A Model for Self-Rolling of an Aluminosilicate Sheet into a Single Walled Imogolite Nanotube

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Introduction and Computational Details

Imogolite nanotubes are attractive because of their potential uses in soil contamination control, as an arsenic scavenger in liquids (where it has shown to be able to retain five times more arsenic than the products in use today), in the containment of oil spills, as a base for creams and drug vehicle, as a transparent additive of polymers and molecular sieves, as a support for insulating polymers and catalysts, and for coating nanowires. Moreover, imogolite is a clay-like nanotube of which the diameter can be controlled. It was discovered in volcanic soils[1], and its structure was given by Cradwick *et al.*[2] in 1972. In 1977 a synthesis protocol was put forward[3]. The chemical formula suggested by Cradwick is $[(OH)_3Al_2O_3SiOH]_{2N}$, with $N = 10$ for natural, and $N = 12$ for synthetic imogolite. For the latter the exterior diameter is of ≈ 2.3 nm and its average length is 100 nm.

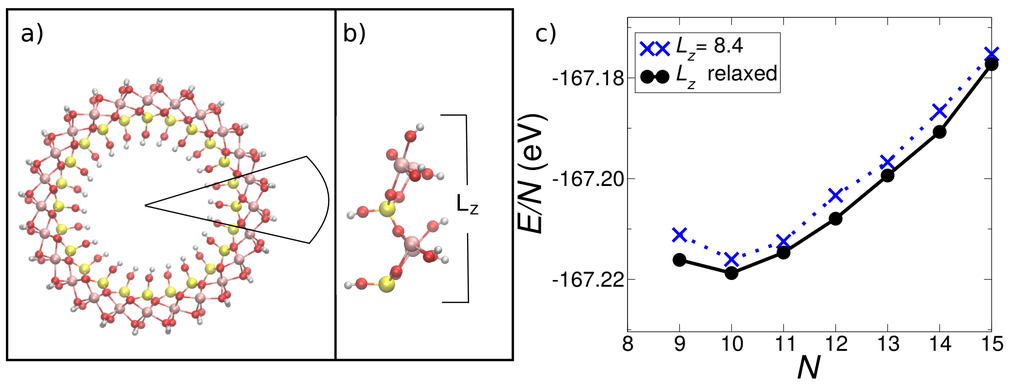

FIGURE 1: (a) Imogolite unit cell with $N = 12$ repetitions of the 28 atom circular sector, of angle $2\pi/N$, marked by the black continuous line. (b) Lateral view of the 28 atom structure that is angularly repeated to form imogolite. Periodic repetitions of the unit cell are imposed in the axial direction. L_z is the axial length of the unit cell. H: light gray, O: red, Si: yellow and Al: pink. (c) Monodispersion concept as modeled with CLAYFF force field. The minimum of energy is for $N = 10$.

We employed the CLAYFF force field[4] to describe the interactions between the atoms. The force field potential with fractional charges assigned to each atom and Lennard-Jones (LJ) (12-6) potentials. The O-H bonds are described by a harmonic bond-stretching term:

$$E = \sum_{i<j} \frac{1}{4\pi\epsilon_0} \frac{q_i q_j}{r_{ij}} + \epsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - 2\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right] + k_{ij}(r_{ij} - r_0)^2,$$

where $\sigma_{ij} = 1/2(\sigma_i + \sigma_j)$ and $\epsilon_{ij} = (\epsilon_i \epsilon_j)^{1/2}$.
The cell sizes were $10 \times 10 \times 5.04$ nm for the model of an isolated imogolite molecule, which were of enough length to be considered as an isolated molecule and to evaluate the Coulomb summation correctly. All calculations were performed with the molecular dynamics program called LAMMPS[5] combined with local developed codes. An equivalent technique to the famous Ewald method was used for the summations of Coulombic interactions as implemented in LAMMPS. The structures were relaxed with the method of modified molecular dynamics known as FIRE[6].

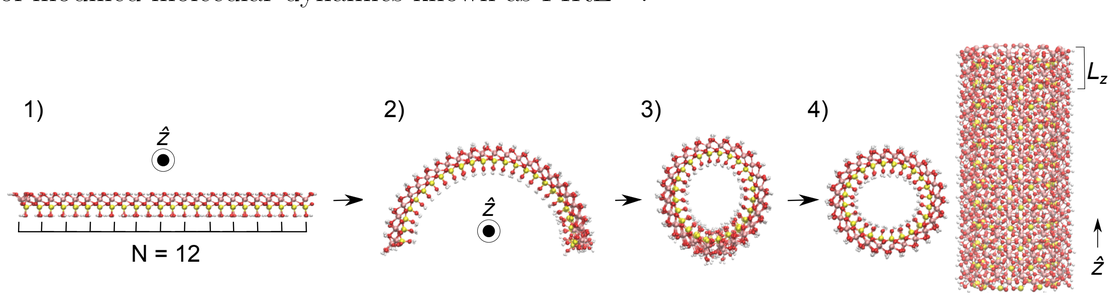

FIGURE 2: Illustration of the imogolite formation process that we simulate. 1) Planar aluminosilicate sheet; 2) Initial scrolling stages; 3) The NT is completed; 4) Axial and lateral view of the NT after relaxation; it is noticed that the defects at the NT seam, illustrated in 3), have disappeared.

In the next sections we present the results of our work. The section *Rolling of imogolite with planar initial conditions* was recently published[7]. The section *Mechanical Properties: Nano-coiling* is in preparation for publication.

Rolling of imogolite with planar initial conditions[7].

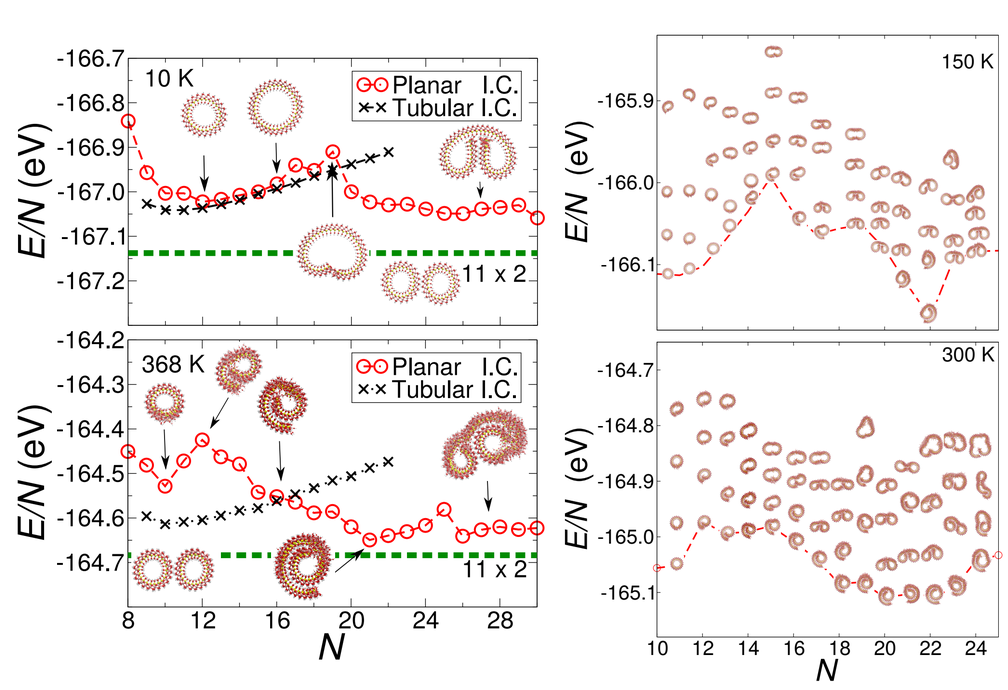

FIGURE 3: Thermodynamic average of E/N for temperatures of 10, 150, 300 and 368 K. The black x correspond to tubular (TIC), and the red circles to planar (PIC), initial conditions. Snapshots of the scrolled conformations, obtained for the minimum energy, are provided for representative N values. The dashed horizontal line corresponds to the total energy of two interacting $N = 11$ NTs at the same temperature.

Mechanical Properties: Nano-coiling[8].

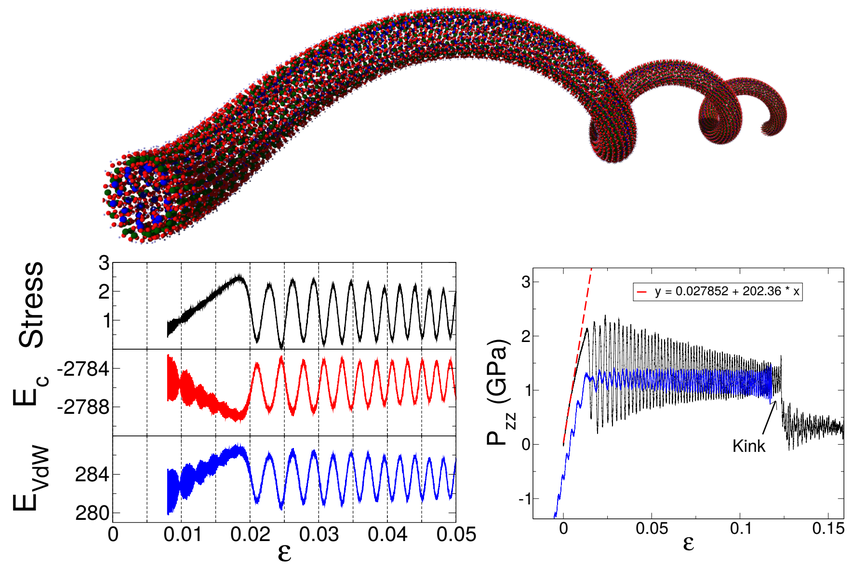

FIGURE 4: P_{zz} vs strain, Young modulus ≈ 200 GPa, this is in good aggrement with previous published results[9]. This case correponds to the compression of the 40 nm imogolite, erate of -1.e-4/ps. Above 0.125 of strain the nanotube begins to break. The units are: Stress in GPa, Coulombian energy (E_c) and Van der Walls energy (E_{vdw}) in eV.

References

[1] N. Yoshinaga and A. Aomine. Imogolite in Some Ando Soils. *Soil Sci. Plant Nutr.*, 8:22–29, 1962.

[2] P. D. G. Cradwick, V. C. Farmer, J. D. Russell, C. R. Masson, K. Wada, and N. Yoshinaga. Imogolite, a Hydrated Aluminium Silicate of Tubular Structure. *Nature Phys. Sci.*, 240:187–189, 1972.

[3] V. C. Farmer, A. R. Fraser, and J. M. Tail. Synthesis of Imogolite: A Tubular Aluminium Silicate Polymer. *J. Chem. Soc. Chem. Commun.*, (13):462–463, 1977.

[4] R. T. Cygan, J. J. Liang, and A. G. Kalinichev. Molecular Models of Hydroxide, Oxyhydroxide, and Clay Phases and the Development of a General Force Field. *J. Phys. Chem. B*, 108:1255–1266, 2004.

[5] S. J. Plimpton. Fast Parallel Algorithms for Short-Range Molecular Dynamics. *J. Comp. Phys.*, 117:1–19, 1995. URL `http://lammps.sandia.gov`.

[6] E. Bitzek, P. Koskinen, F. Gähler, M. Moseler, and P. Gumbsch. Structural Relaxation Made Simple. *Phys. Rev. Lett.*, 97:170201, 2006.

[7] R. I. González, R. Ramírez, J. Rogan, J. A. Valdivia, F. Munoz, F. Valencia, M. Ramírez, and M. Kiwi. Model for self-rolling of an aluminosilicate sheet into a single-walled imogolite nanotube. *J. Phys. Chem. C*, 118(48):28227, 2014.

[8] R. I. González, J. Rogan, J. A. Valdivia, and E. M. Bringa. Aluminosilicate nanotube mechanical properties. *In preparation for publication*, 2015.

[9] Gilberto Teobaldi, Nikolaos S Beglitis, Andrew J Fisher, Francesco Zerbetto, and Werner A Hofer. Hydroxyl vacancies in single-walled aluminosilicate and aluminogermanate nanotubes. *J. Phys.: Condens. Matter*, 21(19):195301, 2009.

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