3114 *J. Phys. Chem. A* **2008,** *112,* 3114−3118

Dissolution of Solid NaCl Nanoparticles Embedded in Supersaturated Water Vapor Probed by Molecular Dynamic Simulations

Alexander Y. Zasetsky,*,[†] James J. Sloan,[‡] and Igor M. Svishchev[†]

Department of Chemistry, Trent University, Peterborough, Ontario, K9J 7B8 Canada, and Department of Chemistry, University of Waterloo, Waterloo, Ontario, N213GI Canada

Received: October 5, 2007; In Final Form: January 3, 2008

The dissolution process for small, on the order of 1000 atoms, crystalline NaCl particles with defects embedded in highly supersaturated water vapor was studied by the molecular dynamics (MD) simulation method. We found that a breakdown of the crystal lattice does not occur unless (1) the thickness of water layer covering the surface of salt particles exceeds several molecular layers and (2) there are a considerable number of defects in the crystal. The collapse of the crystal lattice starts when the amount of water taken up by a salt particle reaches about half (∼50%) of the amount of salt in this particle. The number of defects required to initiate subsequent dissolution of the NaCl crystal on the time scale accessible by our simulations (∼40 ns) is in the range of 10 to 12%. We also report the estimates for the time required to form supersaturated aqueous solutions of NaCl from originally crystalline particles as a function of the number of defects in the crystal.

Introduction

Small aerosol particles suspended in the atmosphere affect the Earth's climate directly by scattering and absorbing thermal solar radiation and indirectly by altering particle formation pathways. Indirect aerosol effects on the climate are also radiative in nature, the optical properties of aerosol particles are affected in a complex (indirect) way by heterogeneous reactions, phase transitions, nucleation, as well as the particle growth and coagulation.[1−3]

Sea salt particles are one of the most abundant atmospheric aerosols. They are composed mainly of water and sodium chloride and can exist as liquid droplets or solid crystals. Being a source of atmospheric chlorine these particles affect the balance of atmospheric ozone. Owing to their ability to release reactive chlorine[4] these particles are thought to promote the oxidation process for organic materials in the atmosphere.[5] Sea salt aerosols also play a central role in the process of cloud formation, acting as cloud condensation nuclei.[6]

The rate of heterogeneous nucleation on these nuclei, in turn, depends on their phase (solid or liquid). The phase transitions of solid salt particles to liquid droplets and vise versa, often termed as deliquescence and efflorescence, are primarily a function of relative humidity (water vapor saturation ratio). These phenomena have been extensively studied experimentally, and their thermodynamic properties at the atmospheric conditions are known with a good accuracy. The kinetics of these transitions, however, is as yet imperfectly understood and is difficult to probe experimentally, and the interpretation of results is not straightforward.[7,8]

The present work aims to examine the initial stage of the dissolution process in nanosized solid NaCl particles embedded in supersaturated water vapor by the MD simulations method. The method has shown to provide valuable molecular level information on a variety of the properties of NaCl aqueous solutions,[9−13] and we use it here to probe the uptake of gaseous water by solid NaCl particles and their consequent transition into liquid aqueous solutions. Note that direct modeling of the dissolution of ideal NaCl crystals, which are unlikely present in the real atmosphere, is very demanding computationally due to the requirements for the system size and simulation time length. An alternative and realistic approach to introduce some amount of defects in the crystal lattice has recently been proposed.[9] The presence of defects (voids) makes it possible to simulate initial stages of the solid to liquid transition on the scale of sizes and times accessible by the MD method.

The motivation behind this work was manifold. First, it is essential to know how much water needs to be taken up by solid NaCl particles in order to start the dissolution process. Second, it is clear that defects in the sodium chloride crystal lattice play an important role in the kinetics of deliquescence. It has recently been reported based on the MD simulations of plane salt-water interfaces[9] that a breakdown of the NaCl crystal requires at least 20% defects to take place. We can expect, however, that in the case of solid salt particles, where the dissolution of the crystal lattice can start at vertexes and edges, a somewhat smaller amount of defects may require to initiate the transition and consequent dissolution of the crystal. Finally, the kinetics of dissolution, at least some estimates of the time required for the crystal lattice to collapse, can be directly obtained from molecular trajectories generated by the MD method.

In the following we shall report the results of large scale MD simulations that are used to study the uptake of gaseous water, formation of the film of liquid water on the surface, and consequent dissolution of crystalline NaCl nanoparticles with defects placed in supersaturated water vapor.

Calculation Details

In the present work we have chosen one of the simplest but, at the same time, one of the most successful water models, the

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* To whom correspondence should be addressed.

[†] Trent University.

[‡] University of Waterloo.

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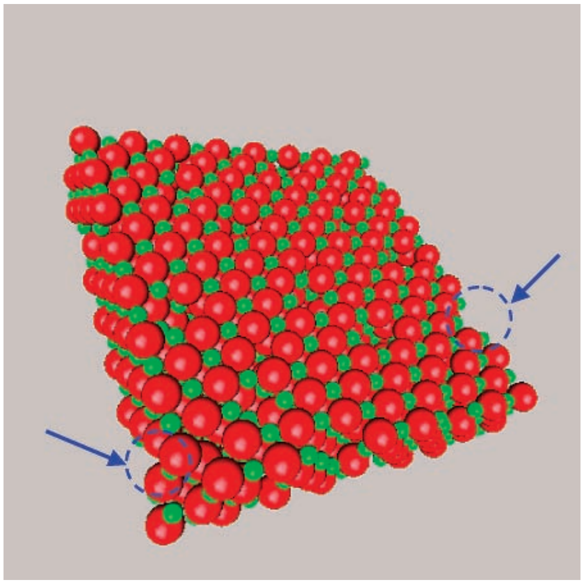


Figure 1. NaCl crystal (460 Na^+ and 460 Cl^- atoms) with 10% defects. Blue arrows indicate defects (voids) introduced.

extended simple point charge (SPC/E) potential.[14] The interaction functions for Na^+-Na^+, Na^+-Cl^-, and Cl^--Cl^- were taken from ref 15. The Lorentz−Berthelot combination rule was applied in the case of the $O-Cl^-$ and $O-Na^+$ interactions. Note that the potential for NaCl[15] was parametrized to accurately reproduce the interaction energy with the SPC water model.

The equations of motion were solved by the Verlet leapfrog algorithm subject to the periodic boundary conditions in a cubic simulation cell with the SHAKE constraint scheme[16] and a time step of 2 fs. The MD simulations have been carried out in the NVT ensemble with temperature controlled by the Nose-Hoover thermostat.[17] The simulations were performed at the temperature of 300 K. We use the spherical cutoff radius of 2.0 nm. A long range correction to the energy and virial was computed by the Ewald method. Using the efficient parallel molecular dynamics code (MolDynaMix) by Lyubartsev and Laaksonen,[18] we have recorded molecular trajectories with the length of 40 ns.

The system was composed of 8096 water molecules, 512 Na^+, and 512 Cl^- ions, minus the number of defects introduced to the crystal. The ideal NaCl crystal was assembled of 8 × 8 × 2 elementary cells with the cubic close packed (ccp) structure. The number of defects we have introduced to a perfect crystal in the present work was 12, 16, and 20%. In order to preserve electro- neutrality and regularity of the system, defects were formed by randomly removing ion pairs from the crystal lattice. An example of the sodium chloride crystal with 12% defects (voids) is shown in Figure 1.

Crystalline NaCl nanoparticles were placed in highly supersaturated water vapor with the saturation value of 10, 50, and 100. We note that events with such high supersaturations do not normally occur in the atmosphere. On the other hand, simulations with a realistic saturation ratio value of about 1 would require enormous computer power and/or simulation time length. It is not yet possible to model the uptake of water vapor (as well as nucleation) at vapor saturations relevant to real atmospheric conditions directly by the MD method. Nevertheless, the use of (unrealistically) high vapor saturation ratios enables to look at the entire process, from the uptake of water vapor by salt particles to the collapse of their crystal lattice, at a molecular level.

A standard approach used in molecular simulations to analyze crystal (order) to liquid (disorder) transitions is that of finding some measure of the order in molecular systems based on the mutual arrangement of neighboring atoms/ molecules. In this work, we analyze atomic structures, or the degree of crystallinity in NaCl particles, by using the local order parameter q_4 suggested in the works.[19,20] This quantity has proved to be very efficient in studying liquid to solid-phase transitions in sodium chloride melts,[20] and we use it here to trace the local order in NaCl particles during the course of computations.

With this aim, we first compute the following quantity ($q_{4m}(i)$) for each atom in a salt particle

$$q_{4m}(i) = \frac{1}{N(i)} \sum_{j=1}^{N} Y_{4m}(\mathbf{r}_{ij}) \qquad (1)$$

where $Y_{4m}(\mathbf{r}_{ij})$ is the angular component of spherical harmonics, $N(i)$ is the number of adjacent atoms, $\mathbf{r}_{ij}$ is the unit vector that indicates the direction between a central atom i and its neighbors j.

The local order parameter $q_4(i)$ is then calculated as

$$q_4(i) = \left(\frac{4\pi}{2l+1} \sum_{m=-l}^{l} \left| q_{lm}(i) \right|^2 \right)^{1/2} \qquad (2)$$

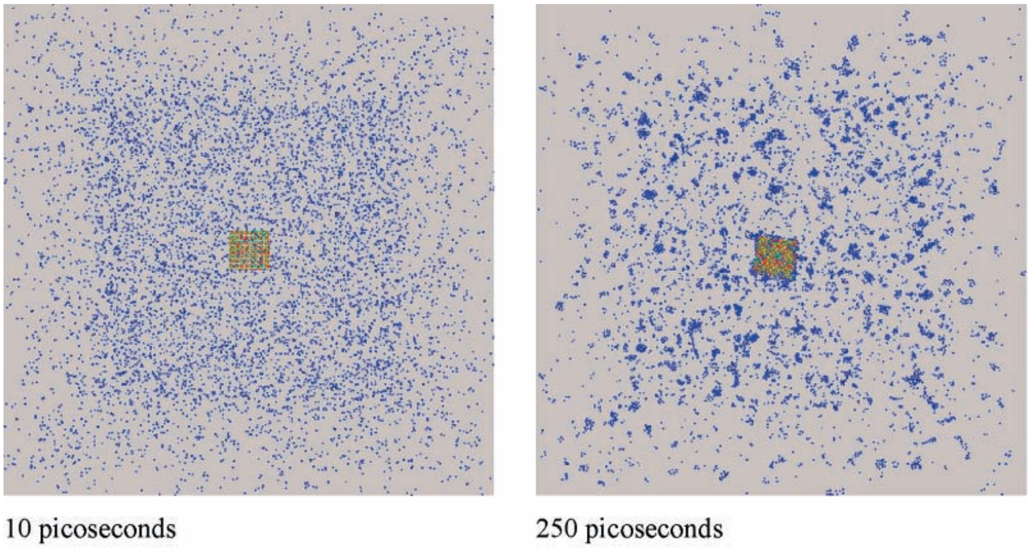
with l equal to 4 in the present study.

It was shown that an atom i is "solid-like" if the scalar product $q_4(i)$ is larger than some threshold value.[20] For the purpose of tracing the time evolution of the "global" order in a salt particle we use the value of parameter $\langle q_4 \rangle$ averaged over all the atoms in this particle.

Results and Discussions

We start the discussion with the process of water vapor uptake by salt particles. Our simulation results demonstrate that, under such high supersaturations, the uptake of water molecules by solid salt particles and formation (nucleation) of pure liquid water droplets in supersaturated vapor occur almost simultaneously. This is illustrated in Figure 2, where four snapshots of the simulated system at 10, 100, 250, and 1000 picoseconds are shown. First signs of condense water nuclei can be seen after approximately 50−100 ps of simulation time. These are small clusters with the size ranging from 2−10 water molecules. The growth and agglomeration of liquid water particles then continues on the time scale of hundreds of picoseconds, and the excess of gaseous water is exhausted, in other words the amount of water taken up by salt particles as a function of time levels off, after about 1 ns for the saturation value of 100. For the saturation value of 10, however, the same process requires about 10 ns to deplete the excess of water in the gas phase and to form liquid droplets and a layer of liquid water on the salt particle surface. We should note that the nucleation and particle growth rates as well as the length of the induction phase (the time period required to detect first nucleation events for a particular cluster size) are extremely sensitive to the value of vapor saturation ratio.

The uptake of gaseous water is the first stage in the dissolution process. At this stage the amount of water taken up by a salt particle is equal approximately to that in water droplets formed homogeneously and simultaneously (see Figure 2). The number of water molecules condensed on the salt particle as a function of time is shown in Figure 3. As it can be seen in the figure, it requires for a salt particle about 1 ns to take up 600 water molecules (which is roughly the limit for the system size and salt particle size used in this work) for the saturation value of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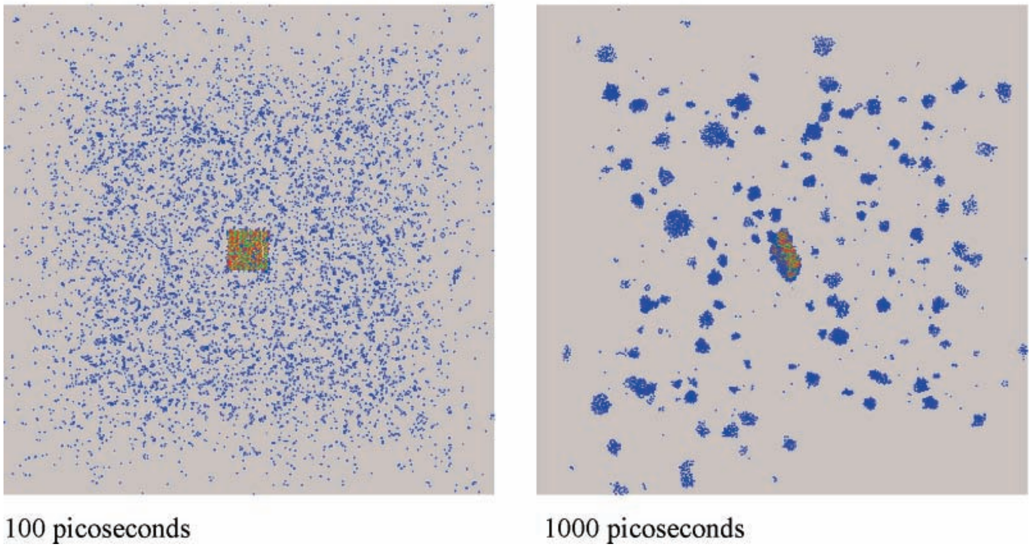
250 picoseconds


100 picoseconds

1000 picoseconds

Figure 2. Four snapshots that show the formation (nucleation) of liquid droplets and water uptake by a NaCl particle from supersaturated water vapor. Molecular system contains 8192 water molecules and 460 Na^+/ Cl^- ion pairs. Water vapor saturation value and number of defects in NaCl crystal are 100 and 16%, respectively. Oxygen atoms are shown by blue spheres. Na^+ and Cl^- ions are shown by green and red spheres, respectively.

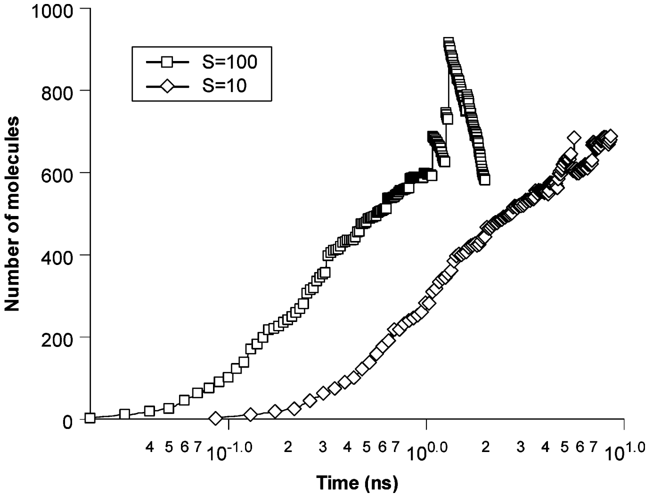


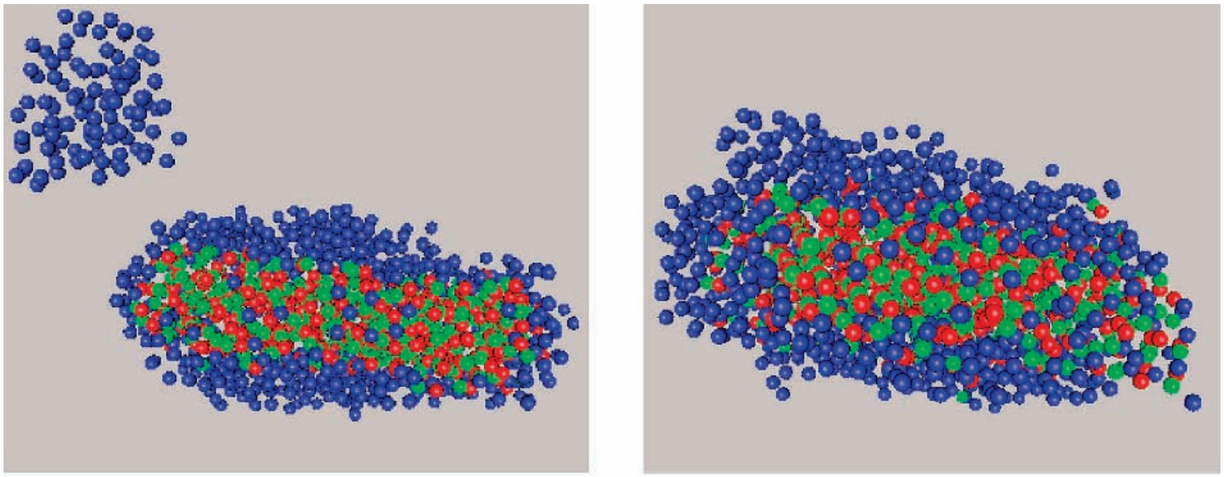
Figure 3. Water uptake by NaCl particles as a function of time and water vapor saturation ratio.

100. In the case of the saturation value of 10, it takes an order of magnitude longer for the system to form the same water layer of about 600 molecules on salt particles.

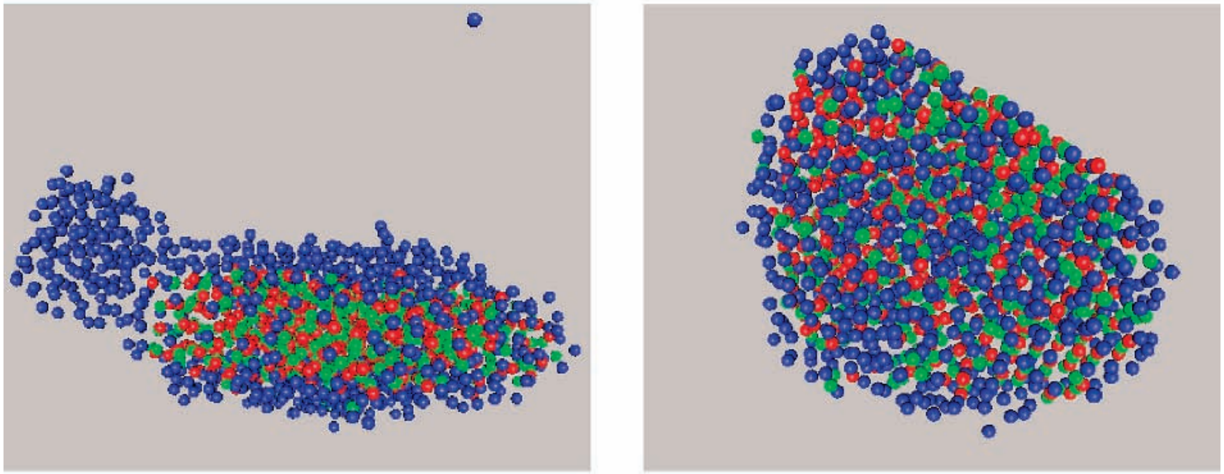
Next stage is diffusion of water molecules through the water-salt interface and the resulting collapse of crystal lattice as such. In order to initiate this phase transformation, a large enough amount of water should be taken up by salt. We found that the crystal to liquid (partially mixed amorphous) transition starts only when a number of water molecules reaches approximately 50% that of a number of atoms in this salt particle. We remind that the results are obtained for NaCl particles composed of about one thousand atoms.

After the condensation process through the addition of single water molecules (monomers) is completed, a further increase in the water content on salt particles progresses via coagulation with liquid water droplets. Such an event is shown in Figure 4, where a water droplet merges a salt particle already covered by water. This figure also illustrates different stages of crystal dissolution for the particle with 16% defects. As it might be expected, the particle shape also undergoes significant changes during this transition. Being plate-like initially, the particle takes on almost spherical shape as soon as the breakdown of crystal lattice is finished.

The rate of salt dissolution is very sensitive to the amount of defects introduced to the crystal lattice. In Figure 5, the degree of crystallinity, which is monitored by the order parameter $< q_4 >$, is plotted as a function of time. It shows that initially



1 nanosecond 5 nanoseconds



2 nanoseconds 10 nanoseconds

Figure 4. Four snapshots that illustrate collapse of NaCl crystal and formation of supersaturated liquid aqueous solution. Original NaCl crystal has 860 ion pairs, corresponding to 16% of defects. Oxygen atoms in water molecules are shown as blue spheres. Na^+ and Cl^- ions are shown by green and red spheres, respectively.

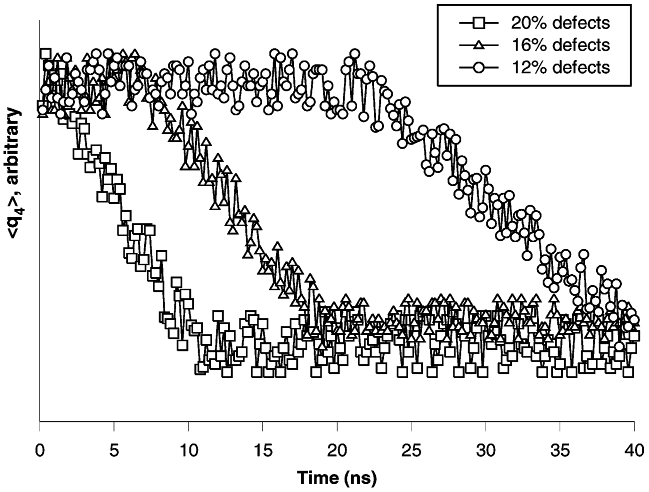


Figure 5. Time evolution of the order parameter $\langle q_4 \rangle$ for solid NaCl particles with a different amount of defects. The parameter $\langle q_4 \rangle$ is computer as the average over all the atoms in the salt particle.

ordered atoms in the NaCl particle, which is characterized by a larger value of parameter $\langle q_4 \rangle$, become disordered after several nanoseconds. It was found that the transition of solid particles covered by water to liquid aqueous solutions occurs on the time scale ranged from 10 ns for the crystal with 20% defects to 40 ns for the crystal with 12% defects. Note again that on the time scale accessible to us complete dissolution of NaCl crystals cannot be achieved, although we have undoubtedly observed the collapse of crystal lattice and the formation of amorphous droplets composed of partially mixed (supersaturated) aqueous solutions of sodium chloride.

Conclusion

We report the results of MD simulations that in our view can facilitate an understanding of very complex and important processes of phase transformations in atmospheric sea salt aerosols. Salt particles were placed in highly supersaturated water vapor. Dramatic changes in the crystalline structure of NaCl aerosol particles have been observed after a large enough amount of gaseous water was taken up by salt. The amount of water required to initiate these structural changes is approximately half as much as the amount of salt. Note that this quantity may possibly be dependent on the size of molecular system, the size of salt particles, and the number of defects used in simulations. As regards the effect of defects, we could only observe a collapse of the crystal lattice if the number of defects introduced to the salt crystal exceeded 10%. The phase (material) thus formed can be referred as partially mixed amorphous or supersaturated aqueous mixtures. It is clear that much more water, in comparison to the amount of NaCl, and much longer simulation runs are needed to arrive at thermodynamically stable saturated aqueous solutions corresponding to the NaCl solubility limit.

In closing this discussion, we would like to point out that despite significant advances in understanding of the deliquescence and efflorescence processes in atmospheric salt aerosols achieved recently, an understanding of the kinetics of these transitions is still some way off. Further progress may, in part, be achieved through the use of computer simulations. Moreover, while a direct probe of the water uptake, nucleation, and salt dissolution by the MD method at realistically low saturations on the order of 1 is extremely computationally expensive, if possible, at present, this is projected to become doable in the not too distant future.

Acknowledgment. Authors are grateful for the financial support of the Natural Sciences and Engineering Research Council of Canada and SHARCNET. SHARCNET (www.sharcnet.ca) is a consortium of universities and colleges operating a network of high-performance computer clusters across south western, central, and northern Ontario.

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