Extending the time scale in molecular dynamics simulations: Propagation of ripples in graphene

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A technique using causal Green's function is proposed for extending and bridging multiple time scales in molecular dynamics for modeling time-dependent processes at the atomistic level in nanomaterials and other physical, chemical, and biological systems. The technique is applied to model propagation of a pulse in a one-dimensional lattice of nonlinear oscillators and ripples in graphene from femtoseconds to microseconds. It is shown that, at least in the vibration problems, the technique can accelerate the convergence of molecular dynamics and extend the time scales by eight orders of magnitude.

Limited time scale[1] is a major unsolved problem in molecular dynamics (MD),[2] which is the most important tool for modeling of physical, chemical, and biological systems. Atomistic or molecular modeling of material properties and physical processes has now emerged as a new scientific discipline because it is a valuable aid and supplement to theoretical and experimental studies. The problem is that the convergence requirements limit the size of the time step in MD, which is, in general, several orders of magnitude smaller than the time scales of physical interest. For example, in the field of nanomaterials and disordered solids, the time steps in MD are limited to a few femtoseconds. On the other hand, many physical processes of interest such as diffusion, radiation damage, formation and growth of defect clusters, wave propagation, phonons, thermal conductance, etc. occur at time scales of nanoseconds to microseconds. Modeling these processes would require $10^6 - 10^9$ time steps, which is a formidable task even for modern computers. This has been a major stumbling block in the science of modeling, and ability to bridge the time scales has remained a long-sought goal.[1]

Here we show that the time scales can be extended by several orders of magnitude by incorporating causal Green's function in MD. We validate our technique by applying it to calculate pulse propagation in a one-dimensional lattice of nonlinear oscillators. Further, we illustrate our technique by modeling propagation of ripples in graphene from femtoseconds to microseconds. Ripples[3] have an important role in determining the stability of graphene and are a subject of strong topical interest. Presently there is no available technique for modeling a process over such an extended range of time. Bridging time scales is even more crucial for atomistic modeling of physical processes in nanomaterials such as graphene because of the obvious difficulties in experimentation at nanoscale.

Many efficient techniques[4–7] have been proposed for improving the temporal convergence of MD. For a review and other references see Ref. 1. These techniques are based upon use of integrators, transformations, and efficient ways of including higher-order terms in time. They result into substantial acceleration of MD but are not adequate to bridge the time scales from femtoseconds to microseconds. Voter *et al.*[1] described an elegant technique to extend MD to several picoseconds using the transition state theory. Our technique is based upon the simple physical idea that the causal Green's function gives the temporal response of a system at all times.

We show that it gives an exact solution of the temporal part of the MD equations for up to quadratic terms in atomic displacements in the interatomic potential. Higher-order terms are then included by iteration. We will refer to our technique as Green's function in molecular dynamics (GFMD). This technique should be applicable to all physical, chemical, and biological systems where MD is used.

In certain class of problems in which the atoms vibrate about an equilibrium site, GFMD gives exact results in the harmonic approximation. Examples of such class of problems are phonon transport, thermal conduction etc., in disordered or finite solids and low-dimensional material systems for which MD has to be used because analytical solutions are not available even in the harmonic approximation. For nonlinear vibration problems, depending upon the anharmonicity, GFMD can accelerate MD by about 8 orders of magnitude, and model processes at microseconds. In other classes of problems in which the atoms are itinerant, such as diffusion or crystal growth, GFMD can be used iteratively and should still accelerate MD by a significant amount.

Consider a set of N interacting atoms. We label the atoms by indices L and L'. We assume a Cartesian frame of reference and denote the position vector of atom L by $\mathbf{r}(L)$ at $t=0$. We denote the displacement and velocity of atom L at time t by $\mathbf{u}(L,t)$ and $\mathbf{c}(L,t)$, respectively. As in classical MD, we need to solve the following equation for $\mathbf{u}$:

$$m_L \frac{\partial^2 u_\alpha(L,t)}{\partial t^2} = -\frac{\partial W}{\partial u_\alpha(L,t)}, \qquad (1)$$

where m_L is the mass of L and W is the total potential energy of the system. We expand W as a Taylor series in powers of $\mathbf{u}$, which gives

$$m_L \frac{\partial^2 u_\alpha(L,t)}{\partial t^2} = f_\alpha(L) - \sum_{L'\beta} \phi_{\alpha\beta}(L,L') u_\beta(L',t) + \Delta f_\alpha(L,t), \quad (2)$$

where α, β $(=1,\ldots,n)$ denote the Cartesian components, n is the number of degrees of freedom for each atom, $-\mathbf{f}$ and $\boldsymbol{\phi}$ are the Taylor coefficients evaluated at $\mathbf{u}=0$ and $\Delta\mathbf{f}$ represents the cubic and higher terms in the expansion of W. For notational brevity, we define nN dimensional vectors $\mathbf{U}(t)$, $\mathbf{C}(t)$, $\mathbf{F}$, and $\Delta\mathbf{F}(t)$ whose αL components are $\sqrt{m_L}u_\alpha(L,t)$, $\sqrt{m_L}c_\alpha(L,t)$, $(1/\sqrt{m_L})f_\alpha(L)$, and $(1/\sqrt{m_L})\Delta f_\alpha(L,t)$, respectively. We also define an $nN \times nN$ matrix $\boldsymbol{\Phi}$ whose $\alpha L, \beta L'$

elements are $\phi_{\alpha\beta}(L,L')$. The formal solution of Eq. (2) in the operator form is

$$\mathbf{U}(t) = \left(\mathbf{I}\frac{\partial^2}{\partial t^2} + \mathbf{D}\right)^{-1}\mathbf{F}_{\text{eff}}(t),\qquad(3)$$

where $\mathbf{I}$ is the unit matrix, $\mathbf{D} = \mathbf{M}^{-1/2}\boldsymbol{\Phi}\mathbf{M}^{-1/2}$, $\mathbf{F}_{\text{eff}}(t) = \mathbf{F} + \Delta\mathbf{F}(t)$, and $\mathbf{M}$ is a diagonal matrix with atomic masses as its elements.

The inverse operator in Eq. (3) is the Green's function, which is defined as a solution of

$$\left(\mathbf{I}\frac{\partial^2}{\partial t^2} + \mathbf{D}\right)\mathbf{G}(t-t') = \mathbf{I}\delta(t-t'),\qquad(4)$$

where $\mathbf{G}(t)$ is the causal Green's function which is 0 for $t < 0$.[8] We take the Laplace transform of Eq. (4) for $t' = 0$. This gives $\mathbf{G}^L(s) = [s^2\mathbf{I} + \mathbf{D}]^{-1}$ where s is the Laplace variable conjugate to t, and the superscript L over a symbol denotes its Laplace transform. The solution of Eq. (3), subject to the initial conditions on $\mathbf{U}$ and its derivative $\mathbf{C}$, is then given by

$$\mathbf{U}^L(s) = \mathbf{G}^L(s)\mathbf{F}_{\text{eff}}^L(s) + s\mathbf{G}^L(s)\mathbf{U}_0 + \mathbf{G}^L(s)\mathbf{C}_0.\qquad(5)$$

To obtain the inverse Laplace transform of Eq. (5), we multiply its both sides by $\mathbf{V}^T$, the transpose of the matrix of eigenvectors of $\mathbf{D}$. This diagonalizes $\mathbf{G}^L(s)$ and gives

$$\mathbf{U}^{*L}(s) = \mathbf{G}_D^L(s)\mathbf{F}_{\text{eff}}^{L*}(s) + s\mathbf{G}_D^L(s)\mathbf{U}_0^* + \mathbf{G}_D^L(s)\mathbf{C}_0^*,\qquad(6)$$

where $\mathbf{U}^{*L}(s) = \mathbf{V}^T\mathbf{U}^L(s)$, $\mathbf{F}_{\text{eff}}^{L*}(s) = \mathbf{V}^T\mathbf{F}_{\text{eff}}^L(s)$, $\mathbf{U}_0^* = \mathbf{V}^T\mathbf{U}_0$, $\mathbf{C}_0^* = \mathbf{V}^T\mathbf{C}_0$, and $\mathbf{G}_D^L(s)$ is a diagonal matrix. Its elements are $[G_d^L(s)]_{ii} = 1/(s^2 + E_i^2)$, where E_i^2 is an eigenvalue of $\mathbf{D}$ and $i = 1, 2, \ldots, nN$. The eigenvalues can be real or complex.

As a numerical approximation, we neglect $\Delta\mathbf{F}$ in $\mathbf{F}_{\text{eff}}$, so $\mathbf{F}_{\text{eff}}^{L*}(s) = \mathbf{F}^*/s$. Then we can obtain the inverse Laplace transform of Eq. (6) analytically. The final result is $\mathbf{U}(t) = \mathbf{V}\mathbf{U}^*(t)$, where

$$U_i^*(t) = -(F_i^*/E_i^2)[\cos(E_i t) - H(t)] + (C_{0i}^*/E_i)\sin(E_i t)$$
$$+ U_{0i}^*\cos(E_i t),\qquad(7)$$

and $H(t)$ is the Heaviside step function.

Equation (7) is an exact solution of Eq. (3) for all values of t if $\Delta\mathbf{F}(t) = 0$. This equation can be used as such for phonon or thermal problems in disordered or finite systems where the harmonic approximation is valid but the problem cannot be solved analytically due to lack of translational symmetry. To account for anharmonic effects, we expand W locally at each time step. We calculate $\mathbf{U}(t)$ from Eq. (7) in steps of $t = 0$ to Δt, and keep Δt small enough so that $\Delta\mathbf{F}(t)$ is negligible during that time. The maximum value of Δt is determined by the value of $\Delta\mathbf{F}(t)$, which depends upon the specific problem. This introduces a constraint on Δt but is much less severe than that in conventional MD.

The convergence of this technique is much faster than MD because of two factors: (i) in the basic MD only the first term on the right of Eq. (2) is retained, whereas GFMD retains up to quadratic terms in the expansion of W, and (ii) the temporal equation in MD is integrated numerically from $t = 0$ to Δt, whereas GFMD gives an exact solution of the temporal equation for up to quadratic terms in atomic dis-
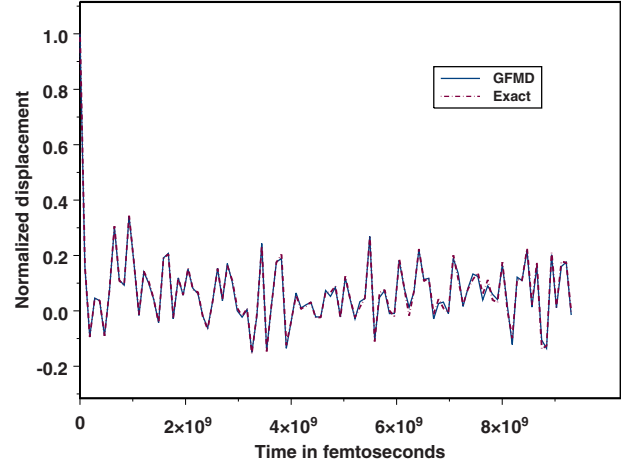

FIG. 1. (Color online) Atomic displacement of the central atom in a one-dimensional lattice as function of time calculated by using GFMD with $\Delta t = 100$ femtoseconds and compared with the exact result. The two curves almost overlap. The displacements are normalized with respect to the initial displacement of the central atom.

placements in W. The basic MD can be accelerated somewhat by using more refined numerical techniques[2] that partly account for the quadratic terms in W by iteration but the numerical integration of the temporal part is a severe constraint on Δt in MD.

Equation (7) requires diagonalization of $\mathbf{D}$ which is an $O(N^3)$ calculation. For many systems of practical interest, the interatomic interaction is short range. In these cases $\mathbf{D}$ is sparse and may be banded. This can reduce the computation to $O(N^2)$ or even $O(N)$. In many cases, N has to be kept small (few hundred atoms) for other computational reasons. In such cases, the time evolution can be conveniently calculated by diagonalizing $\mathbf{D}$ even if $\mathbf{D}$ is not sparse or banded.

An alternative to diagonalization is to use an iterative technique similar to static MD for the space part of Eq. (2), which requires $O(N)$ calculation. We assume $\mathbf{u}(L',t)$ in Eq. (2) to be constant during the interval $t = 0 - \Delta t$ for all L' except $L' = L$. We then solve Eq. (2) using Eq. (7) for the single atom L. This process includes anharmonic effects. In this case $\mathbf{D}$ is only an $n \times n$ matrix ($n = 1 - 3$) and can be easily diagonalized. The actual choice between using full diagonalization or single atom iterative calculation will depend upon the specific problem.

In order to bench mark GFMD, we have applied it to calculate the propagation of a pulse in a one-dimensional lattice of $(2J+1)$ atoms. The model lattice is shown in supplementary Fig. 1.[9] The interaction potential between atoms can be nonlinear. This is a useful model for testing a new technique because its analytical solution is available in the harmonic approximation. It is not possible to benchmark GFMD against MD in more realistic systems because results over such a wide range of time cannot be obtained by using conventional MD.

We label the atoms by L where the central atom is $L = 0$ and the end atoms are $L = -J$ and J. The two end atoms are assumed to be fixed so their displacement is 0 at all times. We generate the pulse in the lattice by displacing the central atom by an amount d. We assume that each atom interacts
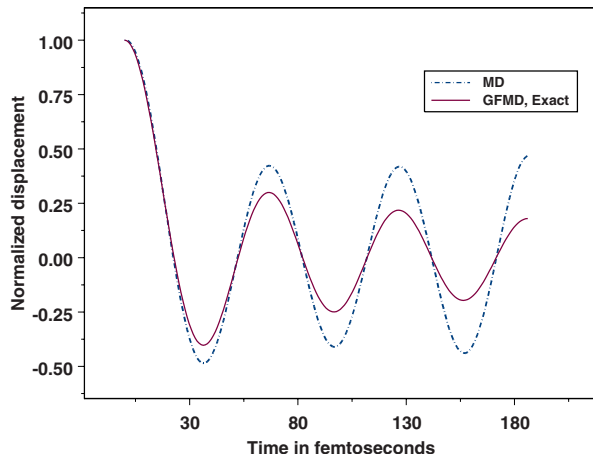
FIG. 2. (Color online) Same calculations as in Fig. 1 compared with results obtained by using basic MD for time step $\Delta t = 1$ fs. The agreement between the two curves becomes increasing worse at longer times and/or for longer Δt.

with its nearest neighbors only. The displacement of the atom L at time t in the harmonic approximation is given by

$$u(L,t) = (d/2J) \sum_{k_i} \cos(k_i L) \cos[\omega(k_i)t], \qquad (8)$$

where $\omega^2(k) = 2(\mu/m)(1 - \cos k)$, μ is the force constant, m is the atomic mass, k is the wave vector, and i is an integer varying from $-J$ to $J-1$. The allowed values of k_i are $(2i+1)\pi/2J$.

We solve the same problem by using GFMD. If d is small enough for the anharmonic effects to be negligible, the GFMD results should agree with the exact harmonic result. This should provide a test of accuracy and the convergence of the GFMD technique. We assume that the atoms interact through the Morse potential $V(x) = -V_0[\exp(-\gamma x) - \exp(-2\gamma x)]$, where x is the distance between two atoms and V_0 and γ are constants. We express x in units of a_0, the interatomic spacing at equilibrium. We choose $\gamma a_0 = \ln 2$ which gives $x = 1$ at equilibrium. We choose $V_0 = 14.375$ eV, $m = 12$ AU, and $a_0 = 1$ Å. These values have been chosen so that the cohesive energy of the model solid is -7.2 eV per atom, which is equal to that of graphene. The resulting value of μ, the nearest neighbor harmonic force constant, is 55.25 N/m. We choose d, the initial displacement of the central atom to be $10^{-4}a_0$. This value is small enough for the anharmonic effects to be negligible to enable a comparison between the GFMD and the exact harmonic result.

The atomic displacements of the central atom calculated by using Eq. (7) along with the exact harmonic results are shown in Fig. 1 for time up to about 10 ms. The displacements are normalized, that is, expressed in units of d. The two curves almost overlap over the entire scale. The same results are shown in Fig. 2 for time until about 180 fs and compared with the results obtained by using the basic MD. This figure shows that the time scale in the basic MD is limited to a few femtoseconds in contrast to several microseconds for GFMD.
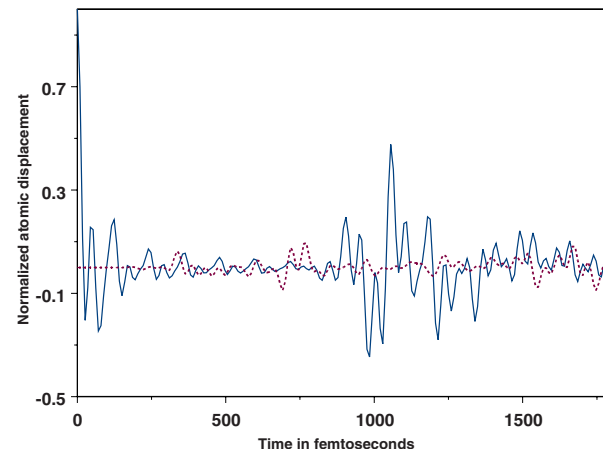

FIG. 3. (Color online) Atomic displacements as function of time in the picoseconds range for the central atom (solid line) and the atom located at about 1.9 nm along the $+X$ axis (dotted line) in graphene. The displacements are normalized as in Fig. 1.

Further, we illustrate GFMD by applying it to calculate the propagation of ripples in graphene. In order to bring out the efficacy of the GFMD technique, we have chosen a particularly simple but realistic and commonly used model potential, the Tersoff-Brenner (TB) potential.[10] In this model the interatomic interactions extend only up to second neighbors of each atom.[11] The X and Y axes are assumed to be in the plane of the graphene sheet and the Z axis along the normal to its plane. The origin of the coordinates is assumed to be at a lattice site. We consider only the atomic displacements in the Z direction to which only the Z components f_z, Δf_z, and ϕ_{zz} contribute and $n = 1$. Propagation of pulses is an important characteristic of a material and is useful in understanding its elastic response and phonon transport. Such a calculation for a finite lattice cannot be done analytically even in the harmonic approximation.

Our model consists of about 1100 carbon atoms located at the equilibrium graphene lattice sites at $t = 0$. As in Ref. 11, the outer atoms within the second-neighbor distance of the outermost vibrating atoms are pegged so that their displacement is zero at all times. The size of the active lattice along the X axis is about 5.52 nm. Propagation is initiated by imposing an initial displacement d in the Z direction on the central atom. The CPU time for these calculations was only a few minutes on a standard 3 GHz desktop.

We account for the anharmonic effects in the Z direction by calculating f_z and ϕ_{zz} for each atom at each time step. These components change at each step due to anharmonicity. A major approximation in these calculations is that the displacements in the Z direction and in the XY plane are not coupled. This is strictly valid only in the harmonic approximation. We, therefore, keep d small so that the coupling between the ZZ and the planar components of ϕ can be neglected at all times.

Figure 3 shows the displacement of the central atom and the atom at a distance of 1.9 nm from the center along the X axis. The displacements have been normalized with respect to $d = 0.01a$, where $a = 1.2563$ Å is half the lattice constant of graphene in the TB model.[11] The time taken by the wave
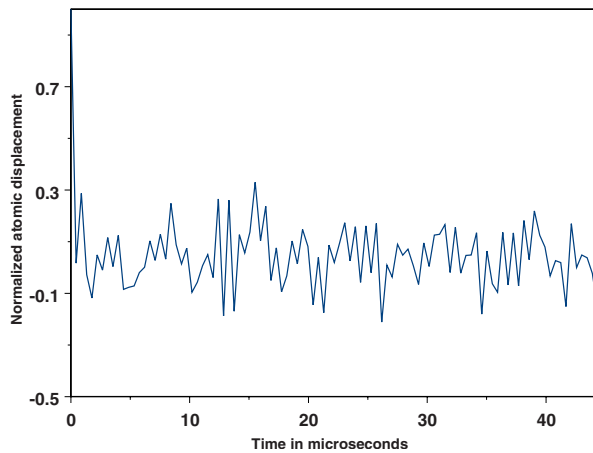
FIG. 4. (Color online) Same as in Fig. 3 for the central atom in the microseconds time range.

FIG. 5. (Color online) Snapshot of normalized atomic displacements in graphene at about 20 ms. Coordinates X and Y are in units of half lattice constant.

to reach this atom is about 320 fs. This is consistent with the maximum group velocity of the wave being 5764 m/s as calculated from the TB model dispersion relation. The boost in the displacement pattern of the central atom at about 960 fs shows the arrival of the reflected wave. This time is also consistent with the maximum group velocity of the wave.

An unusual feature of graphene is that the phonon frequency of the acoustic Z modes has a quadratic and not linear dependence on wave vector in the zero wave-vector limit. Hence, these waves are dispersive even at the center of the Brillouin zone. Their velocity is maximum at an intermediate point in the zone. A pulse generated at $t=0$ on a single atom generates waves of all wavelengths that move with different velocities. The displacement of any atom is the resultant of all these waves and the reflected waves. Figure 4 shows the displacement of the central atom in the microseconds range. Figure 5 shows a snapshot of the ripples or the instantaneous displacements of all atoms in the lattice at about 20 ms. A movie of the propagation of ripples is available in Ref. 9.

An important test of the numerical convergence of the model is the invariance of the total energy of the system at all times. We have calculated the change in the energy of the system at each time step and found it to be less than $10^{-4}\%$. This shows that the GFMD has extended and bridged the time scales at least in these calculations by 8 orders of
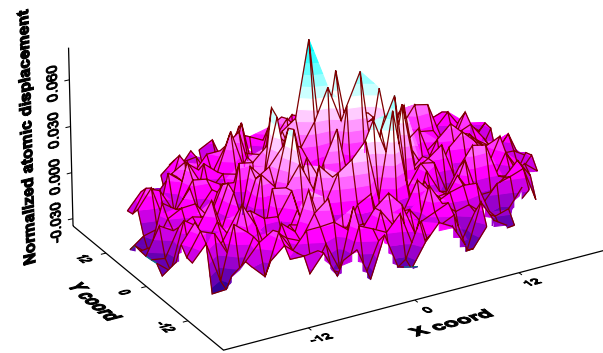
magnitude—from femtoseconds to microseconds. In the basic MD the lack of energy conservation results in an increase in the crystal temperature. This necessitates quenching of temperature that may introduce errors in the displacements. This problem does not arise in the present calculations since the energy is very well conserved. Finally, an additional advantage of GFMD is that the same formulation can be used to bridge the length scales by taking the asymptotic limit of the static part of the Green's function.[12,13]

In conclusion, we have presented a possible solution of the long-standing problem of bridging time scales in atomistic or molecular modeling of nanomaterials by incorporating causal Green's function in MD, which significantly accelerates its temporal convergence. The technique is verified by applying it to calculate pulse propagation in a one-dimensional lattice of nonlinear oscillators. The technique is further illustrated by modeling propagation of ripples in graphene from femtoseconds to microseconds, which is not possible by using any other available technique. In these calculations the total energy is conserved within $10^{-4}\%$, which partially validates GFMD. Thus, in the two model problems considered in this Rapid Communication, GFMD extends the time scales by a factor of 10^8. The technique is general and should be applicable to modeling of time-dependent processes in various physical, chemical, and bio systems in which MD is used.

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