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14. ABSTRACT

Classical molecular dynamics simulations typically require an initial equilibration phase to obtain a suitable starting configuration at the desired temperature and pressure. We have observed in various simulations of molecular crystals that, in some instances, defects spontaneously form when the reactive force field ReaxFF-*lg* is used. The source of defect formation is attributed to improper equilibration of the system. This technical note describes an alternate equilibration method that results in a defect-free crystal after equilibration.

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1. Introduction

Atomistic simulations, including molecular dynamics (MD), have become an important tool for researchers in various disciplines to study complex physical and chemical processes on the molecular scale.[1] However, there are 2 very important factors that affect the quality of the MD results: the description of the interatomic potentials and the initial configuration of the system for the trajectory from which relevant thermodynamic and structural averages will be obtained. The interatomic potentials are typically fitted to results from experiment[2] or quantum-level atomistic simulations,[3] such as density functional theory.[4] ReaxFF[5] and, more recently, ReaxFF-*lg*[6] have emerged as preferred potentials for reactive systems and have been fitted for use in simulations of many types of materials, such as hydrocarbons,[5] energetic materials,[7] semiconductors,[8] and metal oxides.[9] A relevant initial configuration is usually obtained through an equilibration trajectory in which the system is relaxed away from the initial atomic positions and velocities, through integration of the equations of motion. The length of the equilibration trajectory should be sufficiently long to converge to the desired thermodynamic state.

The original parameterization of the ReaxFF-*lg* potential[6] was developed for use in CHNO-type energetic materials but has accurately predicted structural properties of the nonenergetic molecular crystal sucrose ($C_{12}H_{22}O_{11}$), or table sugar. Our simulations of sucrose were started with the experimental configuration, but planar defects were observed to nucleate during the equilibration portion of the simulation. This technical note describes a modification of the equilibration process that produces a defect-free crystal for sucrose using the ReaxFF-*lg* potential.

2. Defect-Free Equilibration

MD simulations of sucrose were initiated using the experimental lattice vectors and atomic positions at 0 GPa.[10] The space group of the sucrose crystal is $P2_1$, with a unit cell containing 2 molecules.[11] The simulation cell is fully periodic, containing $3 \times 3 \times 3$ unit cells, for a total of 2,430 atoms. Figure 1a shows the molecular centers of mass for this configuration, projected onto the *xz*-plane. The timestep of the simulations is 0.1 fs, with thermostating and barostating rates of 0.1 ps and 1.0 ps, respectively. All simulations are performed using the LAMMPS computer code.[12]

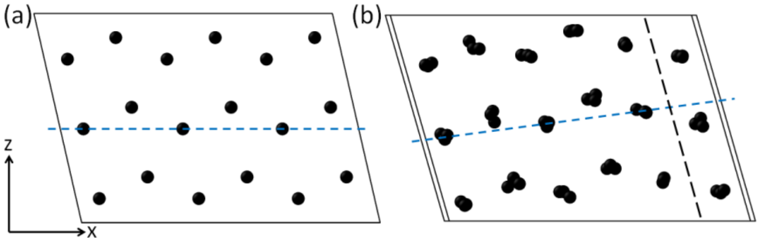

Fig. 1 **a) Initial and b) final configurations of the molecular centers of mass (projected onto the *xz*-plane) for Equilibration 1 using the experimental unit cell with the Goddard model at 0 GPa**

In a similar procedure to that of an earlier study for simulations of energetic molecular crystals using ReaxFF-*lg*,[13] the equilibration starts with microcanonical (NVE) MD with velocity rescaling every timestep for 2.5 ps, followed by isothermal-isochoric (NVT) MD at 300 K for 2.5 ps with no rescaling, then isothermal-isobaric (NPT) MD at 300 K and 0 GPa for 2.5 ps during which the cell angles are fixed but edge lengths are allowed to change. Finally, isothermal-isostress (NsT) MD is performed for 40 ps, during which cell angles are allowed to change along with edge lengths. The first 35 ps of the NsT MD simulation is still considered part of the equilibration; the last 5 ps is the production portion of the trajectories. This equilibration protocol was sufficient to provide initial states converged to proper thermodynamic states for the energetic material cyclotrimethylene trinitramine (RDX).[13,14]

Structural and thermodynamic averages are taken from snapshots created every 500 timesteps over the last 5 ps. Figure 1b shows the final configuration of the molecular centers of mass at the end of the trajectory using this equilibration protocol, denoted “Equilibration 1”; the Table below contains the corresponding lattice constants and angles. The lattice constants, *a*, *b*, and *c*, are all larger than the experimental configuration, resulting in a density of 1.56 g/cm^3. This is 1.89% less than the experimental value of 1.59 g/cm^3. This indicates that the initial system in Fig. 1a (i.e., the experimental configuration) is under compression when the equilibration trajectory initiates. During the NVE portion of the equilibration, in which the volume is fixed and the compressive stress cannot be relaxed in any way other than reorientation and/or deformation of the molecules, this compressive stress causes the crystal to rotate around the *y*-axis, as seen from the dashed blue reference lines in Fig. 1a and 1b. The enforcement of periodic boundaries in the simulation results in a stacking fault, indicated by the black dashed line in Fig. 1b.

Table Crystal parameters after each equilibration, compared to experiment

	Experiment	Equilibration 1	Error[a]	Equilibration 2	Error[a]
a	10.863 Å	11.128 Å	2.44%	11.102 Å	2.20%
b	8.705 Å	8.771 Å	0.76%	8.767 Å	0.71%
c	7.7585 Å	7.784 Å	0.33%	7.649 Å	–1.41%
α	90.0°	89.02°	–0.98°	89.81°	–0.91°
β	102.94°	105.83°	2.98°	101.18°	–1.77°
γ	90.0°	91.42°	1.42°	90.0°	0.0°

[a] Error is equal to the percent difference for the distances and absolute difference for the angles compared to experimental values.

The presence of the defect is an artifact of the equilibration protocol when using an initial highly stressed state. Therefore, it was necessary to develop a procedure that precludes this artifact. This procedure, denoted "Equilibration 2", is as follows: The lattice vectors produced by the simulation resulting from Equilibration 1 are used in conjunction with the experimental fractional positions of each atom to generate a new 3 × 3 × 3 system, as seen in Fig. 2a. This alleviates the compressive stress on the system that was apparent when the experimental lattice vectors of the unit cell were used to construct the simulation cell. This new system is then equilibrated in the same manner as described earlier: 2.5 ps in the NVE ensemble, 2.5 ps in the NVT ensemble, 2.5 ps in the NPT ensemble, and 40 ps in the NsT ensemble. Once again, structural and thermodynamics averages are obtained every 500 timesteps over the final 5 ps of the NsT portion of the simulation. We stress that this trajectory is *not* a continuation of the first equilibration but an entirely new simulation using an initial configuration obtained from Equilibration 1. The molecular centers of mass at the end of this trajectory are shown in Fig. 2b, and we note the absence of any defects in the system. The lattice constants and angles appear in the Table under the column "Equilibration 2". The errors are reduced for all crystallographic parameters except the *c* lattice constant. Surprisingly, the density after the second equilibration is 1.56 g/cm^3, identical to that of the first equilibration, but this is due to offsets in lattice constants and cell angles.

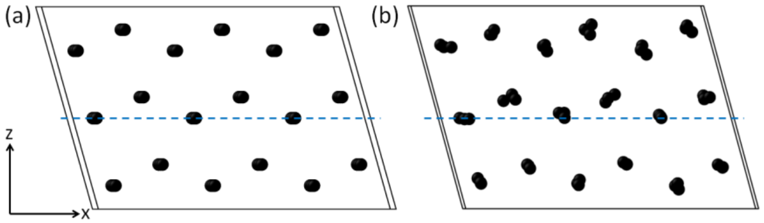

Fig. 2 Same as Fig. 1, with a) the initial configuration generated by combining the experimental atomic fractional coordinates and the lattice vectors from the first equilibration, resulting in b) a defect-free final configuration after Equilibration 2

To ensure that the defect resulting from Equilibration 1 is not an artifact of the small system size, the calculation using Equilibration 1 was repeated on a 15 × 15 × 15 unit cell system (303,750 atoms). The initial molecular centers of mass are shown in Fig. 3a, while the final configuration after Equilibration 1 appears in Fig. 3b. It is clear that defects were generated during the equilibration. In order to perform Equilibration 2, the average unit cell lattice vectors were obtained from the final configuration of the trajectory using Equilibration 1 (Fig. 3b). These were used, along with the experimental fractional atomic positions, to generate a new 15 × 15 × 15 unit cell system. The equilibration trajectory was then repeated. The result of the trajectory using Equilibration 2 is in Fig. 3c. Just as in the smaller system, Equilibration 1 results in a defect system, while Equilibration 2 is a perfect single crystal. This suggests that the phenomenon was not due to size effects and that a double equilibration similar to the process described herein should be performed for simulations of any size.

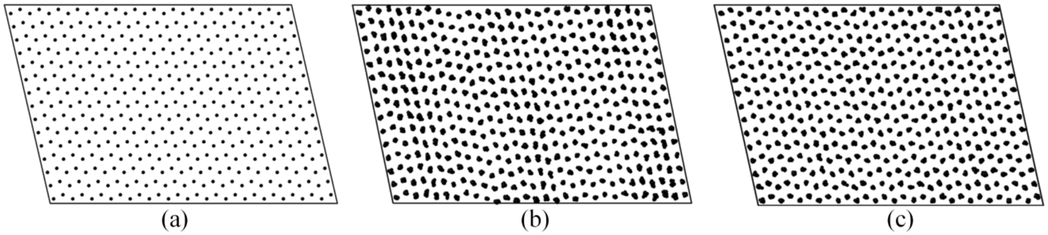

Fig. 3 Same as previous figures, for a larger system (15 × 15 × 15 unit cells): a) initial configuration, b) configuration after Equilibration 1, and c) final configuration after Equilibration 2

This process points to the precarious nature of the ReaxFF potential (which includes the ReaxFF-*lg* formulation) wherein great care must be taken during equilibration to avoid undesirable effects in the system or from the subsequent portion of the simulation in which averages are taken. This especially holds true for studies such as this, where the potential was not fitted for the material of interest—in this case, sucrose. In another study, we have observed the nucleation of a defect region in the energetic material 1,1-diamino-2,2-dinitroethene (FOX-7) using a different parameterization of ReaxFF-*lg* when fitted to RDX information.[13] Once again, we are able to eliminate the FOX-7 defect using the same double equilibration method described here. The nucleation of defects during equilibration does not necessarily bring into question the transferability of ReaxFF or ReaxFF-*lg*, only that care must be taken in setting up the simulation cell used to initiate the trajectories from which relevant structural and thermodynamic properties are obtained.

3. Summary and Conclusion

We have developed an equilibration protocol for ReaxFF-type potentials that is capable of avoiding the nucleation of defects due to highly stressed initial states. The equilibration technique is as follows: A first equilibration (that results in a system with one or more defects) provides lattice vectors that can be used to build a new simulation cell. The trajectory is repeated using the new simulation cell as the initial configuration, resulting in a defect-free system. This technique has been successfully applied to sucrose and FOX-7. We have also shown that the nucleation of defects occurs for larger systems, reducing the likelihood that a size effect is responsible for this phenomenon.

There are numerous parameterizations of ReaxFF and ReaxFF-*lg*, and this technique is likely not necessary for simulations of systems whose thermodynamic and structural states are similar to information used in the fitting. In those cases, the parameterization is expected to result in simulation cells that are not highly stressed. But the ReaxFF force fields used in this work were not parameterized for either sucrose or FOX-7, and the compressive stresses at the outset of the simulations result in the nucleation of planar defects. This technical note clearly shows that some care must be taken during equilibration to get a suitable starting configuration and provides a straightforward means of relaxing systems initially under stress.

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