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Comparison of the Ewald and Wolf methods for modeling electrostatic interactions in nanowires

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SUMMARY

Ionic compounds pose extra challenges with the appropriate modeling of long-range coulombic interactions. Here, we study the mechanical properties of zinc oxide (ZnO) nanowires using molecular dynamic simulations with Buckingham potential and determine the suitability of the Ewald (*Ann. Phys.* 1921; 19) and Wolf (*J. Chem. Phys.* 1999; **110**(17):8254–8282) summation methods to account for the long-range Coulombic forces. A comparative study shows that both the summation methods are suitable for modeling bulk structures with periodic boundary conditions imposed on all sides; however, significant differences are observed when nanowires with free surfaces are modeled. As opposed to Wolf's prediction of a linear stress–strain response in the elastic regime, Ewald's method predicts an erroneous behavior. This is attributed to the Ewald method's inability to account for surface effects properly. Additionally, Wolf's method offers highly improved computational performance as the model size is increased. This gain in computational time allows for modeling realistic nanowires, which can be directly compared with the existing experimental results. We conclude that the Wolf summation is a superior technique when modeling non-periodic structures in terms of both accuracy of the results and computational performance. Copyright © 2010 John Wiley & Sons, Ltd.

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KEY WORDS: Ewald summation; Wolf summation; long-range interactions; nanowires

1. INTRODUCTION

Owing to the difficulties encountered in the experimental investigation of the mechanical behavior of nanomaterials, computational methods play a major role in determining their properties. The relevant methods, involving atomic scale modeling, can be broadly classified into two categories: (i) *ab initio* methods and (ii) Molecular Dynamics (MD) methods based on semiempirical

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two-body, three-body, and many-body potentials (e.g. Embedded Atom Method-based potentials [1] and biomolecular force fields like CHARMM [2]). *Ab initio* methods are known to predict material behavior and properties very accurately but are very expensive computationally and do not allow for modeling of large systems with realistic dimensions (having a few million atoms). On the contrary, MD methods that do not calculate electronic structures completely can be used to model relatively larger systems. In this work, we chose to model zinc oxide (ZnO) as a case study.

Zinc Oxide (ZnO) offers a unique combination of semiconducting and electromechanical properties, which makes it a suitable candidate for various nanoscale applications. ZnO nanowires have attracted much attention in applications in high-power optoelectronic devices, logic circuits, piezoelectric devices, nanoresonators, and electromechanically coupled nanocantilever sensors due to their excellent semiconducting, piezoelectric, and biocompatible properties. Accurate knowledge of their mechanical properties is a crucial factor in designing such devices with predictable and reproducible operation. The small dimensions of the nanostructures, however, raise serious challenges for the experimental investigation of properties relevant to their application. Therefore, a two-fold approach involving computational modeling is relevant and important.

In the context of modeling ZnO, MD methods have been used to predict the mechanical properties of bulk ZnO [3]. The short-range interatomic interactions are usually modeled using a Buckingham-type pairwise potential; however, different mathematical techniques have been developed to efficiently calculate the long-range forces. The traditional Coulomb summation results in a converging equation only under specific conditions. In the literature, this problem is referred to as the Madelung problem [4]. The Madelung problem was solved with the Ewald summation [5], which through certain mathematical manipulations calculates the conditionally convergent $O(r^{-1})$ Coulomb summation. It has been used to model proteins [6, 7], salt compounds [8], semiconductors [9, 10], and other materials. The Ewald summation, however, assumes periodicity of the modeled system and its application in physically non-periodic systems such as liquids, amorphous solids, and nanostructures is questionable [11]. To cope with the problem of non-periodic systems and at the same time to increase computational efficiency, Wolf *et al.* [12] presented a new method for evaluating the Coulomb potential. Wolf's method has gained popularity in recent years and is being widely used. In our recent work, we used this method to simulate tensile tests on nanowires as large as 20 nm in diameter [13, 14]. Using a combined experimental–computational approach, we reported that Young's modulus of nanowires increases with decreasing diameters and the effect is prominent when the diameter is smaller than 80 nm. The observed size effect was explained based on the surface reconstruction and increasing surface-to-volume ratios. The key to model surface effects properly and to model larger nanowires efficiently was the utilization of Wolf's summation method, which will be discussed in this paper.

The objective of this work is to address the applicability of the Ewald summation in modeling non-periodic structures, as little comparison between the Ewald and Wolf summations on non-periodic structures exists in the literature. First, we discuss the theoretical background of the Ewald and Wolf summation techniques. Then the mechanical properties of periodic bulk ZnO structure as predicted by Ewald's methods are presented and compared against the experimental values. Using Ewald's results as a benchmark for modeling bulk ZnO, the optimal mathematical parameters required in the Wolf's formulation are determined. Simulated tensile tests on nanowires ranging from 2.4 to 7.5 nm in diameter using both summation methods are then compared. Finally, the gain in computational efficiency offered by Wolf's summation is reported.

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2. THEORETICAL BACKGROUND

In this section, we briefly present the theoretical basis of the Ewald and Wolf summation methods.

2.1. Ewald summation method

The Ewald summation for calculating long-range coulombic interactions is derived from the Coulomb sum, which gives the resultant total energy of a system of N charges q_i at position r_i:

$$E_{\text{coul}} = \frac{1}{2} \sum_{i=1}^{N} \sum_{j \neq i=1}^{\infty} \frac{q_i q_j}{r_{ij}} \tag{1}$$

Equation (1) is conditionally convergent when the system of charges is truncated to a sphere of radius R_c, as is common in MD simulations. The Ewald summation converts this equation into a sum of convergent equations by performing the following mathematic manipulations [5]:

1. Structural periodicity is enforced and Equation (1) is multiplied by unity by means of the error function and complimentary error function.

$$E^{\text{Ewald}} = \frac{1}{2} \sum_{i=1}^{N} \sum_{j=1}^{N} \sum_{n=0}^{\infty} \frac{q_i q_j}{|r_{ij} + \boldsymbol{n}L|} (erfc(\alpha |r_{ij} + \boldsymbol{n}L|) + erf(\alpha |r_{ij} + \boldsymbol{n}L|)) \tag{2}$$

2. The Fourier transform of the error function term is taken (but not of the complimentary error function term) yielding the final Ewald equation:

$$E^{\text{Ewald}} = \frac{1}{2} \sum_{i=1}^{N} \sum_{j=1}^{N} \sum_{n=0}^{\infty} \frac{q_i q_j}{|r_{ij} + \boldsymbol{n}L|} (erfc(\alpha |r_{ij} + \boldsymbol{n}L|)) - \frac{\alpha}{\sqrt{\pi}} \sum_{i=1}^{N} q_i^2 + \frac{2\pi}{3V} \left(\sum_{i=1}^{N} q_i r_i \right)^2 + \frac{2\pi}{V} \sum_{\boldsymbol{k} \neq 0}^{\infty} \frac{e^{-k^2/4\alpha^2}}{k^2} \sum_{j=1}^{N} q_j e^{-i\boldsymbol{k} r_j} \sum_{j=1}^{N} q_j e^{i\boldsymbol{k} r_j} \tag{3}$$

In Equations (2) and (3), $\boldsymbol{n}$ is a vector denoting the periodic image of simulation box L and $\boldsymbol{k}$ is a reciprocal space vector. In the implementation of the Ewald summation α is picked to be relatively large, such that the Ewald summation converges [11].

2.2. Wolf summation method

The Wolf summation is based on the observation that the Coulombic summation does not converge as a result of the potential non-neutrality of the total charge contained within the spherically truncated system of radius R_c [12]. Furthermore, the Wolf summation relies on the fact that if charge-neutralization of such a system is achieved, the correct equivalent system energy can be computed [15]. Thus, the equation for the Wolf summation is developed in three steps [12].

1. The system contained within R_c is charge neutralized. The charge neutralization is achieved by the use of the key observation that within the sphere of radius R_c, the charges that are not balanced are on the surface of that sphere. As such, when calculating the energy contained

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in that sphere, the Wolf summation subtracts a term representing the energy on the surface of the sphere:

$$E^{\text{charge,neutral}} = \frac{1}{2}\sum_{i=1}^{N}\sum_{j\neq i}\sum_{r_{ij}<R_c}\frac{q_i q_j}{r_{ij}} - \lim_{r_{ij}\to R_c}\frac{q_i q_j}{r_{ij}} \tag{4}$$

The first term of Equation (4) represents the traditional Coulombic sum and is the same as Equation (1), while the second term represents the unbalanced surface charges, which are subtracted from the total energy.

2. As shown by Adams [15], computing the charge neutralized energy of a spherically truncated system (step 1) approximates shifting the correct energy of the system by a constant. This constant can be computed by:

$$E^{\text{shift}} = \frac{1}{2R_c}\sum_{t=1}^{N} q_t^2 \tag{5}$$

Therefore, the approximate correct energy of the spherically truncated system is given by subtracting Equation (5) from Equation (4):

$$E^{\text{Wolf}} = \frac{1}{2}\sum_{i=1}^{N}\sum_{j\neq i}\sum_{r_{ij}<R_c}\frac{q_i q_j}{r_{ij}} - \lim_{r_{ij}\to R_c}\frac{q_i q_j}{r_{ij}} - \frac{1}{2R_c}\sum_{i=1}^{N} q_i^2 \tag{6}$$

3. A damping function is applied in order to make the Wolf summation computationally more efficient. It is important to note that Equation (6) converges to the correct energy value for high values of R_c and in particular when $R_c \gg a$, the interatomic distance [11]. While it is theoretically possible to use Equation (6) directly in computer simulations, R_c would have to be too high for computational efficiency. As such a damping function is applied to Equation (6), yielding the final Wolf summation equation:

$$E^{\text{Wolf}} = \frac{1}{2}\sum_{i=1}^{N}\sum_{j\neq i}\sum_{r_{ij}<R_c}\frac{q_i q_j}{r_{ij}}(erfc(\alpha r_{ij})) - \lim_{r_{ij}\to R_c}\frac{q_i q_j}{r_{ij}}(erfc(\alpha r_{ij})) - \left(\frac{(erfc(\alpha r_{ij}))}{2Rc} + \frac{\alpha}{\sqrt{\pi}}\right)\sum_{i=1}^{N} q_i^2 \tag{7}$$

In Equation (7), variable α is introduced as a damping coefficient. Higher values of α allow convergence for lower values of R_c.

3. COMPUTATIONAL METHODOLOGY

In this work, modeling of ZnO was carried out with large-scale atomic/molecular massively parallel simulator (LAMMPS) developed at Sandia National Laboratories [16, 17]. We augmented the LAMMPS package to implement the Wolf summation method for modeling coulombic interactions.

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Table I. Comparing different bulk material properties as calculated in this work with earlier reported experimental and computational values.

	Material property	Experimental [Ref]	Ewald method		Wolf method
			Reference [1]	This work	This work
Lattice constants (Å) at 300 K	a	3.249 [18]	—	3.212	3.218
	c	5.204 [18]	—	5.149	5.158
	u	0.382 [18]	—	0.380	0.380
Elastic constants (GPa) at 0 K	C_{11}	209.7 [18]	232.5	221.9	209.1
	C_{12}	121.1 [18]	95.2	86.3	89.9
	C_{13}	105.1 [18]	85.6	75.0	71.6
Lattice energy (eV)	E	−42.03 [19]	−39.33	−39.33	−39.34

The atomic interactions were modeled with the Buckingham potential, expressed in Equation (8):

$$E^{\text{total}} = \sum_{i=1}^{N} \sum_{j \neq i}^{\infty} A \exp\left(\frac{r_{ij}}{\rho}\right) - \frac{C}{r_{ij}^6} + E^{\text{long}}(r_{ij}), \tag{8}$$

where r_{ij} is the distance between two atoms in a cell. A, C, and ρ are parameters defining the short-range interactions and $E_{\text{long}}(r_{ij})$ represents the long-range electrostatic interactions based on the ionic charge. $E_{\text{long}}(r_{ij})$ is calculated by Equations (7) and (3) with the Wolf and Ewald summations, respectively. The constants identified by Binks were used in the calculations for modeling the short-range interactions with a cut-off radius of 8.5 Å [3].

To begin, simulations were performed on bulk ZnO using the Ewald summation method, which has been employed earlier [3]. A cell of bulk wurtzite ZnO, with 1440 atoms and periodicity applied on all sides, was initially allowed to relax at 300 K for 30 ps, long enough for the energy and the pressure of the system to stabilize. The lattice constants were measured from the relaxed lattice structure and are summarized in Table I. Then, a quasi-static loading scheme was employed in two steps: (i) the structure was deformed along the a axis in increments of 0.5% strain over a period of 1 ps (ii) the structure was allowed to relax only in the direction of the elastic constant being calculated for 30 ps, under NPT conditions using the Nose–Hoover thermostat [17]. The virial stresses [20] were calculated and plotted against the strain in order to calculate the elastic constants. Elastic constants C_{11}, C_{12}, and C_{13} were calculated in this fashion and are reported in Table I. A good agreement in the lattice and elastic constants was achieved when compared with the previously obtained results using this methodology [3]. The results obtained from modeling bulk ZnO, using Ewald's method, were then used as a baseline to develop parameters for Wolf's method. The calculations performed to identify appropriate parameters required in Wolf's method are described next.

3.1. Determination of the optimal wolf summation parameters

The lattice energy and pressure, when modeled with Wolf's method, were found to be oscillatory functions of the cut-off radius R_c with dependence on the damping coefficient α. Convergence studies were performed in order to determine the optimal values of α and R_c for modeling bulk ZnO accurately. The same cell of bulk wurtzitic ZnO (as described in the previous section) was

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analyzed using Ewald's and Wolf's methods. Energy minimizations were performed at absolute zero temperature. This simulation was performed for two values of α and repeated for increasing values of R_c for both values of α. The lattice energy and pressure as calculated by the Wolf summation were plotted against R_c for the different α values. The results were compared against the Ewald predictions, as the Ewald method suitably applies to periodic structures. The results of this convergence study are shown in Figures 1 and 2.

Figures 1 and 2 show the lattice energy and pressure of bulk ZnO as a function of cut-off radius R_c for multiple values of damping coefficient α, respectively. Convergence is achieved when R_c is much greater than the lattice constant $a = 3.2$ Å, as determined by Demontis *et al.* [11]. Furthermore, the effect of damping coefficient α is evident as a higher value of α leads to faster convergence.

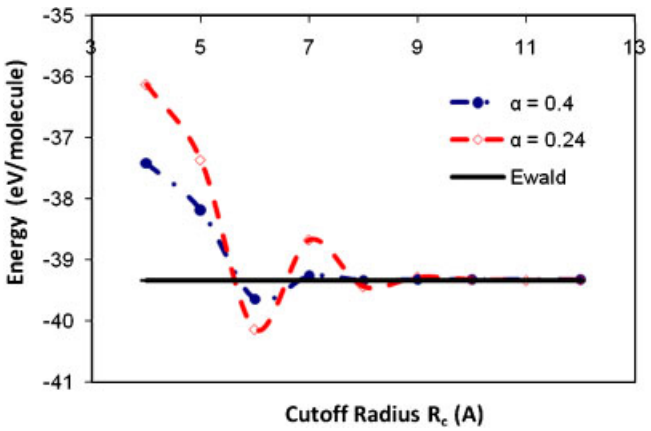

Figure 1. The lattice energy (eV/molecule) of ZnO as modeled with the Wolf summation and Ewald summation.

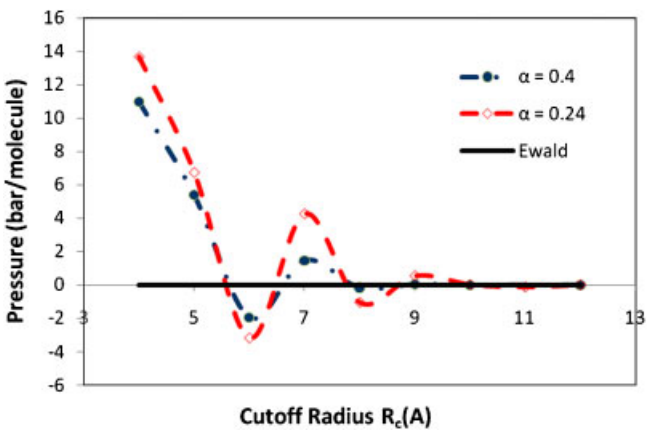

Figure 2. The system pressure (bar/molecule) of ZnO as modeled with the Wolf summation and Ewald summation.

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A tradeoff is observed between the computational efficiency and accuracy. Lower values of R_c improved computational time, but the accuracy is decreased. Given this tradeoff it is important to determine a set of values for parameters α and R_c such that relative computational efficiency and accuracy are maintained.

Given the theoretically predicted $O(N^3)$ relation of computational time to cut-off radius R_c and the importance of computational efficiency, a cut-off radius R_c of 7 Å was selected as optimal. The damping coefficient α was chosen by observing that for $\alpha=0.4$ the summation has converged at $R_c=7$ Å and is sufficiently close ($<1\%$ difference in lattice energies) to the value predicted by the Ewald summation (see Figures 1 and 2). The optimal parameters identified for Wolf's method were then used to calculate the elastic constants for bulk ZnO, which are summarized in Table I for comparison. The Ewald and Wolf summations predict very similar lattice parameters and lattice energy (Table I) in this work and are in excellent agreement with the lattice energy parameters reported in [3] and the lattice energy reported by the CRC Handbook [19]. This indicates that the Wolf summation can predict the bulk lattice properties of ZnO as equally well as the traditionally used Ewald summation. This attests to the Wolf method's suitability and allows its application in predicting further properties of ZnO with high confidence.

The two methods, Ewald and Wolf, were then applied to model [0001]-oriented ZnO nanowires to verify their suitability to predict the material behavior in presence of free surfaces. Nanowires with diameter 5.0 and 7.5 nm were modeled using both the methods. The details of modeling and the results are described in the next section.

3.2. ZnO nanowires Young's modulus

ZnO nanowires orientated along the [0001] crystallographic axis and of hexagonal cross-section (Figure 3) were modeled. Nanowires ranging from 2.4 to 7.5 nm in diameter were modeled using the Ewald and Wolf methods and were compared. Periodic boundary conditions were imposed in the axial ([0001]) direction and an aspect ratio of $\sim 3:1$ was maintained for all simulated nanowires. A quasi-static loading scheme was employed in which a wire was uniformly strained to the desired level over a period of 400 ps under NVT conditions and then allowed to minimize at 0 K. The virial stresses were calculated for each level of strain for all nanowires and Young's moduli were found from the slope of the elastic region of the stress–strain curves.

Figure 4(a) shows the stress–strain response as predicted by the two methods. Zero strain refers to the configuration with lattice constants the same as bulk lattice constants along the axial direction. A compressive stress at 0% strain is the result of surface stresses which decreases with increasing wire diameter. This effect results in the size dependence of the elastic modulus in ZnO nanowires, as described elsewhere [13]. Qualitatively, both the summation methods predict similar surface effects; however, Wolf's method, in contrast to Ewald's method, predicts a perfectly linear elastic response.

Table II compares Young's moduli of different nanowires as predicted by the two methods. For the Ewald results, the modulus is obtained by fitting a linear curve to the stress–strain data. Even though the Ewald summation predicts reasonable Young's Moduli (Table II), the erratic stress–strain response casts doubt to the applicability of the Ewald summation in modeling non-periodic structures. It is noteworthy that the error consistently increases with increasing wire diameter, which suggests that the error associated with Ewald formulation scales with the surface area.

To further understand the differences between the results of the two methods, the radial displacements were analyzed (Figure 5). As the axial dimension is fixed during minimization and defined

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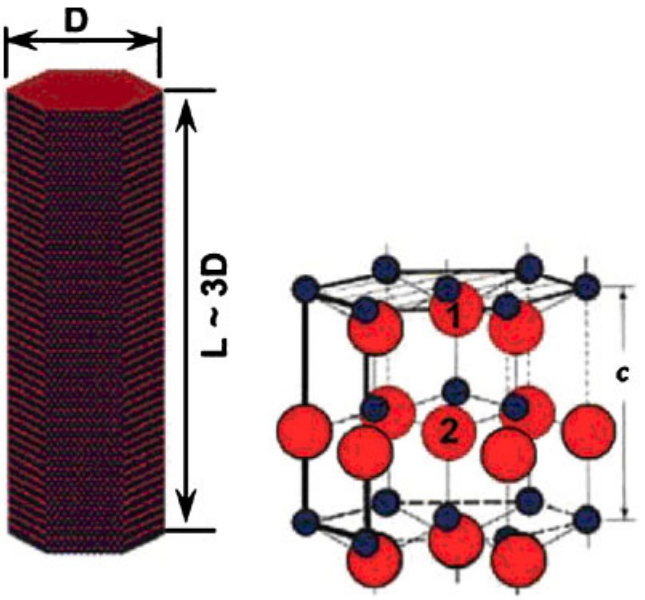

Figure 3. As modeled hexagonal cross-section of a [0001]-oriented ZnO nanowires and a close-up of its wurtzitic atomic structure.

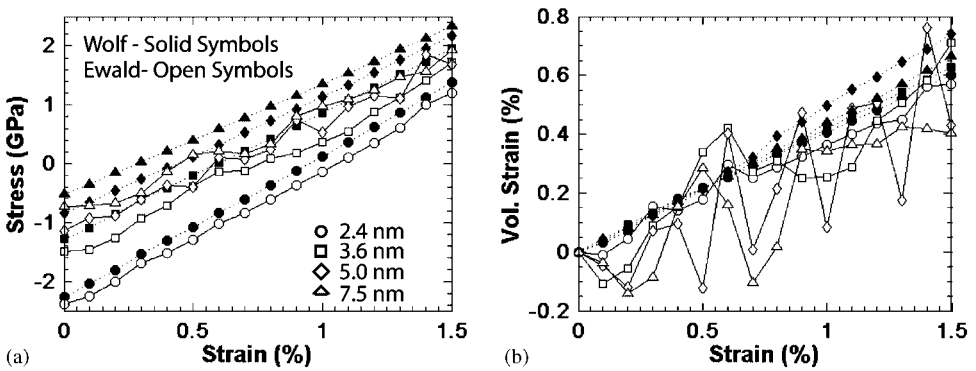

Figure 4. (a) Stress–strain response as predicted by Wolf and Ewald methods for different nanowires and (b) volumetric strain as a function of the applied axial strain for all the nanowires. Same legend applies to both the figures.

by the applied axial strain, the atoms reconstruct in the radial direction in the presence of free surfaces. As shown in Figure 4(b), with increasing strain, Wolf's method predicts a more physical response showing that the nanowire contracts in the radial direction monotonically as the axial strain is increased. This monotonic response is expected as an outcome of Poisson's effect. On the contrary, Ewald's method predicts a fluctuating behavior. This effect of the radial reconstruction is also plotted in the form of volumetric strain in Figure 4(b). The fluctuations in the volumetric response, as predicted by Ewald's method, increase with increasing wire diameter. This confirms

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Table II. Young's modulus of ZnO nanowires as predicted by using the Wolf and Ewald summations.

Wire diameter (nm)	Temperature (K)	Number of atoms modeled	Young's modulus, Ewald summation (GPa)	Young's modulus, Wolf summation (GPa)
2.4	0	2688	239	242
3.6	0	6912	208	214
5	0	23040	194.7	201.4
7.5	0	77760	177.7	190.4

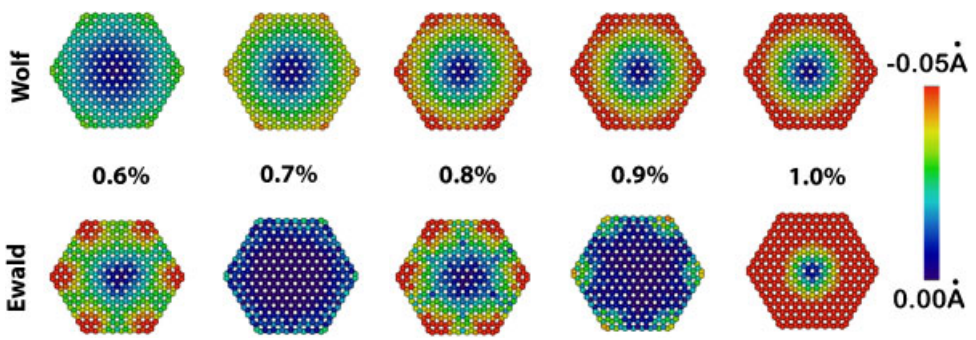

Figure 5. A cross-section of a 5 nm nanowire as simulated with both the Ewald and Wolf summations. The color map shows displacements with respect to the bulk lattice configuration.

Table III. The performance in terms of time taken for each timestep per atom per cpu for nanowires of different diameters.

Nanowire size (nm), Number of atoms	Ewald time (ms)	Wolf time (ms)	Gain
2.4 nm (2688 atoms)	5.8	1.9	3.1
3.6 nm (6912 atoms)	33	6.4	5.2
5.0 nm (23040 atoms)	329	19	17.3
7.5 nm (77760 atoms)	8742	87	100

that Ewald formulation is not capable of modeling free surfaces accurately and the error increases with increasing surface area.

3.3. Computational efficiency comparison

In addition to the inaccuracies associated with Ewald's method in the modeling of non-periodic structures, we observed vast differences in computational times associated with the two methods. The run times for tensile test simulations were recorded for nanowires of different diameters. For a direct comparison of computational times, the simulations were run on 256 processors of the Argonne National Laboratory's Intrepid BG/P system for 5 and 7.5 nm diameter nanowires and on eight processors of our local cluster for 2.4 and 3.6 nm diameter nanowires. Intrepid is the world's fifth fastest supercomputer with 163 840 processors and a peak performance of 557 teraflops [21]. The time required per MD timestep is summarized in Table III. It is important to point out the significant gain in the computational performance achieved with Wolf's method.

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The computational gain increases with the increasing number of atoms, which is consistent with the fact that Wolf's method should scale as order N and Ewald as a higher power of N (N, being the number of atoms in the model).

This significant gain in computational times allowed us to model nanowires as large as 20 nm in diameter, with proper accounting of long-range interactions. The importance of this has been emphasized in our recent work [13], where we bridged the gap between experiments and modeling by presenting a direct comparison. Experimentally, Young's modulus of $\sim$160 GPa was measured via *in situ* tensile tests which agreed very well with the computational predicted value of $\sim$169 GPa at 300 K. Additionally, the size dependence of the elastic modulus was explained based on the surface reconstructions which would not have been possible with Ewald's formulation.

4. CONCLUSION

In conclusion, we establish that the Ewald summation should be applied to non-periodic structures with great caution. While there is a little difference between the Ewald and Wolf summation techniques when modeling bulk ZnO, the Ewald summation does not inspire confidence in modeling nanowires with free surfaces. This is in accordance with the Ewald theory which assumes that the modeled structure is periodic. We showed that while the Wolf summation predicts a linear stress–strain response for ZnO nanowires, the response predicted by the Ewald summation is erratic. The error, as predicted by the Ewald's method, increases with the increasing model sizes. Prior to modeling nanowires, convergence studies were performed in order to determine the ideal parameters of the Wolf summation for modeling ZnO. It was shown that with these parameters the Wolf summation can perform up to 100 times faster than the Ewald summation, depending on the model size. This is a significant advantage over the Ewald summation as it allows for the simulation of experimentally tested nanowires, which would not be possible with the Ewald summation. We judge that the Wolf summation offers a superior alternative when modeling non-periodic structures.

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