infinite expanse of unit cells in the crystal structure of a metal [3]. We will call the volume in which the simulation proper takes place the "simulation box." We assume the electrostatic conditions are similar across the surrounding metallic surface, so we effectively tile copies of the simulation box; the repeated boxes are "images" of the simulation box. Figure 2 gives a visualization of this concept. For SBC, we apply PBC to all sides of the simulation box except the sides parallel to the surface of the metal (the "top" and "bottom" boundaries, see Figure 2). The box is centered on the generated lattice and extends to one-half of the lattice constant beyond the extreme outward-most ions, except for the top boundary, which extends to an arbitrarily chosen height of three times the depth simulated from the metal surface; this ensures there is a sufficient vacuum above the surface of the metal, to simulate the "emptiness" outside the surface of the metal. There are two PBC that are applied to the "sides" of the simulation box: boundary continuity and the minimum image criterion. We accomplish boundary continuity by looping the simulation space: if a particle moves outside the simulation box of length L, we reposition it near the opposing face of the simulation box by adding or subtracting L from the position. The minimum image criterion states that for a particle A in a simulation box, for any interactions with another particle B we use the closest image of the B, and ignore all other images; this models the interaction with particles outside the simulation box. For example, if the distance between two particles is greater than $\frac{L}{2}$, we add or subtract L to the distance such that the interaction

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[3]If ρ_0 is the density of free electrons such that the bulk metal is electrically neutral, the percentage P describes the modified electron density ρ used in the simulation such that: $\rho = P\rho_0$, $0 \leq P \leq 1$. The user changes the value of P and the program calculates ρ. Based on the desired P, the appropriate number of electrons to give an electron density of ρ are used in updating the program.

is between one particle inside the simulation box and a closer image of the other particle outside. Figure 2 gives a visualization of PBC:
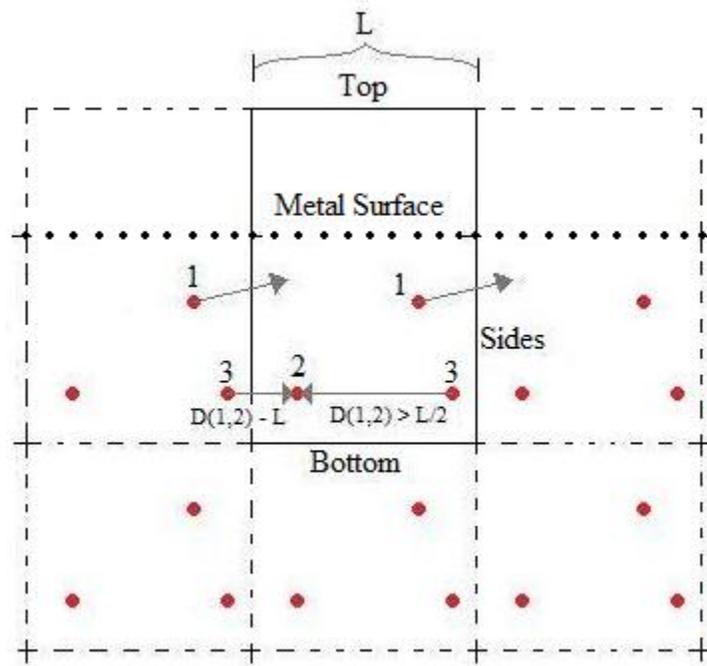

Figure 2: Diagram of SBC. The simulation box is identified by the solid lines, the images by dashed lines, and the metal surface by the dotted line. Both PBC are indicated. The particle 1 displays boundary continuity: as the particle in the simulation box leaves, its neighboring image takes its place. Particles 2 and 3 demonstrate the minimum image criterion: the distance between particles 2 and 3 in the simulation box is greater than $\frac{L}{2}$, so particle 2 interacts with the closest image of particle 3 (to its left) instead of the "real" particle 3 (to its right, in the simulation box).

Unlike side boundaries, the top and bottom boundaries are not treated with the same PBC. At the bottom boundary, we employ the minimum image criterion to simulate the expanse of particles in the interior of the metal, but do not use the continuity condition. Instead, if a particle crosses the bottom boundary, the component of its velocity perpendicular to the surface is reversed, and it is given a random position on the bottom boundary. This simulates a particle leaving the simulation box, and another entering in a different position. The metal surface has no boundary conditions and is open, except for the work function applied here. In case a particle has enough kinetic energy to overcome the work function, at the top of the simulation box, the component of velocity perpendicular to the metal's surface is reversed. The reversal of velocity on the top and bottom boundaries ensures the total number of particles in the simulation remains constant.

To simulate the activation of an external electric field, the number of electrons in the simulation can be changed to a percentage P of the number of electrons required to be electrically neutral. Those electrons that are removed are stored at a location outside the simulation box and are disabled, meaning they are no longer used in any calculations of

the simulation. In this simulation, there are no direct calculations of the effects of the electric field itself, we only simulate it through the decreased electron density. The reason for this method of simulation is the additional complications with the boundary conditions to maintain a constant number of particles.

As a note, because of the small scale of the simulation, the units used in calculation are as follows:

In Simulation	SI Value
unit length	1 angstrom $(\text{Å}) = 10^{-10}$ m
unit mass	electron mass $(m) = 9.11 \times 10^{-31}$ kg
unit charge	electron charge $(-e) = -1.602 \times 10^{-19}$ C
unit time	1 attosecond $(\text{as}) = 10^{-18}$ s

Accordingly, the physical constants such as Coulomb's constant k_e and the Boltzmann constant k_b have been changed to match this scale: $k_e = \frac{1}{4\pi\epsilon_0} = 2.532 \times 10^{-4} \frac{m^3}{e^2 (\text{as})^2}$, and $k_b = 1.515 \times 10^{-9} \frac{m}{K(\text{as})^2}$.

2 Particle Dynamics

The first type of simulation is the particle dynamics simulation [4]. We expect this simulation to be deterministically accurate as the system of particles evolves through time. It is based on classical laws of physics: Coulomb's law($\vec{F_c} = k_e \frac{q_1 q_2}{r_{1\to 2}^2} \hat{r}_{1\to 2}$ where q_1 and q_2 are the charges, $\hat{r}_{1\to 2}$ is a unit vector in the direction from charge 1 to charge 2, $r_{1\to 2}$ is the distance between two interacting particles, and $k_e = \frac{1}{4\pi\epsilon_0}$, where ϵ_0 is the permittivity of free space), Newton's second law($\vec{F}_{net} = \sum \vec{F_c} = m\vec{a}$, where m is the mass of a particle, $\vec{a}$ is its acceleration, and $\vec{F}_{net}$ is the net force), and the equations of motion($\Delta\vec{v} = \int_{t_1}^{t_2} \vec{a}dt$ and $\Delta\vec{s} = \int_{t_1}^{t_2} \vec{v}dt$, where $\vec{v}$ and $\vec{s}$ are the velocity and position vectors, respectively). By adding all the Coulomb interactions together, we can find the net force on a particular particle j at an instant in time due to the interactions with all the other particles:

$$\vec{F_j} = \sum_{i=1}^{N} \vec{F}_{i\to j} = k_e \sum_{i=1}^{N} \frac{q_1 q_2}{r_{i\to j}^2} \hat{r}_{i\to j}, \tag{2}$$

where N is the total number of particles in the simulation and $i \neq j$. Using Eq. (2) and Newton's second law, $a_j = \frac{\sum_{i=1}^{N} \vec{F}_{i\to j}}{m_j}$, we can calculate the acceleration of each particle at every step in the simulation. Using the common approximation of the antiderivatives in the equations of motion:

$$\vec{v} = \vec{a}\Delta t + \vec{v_0} \tag{3}$$

and

$$\vec{s} = \vec{v}\Delta t + \vec{s_0}, \tag{4}$$

we can calculate the new velocities and positions of each particle in the simulation, where $\vec{v}_0$ and $\vec{s}_0$ are the initial velocity and position at the beginning of a reasonably small time interval Δt. For all simulations in this project, this $\Delta t = \frac{1}{100}$ attoseconds. All the particles in the simulation have their positions and velocities updated using Eqs. (2), (3), and (4) at every iteration of the simulation.

3   Monte Carlo

The second simulation type is a Monte Carlo simulation [5]. It is based on statistical physics using the electrostatic energy ($U_c = k_e \frac{q_1 q_2}{r_{1 \to 2}}$) of each particle. The simulation is stochastic and we expect it to be statistically correct. For a particle P in a position i, we can find its electrostatic potential energy U_i with respect to all other particles:

$$U_c = \sum_{j=1}^{N} k_e \frac{q_P q_j}{r_{j \to P}} \tag{5}$$

The particle then makes a hypothetical, random movement to a new position f, at which we can find its new electrostatic potential energy U_f using Eq. (5). The magnitude of the random movement is based on the kinetic theory of matter, so the random movement is given by Eq. (4), using Eq. (1) to find the magnitude of $\vec{v}$. We then find the change in energy, $\Delta U = U_f - U_i$. If $\Delta U \leq 0$, then we accept the random movement, simulating the particle moving to a lower energy state. If the change is greater than zero, we then compare $e^{\frac{-\Delta U}{k_b T}}$ to R_n, where R_n is a random number between zero and one. The exponential function comes from the probability distribution of the possible states of our system as given by Boltzmann statistics [1]. If $e^{\frac{-\Delta U}{k_b T}} > R_n$, then we accept the random movement and the particle's new position is f. If not, then we reject the movement and the particle remains in the position i. For greater positive changes in energy, the exponential function decreases, and the probability of accepting the random movement becomes lower. This process is repeated for each particle in the simulation; thus, the ensemble of particles should eventually evolve into the lowest energy state. To ensure that this minimum energy state is the global minimum rather than a local minimum, if the particles remain in the same state for the duration of five consecutive measurements, every particle is given a random movement based on its statistical average speed; if the ensemble was in its lowest energy state, then it will quickly return to it, if not, the "jolt" enables the particles to attempt to move into a lower energy state.

4   Additional Calculations for Both Simulation Types

Additionally, we include the effects of the work function and the Pauli exclusion principle. The work function Φ is the minimum quantity of energy needed to remove an electron to a point immediately outside the metal [1]. In the PD simulation, we account for this by subtracting the work function from the kinetic energy KE of a particle as it crosses the top boundary of the simulation box. By the conservation of energy: $KE_f = KE_i - \Phi$, and since

$KE = \frac{1}{2}mv^2$, we find the final speed after the work function has been applied to be:

$$v_f = \sqrt{v_i^2 - \frac{2\Phi}{m}} \tag{6}$$

If $v_i^2 - \frac{2\Phi}{m} < 0$, the function is undefined using real numbers, so the velocity defaults to zero, indicating the particle does not have enough energy to escape, and it loses all its energy in the attempt. In the MC simulation, we simply add the work function to U_i if the particle has passed the surface of the metal, making the particle likely to reenter the metal.

To account for the Pauli exclusion principle when the electrons' wavefunctions begin to overlap each other, we construct an approximate function such that its repulsive potential U_r overpowers the Coulomb potential at close distances, and has no effect at large distances. There is no universally accepted method for describing the Pauli repulsion; it is sometimes approximated by r to some relatively large negative power (typically between -8 and -10) [1] although, the Lennard-Jones potential uses a repulsive term with a power of -12. Alternatively, it is approximated using an exponential function [6]. Here, we have chosen the latter approach:

$$U_r = \frac{a_0}{\alpha} e^{\alpha(r_{ion} - r)}, \tag{7}$$

where r is the distance between two interacting particles, r_{ion} is the ionic radius of the metal ions, and α is a constant equal to 1 Å^{-1}, such that the argument of the exponential is unitless and the equation has units of energy. The constant a_0 describes the strength of the repulsion and can be found using the total potential energy U of a simple two-particle system: $U = U_c + U_r$. Because we treat the valence electrons as free, they should begin to overlap the remaining electrons around each ion and be repulsed at a distance equal to the ionic radius r_{ion}. Assuming equilibrium at a separation r_{ion}, the minimum value of U should occur at r_{ion}. We use the first derivative of U to find the value of a_0 such that this condition is satisfied. Also, since the potential due to Pauli exclusion is always repulsive, we take the absolute value, so the resulting value for a_0 is $k_e \frac{|q_1 q_1|}{r_{ion}^2}$.

In the MC simulation, we apply Eq. (7) when the distance between an ion and an electron is r_{ion}. As for the PD simulation, since force is the negative derivative of the potential energy function with respect to position [7], and because the degeneracy pressure is always repulsive, the effective force F_r due to the Pauli exclusion principle is the absolute value of the derivative with respect to position of Eq. (7):

$$F_r = |\frac{dU_r}{dr}| = a_0 e^{\alpha(r_{ion} - r)}. \tag{8}$$

By adding Eq. (8) to Eq. (2), for any particle j closer than the ionic radius to another ion, we find the net force on j due to both Coulomb and Pauli interactions. We then apply Newton's second law and the equations of motion to update the position of j.

5 Results

With the program, we obtain results from each simulation type for several trials. The distance between pairs of adjacent ions is measured and these measurements are averaged

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together. The distances between particles oriented parallel to the metal surface and those oriented perpendicular to it are recorded separately. The change in average separation between neighboring ions is reported as a percentage difference from the original separation (the lattice constant). The measurements for these trials were taken every ten thousand iterations of the simulation. In each of these trials, the electron density drops from 100% (a balance of charge) to 50% (half of the electrons are removed) at the one-hundred thousandth iteration. The different trials are indicated by the difference in color and shape of the data points, the darker shade corresponds to the percent change in ion separation from the lattice constant parallel to the metal's surface and the lighter corresponds to the change perpendicular to the surface. For example, the two blue, diamond-shaped marker data sets are from the same trial, each representing a different set of measurements: the lighter set indicating the average separation change between adjacent ions aligned perpendicular to the metal surface, and the darker set indicating the same measurements for ions aligned parallel to the metal surface. The PD results are shown in Figure (3):
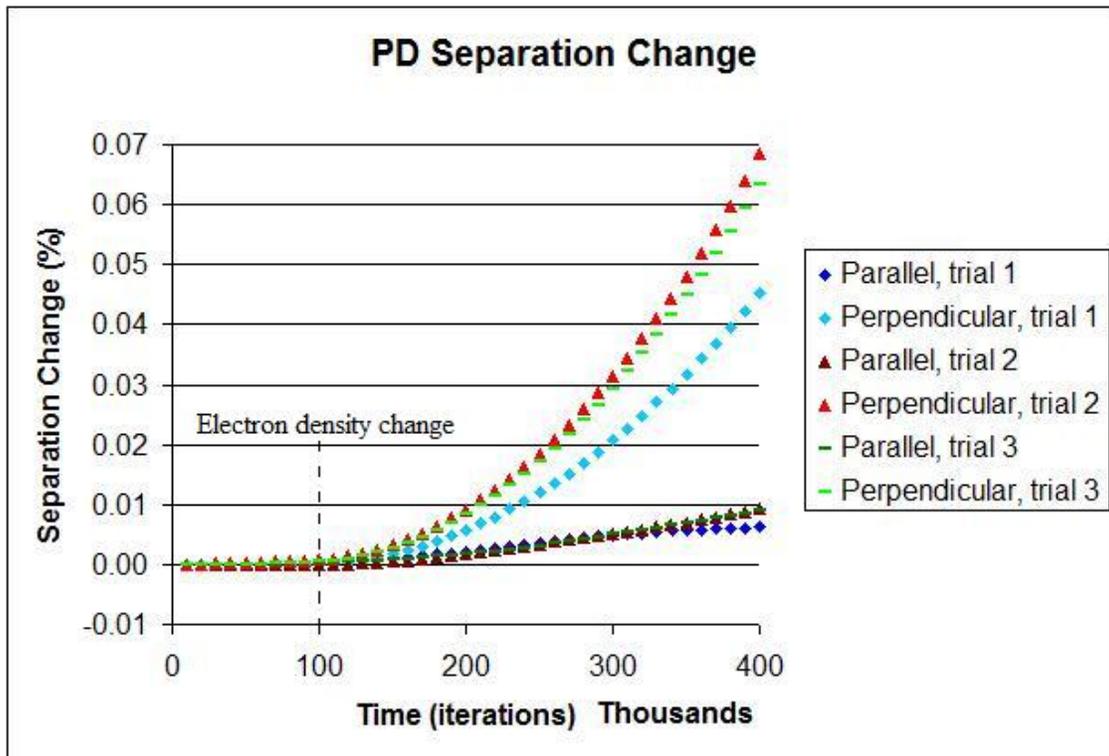

Figure 3: Three PD trial results showing the average change in separation between adjacent ions along directions perpendicular and parallel to the surface of the metal.

Using the PD simulation, we see the average separation of ions increases, as expected. Qualitatively, the largest separation appeared between the surface and second ion layers, and there were fewer electrons in this region than between the other layers.

To test the stability of the simulation, we run a trial where the electron density does not change (a "normal" trial, without an electric field). In this trial, we see a gradual increase in spacing as well; the reason for this is unclear at this time. However, if we compare trials with normal and changed electron densities, shown in Figure (4), we see the ions separate much more quickly in the trial where the electron density decreased. Because we are unsure of the cause of this gradual increase, we are hesitant to claim that this is a systematic error and simply subtract it from the results of a trial where the electron density does change.
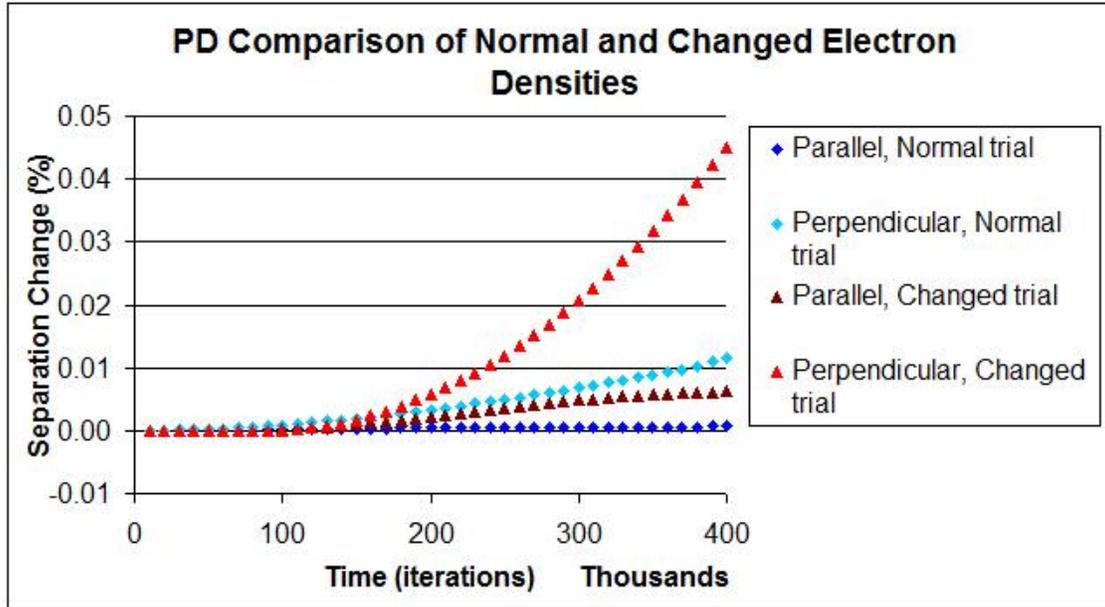

Figure 4: A comparison of PD trials for normal ($\rho = \rho_0$) and changed ($\rho = P\rho_0$) electron densities, showing the separation in adjacent ions arranged both perpendicular and parallel to the surface of the metal.

The changing separation witnessed in the constant electron density trial seems to imply that even under normal conditions, the ions tend to rearrange themselves on the surface: the lattice spacing increases, but the ions retain their location in the lattice. So, the surface of a metal has a less rigid crystal structure than simulated. The lower electron density only seems to expedite the surface deformation. Qualitatively, we see that the deformation largely occurs only in the first and second layers of ions.

For the MC trials, we use the same virtual experiment where the electron density drops from 100% to 50% at the one-hundred thousandth iteration, and measurements are taken every ten thousand iterations. The data is given in Figure (5):
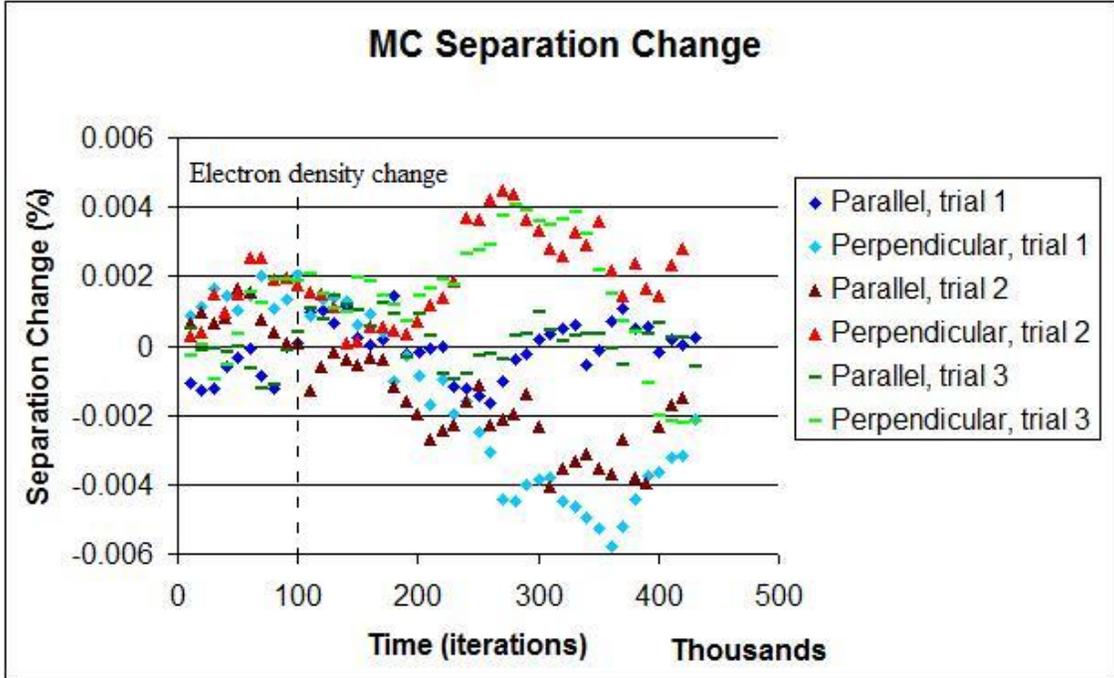
Figure 5: Three MC trial results showing the separation in adjacent ions arranged both perpendicular and parallel to the surface of the metal.

We expect the data to have a lot of variance because of the stochastic nature of the MC simulation. The only consistency between the trials seems to be that after the electron density drops, the ions are more free to move, causing a more pronounced change in separation, both in expansion and contraction. We see that even after the electron density drops, the average separation remains around its original value.

We also note that the scale of the change in separation in the MC simulation is much smaller than that given by the PD simulation. Comparing the two simulation types, the MC does not seem to be as strongly affected by a decrease in electron density as the PD simulation. Clearly, the PD simulation shows an increased rate of changing ion separation for the electron deficient surface of a single-element metal, and the MC simulation shows a comparatively smaller change.

6   Conclusion

In this project we have created a simulation for exploring surface structure of metals. Further research in this topic should include an examination of the crystal structure at the surface of the metal. We also suggest modifying the PD simulation such that it applies an electric field directly to the metal particles (both ions and electrons), rather than simulating the effect of a field using a decreased electron density. This would require a modification of the boundary conditions. It might also be appropriate to use a "graded-density" approach in which the initial electron density changes with depth from "depleted" ($\rho = P\rho_0$) at the

surface to "normal" ($\rho = \rho_0$) several layers of ions into the metal from the surface. We conclude that using the PD simulation has demonstrated the separation in ions expected at the electron-deficient surface of a metal. In fact, this separation not only increased, but the crystal structure of the metal began to break down. Using a MC simulation, we see little effect in decreasing the electron density, except for an increase in deviations from the original ion separation. We hope that we have demonstrated the usefulness of simulations such as this in exploring the atomic-scale behavior of different materials, metals in particular.

Acknowledgments

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