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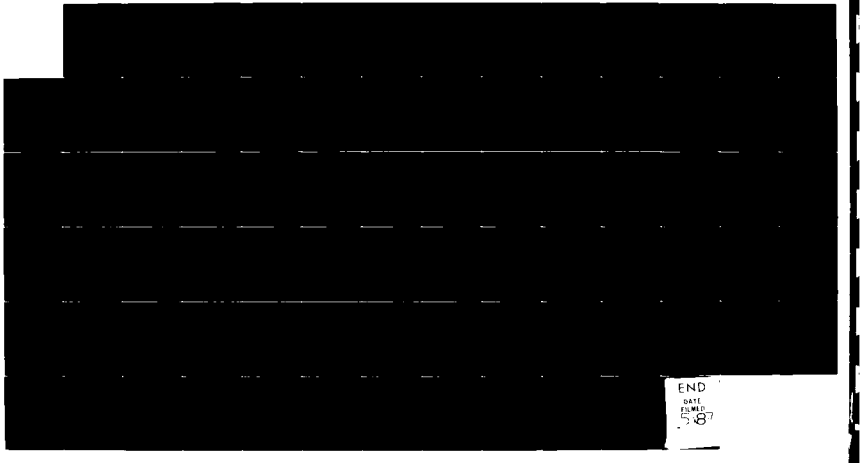

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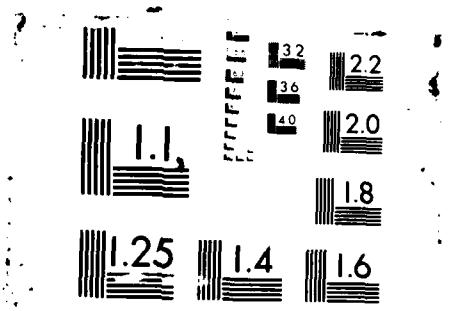

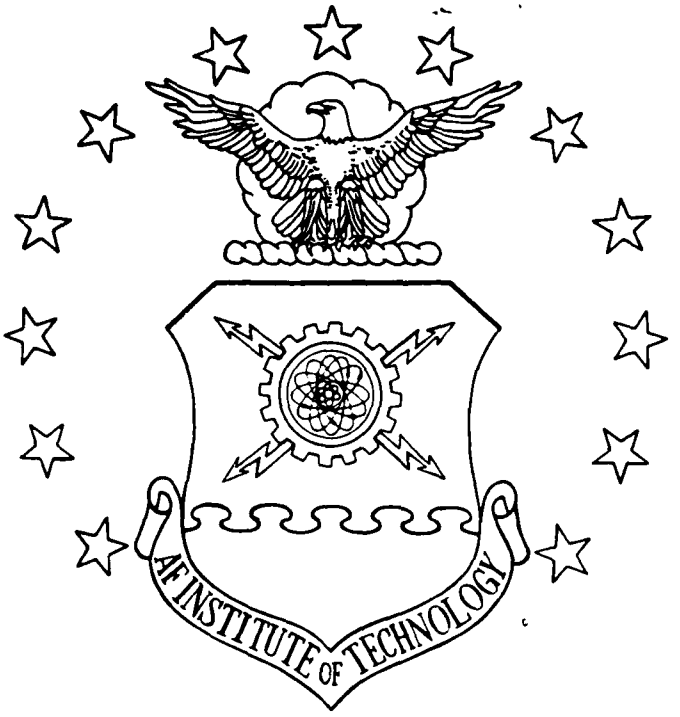

ATOMISTIC SIMULATION OF THE VERIFICATION OF DAGENS' POTENTIALS AND THE ANNEALING OF ATOMIC CLUSTERS

THESIS

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Captain, USAF

AFIT/GNE/ENP/87M-6

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THESIS

Presented to the Faculty of the School of Engineering
of the Air Force Institute of Technology
Air University
In partial Fullfillment of the
Requirements for the Degree of
Master of Science in Nuclear Physics

Debra L. Richlin, B.S.
Captain, USAF

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Preface

The purpose of this study was twofold: to determine the validity of two new silver potentials and to verify a new global minimum configuration technique for silicon. First, molecular statics was used to test two new Dagen silver potentials. In particular this was accomplished by calculating the formation energy of vacancy point defects in the face-centered cubic metal silver via computer simulation. Then, by comparing the results obtained with known experimental data the viability of the new potentials versus the prior version was determined. Second, molecular statics in conjunction with molecular dynamics was used to determine the global minimum configuration of a two dimensional 36 atom cluster using a modified version of Stillinger and Weber's silicon potential. The resulting computational times were then compared to those obtained by utilizing a prior method propossed by Biswas and Haaman utilizing Langevin molecular dynamics techniques (Biswas and Haaman, 1986).

In performing the computer simulation and writing this thesis I thankfully have had a great deal of support and help from others. I am deeply indebted to my faculty advisor, Capt M. Sabochick, for his continuing patience and assistance.

Debra L. Richlin

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Abstract

Two new silver potentials derived by Dagens were validated and a new annealing technique was investigated in this thesis. It was found via a molecular statics technique that the two new silver potentials were less precise than the older silver potential. The calculated vacancy of formation energy of the older silver potential deviated from the experimental value by 21% whereas the two new silver potential values differed by 48% and 64% respectively.

The new annealing technique using a combination of molecular statics and molecular dynamics was found to be approximately ten times faster than a previous method proposed by Biswas and Haaman using Langevin dynamics. In particular, both techniques using a two-dimensional cluster of 36 atoms and a modified version of the Stillinger and Weber silicon potential were tested on the CRAY computer system. The new annealing technique acheived a local minimum configuration of -45.3 eV in 36 seconds of CRAY CPU time while the BH Langevin technique took over 360 seconds of CRAY CPU time to find the same local minimum.

ATOMISTIC SIMULATION OF THE VERIFICATION OF DAGENS' POTENTIALS AND THE ANNEALING OF ATOMIC CLUSTERS

I. INTRODUCTION

Atomistic simulation is the computer simulation of a material as a collection of individual atoms. Two major types of atomistic simulation are molecular dynamics, MD, and molecular statics, MS. Molecular dynamics is used to simulate a material at finite temperatures. Many bulk properties of the material can thus be calculated such as pressure, internal energy and enthalpy. Molecular statics is used to determine stable and metastable atom configurations and is strictly valid only at 0° Kelvin.

MD and MS were employed in completing the two goals of this work. These goals were first to validate Dagens' new silver potentials and second to investigate a possible faster technique for finding global energy configurations.

In atomistic computer simulations the material in question is modeled by individual atoms connected via interatomic potentials. These interatomic potentials dictate how far apart the atoms can be and still react with each other. They also dictate the strength and direction, repulsive or attractive, of the interactive forces (Glasstone, 1979:253-

257). Thus to simulate a real-world material a reliable interatomic potential that correlates well with experimental data is necessarily the cornerstone of a working code.

The potentials used to simulate silver were three noble metal potentials derived from first principles by Dagens (Lam, 1983:2510). The first and oldest of these potentials was tested by Lam (Lam, 1983) to verify its accuracy with experimental data. It was found that for copper the potential agreed quite well, within 10% of the experimental data value for the vacancy energy of formation (the amount of energy required to form a vacancy in a perfect crystal). But for silver the energy of formation was over estimated by 23% when compared with experimental data (Lam, 1983:2514). Subsequently Dagens revised this potential in an attempt to achieve better correlation with experimental data. The two new potentials that he derived were tested as part of this project using a molecular statics approach to find the energy of vacancy formations. This value when compared with experimental data reflected the validity of the two new potentials.

Biswas and Haaman, BH, (BH, 1986:897-898) utilized Lagevin Molecular dynamics to find the global minimum energy configuration of a 32 atom cluster. That is the stable or lowest energy configuration of the system. They used a technique where the atoms were thermally excited to the melt point and then allowed to cool through a series of cooling stages to a global minimum configuration. At each stage of

the cooling process they recalculated the positions of the atoms using Langevin dynamics in conjunction with the Stillinger and Weber silicon potential. To achieve their results BH had to calculate the Langevin equation 200-300 times for each temperature decrement (BH, 1986:897-898). This method, although faster than other techniques, is still somewhat computationally time consuming. The second part of this paper proposed using a combination of molecular statics and molecular dynamics to find the global minimum configuration within less timesteps than those required using the BH Langevin technique.

In their article BH refer to their technique as a means of simulating the annealing of a cluster of atoms (BH,1986). Experimentally annealing is the gradual removing of energy from a heated system until it reaches a stable configuration (Chalmers,1982:109-111). Through a slow annealing process many defects disappear from the crystal as they are given time to recombine, an interstitial with a vacancy, or reposition themselves according to the potentials influence (Corbett, 1986:36). For the purpose of this paper, the cyclic cooling process used in the computer simulations will be referred to as annealing.

Overview.

Chapter 2 describes the interatomic potentials used in this work. The concepts of two body versus three body

potentials and empirical versus non-empirical potentials are discussed. Three of Dagens' two-body non-empirical potentials for silver are presented. Then Stillinger and Weber's, SW, three-body empirical potential for silicon is delineated. The modifications to the SW potential are then described.

Chapter 3 describes the general computational procedures used and the two annealing techniques. Thus MD, MS, Langevin MD, the BH annealing method and a new annealing method are presented.

Chapter 5 presents the results of the verification of Dagens' silver potentials. The calculation of the vacancy energy of formation is covered as well as the methodology used to verify that the computer code was working properly. The results and discussion of the Dagens potential verification is also presented in this chapter.

Chapter 6 contains the results of the comparison of the two annealing techniques. The discussion of these results is also included in this chapter.

The conclusions and recommendations of the present work are given in chapter 7. In particular, recommendations for future work on annealing simulations are made.

II. INTERATOMIC POTENTIALS

Interatomic potentials are used to determine the interatomic forces and energies between atoms. These forces and energies are used by molecular dynamics and molecular statics to calculate both micro- and macro- properties of materials such as the vacancy energy of formation and the global energy configuration of an annealed solid. The results obtained when simulating a particular material relies heavily on the accuracy of the interatomic potentials ability to effectively model the real-world particle interactions (Sabochick, 1985:20).

Two and Three Body Potentials.

Generally potentials are based on the sum of one body, two body, three body etc. interactions between atoms. (SW, 1985) Therefore interatomic potentials can be classified according to the number of atoms that interact with each other at any one time. Materials that can be adequately portrayed by the simultaneous interaction of two atoms utilize the two body term. Materials that are more complex, whose atoms interact with each other in triplets, utilize both the two and three body terms. The latter set are referred to as three body potentials as they include the three body term. These two and three body terms can be expressed via a generic formula.

The general expression is of the form

$$\Phi = \sum_{i} V_1(i) + \sum_{\substack{i\,j \\ i<j}} V_2(i,j) + \sum_{\substack{i\,j\,k \\ i<j<k}} V_3(i,j,k) + \ldots . \qquad (1)$$

The first term describes external and wall forces that interact with the atoms (SW, 1983). As the crystal is normally taken to be isolated from external forces the one body term is usually not included in the potential (SW, 1983).

The second term describes the interactions between pairs of atoms which are not affected by the presence of other neighbors. This two body term is commonly known as a pair potential. Pair potentials are the most widely used potentials. The two body term sufficiently approximates some materials, is easily implemented and computationally faster than more complex potentials (Thee, 1986).

The third or three body term is used when the material has strong directional bonds (SW, 1983). This three body potential is used to stabilize the system and provides the unique geometrical configuration that is an integral part of certain materials such as silicon. In particular, the three body term forces the bond angles to a given value. This term portrays the simultaneous interaction of three atoms bonded together by their individual atomic forces. Implicit in the three body term is thus an angular dependence (Fig 1.) (Sabochick, 1985).

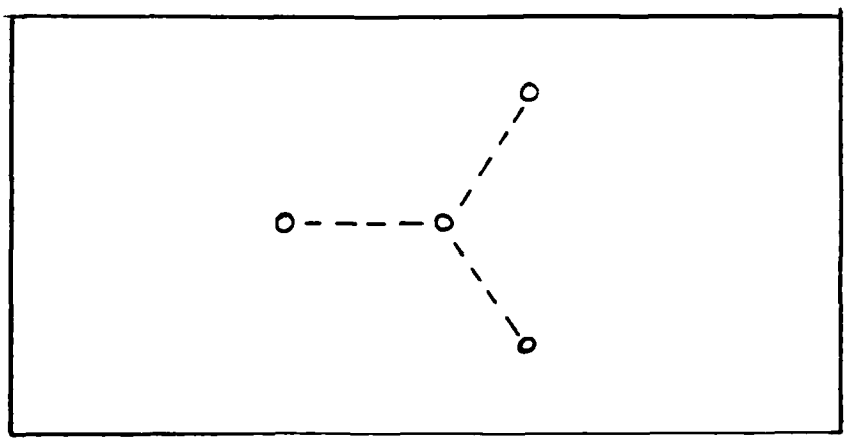

Figure 1. Three body atomic interation. Dotted lines represent interatomic force fields binding the atoms together. The o represents the individual atoms.

Empirical versus Non-empirical Potentials.

Interatomic potentials can also be classified according to the way they are derived. Two classes of potentials are empirical and non-empirical. Empirical potentials are derived by fitting a specific form of a potential such that it will reproduce experimental data. The non-empirical potentials are derived from first principles employing a quantum mechanical treatment of atomic interactions (Sabochick, 1985:20-27).

Although empirical potentials reproduce the data to which they are fitted, they may be inaccurate when modeling other parameters than the ones used for the initial data base. An example of an empirical three-body potential is the Stillinger and Weber potential for silicon (SW, 1983).

One type of non-empirical or first principles potential is derived using the psuedopotential method (Sabochick, 1985 :27-36). These potentials have a number of common properties. One of these common properties is that beyond the first lattice constant the potentials demonstrate oscillatory motion. At large distances these oscillations usually converge to periodic Friedel oscillations (Lam,1983, Sabochick,1986).

The Three Interatomic Dagens' Potentials.

Dagens' potentials were all derived from first principles using the psuedopotential method (Lam, 1983:2504). Figures 2, 3 and 4 portray the three Dagens potentials over different ranges of interatomic distances. Figures 2 and 3 show that the potentials are quite disimilar at $r < a$, where a is one lattice constant. The lattice constant for silver is 4.087 Angstroms. Note in Fig. 3 that the second new potential in this region has a prominent negative well. The old potential is the most strongly repulsive of the three. The first new potential varies only slightly from the old potential in this region. However viewing Fig. 4 one can see that at distances greater than a few lattice constants the new potentials resemble each other while the old potential dominates with pronounced Friediel oscillations. The Friedel oscillation dependence which is prevalent in psuedopotentials can thus be seen in Fig. 4.

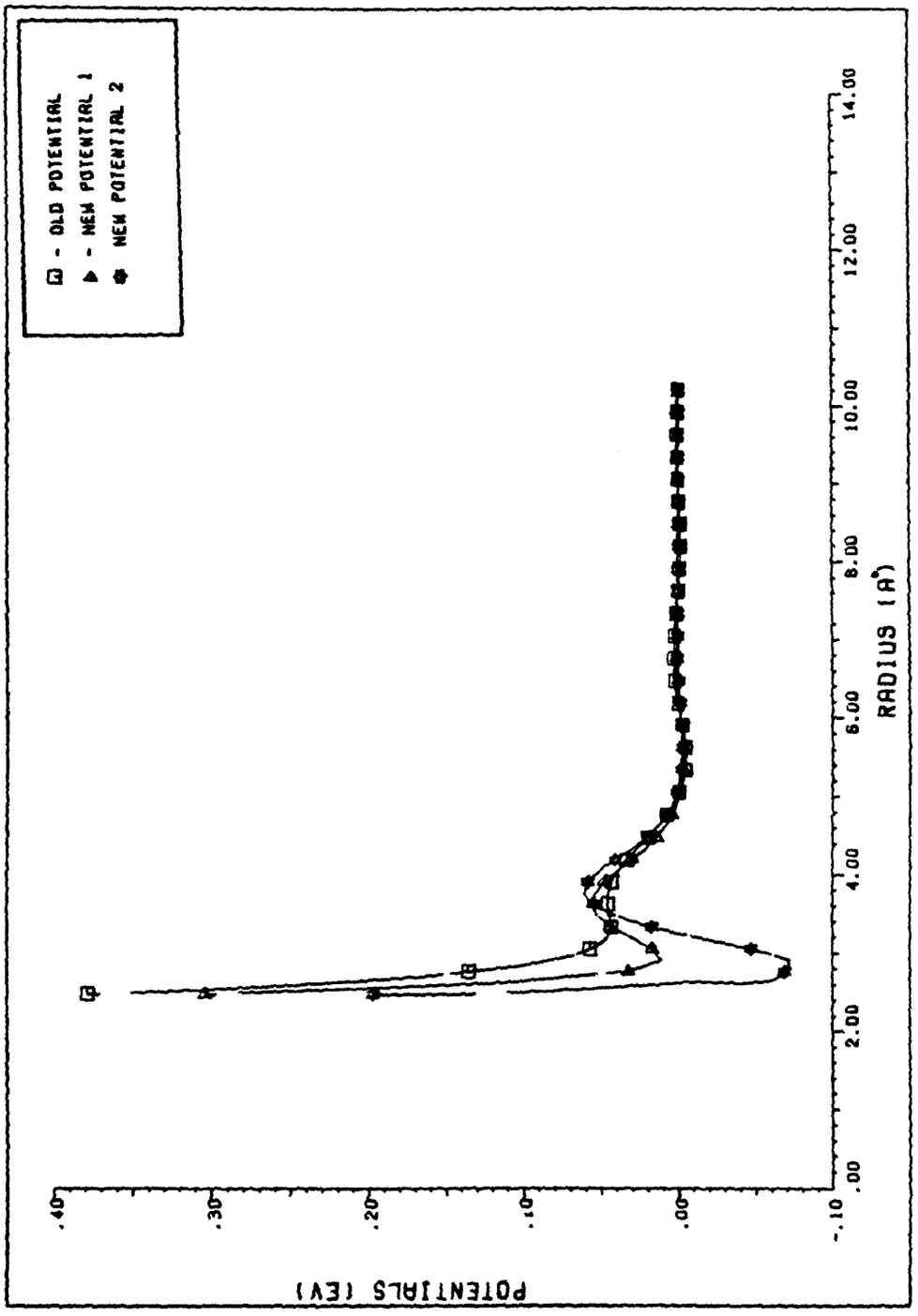

Figure 2. Dagens' Three Silver Potentials.

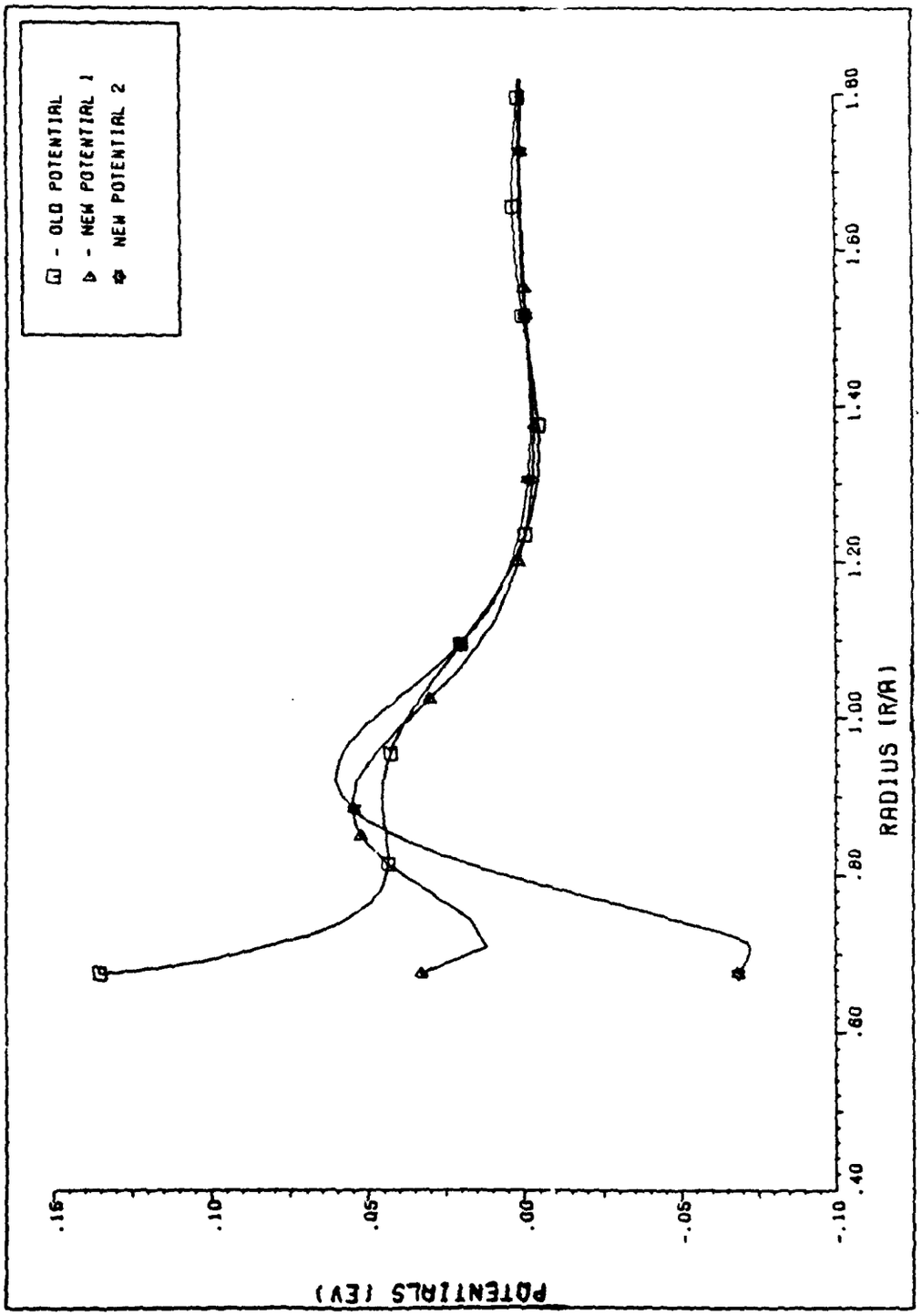

Figure 3. Dagens' Three Silver Potentials (r < 2a). Where a is the lattice constant for silver.

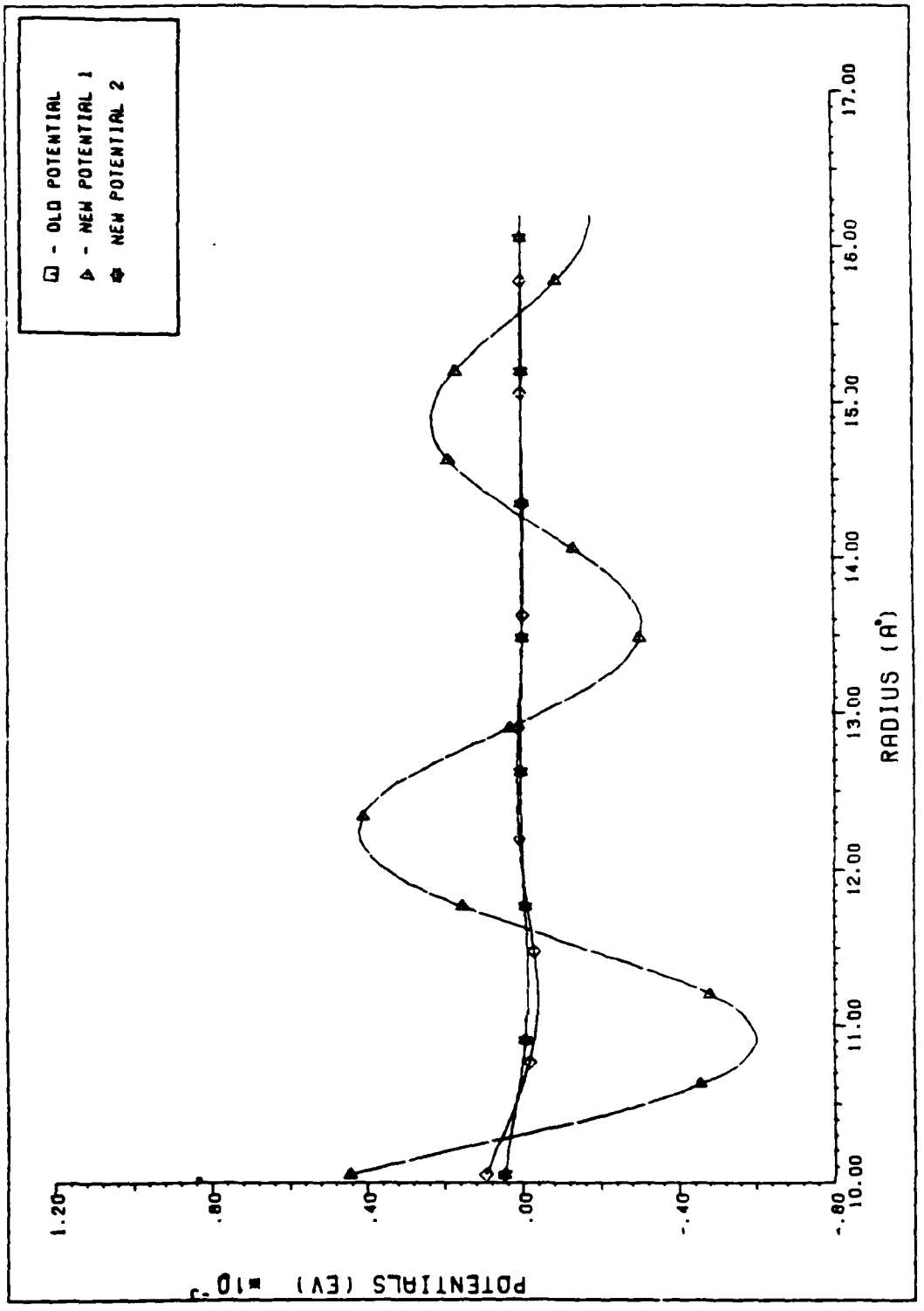

Figure 4. Dagens' Three Silver Potentials (r > 2a). Where a is the lattice constant for silver.

The older version of the interatomic Dagens potential is

$$\emptyset = \{ 1-\exp[-a(r - r_1^2)]\}[(C_1 + \frac{C_1}{r^2}) \frac{\cos(x)}{r^3} + \frac{S_1 \sin(x)}{r^5}]$$

$$+ \sum_n \frac{B_n \exp(-br^2)}{r^{3-n}} + D \exp(-gr) \qquad (2)$$

where $x = Y + 2 k_F r_F$ (k is the zero order Fermi momentum for noble metals) (Lam, 1983). The potential $\emptyset$ is in atomic units with the calculational parameters presented in Table I. The first term in the above equation represents Friedel oscillations at large distances. The second term represents a short range repulsive force. The third term is related to the forces resulting from scattering between two resonant d states (Lam,1983). The old Dagens parameters are presented in Table I.

TABLE I

Interatomic Potential Parameters for Silver (Old Potential)

a	0.1	b	0.109
r_1	3.	B_0	17.669
C_0	0.265	B_1	-0.0459
C_1	-0.265	B_2	-0.2044
S_1	-20.85	B_3	-0.02728
Y	1.429	g	0.8
k_F	0.7189	D	0.2819

The only difference between the two new Dagens potentials are the values of the constant parameters. Thus the two new potentials are of the form.

$$F_{tot} = F_{sp} + F_{dd} \tag{3}$$

where

$$F_{sp}(r) = (f_1 + f_2)\, C + f_3\, (1 - C) \tag{4}$$

where

$$f_i = A_i \exp(-B_i\, r) \cos(K_i\, r + FI_i) \tag{5}$$

$$C = 1/(1 + \exp(2(r-c))) \tag{6}$$

and

$$F_{dd}(r) = [(D0 + D2\, r^2) \exp(-G0\, r) + D1 \exp(-G1\, r)]\, C' + D3\, (1 - C') \cos(K3\,(r - R0)) * \exp(-G\,(r - R0)) \tag{7}$$

where

$$C' = 1/(1 + \exp(2(r-c'))) \tag{8}$$

The above terms involve the corresponding resonant s, p, and d states of the atom. The first term, F_{sp}, is a result of electronic transitions between the resonant s state at one ionic site and the resonant p states at a different ionic site. The second term, F_{dd}, involves the

contributions associated with the scattering between two resonant d states. Table II presents the common parameters between the two new interatomic Dagens potentials, while Tables III and IV present respectively the F_{sp} portion of Dagens potentials 1 and 2 (Lam,1986).

TABLE II

Interatomic Potential Parameters for Silver (F_{dd} part of New Dagens' Potentials)

D0	0.667611	G1	1.763201
D1	16.094525	K3	1.395939
D2	0.308763	G3	0.500000
D3	-0.000011	c'	7.238867
G0	1.481220	R0	10.427867

TABLE III

Interatomic Potential Parameters for Silver (F_{sp} part of New Dagens' Potential 1)

A_1	-27.846879	B_1	1.301653
A_2	0.538025	B_2	0.666321
A_3	-0.008047	B_3	0.405860
k_1	0.654843	FI_1	2.019130
k_2	-0.298960	FI_2	1.745467
k_3	1.1745467	FI_3	-0.020818
c	7.9488		

TABLE IV

Interatomic Potential Parameters for
Silver (F_{sp} part of New Dagens' Potential 2)

A_1	-24.090029	B_1	1.249204
A_2	0.516413	B_2	0.649002
A_3	-0.010724	B_3	0.460805
k_1	0.686321	FI_1	1.932997
k_2	-0.029370	FI_2	0.165145
k_3	1.177000	FI_3	0.279729
c	7.9913		

The Modified Stillinger and Weber Silicon Potential.

The Stillinger and Weber empirical potential, Ø, is composed of a two-body term, f_2, and a three-body term, f_3, as follows:

$$\emptyset = e f_2\left(\frac{r_{ij}}{s}\right) + e f_3\left(\frac{r_i}{s}, \frac{r_j}{s}, \frac{r_k}{s}\right) \qquad (9)$$

where r_{ij} is the radial distance between atom i and atom j. The terms r_i, r_j, and r_k are respectively atoms i, j, and k's radial positions, e and s are energy and length units. The e was chosen as 50 kcal/mole to give f_2 depth of -1 and s was chosen as 0.20951 nm to make $f_2(2^{1/6})$ vanish. Thus a minimum occurs at $r = 2^{1/6}$ and the largest two atom binding

energy is -1. (Dodson,1986) The f_2 term specifies the energy between two atoms as a function of distance. The f_3 term possesses full rotational and translational symmetry (SW, 1983).

The Stillinger and Weber two-body term is

$$f_2(r) = \begin{cases} A(B\,r^{-p} - r^{-q})\,\exp[1/(r-a)], & r < a \\ 0\ , & r > a \end{cases} \qquad (10)$$

and the three-body term is the symmetrized sum

$$f_3 = h(ijk) + h(jik) + h(jki) \qquad (11)$$

where $h(ijk)$ depends on the distances r_{ij}, r_{jk}, and the angle θ_{ijk} (Dodson, 1983). For $r < a$, h has the following form

$$h(r_{ij},r_{jk},\theta_{jik}) = L'\exp\{Y[1/(r_{ij} - a)] + Y[1/(r_{ik}-a)]\} * [\cos(\theta_{jik}) - \cos(\theta_t)]^2 \qquad (12)$$

The parameters that Stillinger and Weber used in the above potentials to simulate silicon are presented in Table V. (SW, 1983). With only a few exceptions these were used as shown throughout this study. Note that all the values are given in reduced units where s = 2.0951 A° and e = 2.167 ev/atom pair (Blaisten-Barojas, 1986).

To give a well defined hexagonal pattern in two-dimensions a number of changes in parameters were necessary

TABLE V

Interatomic Potential Parameters for
Silicon (Stillinger and Weber Potential)

A	7.049556277	L'	21.
B	0.602245584	θ_t	-1/3
q	0.0	p	4.
a	1.80	Y	1.20

during this study. One change shown earlier by Dodson was that the L' term needed to be increased from 21 to a larger value (Dodson chose 60) to adequately model silicon crystal growth (Dodson,1983). The L' term dictates the preference in two-dimensions of the hexagonal structure of the crystal over other atomic configurations. By strengthening the three-body term the hexagonal pattern dominated the atomic cluster. We found L' = 30 to be adequate for the purpose of modeling the two-dimensional melt and subsequent annealing of the simulation material.

Another parameter that was changed during this study was $\cos(\theta_t)$, which also determine the resulting geometry of the solid. Stillinger and Weber used $\cos(\theta_t) = -1/3$ which gives a tetrahedral geometry in three-dimensions. We chose to use a 120 degree angle which will give a hexagonal structure in two-dimensions. The parameters used during this study are presented in Table VI with the two modified parameters changed as specified above.

TABLE VI

Modified Interatomic Potential Parameters
for Silicon (Stillinger and Weber Potential)

A	7.049556277	L'	30.
B	0.602245584	θ_t	-0.5
q	0.0	p	4.
a	1.80	Y	1.20

III. ATOMISTIC SIMULATION

Atomistic simulation is a computer technique whereby a material is simulated via atoms connected by interatomic potentials. These potentials are used to provide force and energy calculations for the computational methods which adjust the atoms positions. These computational methods can be arranged into two general categories. They are molecular dynamics and molecular statics. The latter, molecular statics, was used to verify Dagens' silver potentials. Also a combination of molecular dynamics and molecular statics was used to investigate a new annealing technique. A modified version of molecular dynamics using the Langevin equations was also used in an annealing technique by Biswas and Haaman, BH. The BH technique was used to compare the results obtained with the new annealing technique. Both of these annealing techniques are presented in the latter part of this chapter.

The following paragraph delineates the sections covered in this chapter. The two major sections covered are general computational procedures and the two annealing techniques. Under general computational procedures, molecular dynamics, molecular statics and a modified molecular dynamics technique using Langevin dynamics is covered. Under the two annealing techniques, the BH method using Langevin dynamics and the new annealing method is covered. Each annealing technique is outlined along with particular computational

tools and specific parameters utilized. Finally this chapter concludes with a description of the constraint potential used in the BH Langevin and the new annealing techniques.

General Computational Procedures.

Molecular Dynamics.

Molecular dynamics is a technique whereby one solves Newton's equations of motion for the atom positions and velocities of a system at finite temperatures. For a system of N atoms with velocities v_i and positions r_i the equations of motion are (Thee, 1986:9):

$$\sum_{i}^{N} \bar{F}_i = m \frac{dv_i}{dt} \tag{13}$$

where F_i is the force of atom i with mass m and acceleration dv_i/dt. And

$$\sum_{i}^{N} \bar{F}_i = - \sum_{j \neq i}^{N} \frac{du(r_{i,j})}{dr_{i,j}} \tag{14}$$

where du/dr is the derivative with respect to the atom positions, r, of the interatomic potential, u. Thus

$$m \frac{dv_i}{dt} = - \sum_{j \neq i}^{N} \frac{du(r_{i,j})}{dr_{i,j}} \quad . \tag{15}$$

The above equations were numerically integrated and used along with the interatomic potential to update the atoms positions and velocities. These positions and velocities of the atoms were updated in the molecular dynamics portion of the code for a certain number of time steps. These time steps will be referred to throughout the rest of this paper as N_{steps}.

The general format of the molecular dynamics portion of the code which moves the atoms N_{steps} is presented below.

$$R_i = R_{i-1} + (2v_i + F_i\, dt)(dt/2). \qquad (16)$$

The force, F, is updated by evaluating the positions using an interatomic potential. This new force, F1, is used to calculate the new velocities. These new velocites are then used in the next cycle to calculate the new positions with Eq. (16). The new velocities are, as the mass is set to 1:

$$v_i = v_{i-1} + (F + F1)(dt/2) \qquad (17)$$

The Eqs. (16) and (17) were thus utilized N_{steps} times to move the atoms. This methodology is used until the atoms have moved a given number of steps. Each step is constrained to move within a certain period of time, dt. Thus the atoms move N_{steps} with each step moving in the specified time interval, dt. The particular outline above was used in the molecular dynamics portion of the new annealing technique to move the atoms a prescribed distance

after a defintive amount of energy was applied to the system.

Molecular Statics.

The basic purpose of a molecular statics program is to determine the atomic positions of a system such that the total potential energy is minimized. That is the minimized potential energy system represents stable and metastable configurations of the atoms. The calculated molecular statics stable and metastable configuration results are strictly valid only at the temperature of absolute zero (Sabochick, 1985:64).

Molecular statics has been historically divided into two general categories. The first of these, the quasi-dynamical technique, is a method whereby the Newtonian equations of motion are solved. Utilizing a gradual removal of energy from the system and the continuing solutions of the Newton equations over numerous timesteps the minimum energy configuration is calculated. The second type of minimization techniques do not involve directly the solution of Newton's equations of motion. Instead these minimization techniques use mathematical methods to obtain the minimum energy configurations of the system. These mathematical methods are known as variational methods (Sabochick, 1985:68-70).

Two common quasidynamic methods are the frictional and

v.a. methods. The fictional method allows a braking force to be applied to the atoms which is proportional to the atoms velocities. The rationale for this approach stems from the total energy, which is the sum of the potential and kinetic energies, remaining constant. As the kinetic energy, $mv^2/2$, increases the kinetic energy goes to its maximum value and the potential energy goes to its minimum value. Thus the greatest applied braking force happens when the potential energy is at a minimum which slows down the system near the minimum configuration (Sabochick,1986).

The second method could be termed the velocity and acceleration method or the v.a method. This involves setting the velocity to zero whenever the dot product of the velocity and acceleration becomes negative. The rationale behind this method can be illustrated by considering a bead allowed to slide on a string. (See Fig 5.)

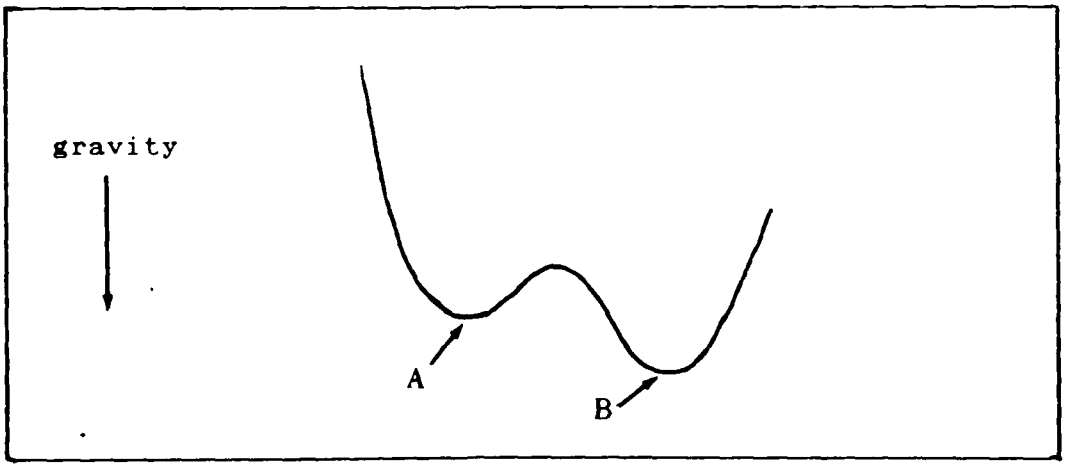

Figure 5. Bead on a Wire. Where point A is a local energy minimum and point B is the global energy minimum.

If there are no frictional forces the bead will cycle along the above path indefinitely. This is precisely the results of a molecular dynamics code if no frictional forces are allowed. Note as the bead passes through the minimum its velocity and acceleration are in opposite directions. At this point setting the velocity equal to zero would force the bead to return to the minimum energy configuration which the bead overshot slightly. One can find the minimum configuration by continuing this process until for example, the maximum force on any atom is below a given value (Sabochick, 1986).

A number of mathematical methods have also been used as minimization techniques. One of these, the method of steepest descent, can be illustrated by using the bead example above. This method looks at the position of the bead, calculates the first derivative and moves the bead in the direction of steepest descent. This is done in very small incremental steps until the bead reaches the minimum energy configuration. Although accurate this method is computationally very time consuming as the time step size must be chosen to be very small to prevent the overshooting of the minimum.

Another mathematical method is the Modified Fletcher Powell, MFP, method. This method is similar to the steepest descent method. The first derivative is calculated and the bead, using the same analogy as before, selects the direction it will move in. However the bead now deals with

a three-dimensional enviroment instead of the prior two-dimensional world. Where formerly the bead saw only lines going up and down it now sees hills and valleys. The MFP method estimates the second derivative of the system. This additional information allows the bead to make a two dimensional selection of the direction it should move in. This method is described in greater detail by Sabochick (Sabochick, 1985:72-79). The Modified Fletcher Powell method was used as the statics portion of the code to verify Dagens potentials and in the new annealing technique.

Note that all of the Molecular Statics techniques presented, even the Modified Fletcher Powell Method, will force the bead into position A. Position A is a local energy minimum while point B is the global energy minimum. The global energy minimum is most desirable to obtain as it is the most stable and thus the most likely configuration of the system. Finding this global minimum will be addressed in the annealing sections of this chapter.

Langevin Dynamics.

Langevin dynamics was used by Biswas and Haaman to find global minimums of three-dimensional clusters of silicon atoms. The utilization of the Langevin equations is associated with the Brownian type of motion that the particles experience as they interact with each other. The equations are derived from the assumption of a very small

time variation associated with a large fluctuating force. The motion of a particle traveling through the atmosphere or through a heated material has these characteristics as it collides frequently with other particles. Also at each collision a large force is transferred to the particle. As this force tends to be in the opposite direction of the general forward path of the particle, the particle is slowed down over time. This viscous motion of the particle with the widely varying applied force is included in the Langevin equation in the following manner:

$$\frac{dv_i}{dt} = - g' v_i + F_i(t) \qquad (18)$$

where g' is the viscous damping force, v is the velocity, $F_i(t)$ is the time dependent force, and dv_i/dt is the time derivative of the velocity commonly known as the acceleration. The force $F_i(t)$ is a time averaged force that depends on the bulk properties of the system (Nichelson, 1983:267-269).

Biswas and Haaman in their article note that both the equipartition of energy theorem and the Maxwellian velocity distribution can be derived from the integrated form of Eq. (16). This implies that the particles described by the Langevin equations will achieve an equilibrium temperature distribution. The BH method using the Langevin equations do not provide accurate instataneous positions and velocities of the particles. Only at temperatures of absolute zero are

their results valid. Also note that the Langevin equations are singly dependent on temperature in BH's work (BH,1986).

Biswas and Haaman modified the above equations to include a position-dependent internal force h(x) which yields the following coupled equations where the i indices have been dropped for convenience. The equations are (Biswas and Haaman, 1986):

$$\frac{dx}{dt} = v \tag{19}$$

$$\frac{dv}{dt} = h(x) - g' v + F(t) \tag{20}$$

Biswas and Haaman noted that numerically integrating the above differential equations yields (Biswas and Haaman, 1986):

$$x(dt) = x_o + (dt/2) [(1 - g' dt) v_o + dt\, h(y_o) + (dt\, e)^{1/2} Z] \tag{21}$$

and

$$v(dt) = v_o + (dt/2) [(1 - g'dt)\ h(y_o) + h(y_o + dt\, v_o) - 2g' [1 - (g' dt/2)] v_o - g' (dt\, e)^{1/2} Z] + (dt\, e)^{1/2} Z \tag{22}$$

where dt is the time step size, g' is the viscous damping

force, x_0 and v_0 are respectively the initial positions and initial velocities. And $h(y_0)$ is the internal force depending upon the positions of the atoms. This is the force calculated from the Stillinger and Weber silicon potential. The e is the product of 2 $g'k_b$ T, where k_b is the Boltzman constant and T is the averaged temperature in degrees kelvin. Finally Z is a single random variable derived from a gausian with mean of zero and standard deviation of 1.0 (BH,1983).

Note that setting the viscous damping force, g', equal to zero reduces the Langevin equations to the more familiar form of molecular dynamics equations presented earlier. The resetting of g' was used to toggle the molecular dynamics code from the Langevin equations to the earlier set of molecular dynamics equations.

The Two Annealing Techniques.

Annealing of crystals has been done practically in industry as a means of strengthening materials. The material is heated to a high temperature at which the crystalline atoms are free to arrange themselves in new patterns. These new atomic arrangements tend to be in the patterns prescribed by the lowest energy minimum of the perfect crystal structure. To achieve an amorphous, non-crystalline arrangement farthest from the perfect crystal structure, the material is cooled very rapidly through a quenching process. If a more perfect crystalline structure

needs to be achieved, as in the case of lenses for telescopes, another process is used. The material is softened through the application of heat and then allowed to cool in gradual stages. The gradual nature of this cooling process allows the atoms time to arrange themselves into their preferred states. This rearrangement tends to form a perfect crystal structure (Chalmers, 1982:109-111).

The perfect crystaline atomic arrangement through the latter annealing process can be modeled via computer simulation. Biswas and Hamaan sugested a technique for modeling the annealing of sililcon utilizing Langevin dynamics. This process is computational time intensive as the atomic positions must be calculated 200-300 times at each temperature increment. Sabochick proposed using a combination of molecular dynamics and molecular statics to model the annealing process. The two techniques are described below along with a number of computational tools used in each technique. The last section of this chapter will deal with the common computational tools used such as the constraining method and related parameters used to hold the atoms together (Biswas and Haaman, 1986).

Biswas and Haaman Annealing Method.

Biswas and Haaman's annealing technique consists of heating the crystal to a melt state and allowing the atoms to reposition themselves at this plateau temperature

utilizing Langevin molecular dynamics. Then they incrementally lower the plateau temperature until the system attains the temperature of absolute zero. At each plateau they allow the atoms to reposition themselves by utilizing Langevin dynamics. This gives a final annealed configuration that they believe is closer to the global minimum configuration than that which would be obtained using molecular statics alone. One time through each temperature plateau calculations will be refered to as a cycle in this paper.

The quality of the annealed configuration depends on the number of incremental temperature plateaus allowed. The smaller the temperature differential is between the plateaus the more perfect the crystal configuration formed. The amount of time an atom stays at the higher temperatures is inversely proportional to the difference in the temperatures at each plateau. At the higher temperatures the atoms have enough energy to avoid being trapped in higher energy metastable states. Unfortunately, as the temperature differential decreases in size, the number of heating and cooling cycles, Ncy, increase. The differential temperature or energy change, Dea, was set before the heating and cooling cycles were implemented. The relationship was:

$$Dea = Ea / Ncy \tag{23}$$

where Ea is the plateau temperature distributed by adding

Ea amount of energy to each atom. At the end of each heating and cooling cycle the temperature is decreased per the following equation:

$$Ea_{new} = Ea_{old} - Dea. \qquad (24)$$

Thus the greater the number of cycles the less the temperature differential between the cycles as mentioned briefly before. By increasing the number of cycles the annealing of the crystal will approach the global minimum configuration. Biswas and Haaman in their article also explain that the random walk nature of the Langevin equations should allow the atoms to anneal out of metastable states. This results from the probability that the walk will be uphill as well as downhill in the potential (Biswas and Hamaan, 1986:896).

Parameters

BH chose their time step size to be small such that g' * dt = 0.2 as this value yielded stable trajectories of the particles. Their initial starting temperatures were set at 0.5 eV and 0.24 eV etc. in reduced units. Temperatures in the range of approximately 1.0 - 2.0 eV they found caused the crystal to disassociate into individual sets of small atom groups (BH,1986). When evaluating the parameters to be used in their technique with our code we found that Ea of 0.5 eV, with Nsteps of 300 and dt of 0.07 caused the cluster to disassociate even using the constraining potential

delineated later. However at Ea of 0.25 eV, Nsteps of 300, and dt of 0.1 the cluster of atoms held together. Thus the latter set of parameters were used in the production runs.

Note the above parameters were given in reduced units where dt of 1 unit is equivalent to 1.85 picoseconds (BH, 1986:897). Once these parameters were set the only variable that was allowed to change was the number of cycles (Ncy) through which the atoms were allowed to be heated and cooled.

BH Computational Tools

Biswas and Haaman state that the general conclusions drawn from their article can be utilized no matter what potential is used to calculate the interatomic forces. Although Biswas and Haaman used Stillinger and Weber's potential, their article implies that they modified the three body term by writing it as the sum of a number of two body terms (Biswas and Haaman, 1986:897). This modification allowed them to calculate the forces and energies in N^2 steps instead of the usual N^3 steps required for the three body term. We used the three body Stillinger and Weber (SW) potential with certain parameter modifications specified in Chapter Two. The SW interatomic potential was used in our code for both techniques. However we also included other modifications to the code that reduced the number of time steps required. These modifications were used in both the new and BH annealing techniques and are described in more

detail by Thee (Thee, 1986:28-36).

New Annealing Method.

The new annealing technique proposed in the present work uses a combination of molecular statics and molecular dynamics. The crystal is heated so that the system is in a liquid amorphous state. This is done by imparting to each atom a high energy. This energy impartation to each of the individual atoms will be referred to, for convenience, as a temperature change. The atoms are then allowed to move according to the dictates of the interatomic potential via the molecular dynamics code. Then to bring the atoms to a metastable configuration the statics code is employed. Note that the statics portion of the code also employs the interatomic potential to bring the atoms down to their lowest energy configuration. The temperature is then incrementally reduced. The above process of utilizing molecular dynamics to move the atoms and molecular statics to reposition the atoms to their metastable state is repeated for this new temperature. This cyclic process is repeated until the decremented temperature reaches absolute zero.

The molecular dynamics portion of the new method allows the atoms the freedom of motion necessary to achieve an annealed crystal. This freedom allows the atoms to rearrange themselves in such a way as to avoid being trapped

in local minimum configurations. BH essentially used this same underlying philosophy in their technique. However to achieve the minimum energy configuration BH had to choose their step size to be extremely small otherwise their integrator would become unstable (BH,1986:897). The smaller the step size, the larger amount of computer time required. As the statics routine forces the atoms to a minimum configuration in a very short period of time this new annealing method should be computationally faster than BH's method.

Parameters

N_{steps}, E_a and dt were the parameters that required setting for the new annealing technique. If dt is extremely small the atoms do not move significantly and the new technique requires a large number of N_{steps} to move the atoms. Recall that the MD portion of the code moved the atoms in such a way that when the statics technique was applied a new minimum configuration was probable at each of the higher temperature plateaus. Thus with too small of a time interval, dt, the system would not anneal properly. On the other hand, if dt is chosen to be too large, the atoms will move too far. This large movement may result in atoms passing through each other. As this process is unrealistic the timestep must be selected such that the atoms move significantly enough to anneal the crystal while still representing the physical boundaries placed on the crystal by classical physics.

These parameters, N_{steps}, dt and E_a are related by a simple formula given below:

$$dist = dt \quad N_{steps} \quad E_a^{1/2} \tag{25}$$

where dist represents the overall distance the atoms in the system have moved. To optimize this distance moved without the atoms passing through each other, the distance was set to 1 unit which is slightly less than the bondlength of 1.12 units. By maximizing E_a, minimizing N_{steps} and using the above formula to calculate dt the parameters were chosen. Thus the parameters chosen for the new annealing technique were N_{steps} of 20, E_a of 0.5 units, and dt of 0.07 units for the first statics runs. Subsequent runs used N_{steps} of 20, E_a of 0.25 and dt of 0.1 (Table VII). This latter set of

TABLE VII
Annealing Comparison Run Parameters. New Tech1 and Langevin1 are respectivey runs made with the new technique and B&H's Langevin technique starting at a metastable state with Potential energy of -44.5934. And similarly the techniques with 2's represent runs made starting at the metastable state having a potential energy of -43.0642.

Parameters	New Tech1	Langevin1	New Tech2	Langevin2
E_a	0.50	0.25	0.25	0.25
N_{steps}	20	300	20	300
Dt	0.07	0.10	0.10	0.10
Gamma	0.00	0.02	0.00	0.02
Rsw	6.21	6.21	7.96	6.21

parameters were used in the BH computation. The second set of data was used in the new annealing technique as the results for E_a of 0.25 was significantly better than runs with E_a of 0.5. Note the above parameters are given in reduced units. Once these parameters were set the only variable that was allowed to change was the number of cycles, Ncy, through which the atoms were allowed to be heated and cooled.

A Procedure Used in Both Annealing Methods.

Constraining Potential.

We found that the addition of a constraining potential subroutine was necessary in the molecular dynamics portion of both techniques. Without the addition of this restraint the results of the BH Langevin and new annealing method's atomic configurations disasociated. That is the resulting system had fragmented into smaller clusters of atoms when an E_a of 0.5 or 0.25 eV was applied. The constraining potential was derived such that within a certain fixed radius the constraining force, F_{con}, and constraining energy, E_{con}, terms were negligible. Outside the chosen radius E_{con} and F_{con} were large enough to effectively return any straying atoms back within the circular boundary defined by the radius. This radius was designated as the switch radius, Rsw, and was used as a toggle parameter distinguish-

ing between the negligible and large constraining potentials.

The energy and force equations are:

$$E_{con} = L_1 r^2 \qquad r \leq rsw \qquad (26)$$

$$E_{con} = a_0 + a_1 + L_1 r^2 \qquad r > rsw \qquad (27)$$

and

$$F_{con} = -2L_1(x_i - x_{avg}) \qquad r \leq rsw \qquad (28)$$

$$F_{con} = -(a_1/r + 2L_2)(x_i - x_{avg}) + (1/N)\sum(a_1/r)(x_i - x_{avg}) \qquad r > rsw \qquad (29)$$

where E_{con} and F_{con} are respectively the constraint energy and force. L_1 and L_2 are respectively the inner and outer radius constraint parameters. The assigned values of these two parameters determine the strength of the force field applied to the atoms under their jurisdiction. As we require a negligible force within Rsw, L_1 is equal to 0.0001. And L_2 is equal to 0.1 as a fairly large force is required outside of the radius Rsw. N in the above equation is the number of particles, a_0 and a_1 are constants selected that the toggle radius values are continuous and smooth. The constraints are:

$$a_1 = 2(L_1 - L_2)\,Rsw \qquad (30)$$

and

$$a_2 = -(L_1 - L_2)\,Rsw^2. \qquad (31)$$

And r_i is the radial distance given by the following equation

$$r_i = [(x_i - x_{avg})^2 + (y_i - y_{avg})^2]^{1/2} \quad (32)$$

where x_i and y_i are the two-dimensional position of atom i in rectangular coordinates. The center of the circular system is represented by x_{avg} and y_{avg}. The equations are:

$$x_{avg} = \sum x_i/N. \quad (33)$$

Note that Eqs. (28), (29) and (33) only present the x component of the force. These equations would thus have to be repeated for the y components.

Rsw was calculated for all but the second BH Langevin runs by calculating the radius of the outer most atom from the center of the initial configuration used. Then a buffer zone of 1.0 was added to this calculated value. For the second Langevin run the value of 6.21 was hand set to provide a tighter boundary.

The above equations were used every time the forces and energies were calculated via the interatomic potentials. If the atom was within the prescribed radius Rsw the change in the total energy and force of the atom cluster was negligible. If on the other hand, the atom was beyond the prescribed radius the interatomic energy, E, and the interatomic force, F_i, terms were updated with a non-negligible additive term.

The equations used to update the potential energy and force are:

$$E = E + \sum E_{con} \tag{34}$$

and

$$F_i = F_i + F_{con}. \tag{35}$$

Note once again only the x component of the force is given. A y component equation is also neccessary to model the two-dimensional 36 atom cluster that was chosen as our test case.

IV. SILVER CALCULATION

Dagens' Potential Calculations.

The purpose of the first part of this thesis is to verify whether two new potentials by Dagens are more accurate than an older potential. The basis for this comparison is the experimental data value of 1.11 eV for the vacancy energy of formation for silver (Lam, 1983:2514). The value for the vacancy energy of formation was computationally calculated for the three potentials and compared to the above experimental data value.

To validate Dagens' potentials the Modified Fletcher Powell, MFP, method of molecular statics, MS, was employed. This method was used as a working molecular statics code was available. In particular, molecular statics was used in conjunction with Dagens' potentials to calculate the energy of formation of a single vacancy.

The energy of formation of a vacancy was calculated by first utilizing a perfect crystal with no defects. The minimum energy of the perfect crystal was then determined by using the MFP MS code. Next one or more of the inner atoms were removed, forming a single or multiple vacancy. The minimum energy of this modified crystal was then calculated. These minimum energies correspond to the stable or metastable states of the system. To calculate the energy of formation of a vacancy, the following mathematical equation

was employed:

$$E_v^f = \frac{1}{2}\sum_{l\neq l'}^{N-1} \phi(|r'_l - r'_{l'}|,n) + (N-1/N)\sum_{l\neq l'}^{N-1} \phi(|r'_l - r'_{l'}|,n)$$

$$+ \frac{1}{2}\left(\frac{-1}{6}\sum_{l} r_l^0 \frac{\phi^{eff}}{r}\right) \qquad (36)$$

where the first term is the minimum energy of the perfect crystal found by using the molecular statics technique previously presented. The second term summation is the minimum potential energy of a crystal with a vacancy, an inner atom removed. This summation term is multiplied by a modifying term. In this term, n is the number of atoms in the perfect crystal and v is the number of vacancies in the modified crystal. The last term is the virial term which compensates for the changed volume of the system. The virial term is calculated during the perfect crystal energy minimization process (Lam,1983).

Code Verification.

To verify that the code was working properly several calculated values were compared with Lam's values for various radius dimensions. The operational computer code

was verified by calculating the vacancy energy of formation for the old potential. This value was compared to Lam's published value (Lam,1983; Lam,1986). This process resulted in close correlation with the values Lam obtained. The results of this check is presented in Table VIII. Lam's data values were based on a 864 atom ensemble with a cut off radius of 11.632 A° (Lam,1983). The calculated values were determined using a 256 atom ensemble with a cut off radius of 6.807 A°.

TABLE VIII

Multiple Vacancy Formation Energies. The table compares Lam's Values for the old Dagen potential values with this projects calculated values.

VACANCIES	LAM'S VALUES	CALCULATED VALUES
SINGLE-VACANCIES	1.37	$1.3\bar{4}$
DI-VACANCIES	2.70	$2.0\bar{8}$
TRI-VACANCIES	3.65	$3.7\bar{7}$
TETRA-VACANCIES	4.62	$4.6\bar{8}$

The cut-off radius is another parameter that can be used as a rough comparison to gauge the accuracy of the code. The cut-off radius is the minimum distance the atoms can be from one another while still experiencing a

negligible force from the interation (Fig 6). Atoms outside the cut-off radius of a particular atom do not affect that particular atom. Also atoms that are within the cut-off radius of a particular atom are influenced by that atom and themselves affect the atom. The cut-off radius for this paper was taken to be a few lattice constants away from any particular atom. Lam also chose the cut-off radius for Dagens silver potentials to be at least twice the silver lattice constant of 4.087 A°. In addressing the verification of the old Lam potential the cut-off radius was set and then refined during the calculation of the vacancy formation energies. Lam calculated the value of the cut-off radius for the 864 atom system to be 11.737 A° (Lam,1983). My calculated values were 6.807 A° for the 256 atom system and 12.248 A° for the 864 atom system.

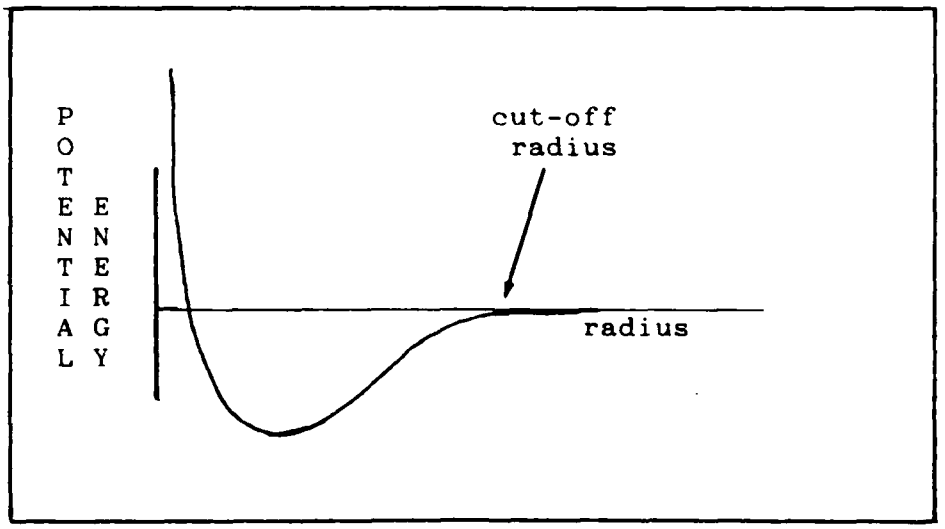

Figure 6. Cut off Radius. Illustrated with a pair potential for two isolated atoms.

Results and Discussion

The computational tools of molecular statics were used to verify Dagens' two new potentials. The results obtained are presented Tables IX and X.

TABLE IX

Vacancy Formation Energy of the Silver Potentials. (256 atom ensemble)

Reference	cut off radius (A)	Virial (eV)	Formation Energy (eV)
Actual Experimental Results	N/A	N/A	1.11
Lam's Results (old potential)	11.737	-2.096	1.37
Calculated Value (old potential)	6.807	-1.991	$1.3\bar{4}$
Calculated Value (new potential 1)	6.923	-0.716	$0.5\bar{8}$
Calculated Value (new potential 2)	7.014	-0.075	$0.3\bar{7}$

The experimental value is the main comparison value. This value, 1.11 eV represents the energy of formation of a single vacancy in a perfect crystal. The removed atom is assumed to have moved from the interior of the system to infinity thus the 256 and 864 atom ensembles should yield

TABLE X

Vacancy Formation Energy of the Silver Potentials. (864 atom ensemble)

Reference	cut off radius (A)	Virial (eV)	Formation Energy (eV)
Actual Experimental Results	N/A	N/A	1.11
Lam's Results (old potential)	11.737	-2.096	1.37
Calculated Value (old potential)	12.248	-2.109	1.41
Calculated Value (new potential 1)	6.923	-0.643	0.51
Calculated Value (new potential 2)	9.869	-0.039	0.31

approximately the same results. The energy of formation is one of the first parameters commonly checked when validating a potential and thus was selected as the first verification point for the Dagens' potentials under consideration.

The calculated values in tabular form on the preceding pages are the values obtained using the molecular statics technique for respectively a 256 atom three-dimensional ensemble and a 864 atom three-dimensional ensemble. Lam's values for his old potential were calculated utilizing a 864

atom three-dimensional ensemble and are as noted above also approximately valid for the 256 atom three-dimensional ensemble.

The last column of data in each table is the comparison values. Note that the two new potential values for the 256 atom ensembles vary respectively by 48% and 67% from the experimental data value. While my calculated value of the old potential varies by only 21%. The 864 atom ensemble yields similiar results. Thus the old Dagens potential portrays more accurately the vacancy formation energy than the two new potentials do. As the vacancy formation energy for the new potentials is less accurate than the previous potentials value, the conclusion was reached that the previous Dagens potential should not be replaced by either of the two new Dagens potentials.

IV. ANNEALING CALCULATIONS

The purpose of the second part of this thesis was to investigate a computationally faster method of simulating the annealing of atomic clusters. This second task required the comparison of a technique presented in an article by Biswas and Haaman and a new anealing technique. The Biswas and Haaman, BH, method utilized Langevin dynamics to anneal the material (Biswas and Haaman, 1986). The new method used a combination of molecular dynamics and molecular statics to simulate the annealing of the material in question. These two techniques were compared on the basis of which method achieved a global minimum or near metastable state computationally faster than the other procedure. Both methods were evaluated using a modified form of the Stillinger and Weber, SW, silicon potential. In general the atoms were thermally excited to the melt point and then allowed to cool through a series of heating/ cooling stages to a global minimum configuration (Biswas and Haaman, 1986).

Our goal in comparing the two techniques was to find the method which reached a particular minimum in the fastest time. Also required was that the atoms anneal to their global minimum configuration or a metastable configuration near the global minimum. The major portion of the code that both the statics and two dynamics routines frequently use is the calculation of the interatomic forces and energies as a function of the atoms' positions. This subroutine, Eval,

required a large portion of computer time as it calculated the energies and forces using the modified SW potential. Keeping track of the number of times this subroutine is called will give a fair estimate of the relative speeds of the two methods. Also as the two methods were tested on the ASD cray computer, actual CPU times are available and provide another data point in estimating the computational intensity of the two methods.

The simulation crystal was chosen to be a 36 atom cluster. It was determined to simulate this crystal in two dimensions as a two dimensional arrangement is easier to plot and visualize than a three-dimensional arrangement. Also a two dimensional arrangement allowed us to hand calculate the minimum configuration. This was accomplished by hand drawing the 'minimum energy' configuration of the 36 atom cluster. Then counting the bondlengths and assigning a value of 1.0 unit to each of them. Through this process the minimum energy configuration value of -46.0 was obtained (See Fig 7).

Listed below are the differences and similarities in the computational implemetation of both the BH and the new technique. First the parameters for each technique varied (Table VII). Next for the Biswas and Haaman technique, Langevan dynamics were used in place of the usual molecular dynamics to anneal the material. Molecular statics was not used in the Biswas and Haaman technique. Finally, the new method employed the use of second order molecular dynamics

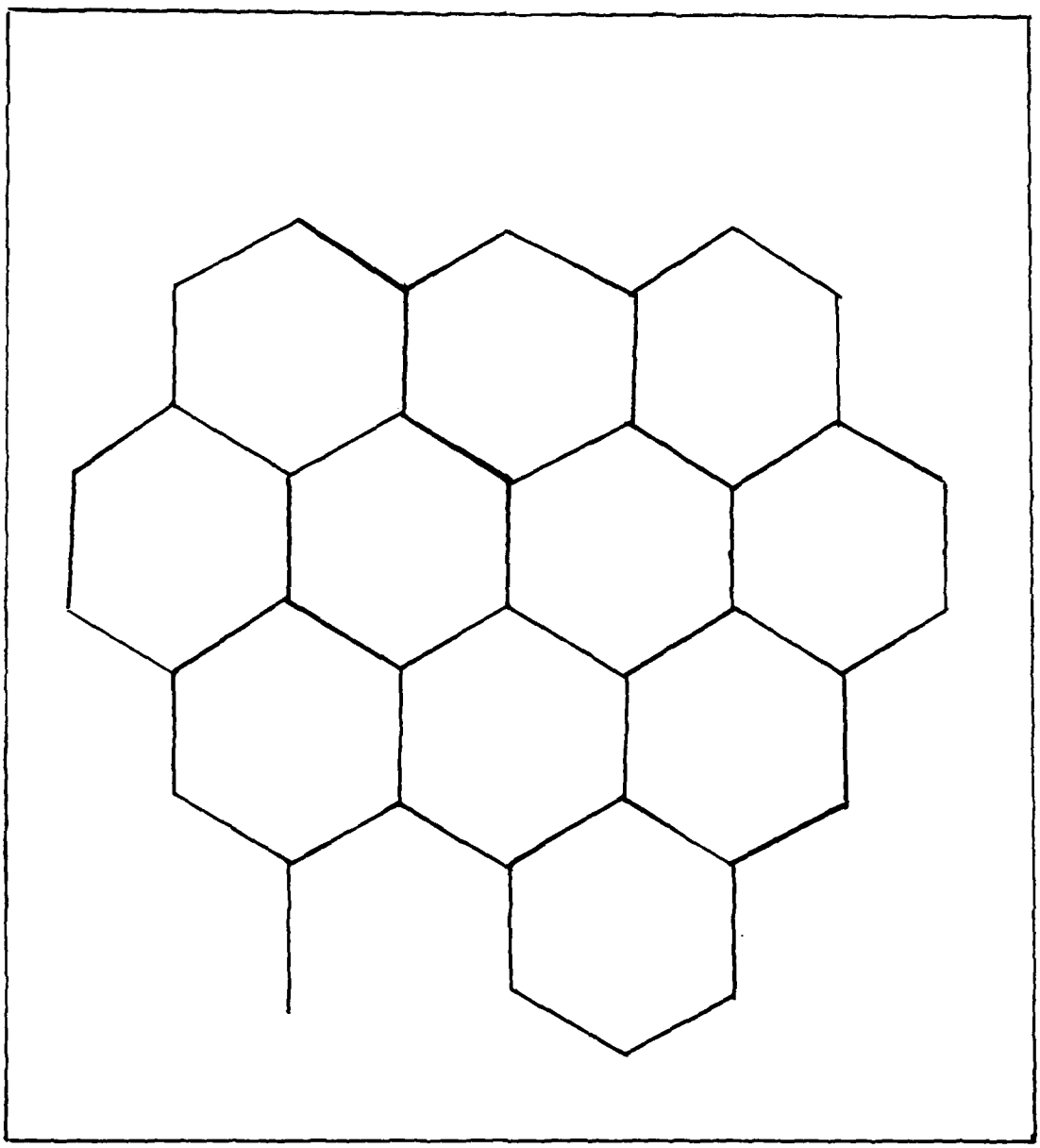

Figure 7. Diagram of Minimum 36 Atom Configuration.

and modified Fletcher Powell molecular statics to anneal the material. The code modification that was used commonly for both annealing techniques was the constraining system boundaries designated by Rsw that contained the system within a circular area. Both methods were run using a two-dimensional crystal of 36 atoms. In both procedures once the parameters were set, the variable used to achieve a better anneal was the increasing of the number of heating and cooling cycles (Ncy). Other than the above, both techniques utilized the same code, therefore a direct comparison of the results from the two procedures can be made.

Two sets of runs were made to test the two-dimensional thirty-six atom clusters. Each set of runs was accomplished using both techniques with the starting positions differing. The new annealing runs were conducted in such a way that after each temperature decrement a metastable state of the atom configuration was found through the MS portion of the code. Thus the minimum energy states tabulated are the lowest energy minimum found by the MS routine. This minimum energy configuration is not necessarily the final state of the atoms at the end of the run. In the BH Langevin method, however, BH specify that the final results at the end of the BH run is the minimum energy results obtained. These are the BH results tabulated.

The first set of runs started from the minimum energy configuration of -44.59 eV. The results of these runs is shown in Table XI and in graphical form in Figures 8 and 9.

TABLE XI

Set 1 Annealing Runs Results. New annealing Technique and BH Langevin Technique results starting from the minimum energy configuration of -44.593 eV.

Ncy	New annealing Technique	BH Langevin Technique
10		Emin = -43.762 CPU = 110 sec Eval = 6000
20	Emin = -44.593 CPU = 20 sec Eval = 1300	Emin = -43.064 CPU = 193 sec Eval = 12000
40	Emin = -45.3141 CPU = 36 sec Eval = 2600	Emin = -43.871 CPU = 359 sec Eval = 24000
80	Emin = -45.248 CPU = 69 sec Eval = 5400	Emin = -45.287 CPU = 715 sec Eval = 48000
160	Emin = -45.329 CPU = 131 sec Eval = 11000	

The second set of runs started from the minimum energy configuration of -43.064. The configuration used was the results of the 20 cycle BH Langevin technique in the first set of runs. The purpose of using the prior BH results was to answer the question, 'Can the two methods achieve the -45.3 minimum state from the -43.064 state?' The results

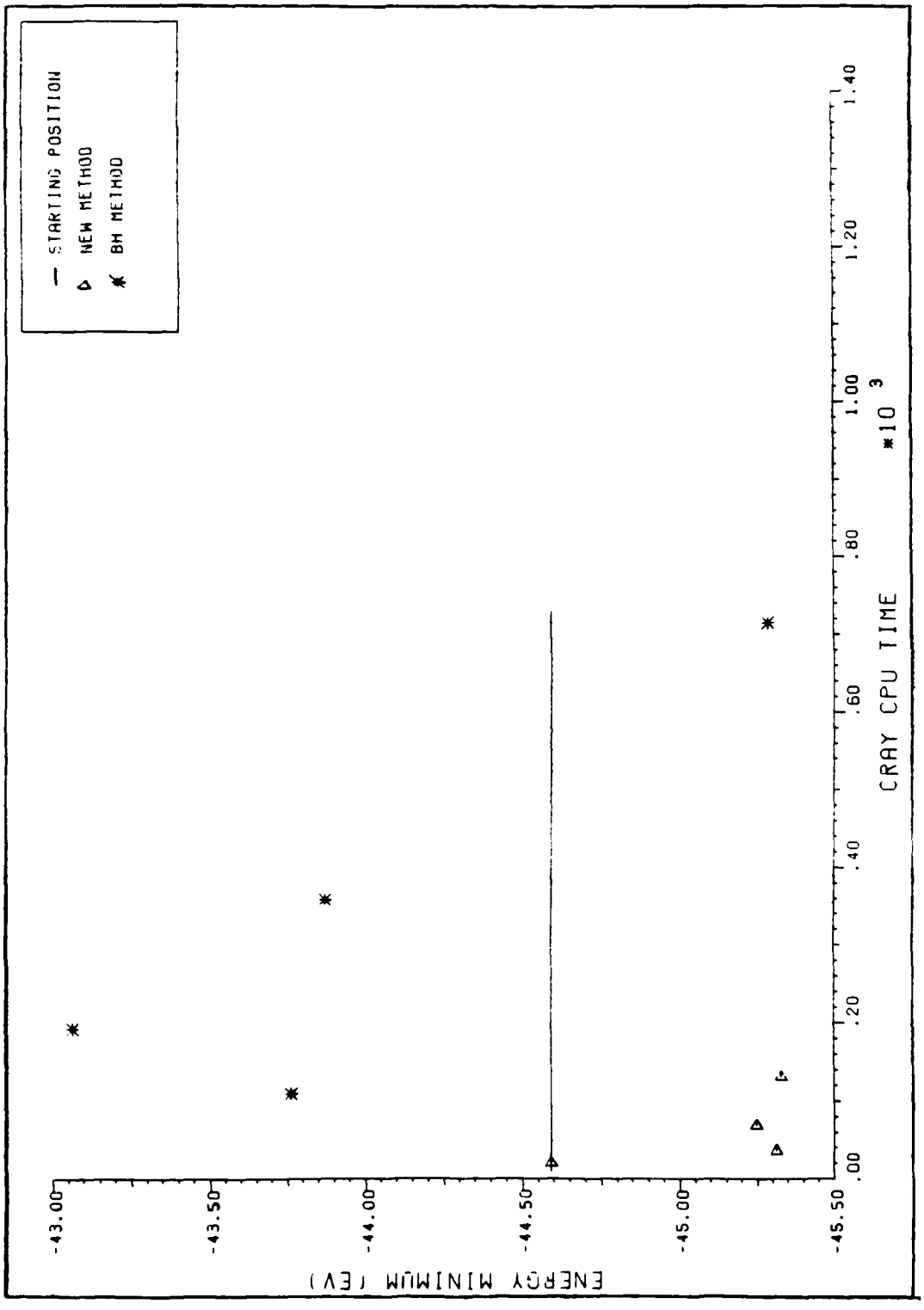

Figure 8. Set 1 Annealing Runs Results. Results starting from the minimum energy configuration of -44.593 eV.

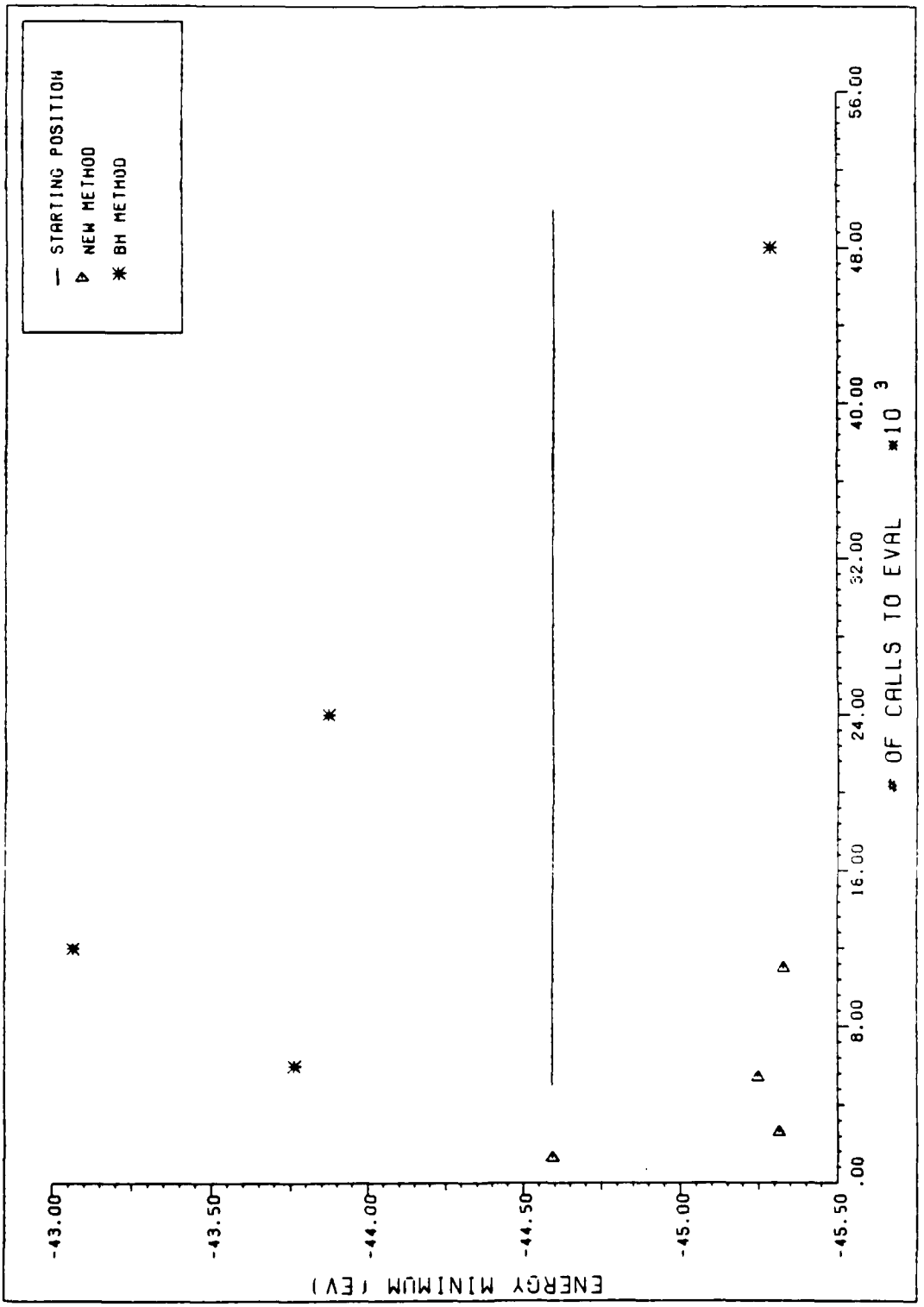

Figure 9. Set 1 Annealing Runs Results. Results starting from the minimum energy configuration of -44.593 eV.

of this new set of runs is portrayed in Table XII and in Figures 10 and 11 on the following pages.

TABLE XII

Set 2 Annealing Runs Results. New annealing Technique and BH Langevin Technique results starting from the minimum energy configuration of -43.064 eV.

Ncy	New annealing Technique	BH Langevin Technique
5		Emin = -42.196 CPU = 62 sec Eval = 3000
10		Emin = -41.771 CPU = 104 sec Eval = 6000
20		Emin = -41.721 CPU = 188 sec Eval = 24000
40	Emin = -44.388 CPU = 38 sec Eval = 2600	
80	Emin = -43.701 CPU = 74 sec Eval = 54000	
160	Emin = -44.351 CPU = 141 sec Eval = 11000	
320	Emin = -45.284 CPU = 287 sec Eval = 23000	

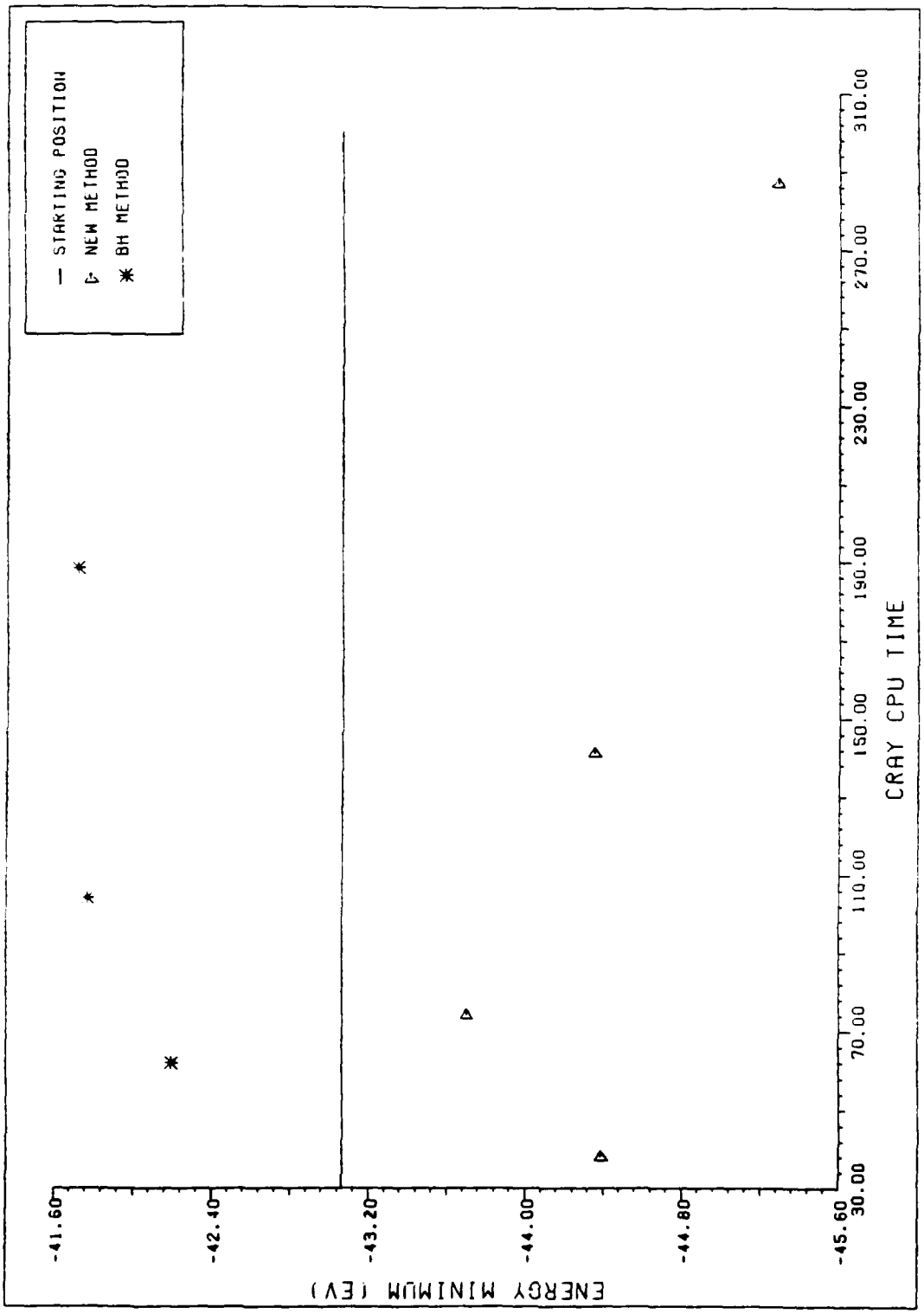

Figure 10. Set 2 Annealing Runs Results. Results starting from the minimum energy configuration of -43.064 eV.

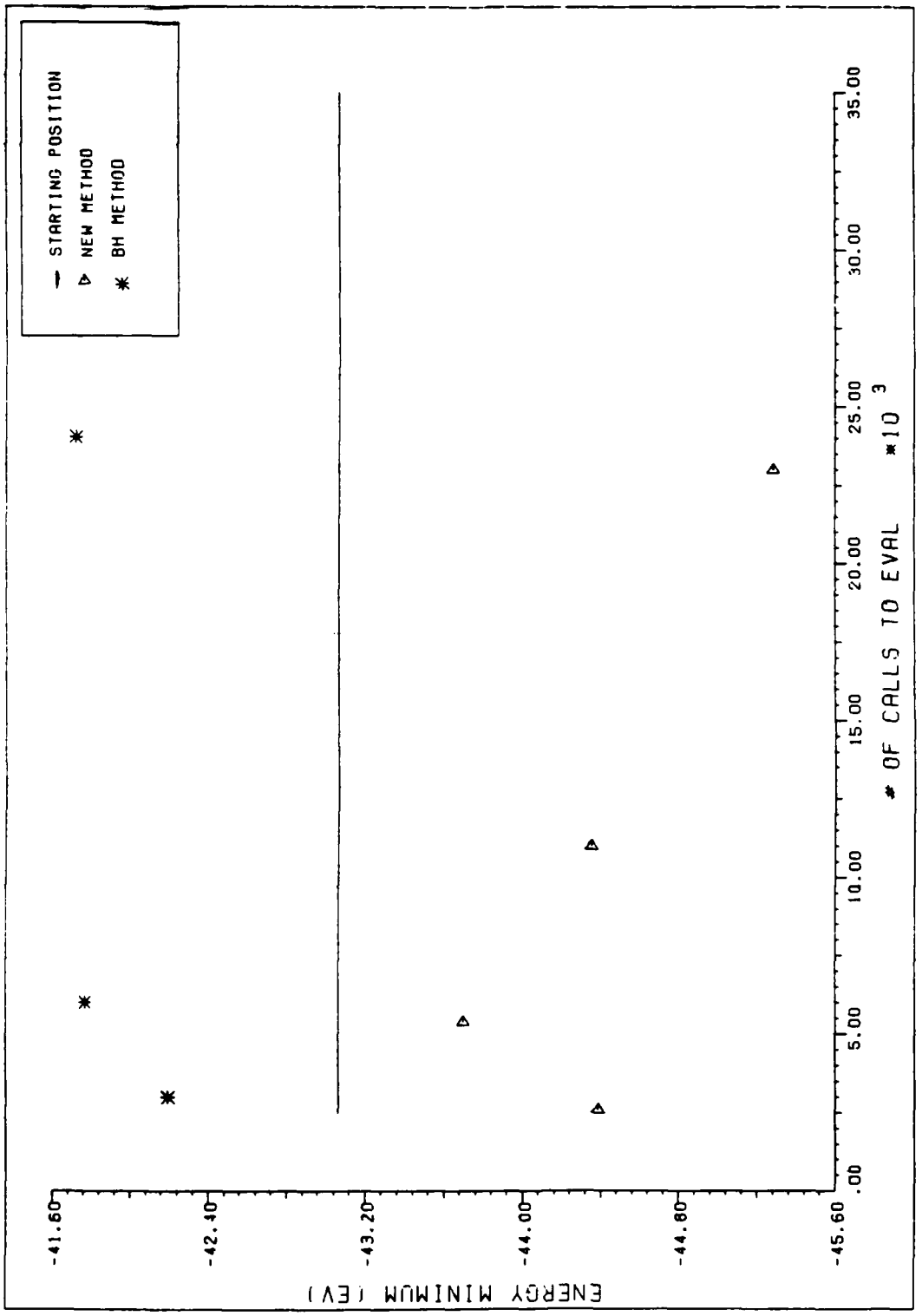

Figure 11. Set 2 Annealing Runs Results. Results starting from the minimum energy configuration of -43.064 eV.

Note that the important comparison parameters in Tables XI and XII are the number of evaluations (Eval) and the CRAY CPU time. The hand calculated minimum energy configuration gave a value of -46.0 Both the new annealing technique and the BH Langevin method achieved -45.3 as their calculated energy minimums in the first set of runs. The important point to note however is the amount of computer time it took each of the two methods to achieve this minimum energy configuration. Where it took the new annealing technique 36 seconds of CPU time and 2600 calls to Eval; the BH Langevin technique reached this minimum energy configuration somewhere between 359-715 seconds and 24000-48000 calls to Eval. Thus the amount of computer time required to reach the same local minimum was approximately a factor of ten difference between the two techniques.

The next set of runs were used as another comparison point. Since the starting configuration was at a higher energy minimum than before it was expected that it would take longer to obtain the local minimum. From Fig. 9 and the data in Table XII one can see that the new technique once again achieved the local minimum faster than the BH Langevin method. Due to a lack of time the BH Langevin runs in set 2 were not extended to the minimum energy configuration value.

A number of two-dimensional plots of the atom configurations accompanying the tabulated energy minimum values, Emin, are shown on the following pages. Note that a slight change in the minimum energy obtained changes the

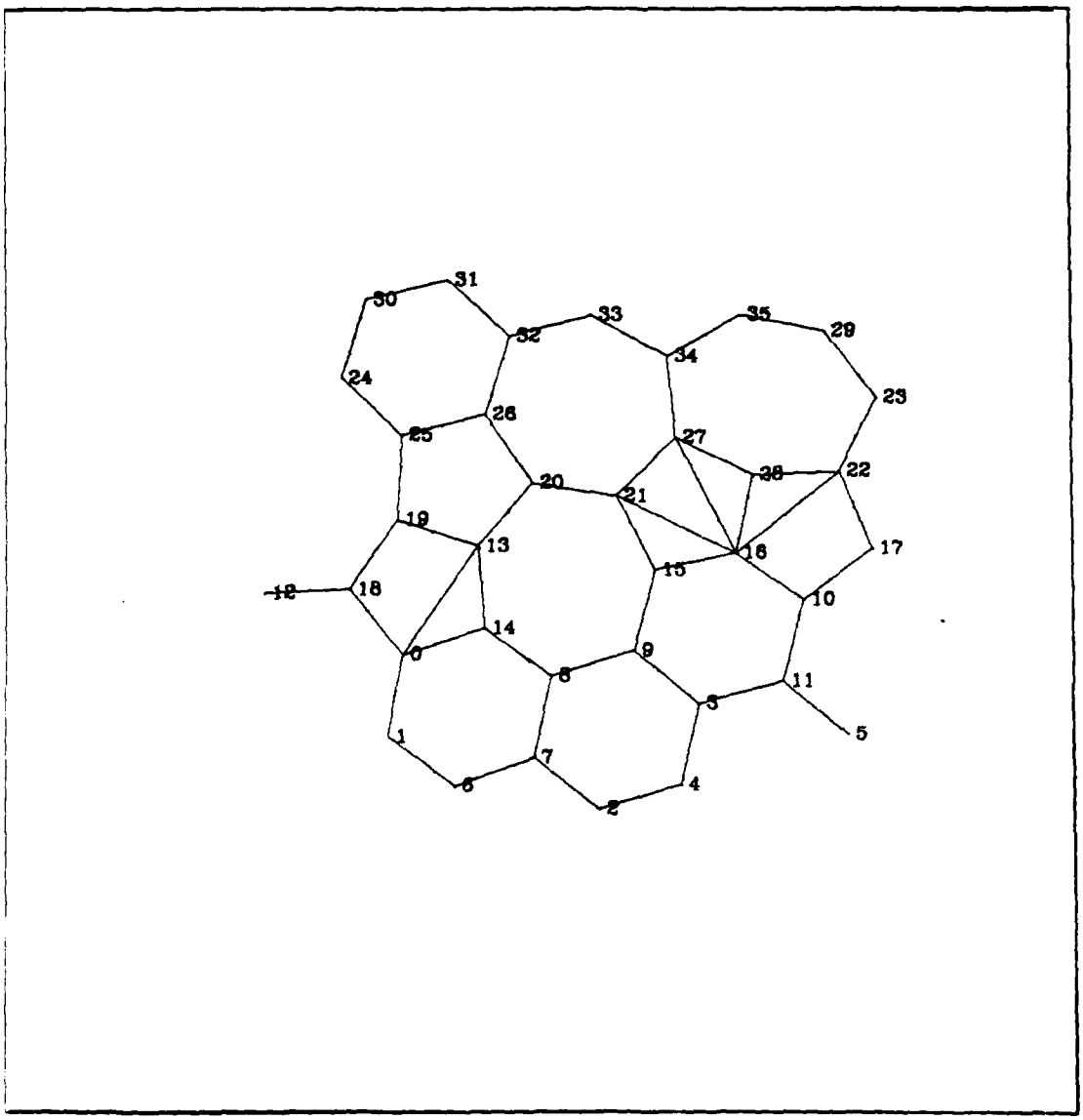

Figure 12. Set 1, New Annealing Technique, cycle 40. New annealing Technique results starting from the minimum energy configuration of -44.593 eV. The above plot corresponds to a minimum energy configuration of -45.314 and took 36 seconds of CRAY CPU time.

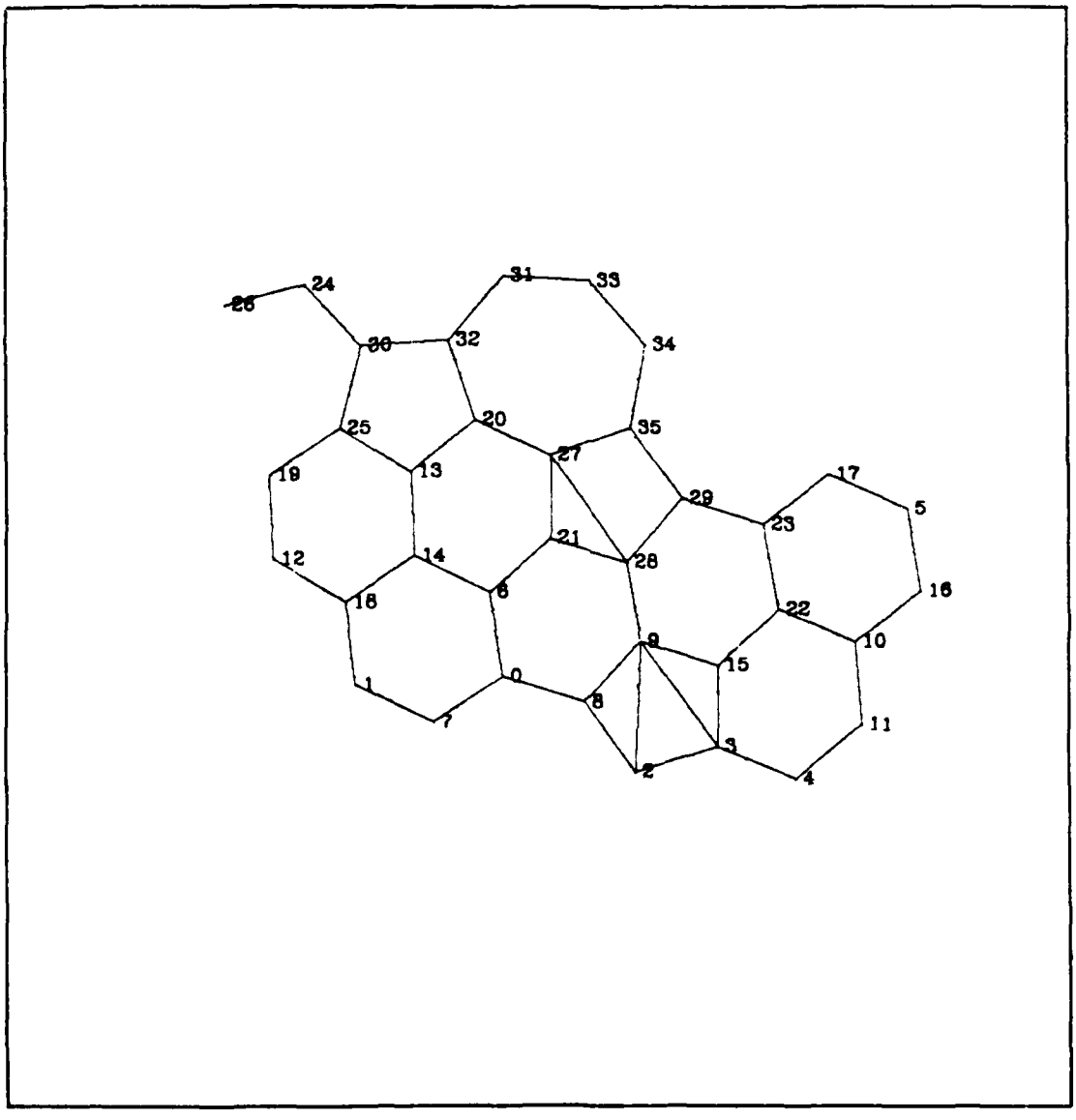

Figure 13. Set 1, New Annealing Technique, cycle 80. New annealing Technique results starting from the minimum energy configuration of -44.593 eV. The above plot corresponds to a minimum energy configuration of -45.248 and took 69 sec of CRAY CPU time.

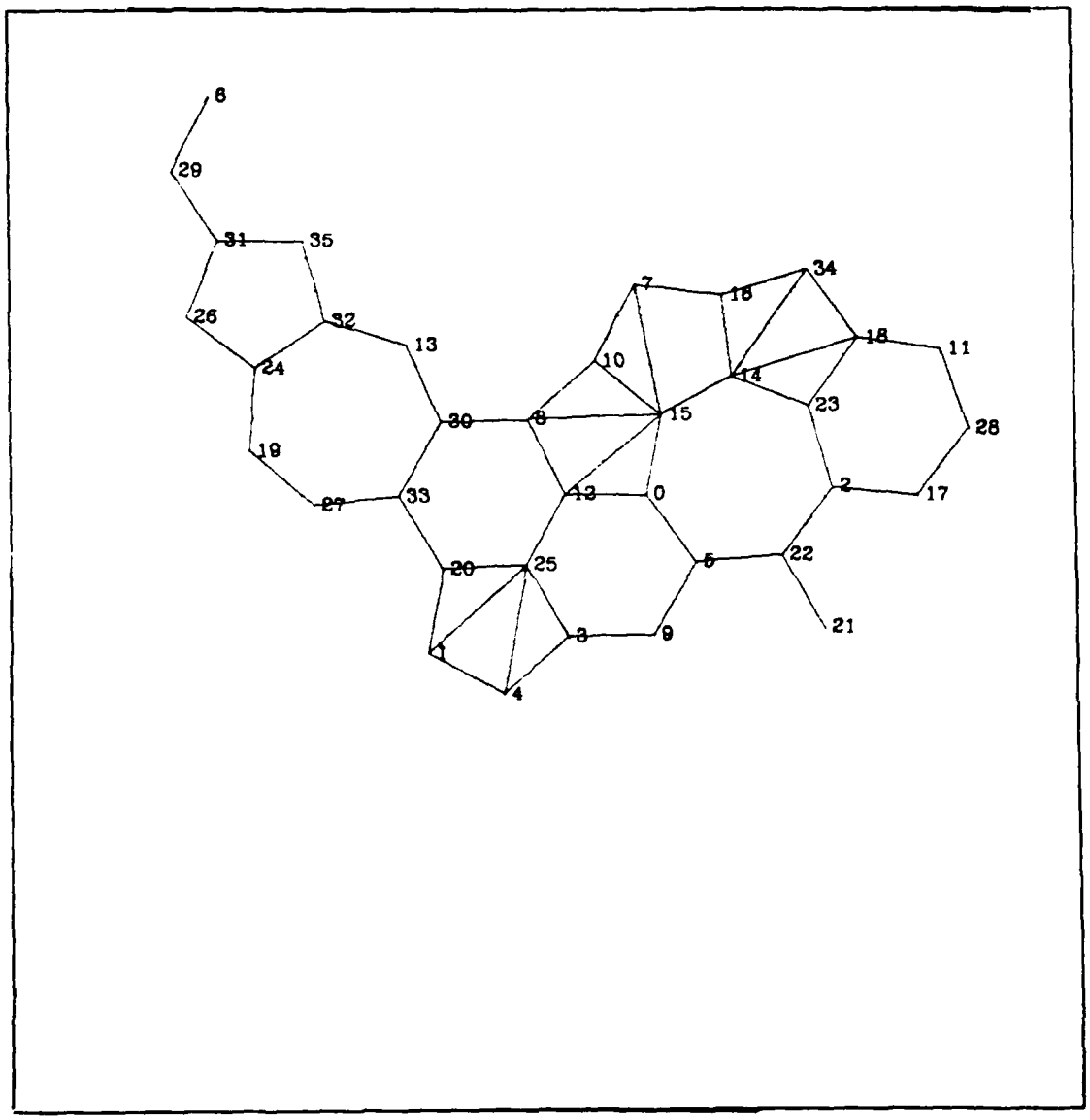

Figure 14. Set 1, BH Langevin Technique, cycle 20. BH Langevin Technique results starting from the minimum energy configuration of -44.593 eV. The above plot corresponds to a minimum energy configuration of -43.064 and took 193 sec of CRAY CPU time.

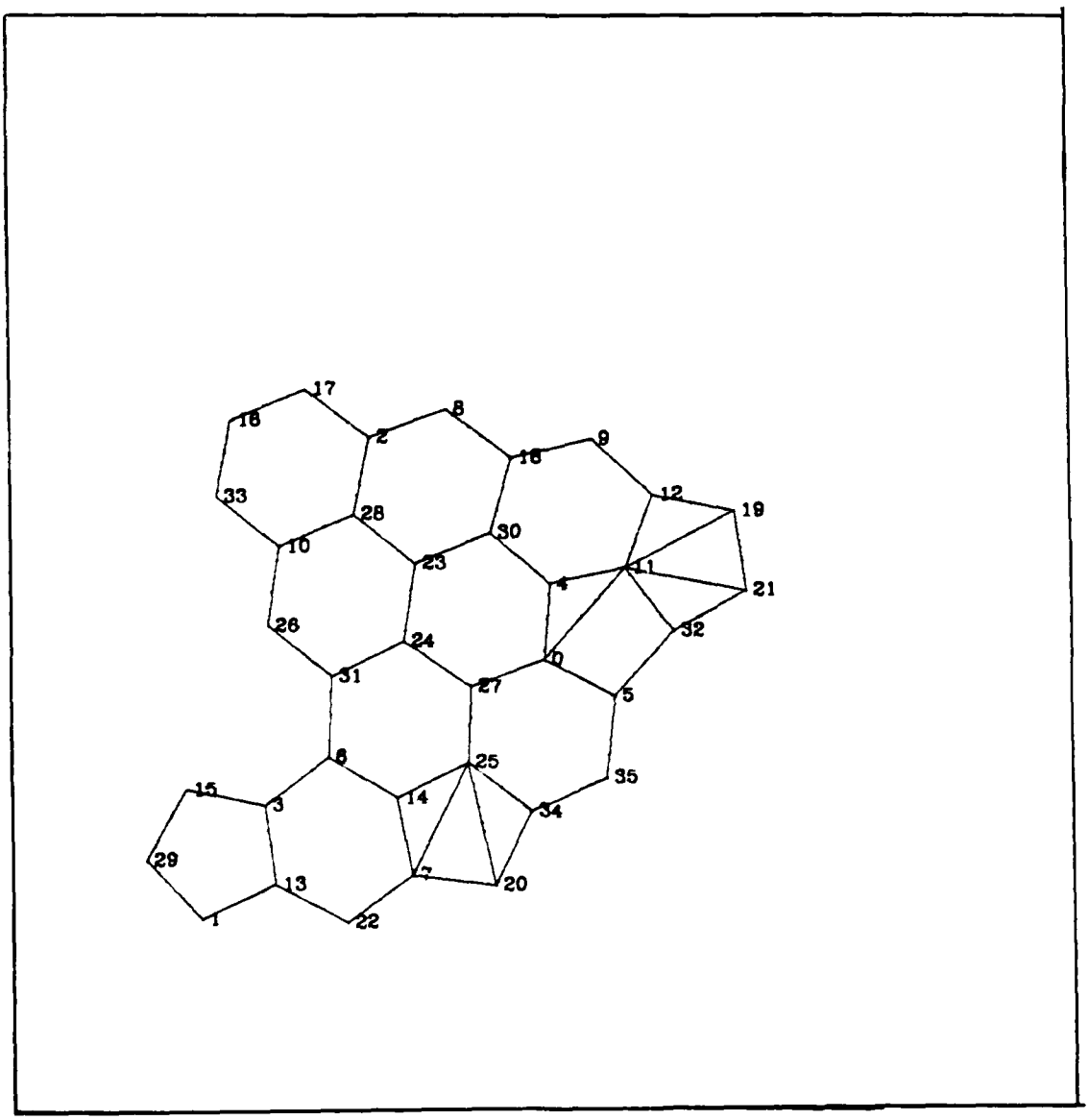

Figure 15. Set 1, BH Langevin Technique, cycle 80. BH Langevin Technique results starting from the minimum energy configuration of -44.593 eV. The above plot corresponds to a minimum energy configuration of -45.287 and took 715 sec of CRAY CPU time.

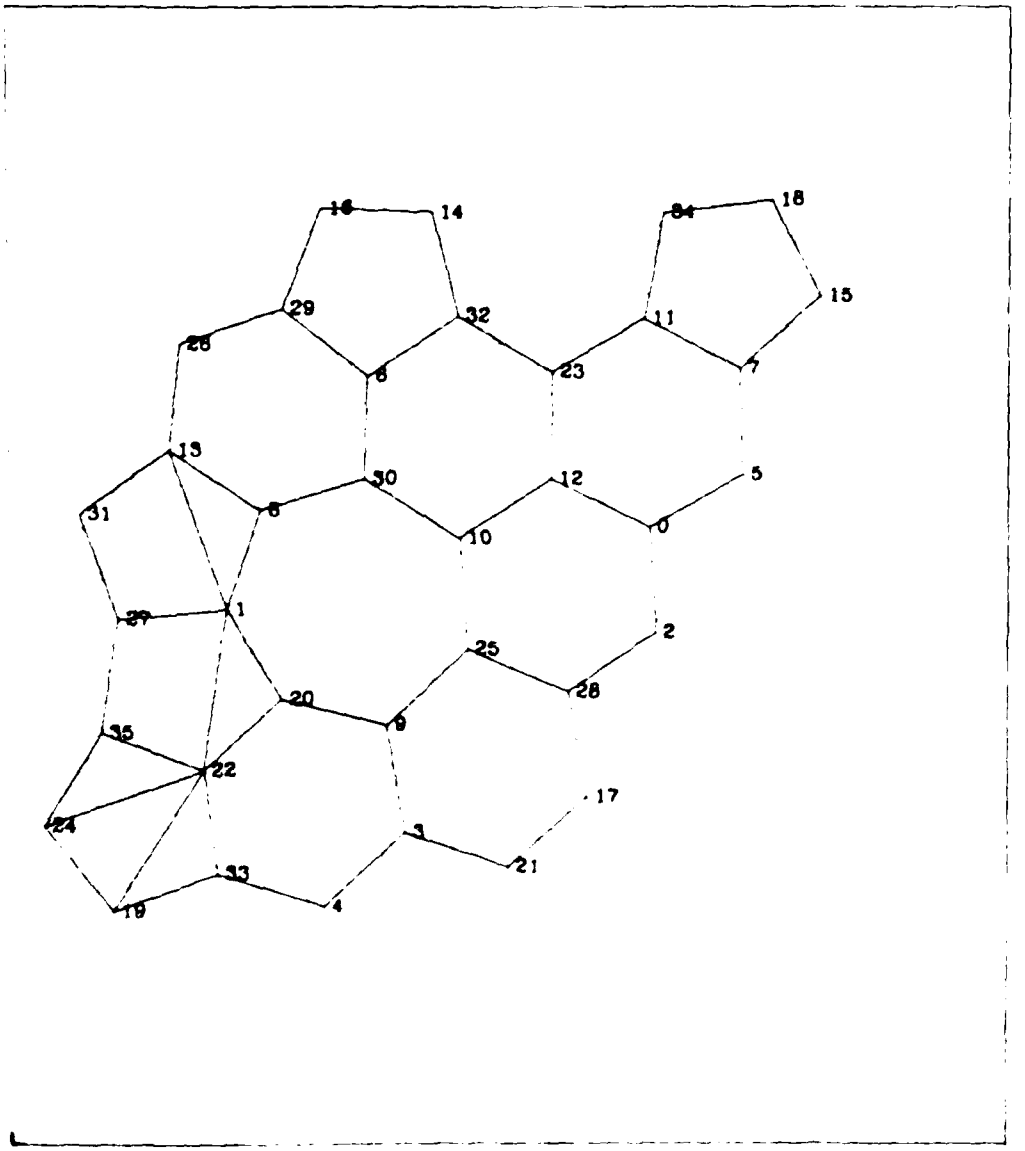

Figure 16. Set 2, New Annealing Technique, cycle 320. New annealing Technique results starting from the minimum energy configuration of -43.064 eV. The above plot corresponds to a minimum energy configuration of -45.284 and took 287 sec of CRAY CPU time.

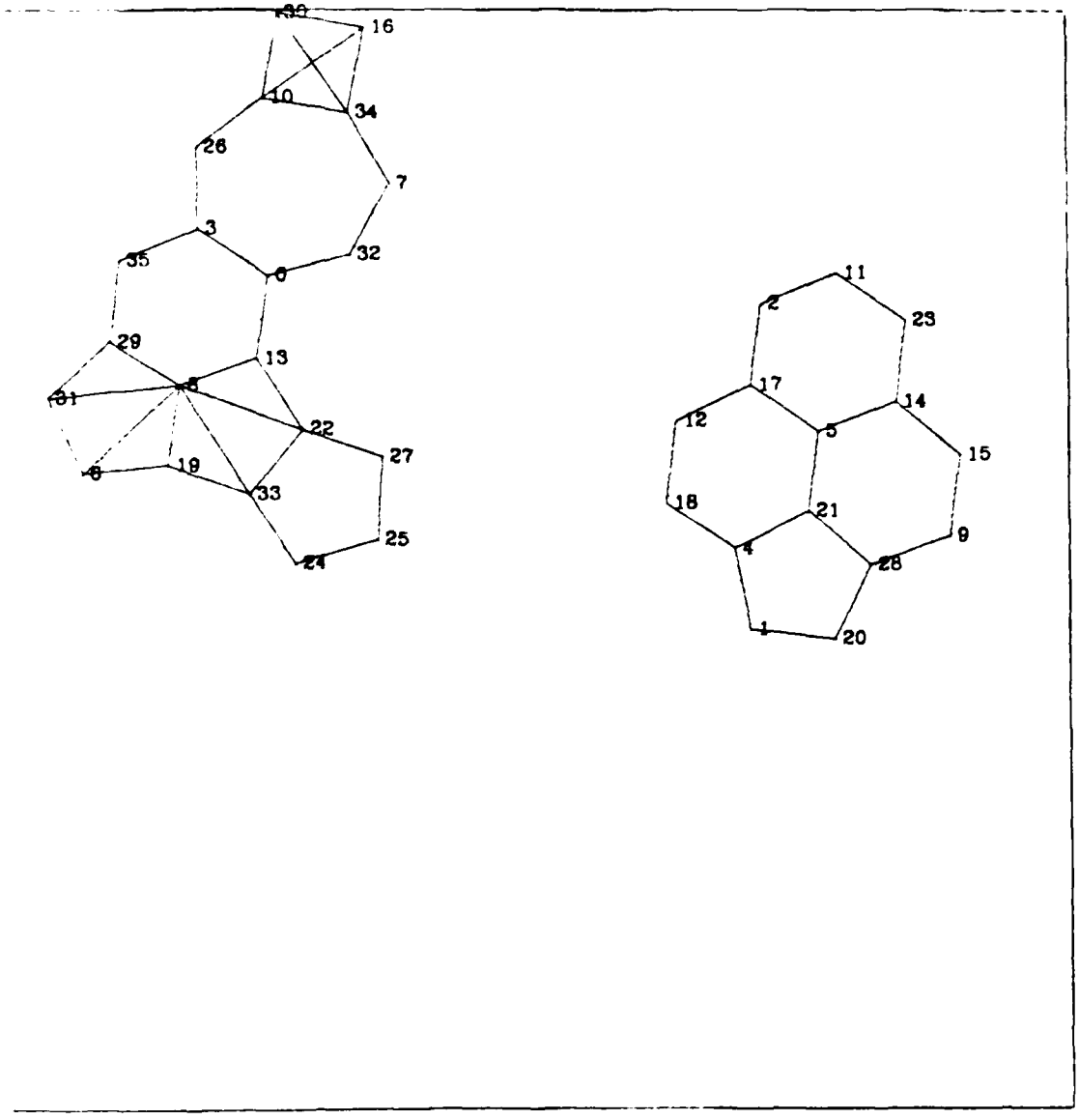

Figure 17. Set 2, BH Langevin Technique, cycle 20. BH Langevin Technique results starting from the minimum energy configuration of -43.064 eV. The above plot corresponds to a minimum energy configuration of -41.721 and took 188 sec of CRAY CPU time.

atomic arrangement of the atoms somewhat. Note also from Fig 16 that the new technique was able to take the higher energy state back down to -45.3 in 287 seconds of CPU time. But, from Fig 17., when we ran the BH Langevin technique the atoms separated into two clusters. By lowering the initial energy and reaccomplishing the run this disassociation may be eliminated. Due to a lack of time we were unable to continue these second set of runs, but the above assumption seems to be valid as the -43.064 eV state was probably passed through on the 80 cycle BH Langevin run in Set 1.

From the small number of data points available the new annealing technique seems to be ten times faster than the BH Langevin method.

VI. CONCLUSIONS AND RECOMMENDATIONS

The purpose of this study was twofold: to determine the validity of two new silver potentials derived by Dagen and to investigate a new technique for finding global minimum configurations. Both of these projects required the use of the atomistic simulation methods of molecular statics and molecular dynamics.

First, molecular statics, MS, was used to test two new Dagens' silver potentials. In particular the formation energy of a single vacancy was calculated using Modified Fletcher Powell, MFP, MS in conjunction with the new Dagens potentials. The two new potential calculated values obtained for the 256 three-dimensional atom ensemble differed by 48% and 67% from the experimental vacancy formation energy value of 1.11 eV. Similarly the calculated new potential values obtained for the 864 three-dimensional atom ensemble differed by 54% and 72% from the experimental value. The calculated vacancy energy of formation value for the previous Dagens potential was found to vary by 21% for the 256 atom ensemble and 27% for the 864 atom ensemble. These results indicate that the old potential correlates more precisely with experimental data than the two new potentials. Thus it is recommended that the older version of the Dagens silver potential continue to be used until a more accurate version is derived.

Second a new technique for simulating the annealing of

a material was investigated, using a combination of molecular statics, MS, and molecular dynamics, MD. The results of this technique was compared with a prior method proposed by Biswas and Haaman utilizing Langevin molecular dynamics techniques (Biswas and Haaman, 1986). In particular, the global minimum configuration of a two-dimensional 36 atom cluster using a modified version of Stillinger and Weber's silicon potential was determined. The resulting computational times of the BH Langevin and the new method were then compared. The resulting data showed that while it took 36 seconds of CRAY CPU time for the new annealing technique to reach a local minimum of -45.3 eV, the BH Langevin method required between 359 to 715 seconds of CRAY CPU time to reach the same local minimum. From these initial data runs it appears that the new technique is ten times faster than the BH Langevin technique. Thus it is recommended that further investigation be made into this new method of simulating the annealing of materials.

The following itemizes a number of recommendations for further investigation of the new annealing technique. Parameters of both techniques need to be optimized more fully. The BH technique was implemented in the last few weeks of the term and parameters were chosen mainly from Biswas and Haamans article. A larger two-dimensional cluster should be annealed as this would indicate what happens at grain boundaries. Finally the code should be extended to three dimensions and the two techniques compared.

In conclusion, two new silver potentials derived by Dagens were tested against experimental data and found to be less precise than the older version of the Dagen silver potential. Also a new annealing technique was compared with, and found to be ten times faster than the BH Langevin annealing method. Investigation of this new annealing method should be persued.

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Two new silver potentials derived by Dagens were validated and a new annealing technique was investigated in this thesis. It was found via a molecular statics technique that the two new silver potentials were less precise than the older silver potential. The calculated vacancy of formation energy of the older silver potential deviated from the experimental value by 21% whereas the two new silver potential values differed by 48% and 64% respectively.

The new annealing technique using a combination of molecular statics and molecular dynamics was found to be approximately ten times faster than a previous method proposed by Biswas and Haaman using Langevin dynamics. In particular, both techniques using a two-dimensional cluster of 36 atoms and a modified version of the Stillinger and Weber silicon potential were tested on the CRAY computer system. The new annealing technique acheived a local minimum configuration of -45.3 eV in 36 seconds of CRAY CPU time while the BH Langevin technique took over 360 seconds of CRAY CPU time to find the same local minimum.


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