Introducing Structural Approximation Method for Modeling Nanostructures

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In this work a new method for analyzing nanostructured materials has been proposed to accelerate the simulations for solid crystalline materials. The proposed Structural Approximation Method (SAM) is based on Molecular Dynamics (MD) and the accuracy of the results can also be improved in a systematic manner by sacrificing the simulation speed. In this method a virtual material is used instead of the real one, which has less number of atoms and therefore fewer degrees of freedom, compared to the real material. The number of differential equations that must be integrated in order to specify the state of the system will decrease significantly, and the simulation speed increases. To generalize the method for different materials, we used dimensionless equations. A fuzzy estimator is designed to determine the inter-atomic potential of the virtual material such that the virtual material represents the same behavior as the real one. In this paper Gaussian membership functions, singleton fuzzifier, center average defuzzifier, and Mamdani inference engine has been used for designing the fuzzy estimator. We also used the Gear predictor-corrector numerical integration method to integrate the governing differential equations. A FCC nano-bar of copper under uniform axial loading along [1 0 0] has been considered. The Sutton-Chen inter-atomic potential is used. The strain of this nano-bar has been calculated using the MD and the proposed method. Comparing the results show that while the proposed method is much faster, its results remain in an acceptable range from the results of MD method.

Keywords: Fuzzy Estimator, Molecular Dynamics, Nanomechanics, Sutton-Chen Potential.

1. INTRODUCTION

In recent years, the interest in sub-micron mechanical devices for application in the nanoelectromechanical systems (NEMS) has been growing due to emerging new technologies which enable us to produce more efficient devices with smaller sizes.[1] Modeling the nanostructures and simulation of their properties is one of the main concerns in the development of such devices. Different methods have been used for modeling nanostructures which can be classified into two major categories. The first class of simulation methods is the one based on computational chemistry.[2, 3] On the other hand, the second class of methods is based on nanomechanics.[4, 5]

The methods based on computational chemistry, such as *ab-initio*,[6–8] Monte Carlo[9, 10] and Molecular Dynamics,[11–13] are heavily computational. These methods require a significant amount of computational resources and take a lot of time. In addition, they only can be used practically for a limited number of molecules. The maximum number of

atoms that can be simulated with this type of method is still less than a billion atoms. The spatial size of this number of atoms is still below sub-microns.[14, 15] For doing the related calculations, super-computers are needed; but the obtained results are accurate.

On the other hand, the methods based on nano- and micro-mechanics, such as Lattice Dynamics[16, 17] and continuum methods,[18, 19] need less computational resources compared to the first class of methods. These methods are faster, but their results are less reliable and commonly approximate.

In this work we will introduce a method, which will take advantage of both methods of computational chemistry and nanomechanics together, while basing it on MD. In the proposed method we will use a virtual material instead of the real one. While the virtual material has fewer degrees of freedom compared to the real material, its behavior is similar to the real one. Here we have used the dimensionless differential equations and inter-atomic potentials in order to generalize the proposed method. In this method an inter-atomic potential for the virtual material is found based on the inter-atomic potential of real material. Then

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this inter-atomic potential has been used for analyzing the corresponding structure for the case of larger structures. It has been shown that the results obtained from the proposed method represent a good accuracy.

To obtain the virtual material corresponding to the real one, we have made some constraints in order to guarantee the same behavior between the real and virtual materials.

2. FUNDAMENTALS AND ASSUMPTIONS

In this section we will introduce the fundamental theories of this method. In addition the assumptions made for finding the approximate structure are clarified.

The first rule for finding the approximate material is that the virtual material must have less number of atoms compared to the real material. Also, it must have the same crystal structure as the real material. The second rule states that while the virtual material must have the same mechanical behavior as the real material it also must be stable.

In the proposed method we used the Born-Oppenheimer assumption.[20, 21] Therefore we can consider the individual atoms as separate bodies interacting via inter-atomic potentials. So, we can use the Newtonian dynamics to study the behavior of the nano-structured material.

The other assumption which was used in this method is the Hartree-Fock assumption.[22] Based on this assumption we can consider the atom's wave function, which is the basis of inter-atomic potentials, as multiples of individual single electron wave functions. The other result is any energy function that satisfies the Schrödinger equation is larger than the actual energy function.

Finally, we will use the Hohenberg-Kohn assumption,[23] which states that the property of each system is based on its energy density function. In addition it states that there is a variational form for the energy density function, which is any other energy function greater than the exact system's energy function.

In the proposed method the number of atoms which the boundary conditions are applied to has a key rule in obtaining correct results. The number of atoms in the virtual material which the boundary condition are applied to, must be such that the ratio of these atoms with respect to the total number of atoms be the same as this ratio for the real material.

3. STRUCTURAL APPROXIMATION METHOD (SAM)

Each inter-atomic potential has two parts, attraction and reaction. The attractive term stems from the attraction force between the electrons and nuclei. On the other hand, the reaction term stems from the electron–electron and the nuclei–nuclei reactive forces. Therefore, each inter-atomic potential, U, can be written as follows:

$$U(r) = A(r) + R(r) \qquad (1)$$

which "$A(r)$" represents the attraction, and "$R(r)$" represents the reaction. The inter-atomic potential function has the minimum value at the equilibrium point. Therefore we have:

$$\left. \frac{\partial U(r)}{\partial r} \right|_{r=r_e} = 0 \rightarrow A'(r_e) = -R'(r_e) \qquad (2)$$

where "r_e" is the equilibrium distance and $\prime$ represents the derivative with respect to "r".

The general form of the potential function for the approximate model can be considered as follows:

$$U_{\text{Apr}}(r) = a(r) \cdot A(r) + b(r) \cdot R(r) \qquad (3)$$

where "$a(r)$" and "$b(r)$" are the coefficients of the attraction and reaction parts, respectively. It is assumed that they are function of inter-atomic distance, i.e., "r".

Due to the Hohnberg-Kohn assumption, the mechanical properties of the material are a function of its energy density. Therefore, the energy density of real and approximated material must be equal. So, we have:

$$\frac{U_{\text{Apr}}}{\Omega_{\text{Apr}}} = \frac{U}{\Omega} \Rightarrow U_{\text{Apr}} = \frac{\Omega_{\text{Apr}}}{\Omega} U \qquad (4)$$

where "Ω" and "Ω_{Apr}" represent the volume of unit cell in the real and approximated materials, respectively. Also, "U" and "U_{Apr}" represent the energy of the real and approximated materials, respectively. For the case of which there is not any atom at the boundaries of the material, the U_{Apr} can be found using even analytical methods. But at the nano-scales, a great number of atoms are placed at the boundaries, and they have a great impact on the properties of the material. In order to find the U_{Apr} the following relation has been considered between the U and U_{Apr}:

$$U_{\text{Apr}}(r^*) = K \cdot U \qquad (5)$$

where "K" is a constant value, "r^*" represents the dimensionless inter atomic distance and is defined as $r^* = r/r_e$.

The goal is finding the appropriate value of "K" such that the mechanical behavior of the approximate structure to become the same as the mechanical behavior of the real material. In order to find the appropriate value of "K", a fuzzy estimator has been designed.

4. FUZZY ESTIMATOR

The input to the fuzzy estimator is the deviation of the property of interest, in this case length of nano-bar, in the approximated structure from the real structure. The output of the fuzzy estimator is the amount of change that should be made in the value of "K", i.e., ΔK. The fuzzy rules are as follows:

$$\begin{cases} \text{If } \dfrac{L_{\text{Apr}} - L_{\text{MD}}}{L_{\text{MD}}} > 0 & \text{then } \Delta K > 0 \\[2mm] \text{If } \dfrac{L_{\text{Apr}} - L_{\text{MD}}}{L_{\text{MD}}} = 0 & \text{then } \Delta K = 0 \\[2mm] \text{If } \dfrac{L_{\text{Apr}} - L_{\text{MD}}}{L_{\text{MD}}} < 0 & \text{then } \Delta K < 0 \end{cases} \qquad (6)$$

These rules are based on the common sense about the stiffness of materials. It states that, "The stiffer the material, the smaller the elongation."

In this work Gaussian membership functions, singleton fuzzifier, center average defuzzifier and Mamdani inference engine has been used.[24] Therefore the change in the value of coefficient, "K", can be found using the following relation:

$$\Delta K = \frac{\sum_{l=1}^{M} \bar{y}^l \mu_{A^l}\big((L_{Apr} - L_{MD})/L_{MD}\big)}{\sum_{l=1}^{M} \mu_{A^l}\big((L_{Apr} - L_{MD})/L_{MD}\big)} \qquad (7)$$

where "M" represents the number of fuzzy rules, "μ_{A^l}" is the value of membership function defined on the input for l-th rule and "$\bar{y}^l$" is the center of the output's membership function, for the l-th rule.

5. DETERMINING THE COEFFICIENT "K"

In this section we will introduce the algorithm which will be used for determining the appropriate value for the coefficient "K". On the first step we have to find the value of property of interest for the real material. For this purpose the molecular dynamics method has been used.
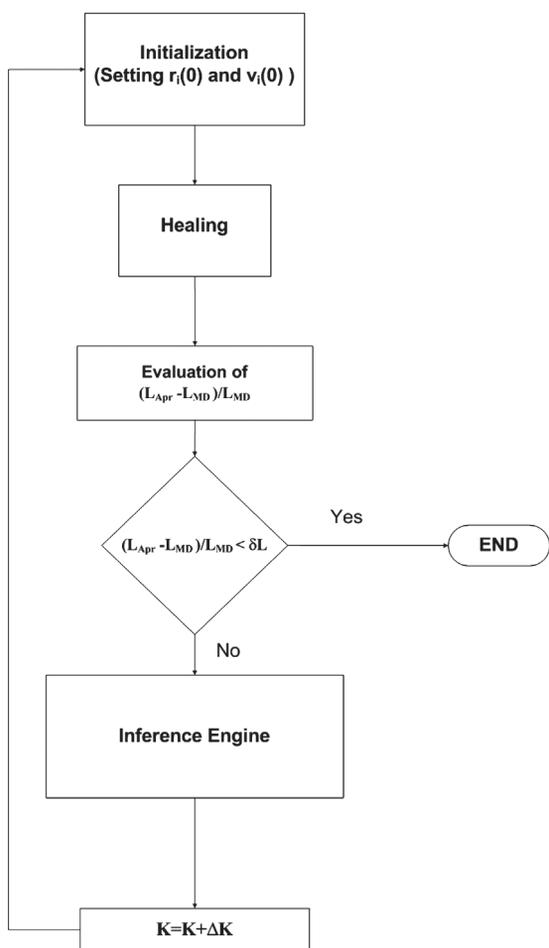

Fig. 1. Schematic of the algorithm for determining the coefficient "K".

After finding the value of property of interest for the real material, the virtual material will be constructed based on the assumptions made. Then we will use the molecular dynamics again to find the same property as the real material but this time for the virtual material. The obtained value will be compared with the value obtained for the real material. The difference between the two values will be passed to the fuzzy estimator for finding appropriate value of coefficient "K". This process continues until the difference between the value of property of interest for the virtual and real material become less than a certain value.

The smaller the difference between the value of property of interest between the real and virtual material, the longer the process of determining coefficient "K" will take.

It should be noted that if the value of property of interest for the virtual material be selected too close to the value for the real material, the proposed algorithm may never converge. This is because of the uncertainties in the system and cut-off and round-off errors.

The schematic picture of this algorithm has been shown in Figure 1.

6. GOVERNING EQUATIONS

The governing differential equations which will be used are the Hamiltonian equations of motion. In order to generalize the solution, we have eliminated the dimension of the governing equations. The dimensionless equations are as follows:

$$H^*\big(r_N^*, p_N^*\big) = \frac{1}{2}\sum_i \big(p_i^*\big)^2 + U^*\big(r_N^*\big) \qquad (8)$$

$$\frac{dH^*}{dt^*} = \sum_i \frac{\partial H^*}{\partial p_i^*}\cdot \dot{p}_i^* + \sum_i \frac{\partial H^*}{\partial r_i^*}\cdot \dot{r}_i^* \qquad (9)$$

$$\frac{dH^*}{dt^*} = \sum_i p_i^* \times \dot{p}_i^* + \sum_i \frac{\partial U^*}{\partial r_i^*}\cdot \dot{r}_i^* \qquad (10)$$

$$\frac{\partial H^*}{\partial p_i^*} = \dot{r}_i^* \qquad (11)$$

$$\sum_i \left(\dot{p}_i^* + \frac{\partial H^*}{\partial r_i^*}\right) \times \dot{r}_i^* = 0 \qquad (12)$$

$$F_i^* = -\frac{\partial H^*}{\partial r_i^*} = -\frac{\partial U^*}{\partial r_i^*} \qquad (13)$$

In Eqs. (8–13), "H" is the Hamiltonian function and "p_i" is the momentum of i-th atom. In addition, while "$\cdot$" represents the product, "$\times$" shows the dot product. The dimensionless parameters are defined in Table I. In addition, "σ" represents the equilibrium distance and "ε" represents the potential well.

It should be noted that the mass of each atom in the approximate structure depends on two parameters:

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Table I. List of dimensionless parameters.

Dimensionless-Parameter's Name	Definition
Relative Distance	$r^* = r/\sigma$
Force	$F^* = F \cdot \sigma/\varepsilon$
Inter-atomic Potential	$U^* = U/\varepsilon$
Velocity	$v^* = v\sqrt{m/\varepsilon}$
Time Step	$\Delta t^* = \Delta t /[\sigma\sqrt{m/\varepsilon}]$
Acceleration	$a^* = a \cdot m \cdot \sigma/\varepsilon$

(I) the mass of atoms in the real structure, (II) Degree of approximation which is used for generating the approximate structure. The general formulation for finding the mass of each atom in the approximate structure is as follows:

$$\frac{m_{\text{Apr}}}{m} = \frac{N}{N_{\text{Apr}}} \qquad (14)$$

where "m" and "m_{Apr}" are the mass of each atom in the real and approximate structure, respectively. "N" represents the equivalent number of atoms in the real structure. "N_{Apr}" represents the equivalent number of atoms in the approximate structure, corresponding to the real structure.

Due to the assumptions we made about the approximate and real structure which states that they have the same crystal structure, the above relation can be simplified for FCC crystal structure as follows:

$$m_{\text{Apr}} = N_{\text{real/Apr}} \cdot m \qquad (15)$$

where "$N_{\text{real/Apr}}$" is the number of real unit cells corresponding to an approximate unit cell. In this paper we have approximated a $2 \times 2 \times 2$ crystal structure, which is equivalent to eight unit cells with a $1 \times 1 \times 1$, crystal structure, i.e., single unit cell. Therefore in this case:

$$N_{\text{real/Apr}} = \frac{8}{1} = 8 \qquad (16)$$

For molecular dynamics simulations, Gear predictor-corrector algorithm[25] is used as the numerical integration method. To model the constant temperature we used the velocity scaling method.[26]
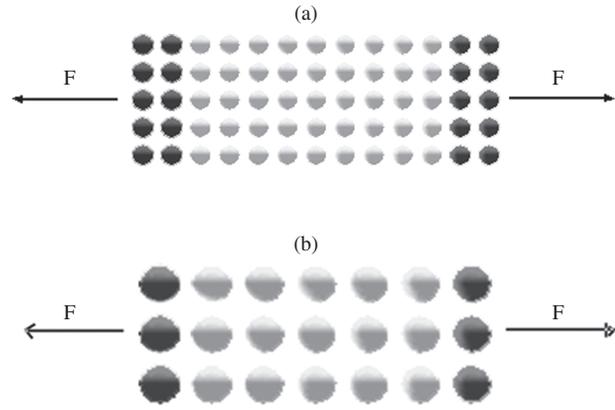
7. CASE STUDY

In this paper a copper nano-bar of FCC crystal structure is considered under uniform axial loading along the x-axis, i.e., [1 0 0].

The Sutton-Chen (SC) inter-atomic potential has been considered which its dimensionless equations are as follows:

$$U^*\left(r_{ij}^*\right) = \left[\frac{1}{2}\sum_i\sum_{j\neq i} V^*\left(r_{ij}^*\right) - c\sum_i \left(\rho_i^*\right)^{1/2}\right] \qquad (17)$$

$$V^*\left(r_{ij}^*\right) = \left(\frac{1}{r_{ij}^*}\right)^n \qquad (18)$$

Fig. 2. (a) Schematic picture of real material, $6 \times 2 \times 2$ unit cells along x-, y- and z-axis. (b) Schematic picture of approximate material, $3 \times 1 \times 1$ unit cells along x-, y- and z-axis. The force is applied to the atoms which has a darker color.

$$\rho_i^* = \sum_{j\neq i}\left(\frac{1}{r_{ij}^*}\right)^m \qquad (19)$$

The cut-off distance for the inter-atomic potential is considered twice as the equilibrium distance of the SC potential, i.e., $r_c = 2 \times r_e$.

Bars with different lengths are considered in this paper. While they are constructed from different number of unit cells along the x-axis but all of them have two unit cells along the y- and z-axis. A schematic picture of the problem configuration and its approximate structure is shown in the Figure 2, for the bar that is constructed from six unit cells along the x-axis.
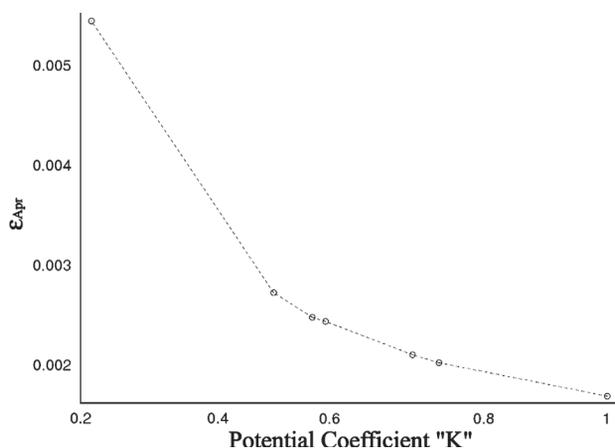
Here a $2 \times 2 \times 2$ crystal structure has been approximated by a $1 \times 1 \times 1$ crystal structure (see Fig. 3). The healing phase and production phase are 100 ps and 1000 ps, respectively.

The applied dimensionless force $F^* = 10$ is considered to be applied at the extreme ends of the nano-bar, along [1 0 0] direction.

Different values of the coefficient "K" are plotted for a single unit cell of virtual material. These values obtained during different iterations of fuzzy estimator. The iteration process ended when difference between the length of
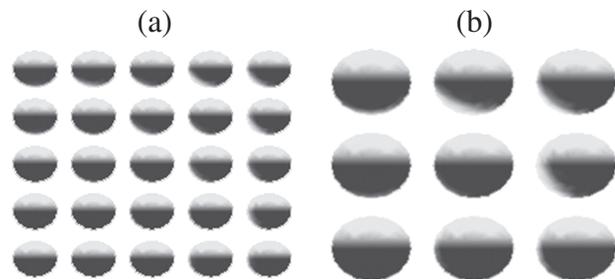
Fig. 3. (a) Real material $2 \times 2 \times 2$ crystal structure, (b) Approximated material $1 \times 1 \times 1$ crystal structure.

Fig. 4. Coefficient "K" obtained from fuzzy estimator, for $1 \times 1 \times 1$ virtual structure.

Fig. 5. Relative error with respect to the number of unit cells along the x-axis of the nano-bar.

real and virtual material, became less than 0.01 of the real material's length.
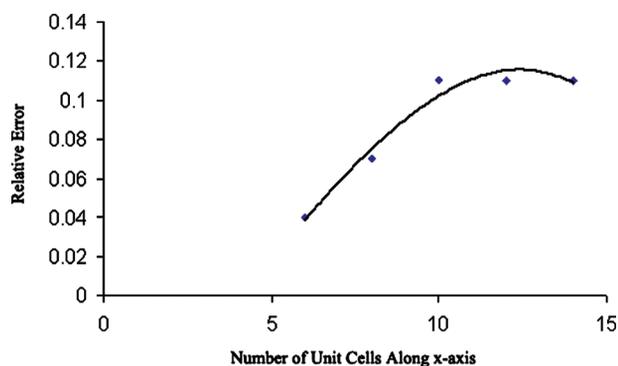
The percentage of atoms that the boundary conditions are applied to must be equal for both the real material and virtual material. In this case while the boundary force should be applied to two layers of atoms at the end of the real nano-bar, it should be applied to only a single layer of atoms for virtual nano-bar.

We also defined 3000001 membership functions on the input of fuzzy estimator. They are equally dispersed on the input range, which is $[-1, 1]$. Beyond this range we used the value of membership function at -1 or 1; it depends on the fact that which one is nearer to the input value.

The strain of virtual material under the applied force is 7.46 Å. Compared to the strain of real material which is 7.4 Å, the virtual material represents about 0.008 deviations with respect to the strain of the real material.

$$\frac{\left| \varepsilon_{\mathrm{MD}} - \varepsilon_{\mathrm{Apr}} \right|}{\varepsilon_{\mathrm{MD}}} = \frac{\left| 7.46 - 7.4 \right|}{7.4} \approx 0.008 \qquad (20)$$

Now, we will use the obtained value of potential coefficient "K", $K \approx 0.48$, to find the strain of the nano-bar made up of virtual material and it is corresponding to the nano-bar of interest. Different nano-bars that are made up of real material and their corresponding approximate structure which are made up of virtual material have been represented in the Table II. Also the duration of each simulation and the evaluated strain are also shown in the Table II. The relative error of the evaluated strains with

respect to the length of nano-bar has also been shown in Figure 5.

In Figure 5 we have shown that the deviation of the evaluated strain for the approximated structure from the strain of the real structure grows up to certain value and it remains constant for the larger systems. Comparing the duration of simulations it can be found that the difference between the simulation time for the real structure and approximate structure grows exponentially.

8. CONCLUSION

In this paper a new method for analyzing the nanostructures has been introduced. This method increases the speed of simulation significantly, while keeps the accuracy of the results in an acceptable range.

In this method the iteration for finding the appropriate value of coefficient "K" continues till the difference between the value of property of interest for the real and virtual material get to a certain value. Therefore the accuracy of the results can easily be improved by reducing the critical value which determines the end of iteration process. But it should be noted that the lower the value of this critical difference, the longer is the process of finding appropriate coefficient "K".

Table II. Simulation results for nano-bars with different lengths. Comparison between MD and proposed SAM.

NO.	Sys.	$\varepsilon_{\mathrm{MD}(\pm 1E-4)}$	t_{MD} (s)	Apr. Sys.	$\varepsilon_{\mathrm{SAM}(\pm 1E-4)}$	t_{SAM} (s)	$(\varepsilon_{\mathrm{MD}} - g\varepsilon_{\mathrm{SAM}})/\varepsilon_{\mathrm{MD}}$
1	$6 \times 2 \times 2$	$\varepsilon = 0/024$	4500	$3 \times 1 \times 1$	$\varepsilon = 0/023$	170	0.04
2	$8 \times 2 \times 2$	$\varepsilon = 0/020$	7700	$4 \times 1 \times 1$	$\varepsilon = 0/0186$	280	0.07
3	$10 \times 2 \times 2$	$\varepsilon = 0/018$	11800	$5 \times 1 \times 1$	$\varepsilon = 0/016$	420	0.11
4	$12 \times 2 \times 2$	$\varepsilon = 0/018$	16800	$6 \times 1 \times 1$	$\varepsilon = 0/016$	600	0.11
5	$14 \times 2 \times 2$	$\varepsilon = 0/018$	22600	$7 \times 1 \times 1$	$\varepsilon = 0/016$	780	0.11

The process of finding the coefficient "K", for the virtual material is time consuming. So this method is recommended for analyzing large systems. For the small systems the classical methods such as molecular dynamics are still preferable.

The proposed method is a significant step toward design and analysis of nanosystems. This method reduces the production costs for products based on nanomaterials. It also provides the tool for analyzing large systems in a reasonable time, with an acceptable accuracy.

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