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Nonlinear Dynamics Analysis through Molecular Dynamics Simulations

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A general goal in multiscale modeling is to analyze macroscale (system-level) phenomena using information on the system at the microscale. In this pedagogical note we revisit the time-stepper approach to performing nonlinear dynamics analysis through the use of a microscopic simulator, molecular dynamics in this case. Using simple illustrative examples we suggest that there are better ways of using a molecular simulator than observing temporal evolution of the system in a hands-off manner alone. Continuum numerical analysis algorithms can be transformed into alternative computational protocols for microscopic solvers: macroscopic nonlinear dynamics information, such as stationary solutions, stability boundaries or similarity exponents, can be obtained through the design and execution of appropriately initialized short bursts of direct microscopic simulation.

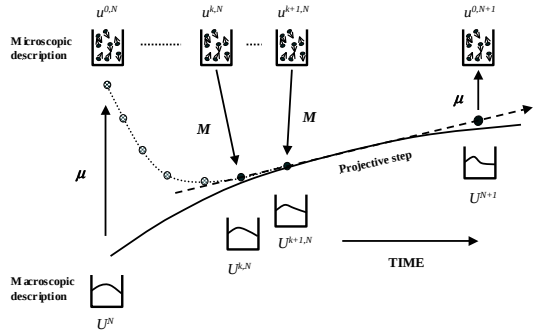
1 Introduction

In the computer-assisted study of nonlinear dynamical systems, direct temporal simulation is not the only available approach. A host of computational tools, such as numerical bifurcation analysis, aimed at efficiently extracting quantitative information have been developed. Such tools include Newton-Raphson and other fixed point algorithms that accelerate the location of steady states, continuation of solution branches in parameter space, eigensolvers that quantify stability, boundary value solvers to accelerate the location of limit cycles, algorithms for codimension-one or higher order bifurcation points to locate transitions, etc. When explicit evolution equations ("macro"-level equations for the purpose of this note) are available, such techniques (given a good initial guess) can be remarkably efficient compared to direct

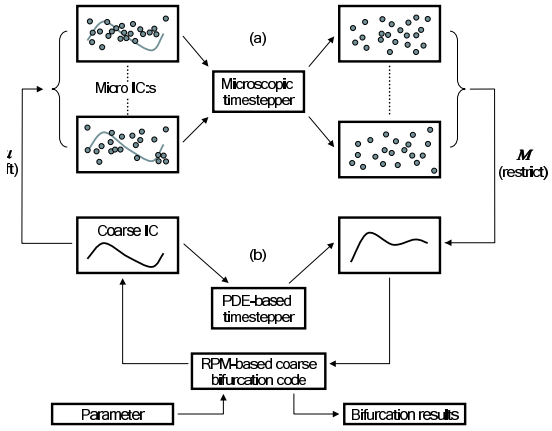
temporal simulation. Over the last ten years, a trend has arisen in continuum numerical analysis towards so-called *time-stepper based* methods, like the Recursive Projection Method (RPM) introduced by Shroff and Keller [SK93], see also [TB00]. These methods are aimed at enabling deterministic dynamic simulators to perform tasks beyond direct temporal simulation: bifurcation analysis, but also long-term prediction, stability analysis, control and optimization. This is achieved through computational protocols implemented through a software superstructure: what, in this discussion, we will call "the wrapper". The wrapper is then a way of combining continuum numerical tools, such as bifurcation analysis techniques, as the *outer* component, with a time integrator (time stepper), as the *inner* component. The functional relation of the two components is indicated schematically in Fig. 1 for the case of coarse projective integration and coarse bifurcation analysis [TQK00, GKT02].

Fig. 1 goes beyond the *deterministic* time-stepper case: it illustrates the use of this wrapper-based computational enabling technology; system level coarse "outer" algorithms (integration, RPM or GMRES-based fixed point location) are wrapped around inner fine scale *atomistic / stochastic* timesteppers. It is interesting that the same wrapper can be operated transparently in two modes, depending on whether a deterministic coarse equation is available or not. For a given set of parameters the time-stepper component is called along with a coarse initial condition, which is evolved forward in time -with a deterministic coarse PDE solver- to produce a coarse output (see the lower part of Fig. 1). The results are processed, and new trial initial conditions are constructed and evolved; after this procedure is repeated a sufficient number of times, bifurcation results are obtained. When a coarse equation is not available the time-stepper protocol operates transparently, but with one additional feature - the "lifting" of the coarse initial condition to one or more consistent microscale initial conditions, and the "restriction" of evolved microscale information back to macroscopic observables.

The lifting step is shown on the left in both parts of Fig. 1. For each microscale initial condition thus produced, the system is evolved forward using the microscopic timestepper, and the evolved microscale conditions are "restricted" to give a coarse output that is then returned to the integration or bifurcation code. Notice that the first mode requires the availability of coarse PDE, whereas such equations are not needed in the second mode: the coarse input-output map for the macroscopic observable has been *estimated* through short computational experimentation with the micro solver. The microscopic timestepper mode implicitly takes into account microscale processes in the bifurcation analysis; it makes the analysis feasible even if the appropriate coarse PDE for the system is not known. On the other hand, it remains to be shown that good results can be obtained using the microscopic timestepper. The distinction between coarse (PDE-based) and detailed (microscopic) timesteppers has been discussed in [TQK00, GKT02, RTK02, MMPK02] and reviewed in [KGHKRT03].



(a)



(b)

Fig. 1. Schematic of timestepper-based numerical computation: (a) coarse integration and (b) RPM-based coarse bifurcation analysis. Macro-initial conditions are *lifted* to consistent microscopic ones, evolved through the timestepper, and *restricted* back to the macroscale. The wrapper is templated on continuum numerical analysis algorithms. It designs and executes these short bursts of computational experimentation with the micro-solver, processes their results, and uses them to estimate the quantities required in the macro-numerics.

We are interested in the use of molecular dynamics (MD) simulation, a well-known method for following the dynamical evolution of a system of atoms and molecules, as the inner, microscopic timestepper. Since molecular dynamics is not designed to perform system-level analysis, running the MD simulation in the conventional manner does not lead naturally to results on nonlinear dynamics behavior on the coarse scale. In what follows we argue that a wrapper can be constructed to enable bifurcation analysis to be performed with MD as the timestepper. We use MD results from existing simulations to illustrate the general utility of the timestepper/wrapper notions, pointing to what has been done (without such notions) to show what more can be done with such notions. While the correspondence and language may not yet be as precise as one would like, it appears that the new connections being made between NLD and MD can be potentially useful.

2 Linking Scales (Practical Determinism)

What is the precise meaning of the statement that "macroscopic equations close at a certain level of description"? Colloquially this implies that one can be practically predictive at that level: given the value of "a few" system observables at a moment in time, one can predict the evolution of these observables at a later time without additional information. If equations for the evolution of these observables are not known, can we put practical determinism (i.e., the information that equations *conceptually* exist) to good use in microscopic simulations ? Our answer is that the timestepper-wrapper method does not require *explicit formulas* for the equations. There are reasons to believe that a time-stepper approach, wrapped around a microscopic simulator, can succeed in solving the equations without writing them down.

The challenge, put in a different way, lies in the linking of micro and macro scales; one would like to make macroscopic predictions on the basis of "just enough" input from the microscale. For our example we consider the prediction of the onset of elastic instability in nanoindentation of a thin-film sample, which leads to the homogeneous nucleation of a dislocation loop, a microcrack or a deformation twin [LVZYS02, VLZYS03, ZLVOYS04]. At the macro scale, the strain induced in the sample may be described in the finite-element method (FEM) by a mesh of grid points (nodes). The FEM governing equations may not be closed because the constitutive (stress-strain) relations capable of describing large-strain deformation at the nodes are generally not known in closed form. On the other hand, MD is a method of simulating the phenomenon at the micro scale without the use of equations describing the manifestation of the instability at the level of macroscopic observables. The challenge is then in passing just enough microscopic information (obtained by running the molecular simulator as parsimoniously as possible in space and time) up to the macro scale, where the manifestation of this instability can be efficiently pinpointed and practically analyzed. If we think of direct dynamic

simulation as "nature", we are in a sense attempting to outsmart nature: obtain the information of interest by doing as little microscopic simulation as possible; hopefully with much less effort than direct simulation of the full system in space, time and parameter space.

Timestepping can thus form the basis of a robust procedure for scale-linking: passing information between the micro- and macroscales. Scale linking is generic to practically all fundamental studies of complex systems behavior. We mention in passing that, while in some problems the relevant macroscopic observables are obvious (e.g. concentration for chemical reactions, or stress and strain in our case), the selection of the right observables (order parameters, phase field variables, reaction coordinates) constitutes an important and difficult part of any procedure for linking scales. This selection determines the level at which we can be practically deterministic.

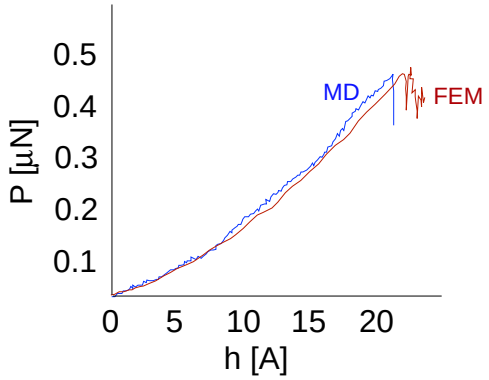


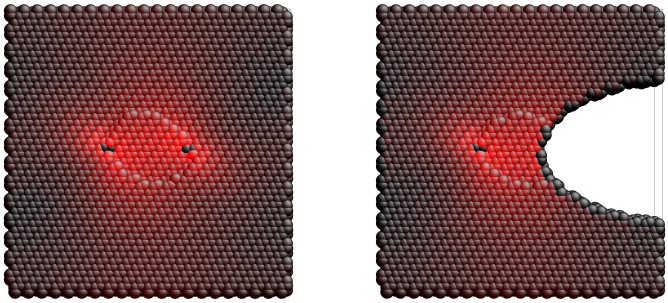
Fig. 2. Nanoindentation displacement-load (h-P) response showing initial elastic deformation of the thin film up to a critical indentation distance where the load suddenly drops (signaling the nucleation of a dislocation loop), prediction by FEM with Cauchy-Born hypothesis (smooth curve) and direct MD simulation (wiggly curve).

Our example of linking scales in the modeling of nanoindentation of metal thin film involves two distinctly different simulation methods, finite-element method (FEM) and molecular dynamics (MD) [LVZYS02, VLZYS03, ZLVOYS04]. The instability in question occurs when the indenter force reaches a critical threshold, or equivalently, when the indenter penetration reaches a critical distance. The resulting phenomenon is a sudden transition from elastic to plastic response of the thin film. To map the nanoindentation study onto the present discussion we regard FEM and MD as the coarse and detailed timesteppers respectively. In FEM the strain at each node is evolved subject to a constitutive relation that specifies the stress field. Since this information is usually not known for strains large enough to induce elastic instability, one can say that determinism does exist but the constitutive relations required

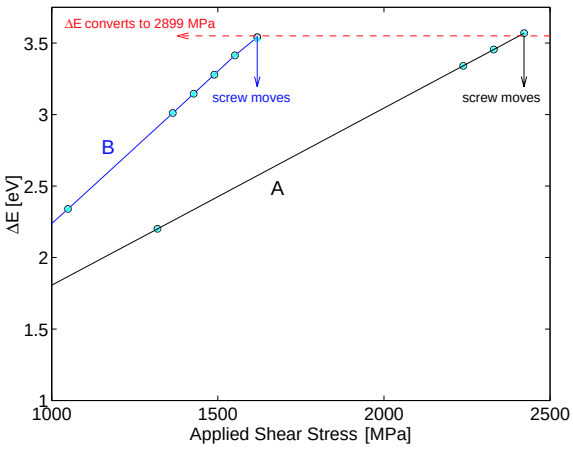
to the close at FEM level are not available. However, in this case it is possible to link FEM with MD using an approach known as the Cauchy-Born hypothesis. In this hypothesis one (a) converts the strain at a given node into a deformation tensor, (b) deforms a perfect crystal according to this tensor, and (c) uses an appropriate interatomic potential to calculate the stress response of the deformed infinite lattice. The resulting stress is then returned to the given node as if it were given by a constitutive relation. By applying this procedure to every node in the FEM calculation and doing it on-the-fly at every step in the evolution one arrives at a prediction of the nanoindentation response. Relative to Fig. 1 we see that the Cauchy-Born hypothesis, steps (a) through (c), are, in effect, the "lifting", "evolving" and "restriction". In Fig. 2 we show a comparison of the predicted response as simulated by the modified FEM, which we denote as interatomic potential FEM, with that obtained by direct MD simulation (detailed timestepper evolution) without projection to the coarse level. This example of linking atomistic (MD) and mesoscale (FEM) illustrates how prediction at the coarse scale can be achieved using the notion of a wrapper. Our use of the Cauchy-Born hypothesis is a special case of a general formulation linking atomistic simulation and FEM, known as the Quasicontinuum Method [TOP96, MT02]. While in this case we evaluate the atomic-level stress immediately upon lifting, in general one may want to run the detailed timestepper a little to "heal" the errors introduced by the lifting process [GKT02].

3 Initializig at Will

In the spirit of linking scales, we now take up the question of how to find the inflection-point and saddle-point configurations of a dynamical system. The premise here is that a saddle point is best located through fixed point schemes (like Newton-Raphson) that exploit macroscopic smoothness through the use of derivatives. Interestingly, under appropriate assumptions on separation between fast attracting and slow repelling time scales, saddles can be located by performing integration of an explicitly available equation *backward in time*. This opens up the intriguing possibility (used in MD studies of alanine dipeptide folding [HK03]) of integrating an equation backward in time to find an unstable solution [GK04]. This can be effected by initializing consistently with a macroscopic observables, evolve microscopically for a short time interval, estimate the time derivative of the macroscopic observables, and use it to project the state of the system for a longer interval *backward in time*. The overall procedure consists of short forward runs, postprocessing of their results, and reinitializations of the system at "effectively earlier in time" values of the macroscopic trajectory. Such a backward integration procedure has been used to escape free-energy minima and explore free energy surfaces; we believe it has potential in detecting transition states and exploring nucleation phenomena.



(a) screw-screw (b) screw-notch



(c)

Fig. 3. Variation of virtual energy release ΔE with applied shear stress for a screw dislocation in silicon in two different microstructure environments (A and B), one in the form of a dislocation dipole, two dislocation cores as shown in (a), and the other in the form of a dislocation core with a notch nearby, as shown in (b). The left dislocation core is seen to to move at the same value of ΔE but different values of the applied shear stress. This signifies ΔE is not affected by the samepl microstructure environment and therefore it can be converted to a value for the Peierls stress that is an intrinsic material property.

Our example for illustrating the advantages of "detailed" system initialization is the determination of the stress required to move an existing, isolated dislocation in a crystal, the so-called Peierls stress in the problem of dislocation dynamics. Since simulations generally can be initialized at will, we take advantage of this flexibility to prepare the crystal model containing a dislocation such that its subsequent behavior provides physical insight. The basic notion of preconditioning the system is not new, yet there are not many simulations that exercise this degree of control in the manner described below. Our simulation consists of setting up two runs, each involving a single dislocation in a lattice with a different sample microstructure environments (denoted as A and B). We subject both systems to incremental values of pure shear to determine the threshold shear stress at which the dislocation will start to move. Given that the two sample environments are quite distinct, it is no surprise that the threshold strain values are different for the two cases. In each run we also calculate the virtual energy release ΔE of the defect by taking a small, localized region around the defect (with dimension about 1 nm) in a manner similar to the J-integral but using atomic sums, and evaluating the energy change within this region plus the border contributions that represent the virtual work done by the environment [Li00]. Fig. 3 shows a plot of the computed local virtual energy releases ΔE with applied shear stress. It is interesting that for the two cases the critical ΔE's for A and B turn out to have the same value. This signifies that even though the sample environments A and B are different, their influences on the local environment of the dislocation is accurately portrayed through the evaluation of ΔE. From the critical value of the virtual energy release, one backs out a value for the Peierls stress, in agreement with results obtained by an entirely different method [Li00, CBCLY01, CBCLY03].

This example illustrates the notion that initializing a microscopic simulation at special initial states (which is effectively impossible experimentally, but eminently doable computationally), evolving for short times and postprocessing the results, can be instrumental in extracting intrinsic properties of the system. By virtue of its invariance to the sample microstructure environment, the procedure demonstrates that the resulting critical energy release ΔE is indeed an intrinsic property of the material. This conclusion could not be reached in a convincing fashion by simply running the simulation of a dislocation dipole in a crystal lattice and determining the apparent critical (supercell-averaged Virial) shear stress at which the dislocation begins to move, due to image dislocation interactions [CBCLY01, CBCLY03]. Our computation of the Peierls stress did not require any knowledge of the coarse theory, i.e. equations of anisotropic elasticity; but it gave the correct coarse result based entirely on numerical evaluations of atomic sums, with a ring size as small as 1 nm. Knowing a functional of the local dislocation environment that correlates with the onset of dislocation motion could form the basis for the systematic exploration of this onset [HSK04].

4 Dynamic rescaling and the formation of singularities.

A third issue we will examine is the question of determining self-similarity and scaling exponents from the system behavior at the onset of explosive instabilities. We believe that it is reasonable to look for rescaling space, time and observables in a way that will transform an apparently violently exploding instability scenario into a smooth stationary one. For our example we have in mind the visualization of a wave instability physically corresponding to the localization of lattice strain, as manifested in the simulation of the homogeneous nucleation of a dislocation loop or deformation twin embryo. We argue that coarse timestepping and successive rescaling (dynamic coarse renormalization) can transform the increasingly steepening of the wave front (which apparently explodes in finite time) to a time-invariant profile [ABK04, SKK03, RM00, RKML03, CBGK03]

Just as in the first example, where the system undergoes an elastic to plastic response transition in the form of dislocation nucleation under indentation, we may also ask for details of the transition from affine shear deformation to the nucleation of a deformation twin, say in the $\{\bar{1}\bar{1}2\}\langle 111\rangle$ shear system of BCC Mo [Chang03]. In contrast to dislocation nucleation which involves the relative shear of two adjacent planes, twinning is a competing process which involves relative shear among three or more adjacent planes. Recent MD simulations have shown that twinning can be homogeneously nucleated by shearing a single crystal [Chang03]. By treating the relative shear between two adjacent planes as a reaction coordinate one can formulate a one-dimensional model (a chain of these coordinates) to visualize the onset of twinning as a dynamical process of strain localization. Fig. 4 shows MD results on dislocation loop / deformation twin nucleation through the profile evolution of a small sinusoidal wave superimposed along the reaction coordinates. What one sees is a four-stage scenario: linear wave, nonlinear wave which begins to steepen, strongly singular behavior just prior to shock wave formation, and emergence of a localized shear. We believe that dynamic renormalization can be applied to these results to show that what appears to be rapidly varying transient behavior, under suitable transformation, is actually a stationary front. Here we seek a fixed point of the composition of the coarse timestepper with dynamic rescaling of the results of coarse timestepping [CBGK03]. The sequence involves lifting from macroscopic observables (deformation field) to consistent molecular configurations, short molecular dynamics evolution, restriction to macroscopic observables, and then *rescaling* of space and the macroscopic observable fields; the latter is performed based on an established, time-stepper based methodology using template functions [RKML03]. Upon convergence, the self-similar shape as well as the exponents of the macroscopically apparent explosion can be estimated for both types of self-similar solutions [Barenblatt96].

We have argued here that timestepper-based methods provide a systematic bridge between molecular dynamics timesteppers and traditional continuum

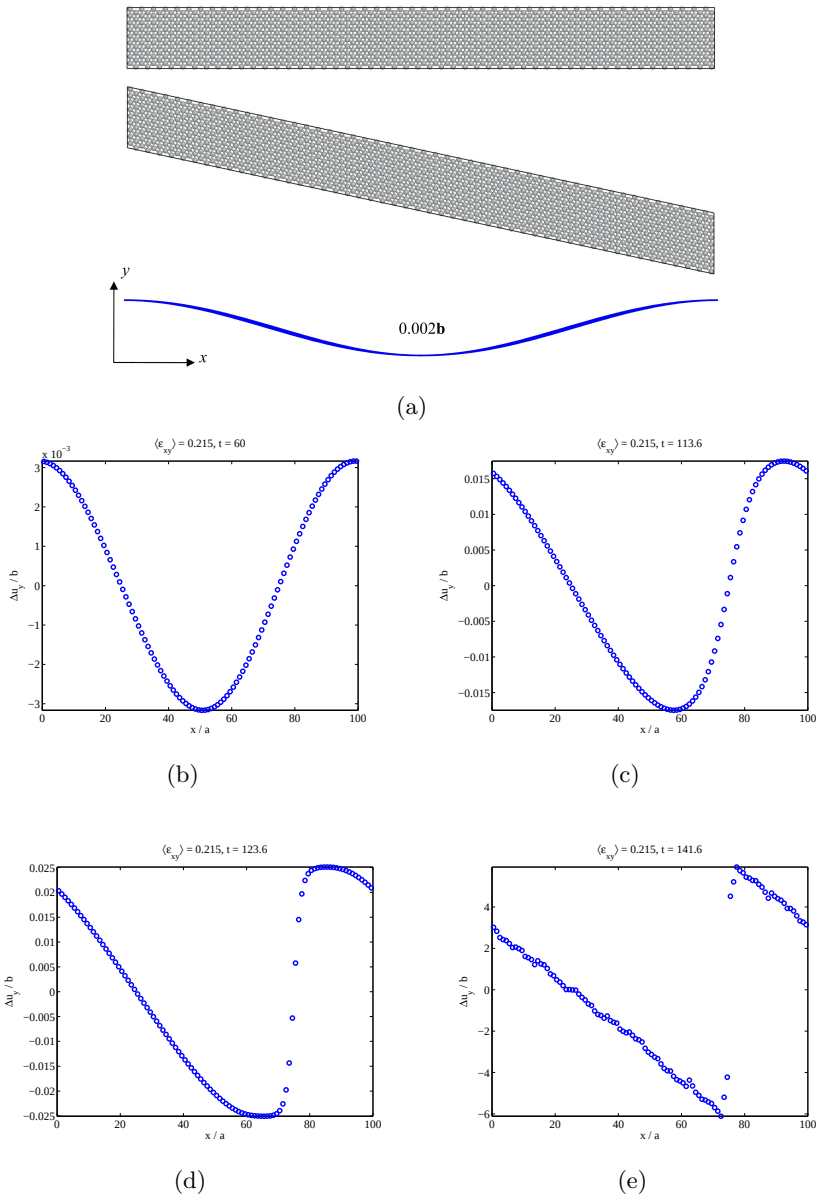


Fig. 4. Visualizing shear strain localization in a crystal under uniform shear deformation. The simulation cell with periodic boundary conditions is shown first undeformed, and then at deformation just before the instability (a), along with an initial sinusoidal shear wave perturbation injected into the system. At the onset of strain localization the perturbation wave profile undergoes four stages of temporal evolution (at a fixed overall strain on the system) that can be classified as linear growth (b), non-linear growth (c), shear-shock formation (d) and formation of an atomic defect, the embryonic dislocation loop / deformation twin (e). After the nucleation, the system strain, previously uniformly distributed, is essentially entirely localized at the glide plane(s) of the dislocation loop / deformation twin.

numerical analysis. Also that, in the presence of coarse determinism at the level of well-chosen observables, mathematical techniques can be translated into protocols for the judicious design of microscopic computational experiments toward system-level analysis goals. Lifting and restriction protocols between macroscopic observables and microscopic initial conditions provide the dictionary that enables the performance of tasks like coarse fixed point and bifurcation computation, coarse integration, optimization and control, as well as coarse dynamic renormalization. This closure-on-demand approach circumvents the derivation of macroscopic closures; by exploiting the existence of practical determinism, it allows us to solve system-level problems with the least possible extent of microscopic simulation. "On the fly" transfer of information across scales, which relies on variance reduction, filtering and estimation, enables the performance of tasks like reverse integration or the location of transition states, would be essentially impossible with direct temporal simulation.

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