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Efficient effective-energy method for lattice-Green's-function simulations of fracture

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This paper discusses a method for finding equilibria within the lattice-Green's-function formulation. The method involves the creation of an energy functional expressed just in terms of a small subset of the ($> 10^6$) total number of degrees of freedom. It is much more efficient and robust numerically than former methods of solution of the Green's-function equations, particularly when the subset becomes $O(10^3)$. The energy functional may be used in conjunction with state of the art conjugate gradient, quasi-Newton or simulated annealing methods to find minimum-energy configurations and compare their energies. In addition, if constraints are placed on the allowed relations between a few of the degrees of freedom then the method may be used to find the energies of unstable equilibria and hence activation energies.

I. INTRODUCTION

There has been much recent interest in using atomic simulations to bridge the gap between the experimental and theoretical descriptions of complex solid state phenomena. An important example is the problem of understanding the factors which determine whether the failure of materials (such as semiconductors or metals) is intrinsically brittle or ductile. It is a difficult problem for simulations because the mode of failure under external stress is the result of interactions at different length scales; the elastic stresses due to cracks and dislocations are long ranged (dying away as $1/\sqrt{r}$ and $1/r$, respectively) but short-ranged interatomic interactions are important at crack tips and within dislocation cores where the elastic solutions are unphysically singular. The lattice-Green's-function method[1] bridges the length scale gap between these two regimes, at present in the static limit. It thus allows for comparisons with the predictions of elasticity-based theories but is also (for a given size of computer) able to treat much larger systems than may be simulated using molecular dynamics. In "nonlinear" regions where atomic distortions from lattice positions are large it uses empirical potentials, and in "linear" regions where strains are small and atomic coordination is unchanged from the unstressed state it uses linear forces determined by force constants derived from the same empirical potentials. The method is applicable to both bulk and surface problems. Figure 1 shows how the regions may be defined when investigating crack problems.

The original lattice-Green's-function work was done using a nearest-neighbor model on a two-dimensional hexagonal lattice and used an iterative equation solver to find system configurations where the sum of the forces on each atom was zero. As we tried to extend this work to longer-ranged and three-body forces, acting on larger numbers of atoms in more general lattices, we discovered that the original solution method was sometimes impractically slow and frequently failed to converge at all if the number of atoms in the nonlinear zone was too large. We have thus developed a modification of the original iterative method with much improved convergence and efficiency properties. It uses the Green's function describing the linear response of the substance to external forces to generate an effective energy function which is minimized to find a state of equilibrium of the system. The minimization can be performed using, for example, conjugate gradient methods. In addition to improving the convergence properties this energy method can be used to calculate energies of activated transition states. The formulation to be derived in this paper is a generalization of calculations made of the activation energy for crack processes made in earlier papers, when the nonlinear region consisted only of one bond.[2] The added feature here is that the energy is used to find the equilibrium configuration of the crack. The equilibrium corresponds precisely

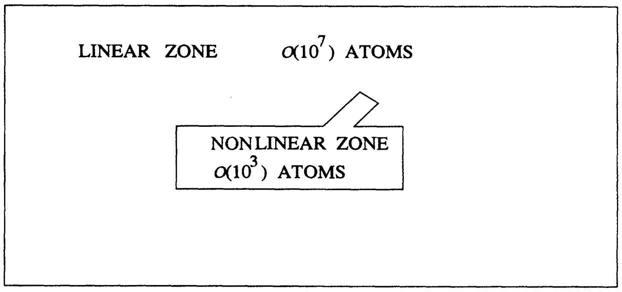

FIG. 1. Separation of the system into "nonlinear" and "linear" regions. The former may contain $O(10^3)$ atoms while the latter may contain $O(10^7)$ atoms for calculations performed on workstations.

to the zero-force condition of the original method but is found more efficiently. Section II of this paper describes the energy-based method in detail. Section III gives a simple example, evaluated analytically, to show how it works. Section IV compares the convergence properties and efficiencies of the old and the new formulations and Sec. V presents conclusions.

II. GREEN'S FUNCTIONS AND THE ENERGY FUNCTIONAL

We now generate the energy functional; at the end of the section we recover the link with the earlier version of the method. We use two notational conventions. First, the subscripts L and NL imply restrictions to the linear and the nonlinear zone degrees of freedom, respectively, while the lack of a subscript implies that there is no such restriction. Second, superscripts describe the nature of the interaction being considered (such as the linear or the nonlinear part of the interatomic interactions, for instance) with no assumption as to where it acts, since that is described by the subscript. By default all interactions are internal unless explicitly identified with the superscript "ext," in which case they are due to forces applied externally, or with the superscript "tot," in which case they include both internal and external interactions.

The internal energy of a system of atoms may be expressed as $E^{\ell} + E^{\mathrm{nl}}$, where the first term is the "linear" internal energy and the the second term is the "nonlinear" internal energy (where linearity or nonlinearity will be seen to refer to the dependence of the corresponding internal *forces* on displacements). Defining $\mathbf{u}$ as the vector of displacements from equilibrium and $\mathbf{\Phi}$ as the spring constant matrix,

$$E^{\ell} = \frac{1}{2}\mathbf{u}\mathbf{\Phi}\mathbf{u}. \tag{1}$$

Differentiating Eq. (1) we obtain the *linear* part of the internal forces which come about from interatomic interactions when the atoms are strained:

$$-\mathbf{F}^{\ell} = \mathbf{\Phi}\mathbf{u}, \tag{2}$$

and combining the last two relations,

$$E^{\ell} = -\frac{1}{2}\mathbf{u}\mathbf{F}^{\ell}. \tag{3}$$

Components of $\mathbf{F}^{\ell}$ are defined as above in both the linear and nonlinear regions.

Our method allows for "exact" representations of the energy in the nonlinear zone. In the present implementation we use empirical potentials for this purpose, and designate the result $E_{\mathrm{NL}}^{\mathrm{exact}}(\mathbf{u}_{\mathrm{NL}})$. (Here $\mathbf{u}_{\mathrm{NL}}$ is the set of deviations from crystal sites of all atoms in the nonlinear zone; the corresponding set of coordinates, for atoms not in general in equilibrium, is $\mathbf{R}_{\mathrm{NL}}$.) The potentials are typically of a general two-body form $\frac{1}{2}\sum_{ij} V_2(\mathbf{R}_i - \mathbf{R}_j)$, of a three-body form $\frac{1}{6}\sum_{ijk} V_3(\mathbf{R}_i, \mathbf{R}_j, \mathbf{R}_k)$, or of the embedded atom form $\sum_i g[\sum_j f(\mathbf{R}_i - \mathbf{R}_j)]$. To obtain the nonlinear energy an additional term E_{NL}^{ℓ} must be subtracted to avoid double counting the "linear" component of the empirical potential which has already been included in Eq. (1). Finally, since the zero of the linear energy corresponds to the unstrained $\mathbf{u} = 0$ configuration, for consistency we subtract a constant $E_{\mathrm{NL}}^{\mathrm{exact}}(\mathbf{0})$ whose value is the total empirical potential energy associated with nonlinear zone atoms only, calculated when $\mathbf{u} = 0$. Its inclusion is strictly necessary only if we wish to compare the energies of different local minima obtained using differently sized nonlinear zones, but it does ensure that $E_{\mathrm{NL}}^{\mathrm{nl}}$ is strictly $O(\mathbf{u}^3)$.

The calculation of E_{NL}^{ℓ}, the "linear" energy in the nonlinear zone, demands care so that no linear contributions from bonds linking the linear and nonlinear zones are included. Let us index atoms as a and b, and index directions (x, y, or z) as i and j, with the atoms at present unrestricted as to location. We may write the total linear energy, Eq. (1), as

$$\begin{aligned} E^{\ell} &= \frac{1}{2}\sum_{i,j,a,b} u_i^a \Phi_{ij}^{ab} u_j^b = \frac{1}{2}\sum_{i,j,a,b} u_i^a \Phi_{ij}^{ab} u_j^b - \frac{1}{2}\sum_{i,j,a} u_i^a u_j^a \sum_b \Phi_{ij}^{ab} \\ &= \frac{1}{2}\sum_{i,j,a,b} u_i^b \Phi_{ij}^{ba} u_j^a - \frac{1}{2}\sum_{i,j,b} u_i^b u_j^b \sum_a \Phi_{ij}^{ba} \\ &= \frac{1}{4}\sum_{i,j,a,b} u_i^a (u_j^b - u_j^a)\Phi_{ij}^{ab} - \frac{1}{4}\sum_{i,j,a,b} u_i^b (u_j^b - u_j^a)\Phi_{ij}^{ba} = -\frac{1}{4}\sum_{i,j,a,b} (u_i^a - u_i^b)\Phi_{ij}^{ab}(u_j^a - u_j^b), \end{aligned} \tag{4}$$

where the second and third equalities use the fact that $\sum_b \Phi_{ij}^{ab} = 0$,[3] and the final equality depends on $\Phi_{ij}^{ab} = \Phi_{ji}^{ba}$,[3] and that

$$\sum_{i,j,a,b} (u_i^a - u_i^b)\Phi_{ij}^{ab}(u_j^a - u_j^b) = \sum_{i,j,a,b} (u_i^a - u_i^b)\Phi_{ij}^{ba}(u_j^a - u_j^b) \quad . \tag{5}$$

Equation (4) is independent of crystal structure and holds, in particular, when there is more than one atom per unit cell. Since the linear energy has now been defined in terms of relative displacements of atoms a and b, this allows us to calculate the required linear energy for the nonlinear zone, by summing over both atoms a and b restricted to be inside the nonlinear zone.

The resulting nonlinear contribution to the interaction energy is

$$E_{\mathrm{NL}}^{\mathrm{nl}} = E_{\mathrm{NL}}^{\mathrm{exact}}(\mathbf{u}_{\mathrm{NL}}) + \frac{1}{4}\sum_{i,j,a,b}^{\mathrm{NL}} (u_i^a - u_i^b)\Phi_{ij}(u_j^a - u_j^b) - E_{\mathrm{NL}}^{\mathrm{exact}}(\mathbf{0}) \quad , \tag{6}$$

where the second term is a sum over atoms in the nonlinear zone only.[4]

This description of the total internal energy is not in principle limited by the use of empirical potentials to calculate the more accurate representation of the energy. One could use density functional theory to calculate the spring constant matrix $\mathbf{\Phi}$ and the energy of the atoms in the configuration given by $\mathbf{u}_{\mathrm{NL}}$. The only problem is the specification of the boundary conditions for the nonlinear zone electronic calculation. It would not be appropriate, for example, to use free boundary conditions for the nonlinear zone cluster since the resulting energy is very different from the energy of the same cluster embedded in the infinite medium. Such care in choosing the boundary conditions is not necessary when using empirical potentials because in that case it is possible to partition the total energy among the separate atoms unambiguously so that the calculated energy for nonlinear zone atoms is independent of factors outside the zone boundary.

In general we are interested in the effect of external forces $\mathbf{F}^{\mathrm{ext}}$ acting on the system. Including these yields

$$E^{\mathrm{tot}} = +E_{\mathrm{NL}}^{\mathrm{exact}}(\mathbf{u}_{\mathrm{NL}}) + \frac{1}{4}\sum_{i,j,a,b}^{\mathrm{NL}} (u_i^a - u_i^b)\Phi_{ij}^{ab}(u_j^a - u_j^b) - E_{\mathrm{NL}}^{\mathrm{exact}}(\mathbf{0}) + \frac{1}{2}\mathbf{u\Phi u} - \mathbf{F}^{\mathrm{ext}}\mathbf{u} \tag{7}$$

for the total energy. Note that the sum over a and b in the second term of this expression is over just nonlinear zone atoms, while the fourth term involves sums over *all* atoms in the whole system. The latter point means that Eq. (7) is a function of a number of variables equal to the total number of degrees of freedom in the system.

To reduce the number of degrees of freedom we proceed as follows. We restrict ourselves to calculating the energy for a restricted subspace of all the possible atomic configurations for the whole system, which contains the sought-after equilibrium. In this subspace the positions of the atoms in the nonlinear zone are arbitrary, but, given these positions, all atoms outside the nonlinear zone must be in zero force positions. Thus

$$\mathbf{F}_L^{\ell} + \mathbf{F}_L^{\mathrm{ext}} = 0, \tag{8}$$

where the subscript specifies that the relation is required to be true only for degrees of freedom in the linear zone. For the restricted set of allowed configurations our new expression will give exactly the same value as before; it is still the energy of the *whole* system[5] (not just of the nonlinear zone) and includes all the internal energy terms which come about in the linear region because of relaxations in response to external forces and to forces exerted on the linear region by the nonlinear region. However, as we now show, the constraint of zero net force on atoms in the linear zone means that their positions do not have to be stored, or even calculated explicitly, in order to obtain the total energy.

In terms of a Green's function $\mathbf{G} \equiv \mathbf{\Phi}^{-1}$, Eq. (2) may be rewritten as $\mathbf{u} = -\mathbf{G}\mathbf{F}^{\ell}$ or in block matrix form as

$$\mathbf{u}_{\mathrm{NL}} = -\mathbf{G}_{\mathrm{NL,NL}}\mathbf{F}_{\mathrm{NL}}^{\ell} - \mathbf{G}_{\mathrm{NL},L}\mathbf{F}_L^{\ell} \tag{9}$$

and

$$\mathbf{u}_L = -\mathbf{G}_{L,\mathrm{NL}}\mathbf{F}_{\mathrm{NL}}^{\ell} - \mathbf{G}_{L,L}\mathbf{F}_L^{\ell} \quad , \tag{10}$$

with the subscripts L and NL referring to the linear and nonlinear regions, respectively. Note that these relations between the displacements, the Green's function and the *linear* part of the internal forces, are *always* valid. They are valid irrespective of whether the system is in equilibrium or not, or of whether there are nonlinear internal forces or not, just by virtue of definitions of $\mathbf{G}$ and $\mathbf{F}^{\ell}$, which do not assume either linearity or equilibrium. This point is crucial to the development which follows.

Rearranging Eq. (9) gives

$$\mathbf{F}_{\mathrm{NL}}^{\ell} = -(\mathbf{G}_{\mathrm{NL,NL}})^{-1}(\mathbf{u}_{\mathrm{NL}} + \mathbf{G}_{\mathrm{NL},L}\mathbf{F}_L^{\ell}) \quad , \tag{11}$$

while substituting the result into Eq. (10) gives

$$\mathbf{u}_L = +\mathbf{G}_{L,\mathrm{NL}}(\mathbf{G}_{\mathrm{NL,NL}})^{-1}(\mathbf{u}_{\mathrm{NL}} + \mathbf{G}_{\mathrm{NL},L}\mathbf{F}_L^{\ell}) - \mathbf{G}_{L,L}\mathbf{F}_L^{\ell} \quad . \tag{12}$$

Using Eqs. (2), (8), (11), and (12) the last two terms in the total energy expression Eq. (7) become

$$\begin{aligned}
E^{\ell} + E^{\mathrm{ext}} &= -\frac{1}{2}\mathbf{F}_L^{\ell}\mathbf{u}_L - \frac{1}{2}\mathbf{u}_{\mathrm{NL}}\mathbf{F}_{\mathrm{NL}}^{\ell} - \mathbf{F}_L^{\mathrm{ext}}\mathbf{u}_L - \mathbf{F}_{\mathrm{NL}}^{\mathrm{ext}}\mathbf{u}_{\mathrm{NL}} \\
&= +\frac{1}{2}\mathbf{F}_L^{\mathrm{ext}}\mathbf{G}_{L,\mathrm{NL}}(\mathbf{G}_{\mathrm{NL,NL}})^{-1}(\mathbf{u}_{\mathrm{NL}} - \mathbf{G}_{\mathrm{NL},L}\mathbf{F}_L^{\mathrm{ext}}) + \frac{1}{2}\mathbf{F}_L^{\mathrm{ext}}\mathbf{G}_{L,L}\mathbf{F}_L^{\mathrm{ext}} + \frac{1}{2}\mathbf{u}_{\mathrm{NL}}(\mathbf{G}_{\mathrm{NL,NL}})^{-1}(\mathbf{u}_{\mathrm{NL}} - \mathbf{G}_{\mathrm{NL},L}\mathbf{F}_L^{\mathrm{ext}}) \\
&\quad -\mathbf{F}_L^{\mathrm{ext}}\mathbf{G}_{L,\mathrm{NL}}(\mathbf{G}_{\mathrm{NL,NL}})^{-1}(\mathbf{u}_{\mathrm{NL}} - \mathbf{G}_{\mathrm{NL},L}\mathbf{F}_L^{\mathrm{ext}}) - \mathbf{F}_L^{\mathrm{ext}}\mathbf{G}_{L,L}\mathbf{F}_L^{\mathrm{ext}} - \mathbf{F}_{\mathrm{NL}}^{\mathrm{ext}}\mathbf{u}_{\mathrm{NL}} \\
&= +\frac{1}{2}\mathbf{u}_{\mathrm{NL}}(\mathbf{G}_{\mathrm{NL,NL}})^{-1}\mathbf{u}_{\mathrm{NL}} - \mathbf{F}_{\mathrm{NL}}^{\mathrm{ext}}\mathbf{u}_{\mathrm{NL}} - \frac{1}{2}\mathbf{F}_L^{\mathrm{ext}}\mathbf{G}_{L,\mathrm{NL}}(\mathbf{G}_{\mathrm{NL,NL}})^{-1}\mathbf{u}_{\mathrm{NL}} - \frac{1}{2}\mathbf{u}_{\mathrm{NL}}(\mathbf{G}_{\mathrm{NL,NL}})^{-1}\mathbf{G}_{\mathrm{NL},L}\mathbf{F}_L^{\mathrm{ext}} \\
&\quad +\frac{1}{2}\mathbf{F}_L^{\mathrm{ext}}\mathbf{G}_{L,\mathrm{NL}}(\mathbf{G}_{\mathrm{NL,NL}})^{-1}\mathbf{G}_{\mathrm{NL},L}\mathbf{F}_L^{\mathrm{ext}} - \frac{1}{2}\mathbf{F}_L^{\mathrm{ext}}\mathbf{G}_{L,L}\mathbf{F}_L^{\mathrm{ext}} \quad .
\end{aligned} \tag{13}$$

Note that the two $\mathbf{u}_{\mathrm{NL}}$-dependent terms proportional to $\mathbf{F}_L^{\mathrm{ext}}$ are equal because of the symmetry of the Green's-function matrix. [The symmetry[3] of Φ means that both $\mathbf{G}$ and $(\mathbf{G}_{\mathrm{NL,NL}})^{-1}$ are symmetric.]

The total energy, the sum of Eqs. (6) and (13), is therefore

$$\begin{aligned} E^{\mathrm{tot}} = &+\left[E_{\mathrm{NL}}^{\mathrm{exact}}(\mathbf{u}_{\mathrm{NL}}) + \frac{1}{4}\sum_{i,j,a,b}^{\mathrm{NL}} (u_i^a - u_i^b)\Phi_{ij}^{ab}(u_j^a - u_j^b) - E_{\mathrm{NL}}^{\mathrm{exact}}(\mathbf{0})\right] \\ &+\left[\frac{1}{2}\mathbf{u}_{\mathrm{NL}}(\mathbf{G}_{\mathrm{NL,NL}})^{-1}\mathbf{u}_{\mathrm{NL}}\right] + \left[-\mathbf{F}_{\mathrm{NL}}^{\mathrm{ext}}\mathbf{u}_{\mathrm{NL}} - \mathbf{F}_L^{\mathrm{ext}}\mathbf{G}_{L,\mathrm{NL}}(\mathbf{G}_{\mathrm{NL,NL}})^{-1}\mathbf{u}_{\mathrm{NL}}\right] \\ &+\left[\frac{1}{2}\mathbf{F}_L^{\mathrm{ext}}\mathbf{G}_{L,\mathrm{NL}}(\mathbf{G}_{\mathrm{NL,NL}})^{-1}\mathbf{G}_{\mathrm{NL},L}\mathbf{F}_L^{\mathrm{ext}} - \frac{1}{2}\mathbf{F}_L^{\mathrm{ext}}\mathbf{G}_{L,L}\mathbf{F}_L^{\mathrm{ext}}\right] \quad , \end{aligned} \tag{14}$$

where the groups of terms in square brackets are the anharmonic, quadratic, linear, and constant terms in $\mathbf{u}_{\mathrm{NL}}$, respectively.

Equation (14) has several noteworthy properties. First, in the limit that the whole system is nonlinear (when there is no $\mathbf{F}_L^{\mathrm{ext}}$) the expression is identical to Eq. (7) as expected. (Recall that $\mathbf{G}^{-1} = \mathbf{\Phi}$.) Second, the last two terms are independent of $\mathbf{u}_{\mathrm{NL}}$ and thus do not have to be included in the functional if it is minimized to find an equilibrium. The most important property, however, is that the result depends entirely on the positions of atoms in the nonlinear zone, with all dependence on atoms outside the nonlinear zone included but invisible. It has reduced the number of effective degrees of freedom by orders of magnitude and thus made minimization searches practical.

We end this section by recovering the link between the energy minimization formulation of the equilibrium condition and the formulation used in earlier work.[1] The equilibrium condition (that there be no force on any atom) is that $-\nabla E^{\mathrm{tot}} = 0$. Note that since Eq. (14) is a function only of degrees of freedom in the nonlinear zone (recall that it assumes that linear zone atoms have rearranged themselves to experience no net force), the gradient involves only derivatives with respect to nonlinear zone degrees of freedom.

Differentiating Eq. (14),

$$\begin{aligned} -\nabla E^{\mathrm{tot}} = &+\mathbf{F}_{\mathrm{NL}}^{\mathrm{nl}}(\mathbf{u}) - (\mathbf{G}_{\mathrm{NL,NL}})^{-1}\mathbf{u}_{\mathrm{NL}} + \mathbf{F}_{\mathrm{NL}}^{\mathrm{ext}} \\ &+\mathbf{F}_L^{\mathrm{ext}}\mathbf{G}_{L,\mathrm{NL}}(\mathbf{G}_{\mathrm{NL,NL}})^{-1}, \end{aligned} \tag{15}$$

where $+\mathbf{F}_{\mathrm{NL}}^{\mathrm{nl}}(\mathbf{u}) = -\nabla E_{\mathrm{NL}}^{\mathrm{nl}}$ [see Eq. (6)]. Setting this expression to zero, rearranging, and using the symmetry of $\mathbf{G}$,

$$\mathbf{u}_{\mathrm{NL}} = +\mathbf{G}_{\mathrm{NL,NL}}[\mathbf{F}_{\mathrm{NL}}^{\mathrm{ext}} + \mathbf{F}_{\mathrm{NL}}^{\mathrm{nl}}(\mathbf{u})] + \mathbf{G}_{\mathrm{NL},L}\mathbf{F}_L^{\mathrm{ext}} \tag{16}$$

in equilibrium. Comparing this nonlinear zone equilibrium condition to Eq. (9) — a general expression for $\mathbf{u}_{\mathrm{NL}}$ which did not assume equilibrium — we see that

$$\mathbf{F}_{\mathrm{NL}}^{\ell} + \mathbf{F}_{\mathrm{NL}}^{\mathrm{nl}} + \mathbf{F}_{\mathrm{NL}}^{\mathrm{ext}} = 0 \quad , \tag{17}$$

the expected force condition for equilibrium. Substituting this relation and Eq. (8), the equilibrium condition on forces in the linear zone, into Eq. (10), the earlier expression for $\mathbf{u}_L$, gives

$$\mathbf{u}_L = +\mathbf{G}_{L,\mathrm{NL}}[\mathbf{F}_{\mathrm{NL}}^{\mathrm{ext}} + \mathbf{F}_{\mathrm{NL}}^{\mathrm{nl}}(\mathbf{u})] + \mathbf{G}_{L,L}\mathbf{F}_L^{\mathrm{ext}} \quad . \tag{18}$$

Equations (16) and (18) may be combined giving

$$\mathbf{u} = \mathbf{G}[\mathbf{F}^{\mathrm{ext}} + \mathbf{F}^{\mathrm{nl}}(\mathbf{u})] \quad , \tag{19}$$

which is the self-consistent equation for equilibrium solved iteratively in previously published work.[1,6] It must be noted that one evaluation of Eq. (19) is somewhat less costly than one evaluation of the total energy expression. Nevertheless, our experience has shown much enhanced ability to find an equilibrium and very large decreases in computer time to find it when using the conjugate gradient method and Eq. (14) rather than iteratively solving the self-consistent equation. These advantages are described in detail in Sec. IV.

The above method relies on the atoms in the linear zone being sufficiently accurately described by the linear approximation. Understanding the limits of the accuracy of this approximation is necessary for both the energy and self-consistent force formulations; we discuss it here because it has not been analyzed in detail previously. Specifically, the approximation requires that the factors $u_i^a - u_i^b$ in the linear energy expression Eq. (4) (the relative displacements in the ith direction of atoms a and b) must be small enough, for all atoms a, b in the linear zone and for all directions i, that in describing the energy it is sufficient to include them just to quadratic order. Thus, both the strain (symmetric) and rotation (antisymmetric) parts of the displacement gradient tensor outside the nonlinear zone must be small. While the condition that strains be small should be familiar the rotation condition may not be so familiar, though it must always be considered for rotated lattices even if atomic separations remain close to unstrained lattice values. It is most easily understood using the example of an isolated dimer in two dimensions bound by a linear spring with spring constant k.

Consider two atoms [see Fig. 2(a)] at equilibrium separation r_0, initially aligned along the x axis, with one atom fixed at the origin. The energy is $\frac{1}{2}k[\sqrt{(r_0 + u_x)^2 + u_y^2} - r_0]^2 = \frac{1}{2}k(u_x)^2 + O(u_x u_y^2)$, where u_x and u_y are deviations from the initial positions in the x and y directions, respectively. Now rotate the dimer about the origin so that one atom remains at the origin and the second is

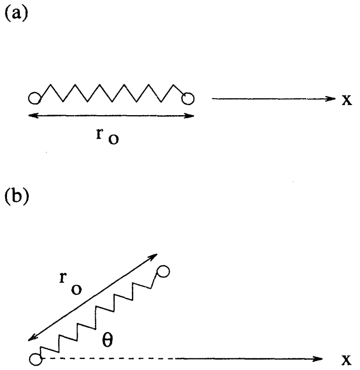

FIG. 2. Dimer configurations used in the model calculation to demonstrate the importance of lattice rotation in limiting the accuracy of the linear approximation.

at $(r_0\cos\theta, r_0\sin\theta)$, as in Fig. 2(b). The true energy is still zero, but its value calculated to second order in u_x (which is equivalent to its description by a Green's-function energy expression) is $\frac{1}{2}kr_0^2(1-\cos\theta)^2$ and thus gets progressively less accurate $[O(\theta^4)]$ as the rotation gets larger. Now stretch the dimer to a length of $r_0+\delta$. Then $u_x = (r_0+\delta)\cos\theta - r_0$ and the true energy is $\frac{1}{2}k\delta^2$, but the energy to second order in u_x is

$$\begin{aligned} E &= \frac{1}{2}ku_x^2 \\ &= \frac{1}{2}k[r_0^2(1-\cos\theta)^2 + 2\delta r_0(\cos\theta-1)\cos\theta + \delta^2\cos^2\theta], \end{aligned} \tag{20}$$

which leads to an error $O(\theta^2)$.

Consider next a trimer, say, lying in the x direction. Then additional energy terms for the third atom in the trimer must be added for the additional bond, corresponding to those already written in Eq. (20). When a rigid rotation occurs the x components of the interatomic separations are reduced below their equilibrium values and so, in the linear approximation in which we work, the internal interactions generate expansive forces to counterbalance the effective compression. The central atom in the trimer does not feel these forces due to symmetry, however. By similar arguments, for a rotated bulk lattice the Green's-function approximation will generate a uniform expansion in the solid. With this uniform expansion no net forces will be generated at any atom, and nothing will happen. However, symmetry-breaking strains added to the rotation will contain rotation-induced errors in the Green's-function representation of the energy and forces. More seriously, at any surface in the lattice, the effective pressure generated by the rotation will generate a surface force due to the destruction of the symmetry at the surface. Thus, a surface site will have errors of order $O(\theta^2 u)$ in the energy generated using the Green's-function description when rotation and strain u are combined, and of order $O(\theta^4)$ on a surface when rotated without strain.

It is therefore necessary to evaluate components of Eq. (19) for atoms near the nonlinear zone after a local minimum has been found. If the resulting displacement gradients and rotations in the linear zone are too large then the calculation must be repeated with a larger nonlinear zone.

III. EXAMPLE: THE FOUR-ATOM RING

To understand the energy functional better, consider a simple example: four identical atoms in a linear chain with periodic boundary conditions, treated within a nearest-neighbor two-body model. To reduce computational effort (as is necessary for large periodic systems) we work in $\mathbf{q}$ space so that the Fourier transform of the spring constant matrix $\tilde{\Phi}_{ij}(\mathbf{q}) \equiv \sum_a \Phi_{ij}(\mathbf{R}_a, \mathbf{0})e^{i\mathbf{q}\cdot\mathbf{R}_a}$ is block diagonal. (The blocks are of side mp, for atoms free to move in m dimensions with p atoms per unit cell.) We use tildes to denote Fourier space quantities.

Taking the nearest-neighbor separation to be 1, we chose $V_2(1+u) = (1/2)ku^2 + \alpha u^4$ as a model potential. Values of the spring constant matrix depend only on the separation between the atoms. Defining $\Phi(|m-n|) \equiv \Phi_{m,n}$,

$$\Big[\Phi(0), \Phi(1), \Phi(2), \Phi(3)\Big] = \Big[2k, -k, 0, -k,\Big] \tag{21}$$

(recalling the periodic boundary conditions). At this point a complication arises. In $\mathbf{q}$ space the diagonal components of the $\tilde{\mathbf{\Phi}}$ matrix are

$$\Big[\tilde{\Phi}(0), \tilde{\Phi}(\pi/2), \tilde{\Phi}(\pi), \tilde{\Phi}(3\pi/2)\Big] = \Big[0, 2k, 4k, 2k\Big] \tag{22}$$

(all off-diagonal elements vanish), so that the matrix cannot be inverted because of the $\mathbf{q}=\mathbf{0}$ translational mode. As explained in the Appendix we therefore calculate the Green's function omitting its $\mathbf{q}=\mathbf{0}$ component in the back Fourier transform from $\mathbf{q}$ to real space, and use those values in subsequent calculations. The resulting matrix, designated $\mathbf{G}^{\infty}$ in accordance with the Appendix notation, is (in real space)

$$\begin{aligned} &\Big[G^{\infty}(0), G^{\infty}(1), G^{\infty}(2), G^{\infty}(3)\Big] \\ &\qquad = \left[\frac{5}{16k}, -\frac{1}{16k}, -\frac{3}{16k}, \frac{-1}{16k}\right] \ . \end{aligned} \tag{23}$$

We now consider the following problem. Designate two neighboring atoms (atoms 1 and 2) to be in the nonlinear zone, and the other two atoms to be in the linear zone. Figure 3(a) shows the equilibrium configuration. We calculate the energy of the system when each atom in the nonlinear zone is moved towards the other by distance v so that $\mathbf{u}_{\rm NL} = (v, -v)$ and additionally these atoms are subjected to external forces of magnitude fk acting in the same direction as their direction of displacement so that $\mathbf{F}^{\rm ext} = (fk, -fk, 0, 0)$ [Fig. 3(b)]. Noting that

$$(\mathbf{G}^{\infty}_{\rm NL,NL})^{-1} = \begin{pmatrix} \frac{10}{3}k & \frac{2}{3}k \\ \frac{2}{3}k & \frac{10}{3}k \end{pmatrix}, \tag{24}$$

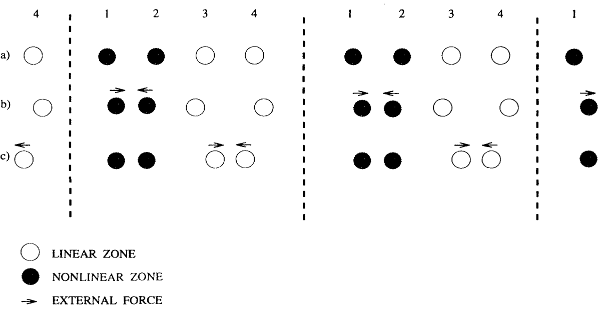

FIG. 3. Periodic array of four atoms used for the model total energy calculation. (a) shows the equilibrium configuration when no external forces are applied. (b) shows the configuration for the first model problem when external forces are applied in the nonlinear zone. (c) shows the configuration for the second model problem when forces are applied in the linear zone.

we now evaluate the total energy using the energy expression Eq. (14):

$$E^{\rm tot} = 16\alpha v^4 + \frac{8}{3}v^2 k - 2fkv \quad . \tag{25}$$

This is identical to the energy obtained by solving for the zero-force positions of $\mathbf{u}_L$ and using the whole Hamiltonian, illustrating that using $\mathbf{G}^\infty$ introduced no error.

A related problem [Fig. 3(c)] is to calculate the energy for the system with $\mathbf{u}_{\rm NL}$ unchanged but with the external forces imposed outside the nonlinear zone instead of inside it: $\mathbf{F}^{\rm ext} = (0, 0, fk, -fk)$. The anharmonic and harmonic terms are unchanged from the first problem but there are new linear and constant contributions to the total energy. Equation (14) gives

$$E^{\rm tot} = 16\alpha v^4 + \frac{8}{3}v^2 k + \frac{2}{3}fkv + \left[\frac{1}{24}f^2 k - \frac{3}{8}f^2 k\right] \quad . \tag{26}$$

Once again this agrees with the direct calculation using the full Hamiltonian.[7]

IV. COMPARISONS OF OLD AND NEW METHODS

To compare the efficiencies of the old and new methods we find equilibria for cracks of varying lengths. For consistent comparison we use the same Green's function and the same force law routines in all the calculations. The original relaxation method involves iteratively calculating

$$\mathbf{u}(i+1) = \mathbf{u}(i) + \alpha\Big\{\mathbf{G}[\mathbf{F}^{\rm ext} + \mathbf{F}^{\rm nl}(\mathbf{u}(i))] - \mathbf{u}(i)\Big\} \tag{27}$$

until $tol \equiv \{\mathbf{G}[\mathbf{F}^{\rm ext} + \mathbf{F}^{\rm nl}(\mathbf{u}(i))] - \mathbf{u}(i)\}^2$ is less than some predetermined constant chosen to reflect machine precision. The constant α may be varied between 0 and 1 during the course of the minimization. (The optimum way to do this is discussed below.) This method uses a standard conjugate gradient routine which requires input of an initial guess for the reduction in energy between the input atomic configuration and the equilibrium, and of a (small) tolerance related to the sum of the squares of the forces in the supposed equilibrium (which should be zero). This tolerance is also limited by machine precision.

While the two tolerances on having found the equilibrium are not identical, they are in fact closely related since the vector of the relevant conjugate gradient "forces" is given (for the case when all external forces are applied in the nonlinear zone) by $\mathbf{F}^{\rm ext} + \mathbf{F}^{\rm nl} - (\mathbf{G}_{\rm NL,NL})^{-1}\mathbf{u}$, as can be seen from Eq. (15). Squaring this gives a quantity close to the quantity *tol* used as a test for equilibrium in the iterative method except for multiplicative factors of order $\mathbf{G}^2$, which for our test case are typically of order 1. Thus the fact that different criteria are used for the two methods should generate only small errors when making quantitative comparisons of their relative efficiencies. Quantitative tests confirm this. Table I shows that the number of iterations needed for convergence using the conjugate gradient algorithm increases only slowly as the tolerance is tightened. (The smallest value for the tolerance in the table is the limit for which machine precision did not affect the accuracy.) Thus the precise value of the convergence test has only a small impact on the run time.

The initial test problems (run here with a bulk Green's function rather than with a crack Green's function) use nearest-neighbor pair forces between atoms in a hexagonal lattice with nonlinear zones of different sizes. The applied external forces are such as to open a crack over a substantial fraction of the nonlinear zone in each case, and the initial configuration is the elastic solution to the relevant problem. Figure 4 shows the CPU time for convergence (on a Silicon Graphics R4000 workstation) as a function of the number of degrees of freedom in the nonlinear zone. The figure shows three curves for the iterative method, corresponding to $\alpha = 0.1, 0.5$, and 1, and one curve for the conjugate gradient method.

Figure 4 shows that in all cases the conjugate gradient energy method takes much less time than the relaxation method. (It should be noted that it takes about 20 s to read in the very large Green's-function file at the begin-

TABLE I. Number of energy-function calls as a function of the input tolerance for convergence for a crack problem using the conjugate gradient method. The output energy on "convergence" is also given to show the relation of the error in the energy to the tolerance for this problem.

Tolerance	Number of iterations	Output energy
10^{-4}	170	-16.888 89
10^{-5}	182	-16.888 965
10^{-6}	195	-16.888 970
10^{-7}	211	-16.888 9721
10^{-8}	227	-16.888 97228
10^{-9}	245	-16.888 9722975
10^{-10}	253	-16.888 97229789
10^{-11}	259	-16.888 972297908

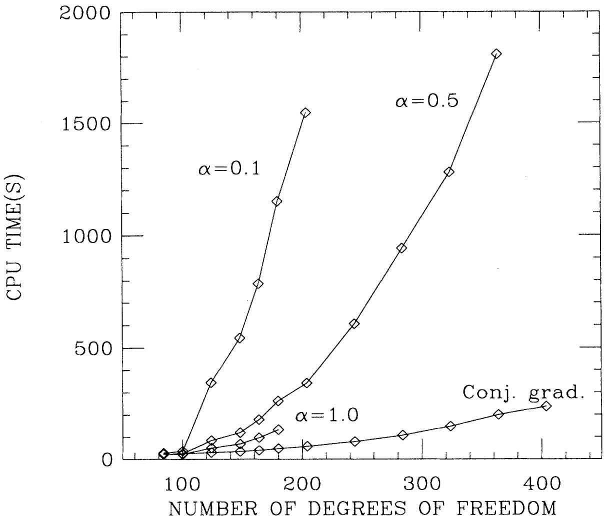

FIG. 4. Time to convergence in seconds for crack problems with different numbers of degrees of freedom using the conjugate gradient method and the relaxation method with three different values of the constant α.

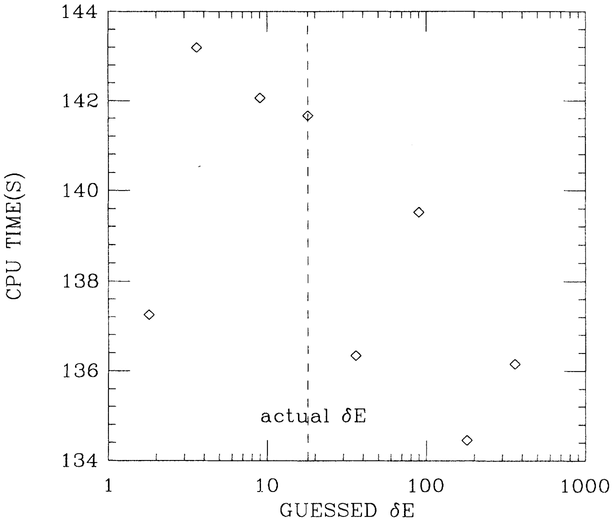

FIG. 5. Time to convergence in seconds as a function of the size of the convergence tolerance used by the conjugate gradient method for a crack problem.

ning of each calculation. Thus the actual computation time is even smaller than it seems in the graphs—only about 10 s for the problem with just 124 degrees of freedom when using the conjugate gradient method, for example.)

The iterative method is considerably more delicate to use than the conjugate gradient method. Figure 4 shows that the time to convergence is strongly dependent on the value of α chosen (which is held constant during each relaxation). In general, the smaller the α value, the longer to convergence, as would be expected since smaller α involves taking smaller steps towards the equilibrium. However, it is not feasible to take large α in general. For example, when the value $\alpha = 1$ was tried on a small sample of 102 atoms the system had not converged even after 20 000 iterations and more than 4000 s of CPU time. The solution in this case would be to change α to a smaller value as the system got closer to equilibrium. For simple cases such a strategy is possible (and was in fact used when finding equilibria for the earlier published work; there, however, the time to convergence was much reduced by using a crack Green's function). There is, however, no general procedure for determining when and how to change α. Thus, efficient use of the method, using optimum α values to minimize CPU time for a given run, demands much prior experience using similar force laws and similarly shaped and sized nonlinear zones. Furthermore, when the interatomic forces are chosen to be longer ranged and there are large numbers of degrees of freedom in the nonlinear zone it is found that moderately large values of α (such as 0.5) frequently lead to the whole system blowing up after significant amounts of CPU time.

When we consider the conjugate gradient method there is no sensitive dependence on a numerically required input parameter, analogous to α in the iterative method. Figure 5 shows the CPU time for convergence as a function of the guessed difference ΔE between the input and equilibrium energies. The time is unrelated to the actual ΔE (which is in this case 18 energy units) over a range of input guessed ΔE's of more than two orders of magnitude spanning the correct value. This makes the energy-based method much more robust than the former method. Furthermore, our experience has shown that this method is much less likely to fail to find a minimum at all by reaching a state where the system has blown up.

V. CONCLUSIONS

We have developed a method, using an energy functional and conjugate gradients, for finding the equilibria of a large number of atoms using Green's functions. It is seen to be faster, easier to use, and able to find equilibria for much larger numbers of degrees of freedom than the old method, to which it is, however, equivalent at equilibrium. The actual time (and also the scaling of the time as a function of size) depends in an intricate way on the force law (particularly on the number of neighbors per atom) and on the size of the nonlinear zone. For crack problems the time is reduced by using a crack Green's function instead of a bulk Green's function. The method extends the usefulness of the Green's function approach because it may be used to calculate activation energies. This can be done by calculating the minimum of the energy when a constraint on relative displacements of the atoms is imposed to ensure the symmetry of the state at the top of the energy barrier. Finally, it is useful to note that while at present we use the conjugate gradient method to find minima, the fact that we have defined both an energy functional and its derivatives makes it equally possible to use quasi-Newton or simulated annealing methods instead. Thus this approach to solving the equilibrium equations provides increased possibilities of locating hard to find minima and of comparing their relative energies.

ACKNOWLEDGMENTS

It is a pleasure to acknowledge discussions of the Green's-function methodology, and how it compares with more standard molecular dynamics approaches, with Dr. Robin Selinger of NIST. As a result of these discussions, we were motivated to work out the accuracy limitations of the Green's-function methodology more carefully, as reported in this paper. We gratefully appreciate support from the Office of Naval Research under Grant Nos. N00014-92-J-4049 (at Washington University) and N00014-92-F-0098 (at NIST).

APPENDIX

This appendix shows how to calculate the Green's function, defined as the inverse of the force constant matrix, in spite of the fact that the force constant matrix is singular. The procedure used, which is justified in detail below, is to omit the $\mathbf{q} = \mathbf{0}$ term in the back Fourier transform from $\mathbf{q}$ to real space.

First note that the $\mathbf{\Phi}$ matrix is *always* singular, whatever the force law or lattice. This is so because its $\mathbf{q} = \mathbf{0}$ term $\tilde{\Phi}_{ij}(0) = \sum_a \Phi_{ij}(\mathbf{R}^a, \mathbf{0})$ is always zero.[3] This means that the $\mathbf{q} = \mathbf{0}$ component of the Green's-function matrix $\tilde{\mathbf{G}}(\mathbf{0}) \equiv [\tilde{\mathbf{\Phi}}(\mathbf{0})]^{-1}$ does not exist. The solution is to note that we use Green's functions only when the sum of all externally imposed forces is zero, to find equilibria. In such cases the Fourier transform of the force vector $\tilde{\mathbf{F}}^{\rm ext}(\mathbf{0}) = \mathbf{0}$. Newton's third law ensures, on the other hand, that $\tilde{\mathbf{F}}^{\rm nl}(\mathbf{0})$, given by the sum of the nonlinear forces over the nonlinear zone, must also be zero. For a system whose Green's function has translational symmetry the convolution theorem allows us to rewrite Eq. (19) as

$$\mathbf{u}(\mathbf{q}) = \tilde{\mathbf{G}}(\mathbf{q})[\tilde{\mathbf{F}}^{\rm ext}(\mathbf{q}) + \tilde{\mathbf{F}}^{\rm nl}(\mathbf{q})] \qquad \forall \mathbf{q}, \tag{A1}$$

showing that the behavior of $\tilde{\mathbf{G}}(\mathbf{0})$ may be ignored when calculating atomic positions since it just multiplies a quantity which is zero. Hence treating $\tilde{\mathbf{G}}(\mathbf{0})$ "incorrectly" has no effect on the resulting equilibria, at least for systems which before loading have translational symmetry.

We now describe the way in which we treat $\tilde{\mathbf{G}}(\mathbf{0})$. First define a projection operator $\hat{\mathbf{P}} \equiv \sum_i |\mathbf{q} = \mathbf{0}, i\rangle\langle \mathbf{q} = \mathbf{0}, i|$, where the sums are, for example, in three dimensions, over the directions x, y, and z. Its real space matrix elements are given by

$$\begin{aligned} \mathbf{P}_{i,j}(\mathbf{R}^a, \mathbf{R}^b) &= \frac{1}{N} \sum_{\mathbf{q}_1 \mathbf{q}_2} \tilde{\mathbf{P}}_{i,j}(\mathbf{q}_1, \mathbf{q}_2)\, e^{-i\mathbf{q}_1 \cdot \mathbf{R}^a}\, e^{-i\mathbf{q}_2 \cdot \mathbf{R}^b} \\ &= \frac{1}{N} \sum_{\mathbf{q}_1 \mathbf{q}_2} \delta_{\mathbf{q}_1, \mathbf{0}} \delta_{\mathbf{q}_2, \mathbf{0}} \delta_{i,j}\, e^{-i\mathbf{q}_1 \cdot \mathbf{R}^a}\, e^{-i\mathbf{q}_2 \cdot \mathbf{R}^b} \\ &= \frac{1}{N} \delta_{i,j} \qquad\qquad \forall \mathbf{R}^a, \mathbf{R}^b \quad , \end{aligned} \tag{A2}$$

where N is the number of distinct $\mathbf{q}$ values, and the normalization ensures that $(\hat{\mathbf{P}})^2 = \hat{\mathbf{P}}$. Now define a perturbed force constant matrix $\mathbf{\Phi}^\beta \equiv \mathbf{\Phi} + \beta \mathbf{P}$, so that the perturbation removes the singularity. In $\mathbf{q}$ space the perturbed matrix is block diagonal with $\beta \mathbf{P}$ nonzero only for $\mathbf{q} = \mathbf{0}$, and $\mathbf{\Phi}$ nonzero only for $\mathbf{q} \neq \mathbf{0}$. This means that in a system with translational invariance $(\mathbf{\Phi}^\beta)^{-1}$ is the sum of the inverses of its two components, provided that when we Fourier transform back to real space we omit the $\mathbf{q} = \mathbf{0}$ term in the calculation of $(\mathbf{\Phi})^{-1}$. Defining $\mathbf{G}^\beta \equiv (\mathbf{\Phi}^\beta)^{-1}$, and noting that the $\mathbf{P}$ piece does not contribute to the inverse when $\beta = \infty$, it is clear that

$$\mathbf{G}^\beta = \mathbf{G}^\infty + \frac{1}{\beta} \mathbf{P} \quad . \tag{A3}$$

The physical value of β is zero but we choose to carry out the calculations with the "incorrect" $\beta = \infty$, so that the choice can be implemented simply by using the unperturbed $\mathbf{\Phi}$ matrix and omitting the $\mathbf{q} = \mathbf{0}$ term in the Fourier transform of $\tilde{\mathbf{G}}$.[8] (This has been discussed in an earlier paper from a different point of view.[1])

It is frequently of interest to compare the energies for different local minima, for example, to see which of several local minima is most likely to be global. We need therefore to show that the energy functional, Eq. (14), and not just the atomic configuration, is unaffected by the $\mathbf{q} = \mathbf{0}$ perturbation. This is complicated by the fact that the boundaries of the nonlinear zone break the translational symmetry and thus the factor $(\mathbf{G}_{\rm NL,NL})^{-1}$ means that convolution theorem arguments cannot be used for the energy expression.

We proceed as follows. Define $\psi \equiv (\mathbf{G}^\infty_{\rm NL,NL})^{-1}$ and $\mathcal{P} \equiv \mathbf{P}_{\rm NL,NL}$, the nonlinear zone submatrix of $\mathbf{P}$, so that $\mathcal{P}^2 = \gamma \mathcal{P}$, where the factor γ comes from the differences in size of the supercell and the nonlinear zone. Then, if $\mathbf{I}$ is the appropriately dimensioned identity matrix, Eq. (A3) gives

$$\begin{aligned} (\mathbf{G}^\beta_{\rm NL,NL})^{-1} = \left[\mathbf{G}^\infty_{\rm NL,NL} + \frac{1}{\beta}\mathcal{P}\right]^{-1} &= \psi \left[\mathbf{I} + \frac{1}{\beta}\mathcal{P}\psi\right]^{-1} \\ &= \psi - \frac{\psi \mathcal{P} \psi}{\beta} + \frac{\psi \mathcal{P}}{\beta^{1/2}\gamma} \left(\mathbf{I} + \frac{\mathcal{P}\psi\mathcal{P}}{\beta\gamma}\right)^{-1} \frac{\mathcal{P}\psi\mathcal{P}}{\beta\gamma} \frac{\mathcal{P}\psi}{\beta^{1/2}} \\ &= \psi - \frac{\psi \mathcal{P} \psi}{\beta} + \frac{\psi \mathcal{P}}{\beta^{1/2}\gamma} \sum_{\lambda_\nu \neq 0} \left(1 - \frac{\beta\gamma}{\lambda_\nu} + O((\beta\gamma)^2)\right) |\nu\rangle\langle\nu| \frac{\mathcal{P}\psi}{\beta^{1/2}}, \end{aligned} \tag{A4}$$

where $|\nu\rangle$ is an eigenket of $\mathcal{P}\psi\mathcal{P}$ with eigenvalue λ_ν, and the sum is over all $|\nu\rangle$ with nonzero eigenvectors. Taking the limit $\beta \to 0$,

$$(\mathbf{G}^{0}_{\mathrm{NL,NL}})^{-1} = \psi - \psi \mathcal{P} \sum_{\lambda_\nu \neq 0} \frac{|\nu\rangle\langle\nu|}{\lambda_\nu} \mathcal{P}\psi. \tag{A5}$$

[Note that $\mathcal{P}(1-\sum_{\lambda_\nu \neq 0} |\nu\rangle\langle\nu|)\mathcal{P} = 0$.] In general the second term will not be zero, suggesting that using $(\mathbf{G}^{\infty}_{\mathrm{NL,NL}})^{-1}$ in the total energy expression will give incorrect energies. Consider, however, cases where $\mathbf{F}^{\mathrm{ext}}_{\mathrm{NL}}(\mathbf{q})$ and $\mathbf{F}^{\mathrm{ext}}_{L}(\mathbf{q})$ *separately* vanish for $\mathbf{q} = \mathbf{0}$. Then premultiplying Eq. (15) by $\mathcal{P}$ gives

$$-\mathcal{P}\nabla E^{\mathrm{tot}} = -\mathcal{P}\psi \mathbf{u}_{\mathrm{NL}}, \tag{A6}$$

so that $(\mathbf{G}^{0}_{\mathrm{NL,NL}})^{-1}\mathbf{u}_{\mathrm{NL}} = (\mathbf{G}^{\infty}_{\mathrm{NL,NL}})^{-1}\mathbf{u}_{\mathrm{NL}}$ if the system is in a minimum or at a saddle point of the total energy.

We have therefore shown that if the overall Green's function has translational symmetry then the atomic positions in zero-force configurations are correctly given by using $\mathbf{G}^{\infty}$ instead of $\mathbf{G}^{0}$, and furthermore that if the sums of the applied forces inside and outside the nonlinear zone separately vanish, then the energies for these configurations are correct for any shape of the nonlinear zone. The arguments may be extended to systems where the Green's function no longer has translational symmetry, as, for example, when a crack Green's function is used. For this case [using the fact $\tilde{\mathbf{\Phi}}(\mathbf{q},\mathbf{0}) = \tilde{\mathbf{\Phi}}(\mathbf{0},\mathbf{q}) = \mathbf{0}$], it can be shown that all the above conclusions still hold.

We now apply this procedure to the four-atom example, giving

$$\left[\Phi^{\beta}(0), \Phi^{\beta}(1), \Phi^{\beta}(2), \Phi^{\beta}(3)\right] = \left[2k + \frac{\beta}{4}, -k + \frac{\beta}{4}, \frac{\beta}{4}, -k + \frac{\beta}{4}\right] . \tag{A7}$$

The Fourier transform is

$$\left[\tilde{\Phi}^{\beta}(0), \tilde{\Phi}^{\beta}(\pi/2), \tilde{\Phi}^{\beta}(\pi), \tilde{\Phi}^{\beta}(3\pi/2)\right] = \left[\beta, 2k, 4k, 2k\right], \tag{A8}$$

so that

$$\left[G^{\beta}(0), G^{\beta}(1), G^{\beta}(2), G^{\beta}(3)\right] = \left[\frac{1}{16}\frac{4k+5\beta}{k\beta}, \frac{1}{16}\frac{4k-\beta}{k\beta}, \frac{1}{16}\frac{4k-3\beta}{k\beta}, \frac{1}{16}\frac{4k-\beta}{k\beta}\right] . \tag{A9}$$

The limit of this expression as $\beta \to \infty$ is used in the energy calculation in Sec. III.

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[1] R. Thomson, S. Z. Zhou, A. E. Carlsson, and V. K. Tewary, Phys. Rev. B **46**, 10613 (1992).

[2] R. Thomson, in *Solid State Physics*, edited by H. Ehrenreich and D. Turnbull (Academic, Orlando, FL, 1986), Vol. 39, p. 1.

[3] Two properties of the force constant matrix used in this paper are that $\Phi^{ab}_{ij} = \Phi^{ba}_{ji}$ and that $\sum_b \Phi^{ab}_{ij} = 0$. The first is true because $\mathbf{\Phi}$ is a matrix of second derivatives. The second follows from the fact that if the whole crystal is moved by an arbitrary fixed amount so that the atoms remain in equilibrium, then the ith component of the linear force on the atom a, given by $-u_j \sum_b \Phi^{ab}_{ij}$, must be zero. In addition, note that the derivation of Eq. (4) is simplified for the case of one atom per unit cell by noting that in that case $\Phi^{ab}_{ij} = \Phi^{ba}_{ij}$, by the inversion symmetry of any Bravais lattice.

[4] When calculating the nonlinear energy, the inclusion of linear bonds only when both atoms are in the nonlinear zone is paralleled by the inclusion of pair potential terms only when both atoms are in the nonlinear zone. For three-body and embedded atom potentials the correct treatment of those terms when some atoms are inside and some atoms are outside the nonlinear zone is more complicated. It will not be further discussed here. An additional complication comes about, even with pair forces, when the force ranges beyond nearest neighbors, so that the equilibrium separation is no longer given by the length corresponding to the pair force minimum but is instead determined by a balance of forces from atoms at different separations. In this case, even if no external forces are applied and we consider what should be the equilibrium configuration, the establishment of the nonlinear region breaks the symmetry and hence leads to boundary atoms experiencing nonzero forces. These must be subtracted in finding the true equilibria and hence they give rise to an extra term, proportional to $\mathbf{u}$, which must be added to the total energy functional.

[5] For an isolated system it is clear what the *whole* system is. More commonly, however, the Green's-function method is used for systems with periodic boundary conditions; in such cases the energy is actually the correct value for all atoms in one supercell.

[6] S. J. Zhou, A. E. Carlsson, and R. Thomson, Phys. Rev. B **47**, 7710 (1993); S. J. Zhou, A. E. Carlsson, and R. Thomson, Phys. Rev. Lett. **72**, 852 (1994).

[7] It is, however, possible to construct configurations for which the out-of-equilibrium energy calculated using $\mathbf{G}^{\infty}$ gives the wrong answer (because of the neglect of the $\mathbf{q} = \mathbf{0}$ terms) This is so even though energy minimization gives the correct *equilibrium* positions and energies. Consider an asymmetric problem: four atoms as before, but with atoms 1, 2, and 3 in the nonlinear zone and only atom 4 in the linear zone. No external forces are applied and the atomic configuration in the nonlinear zone is taken to be $\mathbf{u}_{\mathrm{NL}} = (v, -v, 0)$. In order for the fourth atom to experience no force it must move by $v/2$ to be equidistant from atom 3 and the atom corresponding to atom 1 in the next cell. Note, however, that using Eq. (12) and $\mathbf{G}^{\infty}$ shows erroneously that it does not move at all, since moving it leads to a nonzero $\mathbf{q} = \mathbf{0}$ component of the displacement. [Using Eq. (12) is laborious,

but the simpler Eq. (19) does not apply here because the specified nonlinear zone positions mean that the atoms are not in equilibrium without external loading.] Similarly the energy obtained by using Eq. (14) is $3kv^2 + 17\alpha v^4$ while the true energy adding up bond energies is $3\frac{1}{4}kv^2 + 17\alpha v^4$. The difference may be completely accounted for by the error in the assumed position of atom 4. The point is that the proof in the Appendix for the correctness of the energy applies only for the zero-force condition, which is not met in this case.

[8] To understand this further note that the $\mathbf{q} = \mathbf{0}$ value

$$\tilde{\mathbf{G}}^{\infty}(\mathbf{0}) = \lim_{\beta \to \infty} \begin{pmatrix} \beta & 0 & 0 \\ 0 & \beta & 0 \\ 0 & 0 & \beta \end{pmatrix}^{-1} = \mathbf{0} \quad ,$$

while $\mathbf{G}^{\infty}(\mathbf{q}) = \mathbf{G}^{0}(\mathbf{q})$ for all nonzero $\mathbf{q}$.