

Comparison of Solution Schemes for Atomic Simulation Problems

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A comparison is made between various solutions methods which have been used to find equilibrium configurations in atomic simulation studies. It is found that the conjugate gradient scheme is best although a small modification is necessary from the usual formation to produce good convergence. Low-lying metastable configurations are readily produced and it appears that none of the solution methods used can guarantee a true lowest energy state. Several numerical integrators, used in dynamic simulations and some of the static solution techniques, are also examined and the most appropriate to use in each situation is determined. © 1985 Academic Press, Inc.

INTRODUCTION

The study of materials and their associated defects at the atomic level by computer simulation is a relatively new field of materials research. Materials are studied at this level in order to better understand their macroscopic properties, such as mechanical strength, by observing their behaviour on the microscopic level. Since it is very difficult to examine real materials on this small scale, this work is most easily accomplished by studying model materials using computer simulation.

In a typical atomic simulation problem, a small region of the material is modelled by a set of mass points, representing the atoms, connected by non-linear springs, representing the atomic bonds. The interatomic potentials to be used for these springs are determined from fundamental quantum mechanical considerations or, more commonly, by empirically fitting to known macroscopic properties. This model may represent a gas or liquid [1], a perfect crystal [2], or a crystal containing a defect such as crack or dislocation [3]. The simulations may be divided into two types, static and dynamic. In a static simulation, only the equilibrium arrangement of atoms in the model is found. This permits the determination of the

energy and equilibrium structure of crystal defects [3]. In a dynamic analysis, the motion of the atoms with time is followed and it is the properties of this motion which are of interest. This may be to study the motion of crystal defects [4], nuclear radiation damage [5], or various thermodynamic and lattice dynamic properties [2]. The limiting factor in atomic simulations is computer cost. If computer cost could be reduced, it would be possible to solve larger, more complex models which would improve the accuracy of the results.

Three solution methods are in general use for static solutions and they will be referred to here as simultaneous quenching, individual quenching, and the conjugate gradient method. All start with the model near the final equilibrium position and continuously force it closer to equilibrium. The starting position may be set by using the linear elastic solution for the defect being analysed, for example. Simultaneous quenching [3] involves integrating the equations of motion of the model until the total kinetic energy of the system reaches a maximum. At this point, all velocities are set to zero and the procedure is then repeated. The action of setting the velocities to zero is known as quenching since, at the macroscopic level, this is equivalent to suddenly dropping the temperature to absolute zero. Each of these quenching operations removes some excess energy from the system and, thus, the system continually approaches equilibrium. Individual quenching [4] is similar to this except that each atom is individually quenched, or stopped, when its kinetic energy is a maximum. The conjugate gradient method [6] is an optimization technique which is used to find equilibrium positions defined as potential energy minima. It involves a search through the multi-dimensional configuration space of the system along directions which are constrained to be orthogonal to all previously searched directions. This has been found to give considerably better performance than a simple steepest descent approach. Johnson [7] used a simpler optimization routine for simple crystal defects but general experience with optimization procedures [8] indicates that the conjugate gradient method should be better for complex problems, so Johnson's method was not considered.

This paper presents a systematic comparison of the three static solution techniques described above by examining the solution time required for various problems. Prior to this, a comparison is made of several integration schemes which may be used to solve the equations of motion of the model. This is necessary since both quenching procedures use these integrators and the maximum time step which may be used with them determines how well the quenching procedures will compare to the conjugate gradient scheme. Since this is the primary reason for this test, elaborations such as tunable integrators [9] or variable step sizes were not considered. In spite of this, the results should be of interest for choosing an integration scheme for use in those dynamic problems in which it is desired to observe the model for a given real time, such as those involving studies of defect motion. In dynamic studies in which the evaluation of thermodynamic properties is the primary interest, this may not be the main consideration. Then a given number of integration steps may be desired and this study of the efficiency of integration schemes is of less significance.

INTEGRATION SCHEME TESTS

The pertinent quantity to be used in comparing the relative merits of various integration schemes is the number of interatomic force evaluations per unit model time, since almost all the computer cost is involved in the calculation of these forces. The inverse of this quantity, h/n , where h is the length of the time step used in the integration procedure and n is the number of force evaluations per step, may be considered a figure of merit with computer cost inversely proportional to h/n . For dynamic problems the limiting factor is usually the accuracy of the integration procedure, which must be within the limits of accuracy desired for the simulation. When the integration scheme is used as part of a quenching operation for static solutions, accuracy is not important unless it is very poor since any errors in the model state introduced by the integration scheme will be eliminated, just as the initial error is eliminated as the model approaches equilibrium. The significance of the accuracy of the integration scheme may be assessed by comparing the error introduced into the system by the inaccuracy of the integration scheme with the rate of removal of this error by the quenching algorithms. These are both examined below. The former can be obtained from Fig. 3 and the latter from Figs. 4-7. The rate of decrease of error in the quenching algorithms is at least 20 times the possible rate of increase by any of the integration schemes tested, indicating that the accuracy of the integration scheme is not of great significance when it is used as part of a quenching algorithm. The limiting factor on h/n for static solutions is, then, the system stability limit regardless of accuracy.

The relative merits of different integration schemes are problem dependent [10] and very difficult to determine analytically. As a result, comparison must be made by numerical experiments and several tests of this type are available [10, 11] from which some general conclusions may be drawn. Most of these numerical tests involve only a few degrees of freedom. Beeman [12], however, has presented the results of test of a variety of predictor-corrector methods on a simulation of liquid argon involving several hundred degrees of freedom. The primary interest of the present paper is in the simulation of defects in solids such as iron. This differs from simulations of liquids or gases such as those considered in [12] by using interatomic potentials which are generally steeper at small separations and which have shorter cutoffs. Also, of course, the ratio of kinetic to potential energy in a solid differs considerably from that in the corresponding liquid. These differences will affect the stability limits of the numerical integration procedures, so it is useful to re-examine their behaviour for the case of the simulation of solids. We do so in this section. We also examine a slightly wider range of integration schemes than that studied by Beeman, although he provides more detail on predictor-corrector methods than we do. Several integration schemes have been used in the simulation of solids, by far the most common of which is a simple 2-step difference formula [5]. This will be compared to several others selected from the literature. All the integration schemes tested are summarized in the Appendix.

To select methods which may be applicable, the characteristics of the model

being solved must be considered. Techniques useful for stiff differential equations need not be considered, since the time scale of interest is that of the smallest time constant. The equations are purely second order with no first order components, so only those methods developed particularly for this type of problem will be tested. Most previously published comparisons are for integrators of sets of first-order differential equations only. The results are probably qualitatively applicable to similar second-order solvers, however, so these previously published comparisons will be used as a basis for initial selection of the methods to be considered here.

As stated above, most simulations have used a simple 2-step difference scheme (see Appendix Eq. A1). Many other simple difference schemes are possible, all more elaborate than the 2-step, and a 5-step one (Eq. A2) was chosen as representative of this class [10]. The other main classes are the Runge-Kutta and the predictor-corrector methods. The general conclusions of Lapidus and Seinfeld [10] for the Runge-Kutta methods are that, for the accuracy level needed here, which is relatively low compared to that needed for many other problems, the accuracy at a given value of h/n is nearly independent of the order of the integration scheme used. Similarly the stability limits expressed as h/n are also nearly independent of order. As a result only one Runge-Kutta method, of third order (Eq. A3), was selected for the test [13]. Lapidus and Seinfeld also concluded that, of the predictor-corrector methods, the Adams methods are best in general. The Adams methods are characterized by the number of steps used, q , and the number of iterations of the corrector, s . A comparison of different Adams methods on several problems [11] led Hull and Creemer to conclude that as q increased, the error and stability decreased for a given computer cost. This is consistent with the result of the tests by Beeman [12]. Thus it would be expected that a high q method would be better for accuracy in those dynamic problems in which accuracy requirements dominate, while a low q would give greater stability for static problems. The effect of changes in s was less consistent in [11], with $s=1$ better for some problems and $s=2$ better for others. A $q=4$ (Eq. A5) and a $q=6$ (Eq. A6) method were selected and both were tried with $s=1$ and 2. The two $s=2$ schemes were not found to be competitive in either accuracy or stability when tested and so will not be considered further. The Nordsieck [13, 14] modification of the Adams method was used since it permits simultaneous possession of the atom positions and their derivatives and, therefore, of the system potential and kinetic energies. Also changes in the step size are easier to implement than for the basic Adams method and this may be of use in some problems although it is not pursued here. Finally a hybrid scheme developed especially for high efficiency with second-order equations in problems of astronautics [15] was tested (Eqs. (A7) and (A8)). This has characteristics of both Runge-Kutta and predictor-corrector methods.

The tests were performed on the model crystal shown in Fig. 1 which represents two planes of atoms in bcc α -Fe. The atomic motions are restrained to lie in these planes so the material may be considered to be in plane strain. The interatomic potential used is the Johnson-I potential [7], shown in Fig. 2. The time step lengths used could be scaled for other materials to a first approximation by $\sqrt{m_d/k}$, where

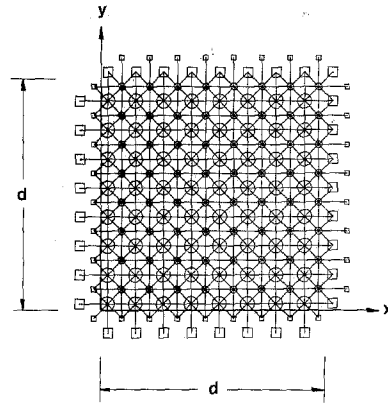


FIG. 1. Model used. The free atoms are marked by circles, boundary atoms by squares. The smaller markers are in a plane below that of the larger. Interatomic bonds are shown as straight lines.

m_a is the atomic mass and k is some effective spring constant of the bonds. Some experimentation may of course be necessary. The size of the models used in atomic simulations varies over a wide range, but the one used here is typical of the smallest which have been used. It contains 194 atoms in total of which 128 are free to move. The 66 boundary atoms are rigidly fixed at the positions needed to apply the desired boundary loads to the model. In actual simulations some form of flexible

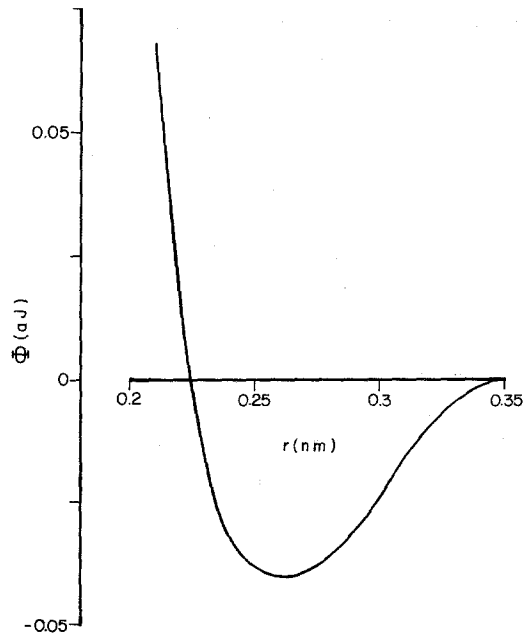


FIG. 2. Johnson-I interatomic potential.

boundary scheme is useful to get more accurate results, but either these update the positions of the boundary atoms only at long time intervals while holding them fixed between these updates [16], or the boundary motions are defined by other degrees of freedom which are treated in the same way as the atom positions [17]. Thus the computer time needed for a model with rigid boundary conditions is representative of that for a model with flexible boundaries, so that these were not considered in this test. The time for one evaluation of all interatomic forces was about 0.6 s on a CDC 6400 computer. This time is proportional to model size and to the complexity of the interatomic potential used. More complex potentials would be desirable but they have been restricted by computer cost in the past. However, sizes more than 10 times larger than that tested here have been used in some cases [17]. It is felt that changes in size should not affect the relative merits of various integration schemes or static solution methods although no tests were made of this. Future work could test this point.

The integration schemes were compared by checking their stability limits and the accuracy of energy conservation which they maintained while simulating the thermal vibrations of the model of Fig. 1. Energy conservation was checked since it is a single number characterizing the whole system accuracy, it is simple to evaluate, and it is often the physical property which is of primary interest, for example, in thermodynamic simulation of saddle point energies for defect motion. For this test, the atoms were first displaced from their equilibrium positions by normally distributed amounts such that the extra energy added to the system was equal to 1 aJ ($1 \text{ aJ} = 10^{-18} \text{ J}$). This is approximately the energy the crystal would possess at room temperature. It was chosen as being typical of the energies which might be examined in a thermodynamic analysis, as well as the energy excess which might be present in a model during the course of a static solution. For instance, it is about twice the excess energy which must be removed from the crystal for a crack problem at two times the Griffith stress intensity factor. The factor of two in energy should account for the presence of some bonds which are very highly stretched in such defect problems which do not appear in thermal vibrations.

The simulation was carried out with each integration scheme for a model time of 3500 fs ($1 \text{ fs} = 10^{-15} \text{ s}$). This time was chosen as the time needed for very accurate static solutions. This can be seen from the results of the static solution tests presented later. This length of time is also enough to permit a shear wave to propagate about 40 lattice parameters and, since the speed of crack propagation or dislocation motion is of this order of magnitude, it should be sufficient for dynamic studies of defect motion as well. For shorter times, the stability limits may appear to be extended slightly since some cases appeared stable for several hundred fs before finally diverging.

Each integration scheme was tested with step sizes of 3, 6, 9, 15, 21, 30, and 45 fs, at least. The rate of increase of energy error with model time was roughly linear for almost all cases. The few exceptions were isolated and did not affect the relative standing of the methods involved. Thus comparing errors at the endpoint of the simulations is sufficient to rank the methods. This error is presented in the form

$r/(KT)$, where r is the energy error at the end of the simulation, K is the maximum system kinetic energy (which is 1 aJ in these tests), and T is the time of the simulation (3500 fs). This is plotted against the measure of computer cost, h/n , both on logarithmic scales, in Fig. 3.

From Fig. 3 it can be seen that the $q=4$, $s=1$ Nordsieck method has the greatest stability and therefore should be best for static solutions. The commonly used 2-step difference formula is next best. It is in fact more accurate than the Nordsieck method over most of the range of step sizes but as stated earlier this factor is negligible for static solutions. The Nordsieck scheme does use slightly more memory than the 2-step difference and this may be a problem in some cases. The 5-step difference and the Runge-Kutta methods are also acceptable while the hybrid scheme and the $q=6$, $s=1$ Nordsieck are significantly worse. Step sizes which have been used in simulations are not always stated in published work but the largest is apparently 17 fs [3] used in an iron dislocated problem for the 2-step difference scheme. This is very near the stability limit found here for this method and confirms the general applicability of the results for different problems.

The best method to be used for a dynamic analysis depends on the accurately level needed. An order of magnitude estimate for this may be made as follows. Suppose the material properties are known to 1% and it is desired that the integration scheme accuracy be comparable to this. If $r/K=0.01$ at a time of 3500 fs, then $r/(KT)=2.9E-6 \text{ fs}^{-1}$. At this accuracy and higher, the $q=6$, $s=1$ Nordsieck and the 5-step difference schemes are best. At lower accuracies the 2-step difference becomes best with the 5-step difference very close. The others are generally within a factor of 1.5 of the best methods in computer cost except for the Runge-Kutta which is as much as 5 times costlier at some accuracies.

In conclusion, if a single method is desired for static and dynamic analyses, the 2-step or 5-step difference schemes are probably the best. The former has a smaller memory requirement. For static analyses alone, the $q=4$, $s=1$ Nordsieck is slightly

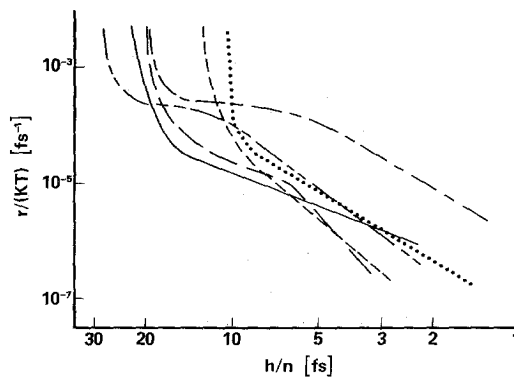


FIG. 3. Results of integration scheme tests: (—) 2-step difference; (---) 5-step difference; (- - -) Runge-Kutta; (- · - ·) $q=4$, $s=1$ Nordsieck; (· · ·) $q=6$, $s=1$ Nordsieck; (···) hybrid.

better than the 2-step difference method. The integration time step used must be less than 20 fs for stability for the Nordsieck case and 10 fs should provide a sufficient safety margin to ensure stability under all conditions. No instabilities have ever been observed using 10 fs on a wide variety of problems, while instability has occurred occasionally when 20 fs has been used, and once with 15 fs. For those dynamic analyses dominated by accuracy rather than stability considerations, the lowest cost integrator for a given accuracy should be selected. From Fig. 3, this can be seen to be either one of the difference schemes or the $q=6$, $s=1$ Nordsieck method. The step length for any degree of accuracy can be read off Fig. 3 and scaled for other materials as mentioned above.

STATIC SOLUTION TESTS

In this section the three static solution methods will be compared. The model used is the same one used for the test of integration schemes. The computer time required to approach equilibrium will be determined for four problems. In three of the problems the boundary atoms were fixed at the perfect crystal positions. The free atoms were given initial displacements which were sinusoidal in form.

$$\begin{aligned} u &= A \sin(m\pi x/d) \sin(m\pi y/d) \\ v &= B \sin(m\pi x/d) \sin(m\pi y/d) \end{aligned} \quad (1)$$

where (u, v) is the displacement of the atom at (x, y) . B was set equal to $A/2$ so that the displacement vectors did not lie along a high symmetry axis such as the $[110]$ direction. The value of A was chosen so that the total energy which had to be removed from the crystal was 5 aJ. This is larger than the energy excess in most static solution problems so that the efficiency of the solution schemes over a wide range of energy levels could be observed. Values of 1, 2, and 3 were used for m . This form of test problem was chosen so that the effect of different spatial frequencies in the initial position errors for static problems could be determined. Also, since the final position which was sought was the perfect crystal position, no problems of alternate minima were encountered which can be seen in more complex problems. The final problem on which the solution schemes were compared was a crack tip problem. For this, the boundary atoms were set at the positions specified by linear elastic fracture mechanics as were the initial positions of the free atoms. The system was then relaxed from this position. The energy which had to be removed was about 0.063 aJ for a stress intensity factor equal to the Griffith value.

The conjugate gradient method had to be modified in one way from that presented by Sinclair and Fletcher [6] in order to get efficient convergence. It was found that the unmodified method hung up at non-equilibrium points which it only slowly passed. To avoid this, the series of conjugate directions had to be restarted periodically, much more often than suggested by the tolerances of Sinclair and Fletcher. A restart every 10 steps was satisfactory.

The results are shown in Figs. 4-7. Each figure gives the results of one of the test problems. The horizontal axis in each plot is a measure of computer time expended. This is expressed as the number of interatomic force evaluations made. The integration scheme used for the two quenching solution methods was the $q=4$, $s=1$ Nordsieck with a time step of 10 fs. Increasing the step length would proportionally decrease the computer time needed to reach a given level of accuracy for the two quenching methods thus making them more attractive vis-a-vis the conjugate gradient method. The test of integration schemes described above indicates that this could be done although by less than a factor of 2. To do so would remove the safety factor on the stability limits of the integration and so would not be advisable. Part (a) of each figure is a plot of energy error in the solution against computer time used. The energy error expressed as $(C-E)$, where C is the potential energy of the system in its current configuration and E is the potential energy of the system at the final equilibrium configuration. E was determined to sufficient accuracy from a very accurate solution for each case. Part (b) of each figure is a plot of the sum of the squares of the forces on all atoms, $|\bar{F}|^2$, against computer time. At equilibrium, this should be zero of course.

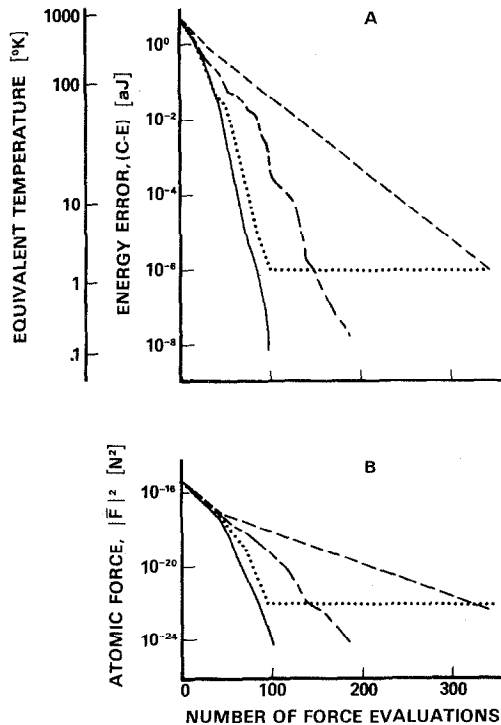


FIG. 4. Results of solution test. Sinusoidal initial displacements, $m=1$. The integration step length used with the two quenching algorithms = 10 fs: (—) modified conjugate gradient; (— —) simultaneous quenching; (- - -) individual quenching; (···) unmodified conjugate gradient.

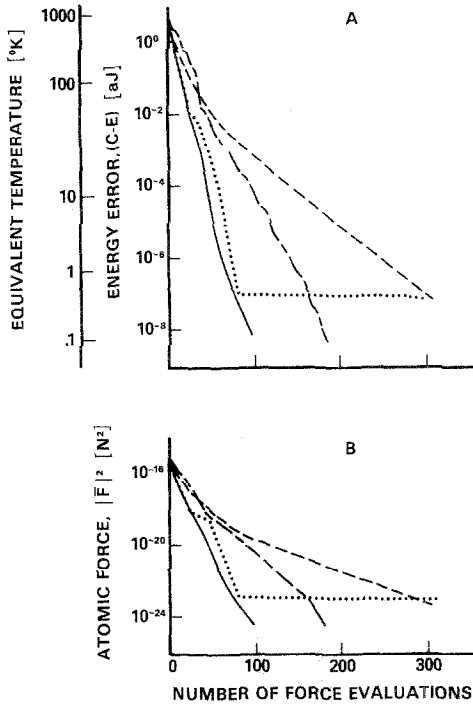


FIG. 5. Same as Fig. 4 except $m = 2$.

The results show that for all cases, the errors decreased approximately exponentially with computer time. This knowledge enables a prediction to be made of the time required to reach a given accuracy level once a solution has been started. This may be useful in scheduling. In addition, for the sinusoidal initial displacement problems, the modified conjugate gradient method was best, followed by the simultaneous quenching and the individual quenching methods. Increasing the integration step size for the simultaneous quenching method could make it more efficient but not so much so that it would become best without introducing the possibility of numerical instability. The poor performance of the individual quenching was surprising in view of its widespread use. It may do much better if more than one atomic mass were present or if longer range forces were used. This is a point which could be examined in the future. The unmodified conjugate gradient method reached stages in the solution at which the change in position of the system during each step became very small. This causes the plateaus in the energy and force curves which were not passed in the time studied. For each method, the time to reach a given accuracy was shortest for the highest spatial frequency, $m = 3$, and largest for the lowest frequency, $m = 1$. Thus if any trade-off were possible, initial conditions should be chosen to minimize the low spatial frequencies in the initial errors. This may be of interest to proposals [18] to combine the present solution

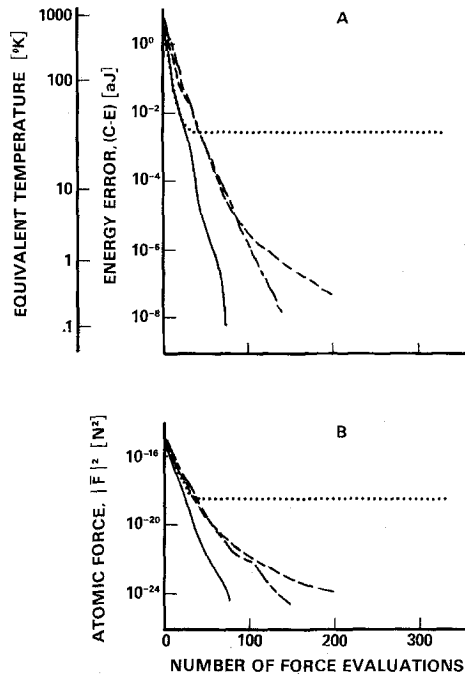


FIG. 6. Same as Fig. 4 except $m = 3$.

methods with the so-called "lattice statics" models. The change in solution as the spatial frequency changed was least for the modified conjugate gradient method and greatest for the individual quenching method.

For the crack tip problem, the curves are more complex but the same or better efficiency holds for the solution methods, so this result is probably applicable. The plateaus in the unmodified conjugate gradient curves are again seen. The force magnitude plot of Fig. 7(b) shows that the plateau was passed and a fairly accurate equilibrium position was achieved at about 320 force evaluations. The reason that the steep drop off was not observed in the energy plot of Fig. 6 is that the equilibrium position which was found by this method was different from that found by the others. The energy difference between the two equilibria is 0.00017 aJ. The curves for the other methods seem to have kinks at this point, indicating that they too may have felt this alternate equilibrium point. This would seem to confirm the statement of Beeler [19] that "of all the methods available for computing defect equilibrium configurations, the artificial dynamic method [the quenching methods used here] is the only one which will not only converge to the lowest energy configuration and not to some low metastable configuration." That this is not true in general, however, can be seen in the crack problem at a stress intensity factor of twice the Griffith value. The

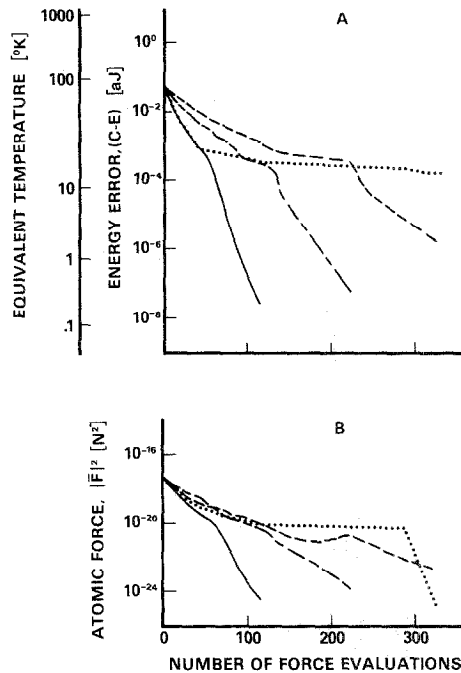


FIG. 7. Same as Fig. 4 except for crack tip problem at the Griffith stress intensity factor.

does not propagate because of the lattice trapping effect. The accuracy versus computer time curves are similar to those already given and so will not be presented. In this case, however, three different equilibria were found. The lowest in this case was found by the two conjugate gradient methods. The simultaneous quenching method converged to an equilibrium configuration 0.0005 eV above this and the independent quenching method to one 0.0126 eV above the conjugate gradient solution.

Figure 8 shows two of these equilibrium positions and the unbroken bonds in each case. The differences can be seen mainly in the area between the crack tip and the lower right corner of the model. These are real, separate equilibrium positions made possible by the presence of a non-linear interatomic potential, and they are not merely artifacts of the solution method used. The presence of these alternate equilibria may be important in computer simulation studies. Saddle point energy for crack propagation and thermally activated defect motion, for example, may be significantly different for the separate equilibria. No solution method apparently can be counted on to give true lowest energy configurations. The problem considered here is of course a simple one and cannot be considered representative of a true crack tip situation. The main problems are the small size and the rigid boundaries, but improving these points would increase the number of degrees of freedom and increase the region of crystal affected by the non-linear crack tip field, so that

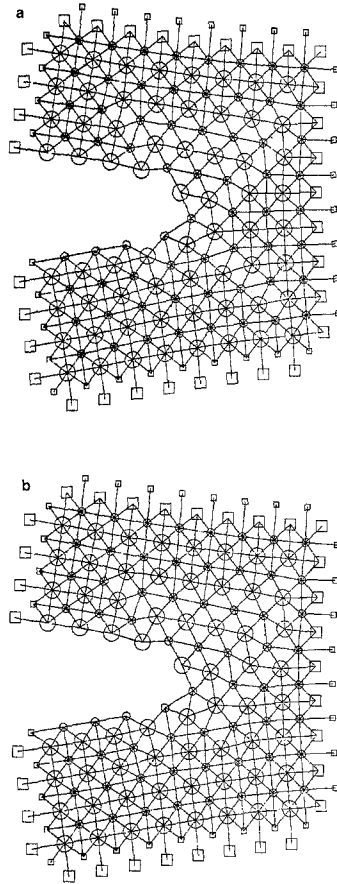


FIG. 8. Alternate equilibria for crack tip problem at twice the Griffith stress intensity factor: (a) modified conjugate gradient solution; (b) individual quenching solution.

the number of alternate equilibria possible may increase. The fact that alternate equilibria are so easily produced even for such a simple problem as this indicates that they may be more common than is usually considered.

The final point which will be considered is the relation between the energy error ($C-E$) and the sum square of the atomic forces $|\bar{F}|^2$ as the system approaches equilibrium during a static solution. The former quantity cannot, of course, be known before the solution is completed since E is the final equilibrium energy, but the latter is easily calculated at any time and it has in fact been used [6] to determine the point at which the solution may be stopped. It can be used with all solution methods considered here. Other stopping criteria involving the use of kinetic energy in the system are more common for the quenching methods [3, 4] but these cannot be used for the conjugate gradient scheme. The criteria and the

values used as tolerances in them have apparently been chosen fairly arbitrarily in the past. Figure 9 is a plot of $(C-E)$ versus $|\bar{F}|^2$ for all solution schemes on all problems tested here. A point is plotted for each after every 20 force evaluations with the exception of the unmodified conjugate gradient scheme for the crack tip problem which converged to a metastable equilibrium. It can be seen that the force and energy are very strongly correlated for all cases. If a single interatomic bond is represented to a first approximation by a linear spring, we would have

$$e = f^2/(2k) \tag{2}$$

where k is the spring constant, e the potential energy, and f the force in this bond. If all bond springs were similar, the total energy above the equilibrium state and the sum square of all forces should behave in the same way. Figure 9 contains plots of the above equation for k s of 39.3 and 15.7 N/m. These are the spring constants for small displacements of the nearest and second nearest neighbour bonds in this model at the perfect crystal lengths. This can only be a very rough approximation to the true situation as a system such as the one used here approaches equilibrium of course. In crack problems for example, there is a general stretching of all bonds and a corresponding decrease in spring constant since the bonds are non-linear. Also, the fact that all springs are not alike even if no changes occurred would mean that no single value of k could characterize the system for all energies. Nevertheless,

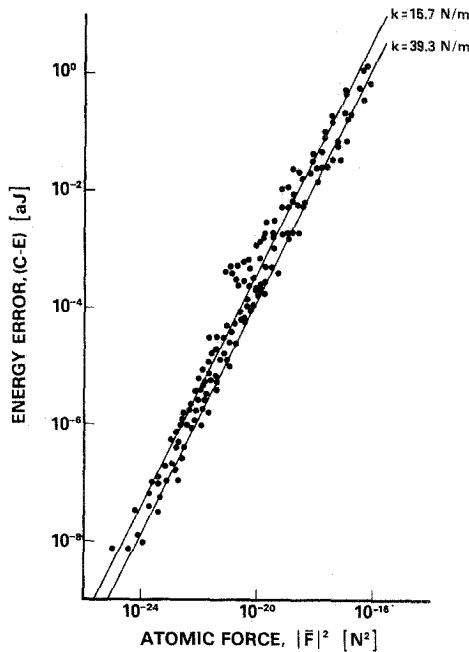


FIG. 9. Energy error versus sum of squares of atomic forces for all cases.

the correspondence between the observed points and the curves is quite good for the crack problem. This ability to estimate the actual value of the energy makes the force criterion an excellent one to use to determine when a solution reached a sufficient level of accuracy.

CONCLUSIONS

The tests presented in this paper have shown that the selection of the optimization method for solution of an atomic simulation problem can result in a decrease in computer time used by factors of 2 or 3 over that required by other, often used methods. For dynamic analyses where accurate solution of the equations of motion of the system is desired, the integration schemes which provide the best performance are the 2-step and 5-step difference formulas at low accuracies and the 4-step difference and $q=6, s=1$ Nordsieck at high accuracies. If one of the quenching methods are being used for static solutions, the $q=4, s=1$ Nordsieck method followed by the 2-step difference scheme. The integration step sizes may be determined from Fig. 3.

For static solutions, the conjugate gradient optimization scheme has proved to be better for all test problems than either of the quenching methods. It was found, however, that the series of conjugate directions had to be restarted much more often than suggested by Sinclair and Fletcher in order to get efficient convergence (about every 10 steps). Simultaneous quenching was better than individual quenching for all cases. It may be that in problems where more than one mass is present, individual quenching could be superior although this was not tested. For all solution methods, the higher spatial frequency components of the position errors were removed before the lower ones. This difference in spectral content is especially important for the quenching schemes, less so for the conjugate gradient method. The test problems chosen here were fairly elementary but it is hoped that the results are of general applicability. Future work could check the effect of problem size on solution efficiency and could determine if the addition of flexible body simulation schemes has effect on it. The ease with which alternate equilibrium positions were obtained indicates that this problem may be of some importance. Judging from the limited experience presented here, no static solution method appears to guarantee the true lowest energy state. The differences in energy between the various equilibrium positions are fairly small but may become important when questions of thermally activated motion are considered, for example. Further exploration of this point would be in order. Finally, the use of the sum of the squares of the unbalanced forces on all atoms appears to be a good criterion to use to determine when sufficient accuracy has been reached in a static solution.

APPENDIX

The numerical integrators tested in this work are described in this Appendix. In what follows, each degree of freedom of each atom is treated identically and its value at time t represented by $x(t)$. Its derivatives with respect to time are \dot{x} , \ddot{x} , \dddot{x} , x^{iv} , and x^v . The force on this atom in the direction of the degree of freedom x is F . This is calculated for all atoms when all degrees of freedom x , i.e., the positions of all atoms in each coordinate direction, are given. Since it is a function of the atomic coordinates, it is specified $F[x]$ but it must be emphasized that this is a vector

relation. All forces F may be calculated when and only when all degrees of freedom x have been specified. The integration time step used is h . The atomic mass is m_a .

Two-step Difference

The form used here is equivalent to that given in [5] but is written in a different notation for easier comparison to the other methods:

$$x(t+h) = 2x(t) - x(t-h) + h^2\ddot{x}(t). \tag{A1}$$

Five-step Difference [10, p. 27]

$$\begin{aligned} x(t+h) = & 2x(t) - x(t-h) + h^2/240[299\ddot{x}(t) - 176\ddot{x}(t-h) \\ & + 194\ddot{x}(t-2h) - 96\ddot{x}(t-3h) \\ & + 19\ddot{x}(t-4h)]. \end{aligned}$$

Runge-Kutta [13, p. 49]

This is a third order Runge-Kutta scheme for second-order differential equations:

$$\begin{aligned} k_1 &= h_2F[x(t)]/(2m_a) \\ k_2 &= h^2F[x(t) + 2h\dot{x}(t)/3 + 4k_1/9]/(2m_a) \\ x(t+h) &= x(t) + h\dot{x}(t) + (k_1 + k_2)/2 \\ \dot{x}(t+h) &= \dot{x}(t) + (k_1 + 3k_2)/(2h). \end{aligned} \tag{A3}$$

It can be seen that two force evaluations are required per time step for this method.

Nordsieck Methods [14; 13, p. 148]

These are equivalent to Adams methods but are written in a slightly different form mainly to facilitate changing the step size. They are predictor-corrector methods. If the predictor operation is specified by P , the corrector by C , and the evaluation of the forces by E , then a single application of each may be expressed PEC . This is an $s=1$ scheme. If the corrector is applied twice, $s=2$ and we have $PECEC$ or $P(EC)^2$. In general, changes in s are described by $P(EC)^s$. The number

of force evaluations per step equals s . The P and C operations for the $q=4$ and $q=6$ methods are described below where

$$\begin{aligned} y_0 &= x & y_3 &= \bar{x}h^3/6 \\ y_1 &= \dot{x}h & y_4 &= x^{iv}h^4/24 \\ y_2 &= \bar{x}h^2/2 & y_5 &= x^v h^5/120. \end{aligned} \quad (\text{A4})$$

Superscript p refers to predicted values, c to corrected values.

$q=4$ predictor:

$$\begin{aligned} y_0^P(t+h) &= y_0(t) + y_1(t) + y_2(t) + y_3(t) \\ y_1^P(t+h) &= y_1(t) + 2y_2(t) + 3y_3(t) \\ y_2^P(t+h) &= y_2(t) + 3y_3(t) \\ y_3^P(t+h) &= y_3(t). \end{aligned} \quad (\text{A5})$$

$q=4$ corrector. From $y_0^P(t+h) = x^P(t+h)$, get the predicted force, $F^P[x^P(t+h)]$, at $t+h$. Calculate $W = F^P h^2 / (2m_a) - y_2^P(t+h)$. Correct all y s by setting $y_i^C(t+h) = y_i^P(t+h) + c_i W$, where

$$\begin{aligned} c_0 &= \frac{1}{6} & c_2 &= 1 \\ c_1 &= \frac{5}{6} & c_3 &= \frac{1}{3}. \end{aligned}$$

$q=6$ predictor:

$$\begin{aligned} y_0^P(t+h) &= y_0(t) + y_1(t) + y_2(t) + y_3(t) + y_4(t) + y_5(t) \\ y_1^P(t+h) &= y_1(t) + 2y_2(t) + 3y_3(t) + 4y_4(t) + 5y_5(t) \\ y_2^P(t+h) &= y_2(t) + 3y_3(t) + 6y_4(t) + 10y_5(t) \\ y_3^P(t+h) &= y_3(t) + 4y_4(t) + 10y_5(t) \\ y_4^P(t+h) &= y_4(t) + 5y_5(t) \\ y_5^P(t+h) &= y_5(t). \end{aligned} \quad (\text{A6})$$

$q=6$ corrector. From $y_0^P(t+h) = x^P(t+h)$, get the predicted force, $F^P[x^P(t+h)]$, at $t+h$. Calculate $W = F^P h^2 / (2m_a) - y_2^P(t+h)$. Correct all y s by setting $y_i^C(t+h) = y_i^P(t+h) + c_i W$, where

$$\begin{aligned} c_0 &= \frac{3}{16} & c_3 &= \frac{11}{18} \\ c_1 &= \frac{251}{360} & c_4 &= \frac{1}{6} \\ c_2 &= 1 & c_5 &= \frac{1}{60}. \end{aligned}$$

Hybrid [15]

Note that there are some errors in the formulas given in [15]. The second derivatives below are calculated by $\ddot{x} = F[x]/m_a$. First, the non-step point

$$\begin{aligned}
 x(t + 0.7h) = & \alpha_1 x(t) + \alpha_2 x(t - h) + \alpha_3 x(t - 2h) \\
 & + \alpha_4 x(t - 3h) + h^2[\beta_1 \ddot{x}(t) \\
 & + \beta_2 \ddot{x}(t - h) + \beta_3 \ddot{x}(t - 2h) + \beta_4 \ddot{x}(t - 3h)] \quad (A7)
 \end{aligned}$$

where:

$$\begin{aligned}
 \alpha_1 = & -1.9320993 & \beta_1 = & 0.8625005 \\
 \alpha_2 = & 6.4719549 & \beta_2 = & 3.0303805 \\
 \alpha_3 = & -3.4476119 & \beta_3 = & 0.4336798 \\
 \alpha_4 = & -0.0922437 & \beta_4 = & -0.0072178.
 \end{aligned}$$

Then the full step

$$\begin{aligned}
 x(t + h) = & \gamma_1 x(t) + \gamma_2 x(t - h) + \gamma_3 x(t - 2h) + \gamma_4 x(t - 3h) \\
 & + h^2[\delta_1 \ddot{x}(t) + \delta_2 \ddot{x}(t - h) + \delta_3 \ddot{x}(t - 2h) + \delta_4 \ddot{x}(t - 3h)] \\
 & + h^2 \delta \ddot{x}(t + 0.7h)/m_a \quad (A8)
 \end{aligned}$$

where

$$\begin{aligned}
 \gamma_1 = & 2.0580497 & \delta_1 = & 0.7044318 \\
 \gamma_2 = & -0.9634579 & \delta_2 = & 0.0872588 \\
 \gamma_3 = & -0.2472333 & \delta_3 = & -0.1544589 \\
 \gamma_4 = & 0.1526415 & \delta_4 = & -0.0095188 \\
 & & \delta = & 0.1615960.
 \end{aligned}$$

Two force evaluations per time step are required by this method.

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