Louisiana Alliance for Simulation-Guided Materials Applications

Modelling Molecular Diffusion in Confined Geometries

Summer RET Project 2014

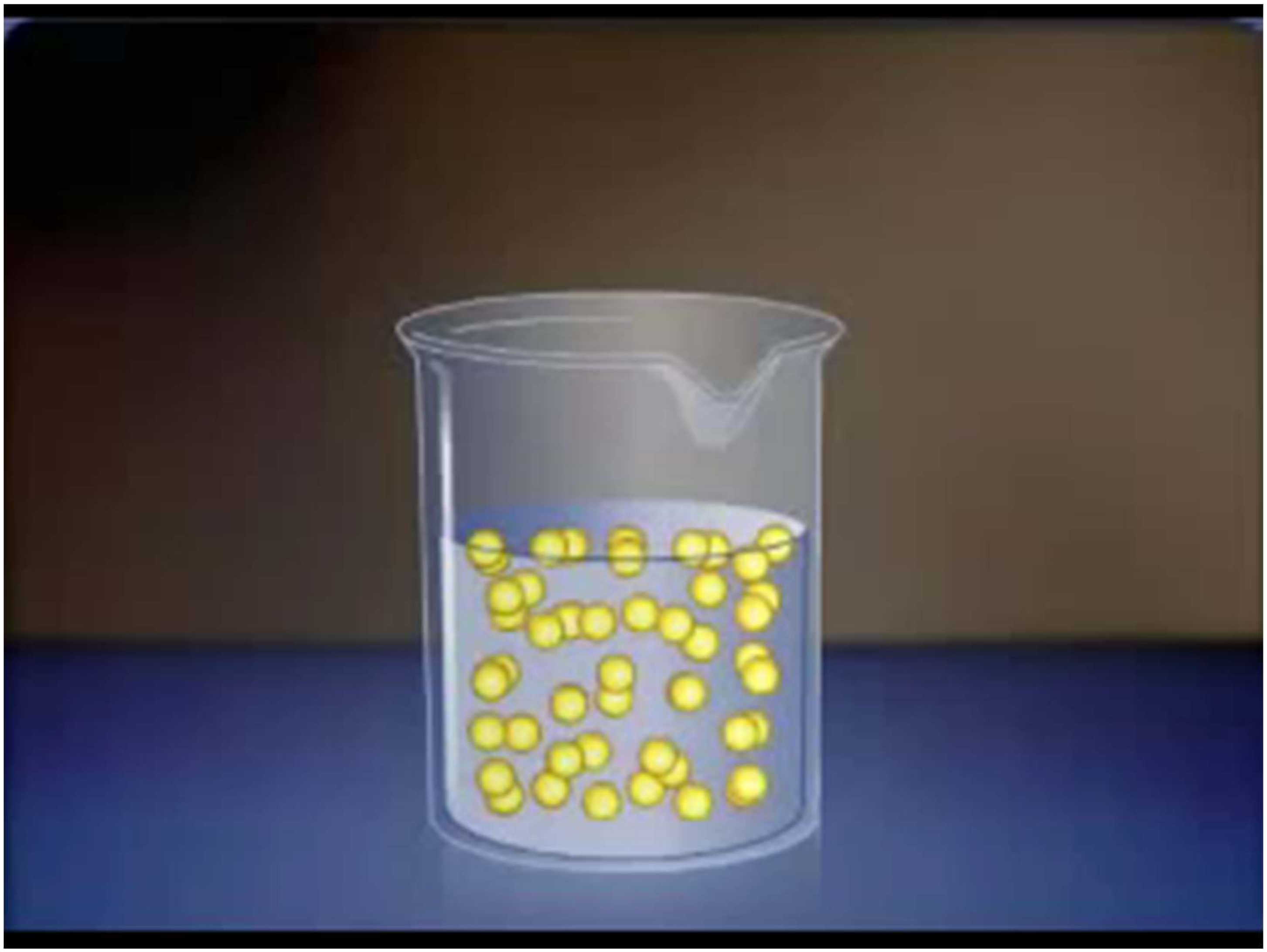
Mary Beth McCoy

Advisor: Dr. Pedro Derosa

PhD Candidate: Divya Elumalai

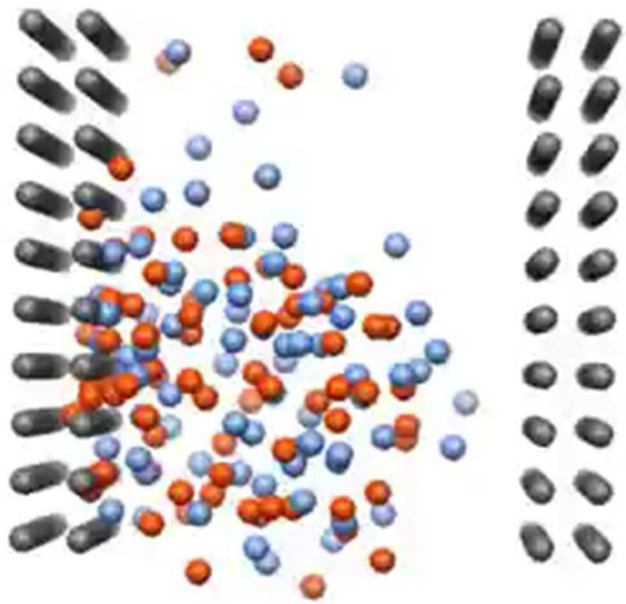
Introduction: play the video "Nanotechnology."

Diffusion



Free Diffusion vs Confined Diffusion the Difference

Confined Diffusion



Introduction

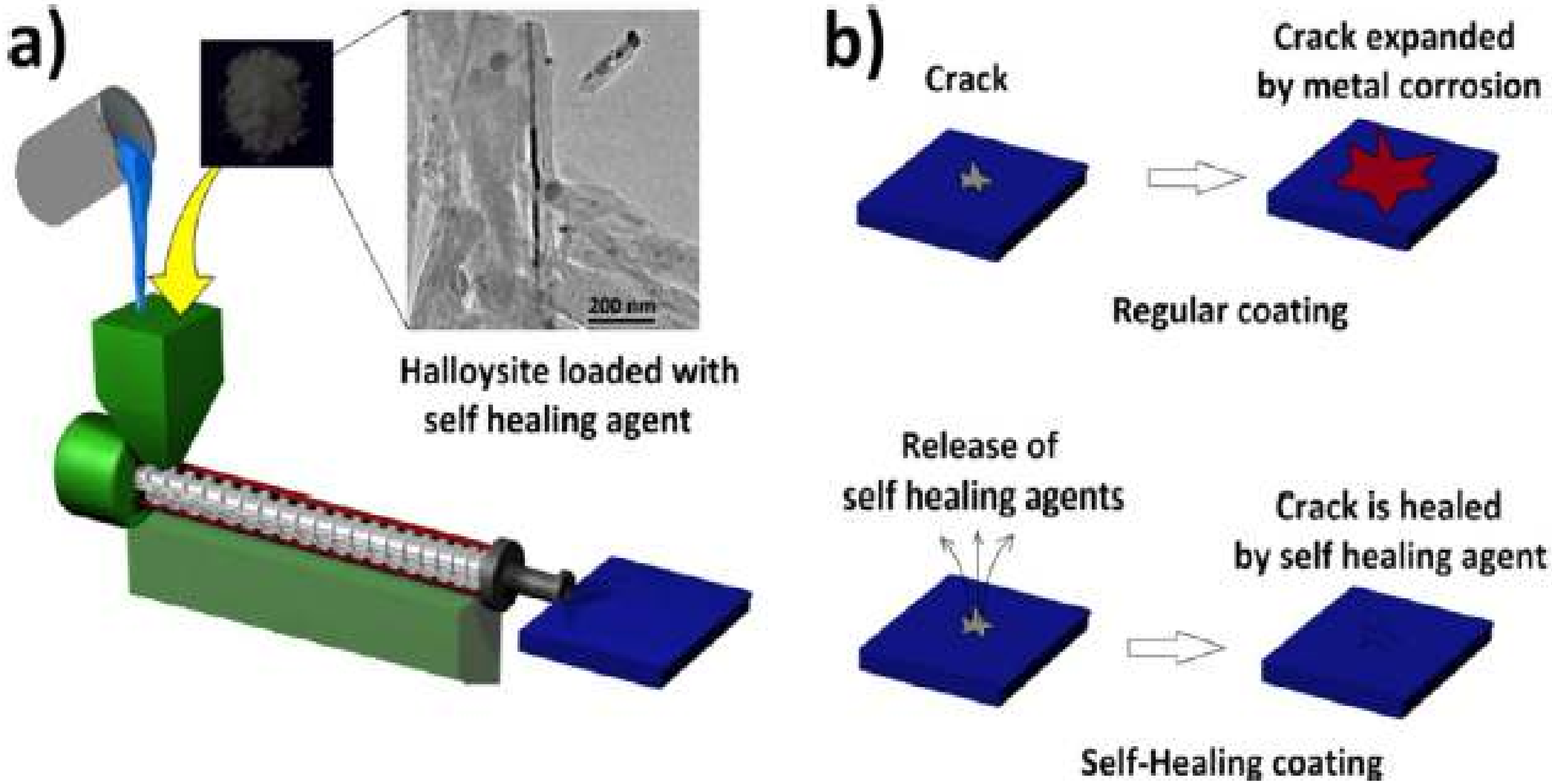
- Nanotubes as controlled release containers have been utilized for applications ranging from drug delivery, cancer therapy, vaccine delivery, imaging and diagnostics to enhancing the lifespan of rust coating in hazardous environments and self healing composites.
- The use of Halloysite nanotubes in such storage and delivery based application has increased, because Halloysite NTs are known to be less cytotoxic than CNTs.
- The overall objective of this research project is to understand transport properties such as adsorption and diffusion in Halloysite nanotubes, and to study the interactions governing transport in nanotubes. Enabling and guiding potential applications in the process.
- Applications such as :
  - Enhancing the lifespan of rust coatings in hazardous environments,
  - Self healing composites and polymers,
  - Sustained/controlled drug delivery.

Why do we need to controlled release?

Let us consider Drug Delivery.

- Controlled release means the delivery container is formulated so that the required amounts of the drug are released slowly over time.
- Such a delivery has the advantage of having to take the drugs at less frequent intervals than **immediate-release** (**IR**) formulations of the same drug. It also means that there may be fewer side effects as the levels of the of drug in the body are more consistent in extended release formulations.
- If the delivery mechanism is such that there is targeted delivery to the required "site". The advantage is the problem of "dose dumping" and "saturation" are overcome. This also avoids the problem of having to increase dosage to over come the immunity the disease and the body builds.

Scheme 1. (a) Preparation of Halloysite-Polymeric Coating, and (b) the Behaviors of the Regular and Self-Healing Coatings in Corrosion Process



E. Abdullayev, V. Abbasov, A. Tursunbayeva, V. Portnov, H. Ibrahimov, G. Mukhtarova, and Y. Lvov, "Self-healing coatings based on halloysite clay polymer composites for protection of copper alloys.," *ACS Appl. Mater. Interfaces*, vol. 5, no. 10, pp. 4464–71, May 2013.

Objective

To study how the release profiles of molecules scale with respect to: the number of particles diffusing out of the nanotube, the radius of nanotube and the length of nanotube, under constant density conditions.

Skills I Acquired

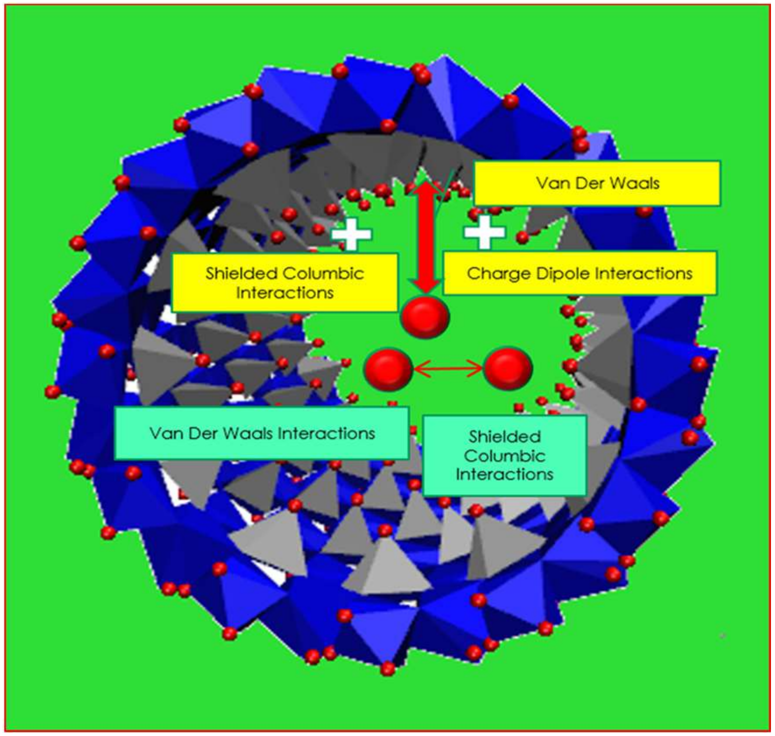
- How to submit Jobs to Unix Clusters using Shell script (PBS) Files and MATLAB executables.
- How to transfer input to and output from Unix clusters(LONI).
- How to perform basic statistical analysis using MATLAB code (provided)
- How to analyze data in excel.

Job Description

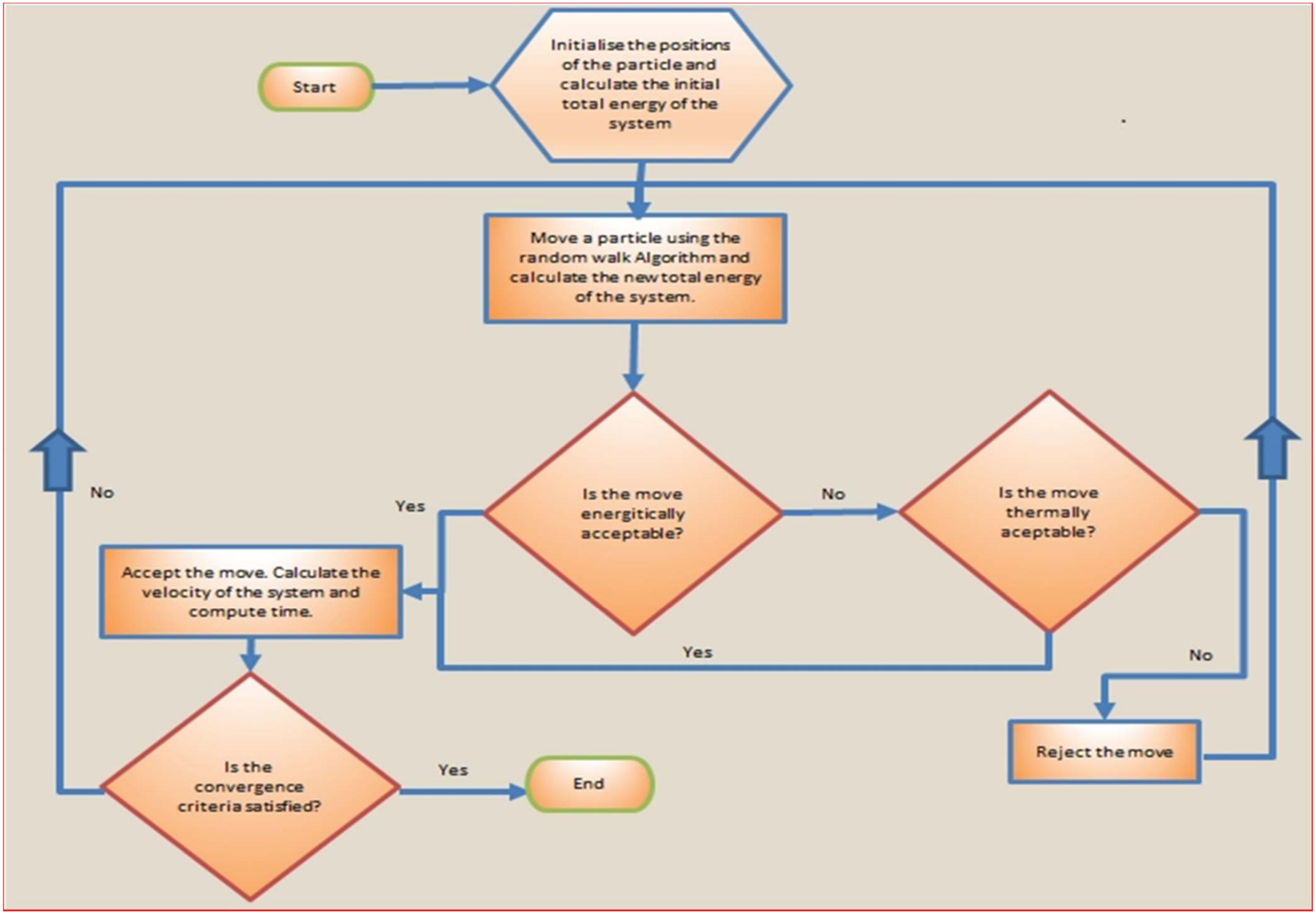
We submitted simulations for 10, 20, 50 , and 100 particles in Cerberus to study the diffusion of these particles out of halloysite nanotubes of corresponding lengths.

Methodology

- A Metropolis Monte Carlo model implementing a random-walk algorithm to generate the most probable motion of particles in the nanotube is utilized.
- The motion is accepted if the move is energetically viable, taking into consideration the contributions from ambient (system) temperature.
- The total energy term has contributions from Van Der Waals interactions, Shielded Columbic interactions, and dipole-charge interactions.

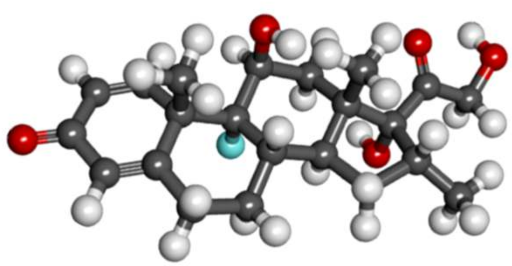


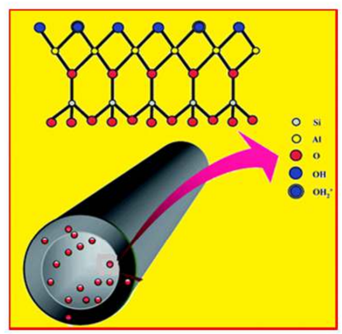
Algorithm

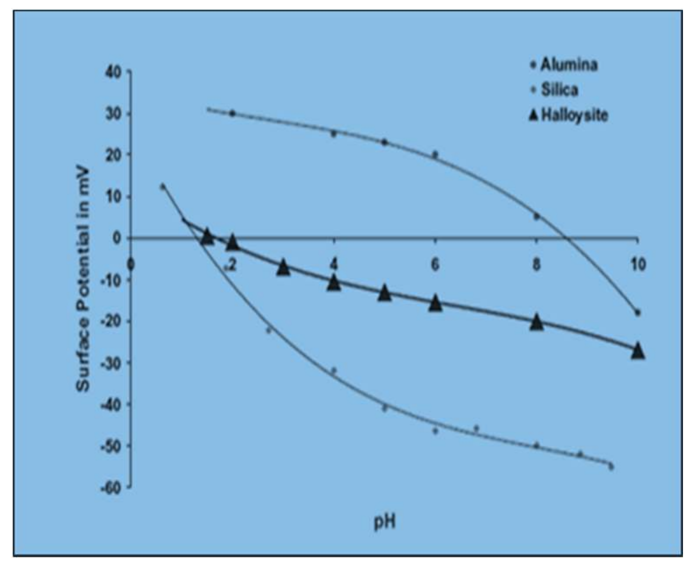

Start
Initialise the positions of the particle and calculate the initial total energy of the system
Move a particle using the random walk Algorithm and calculate the new total energy of the system.
Is the move energitically acceptable?
No
Is the move thermally aceptable?
Yes
Accept the move. Calculate the velocity of the system and compute time.
Yes
No
Reject the move
No
Is the convergence criteria satisfied?
Yes
End

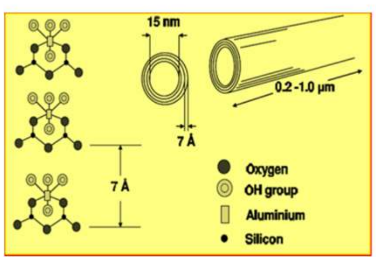
Dexamethasone	$C_{22}H_{29}FO_5$
ζ (pH 7.5)	-35 mv
Refractive Index	1.592
Refractivity	102.493 cm^3
Molar Volume	296.2×10^{-6} m^3
Density	1.3 g/cm^3
Polarisability	39.7×10^{-24} cm^3
Molecular Weight	392.47 Da
Molecular Radius	0.48767×10^{-9} m
ε_r	2.0
Specific Gravity	2.53 g/cm^3

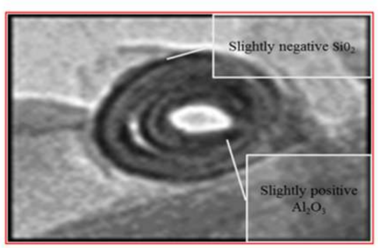
Halloysite	$Al_2Si_2O_5(OH)_4.2H_2O$
Refractive Index	1.54
Molecular Weight	264.2 Da
Average Inner Lumen Radius	15×10^{-9} m
Average Outer Radius	50×10^{-9} m
Specific Gravity	2.653 g/cm^3

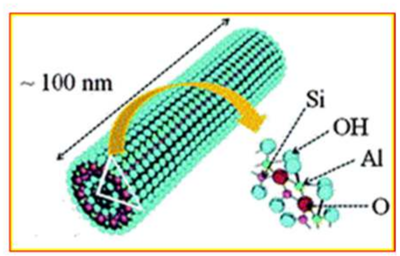


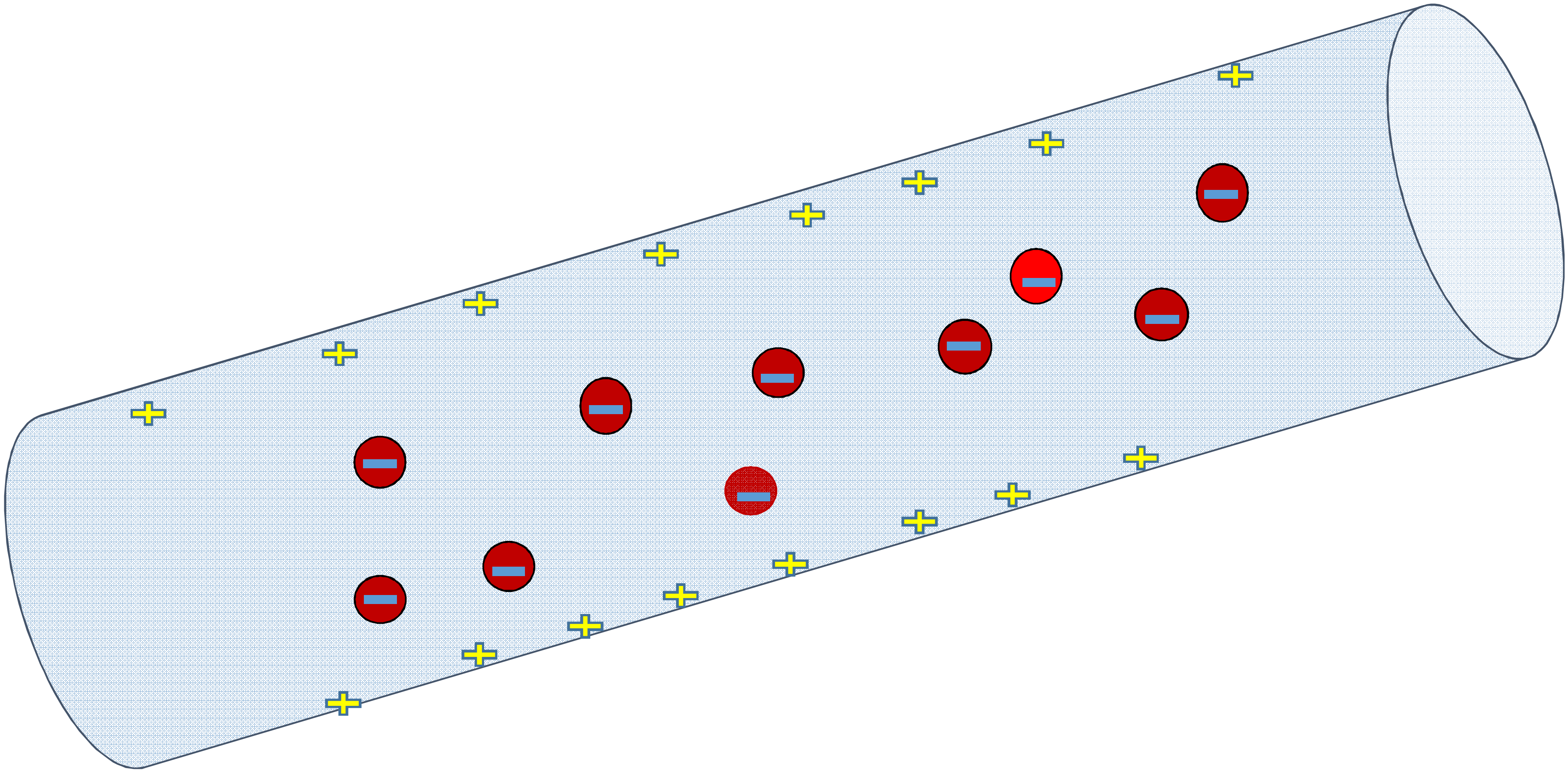




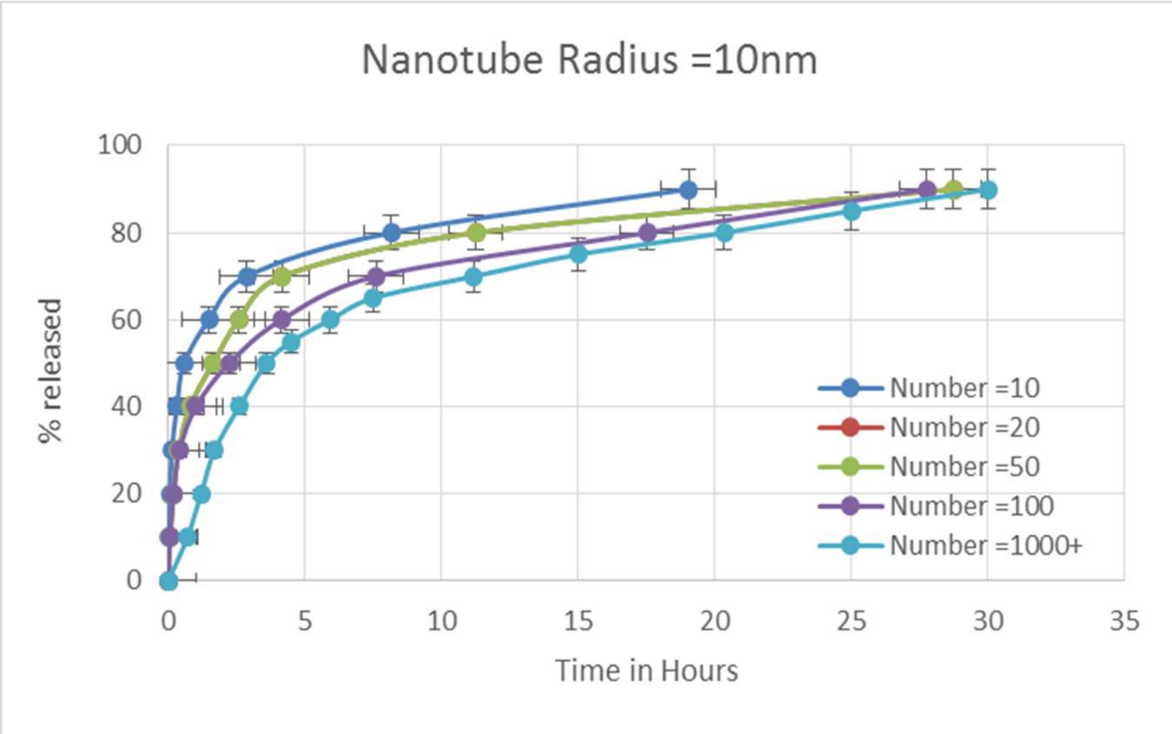








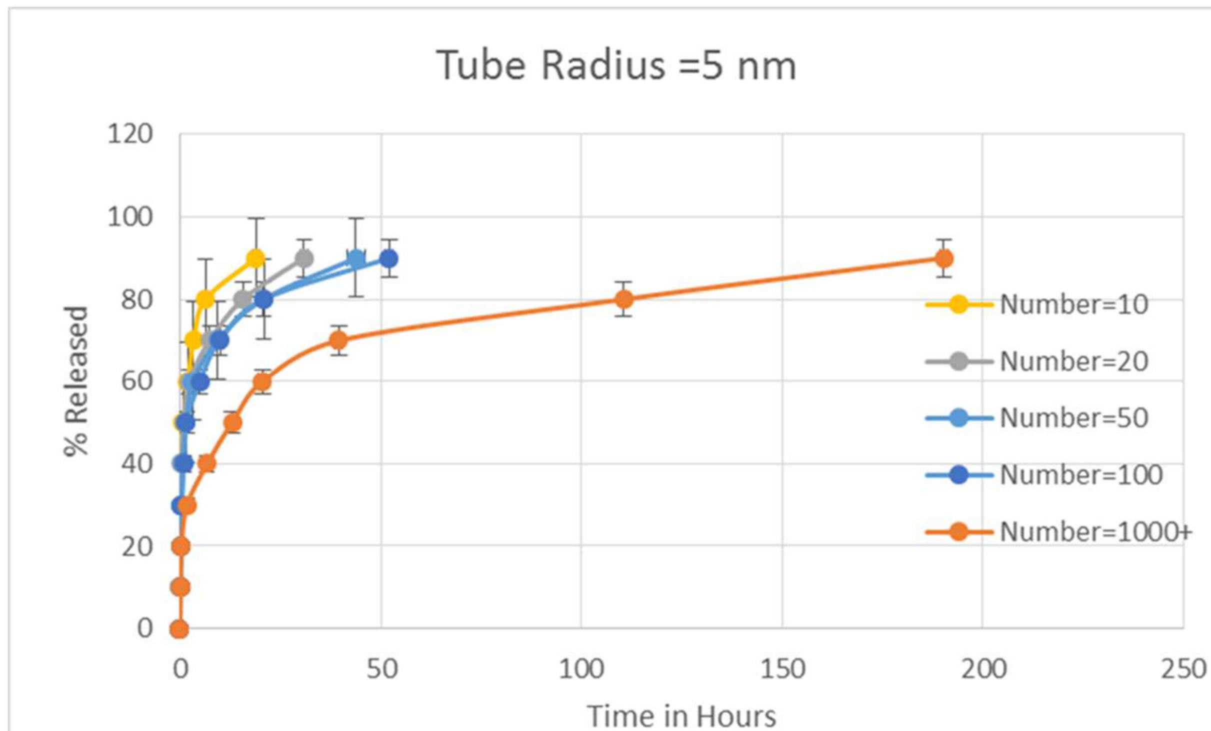
A typical simulation for attractive interaction between particles and the wall.

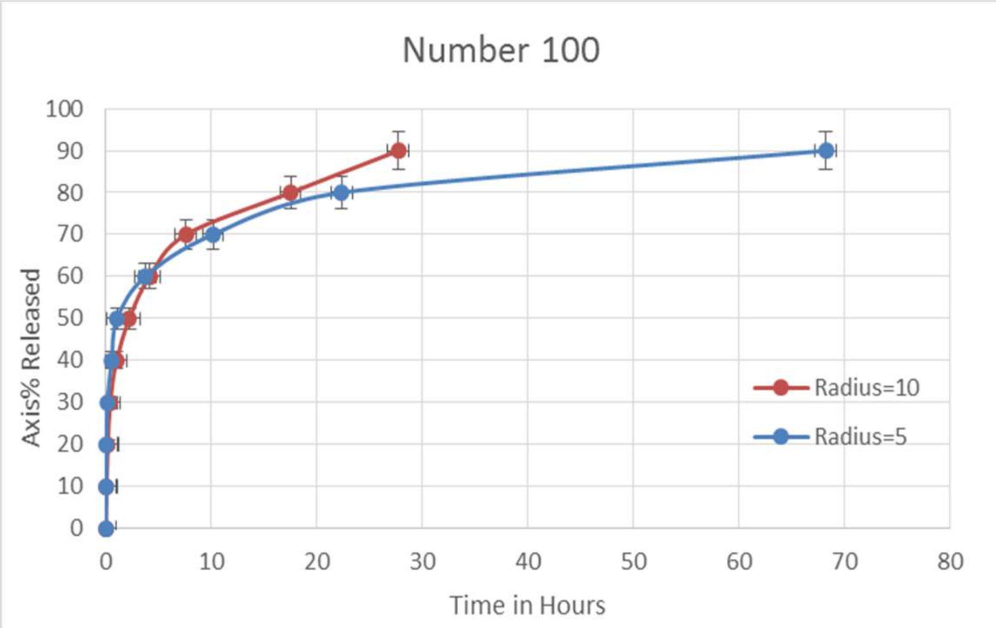


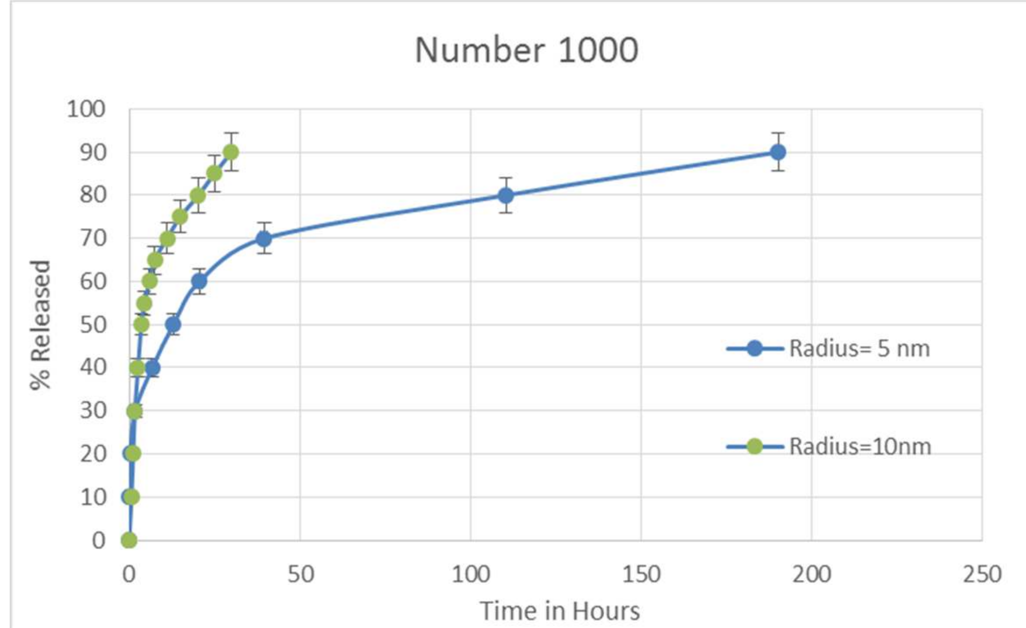
Radius of Nanotube	10 nm
Length of nanotube (nm)	Number of Particles #
23	10
45	20
113	50
225	100
1000	1000+

Release profiles of 10, 20, 50 , 100, 1000+ ~ 1 nm charged particles from Halloysite nanotubes with radii 5nm and 10 nm

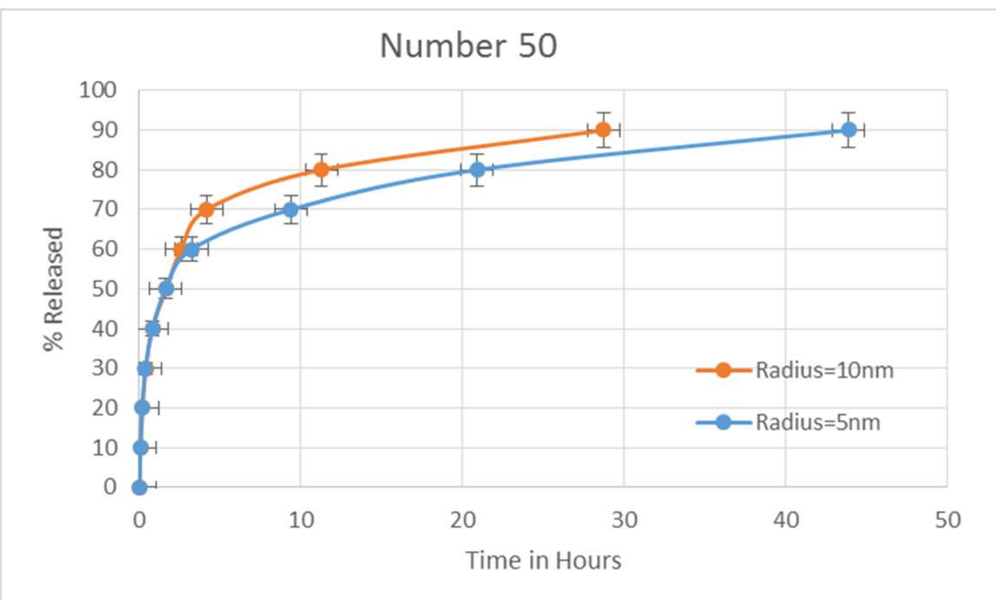
Radius of Nanotube	5 nm
Length of nanotube (nm)	Number of Particles #
90	10
180	20
450	50
900	100
1000	1000+

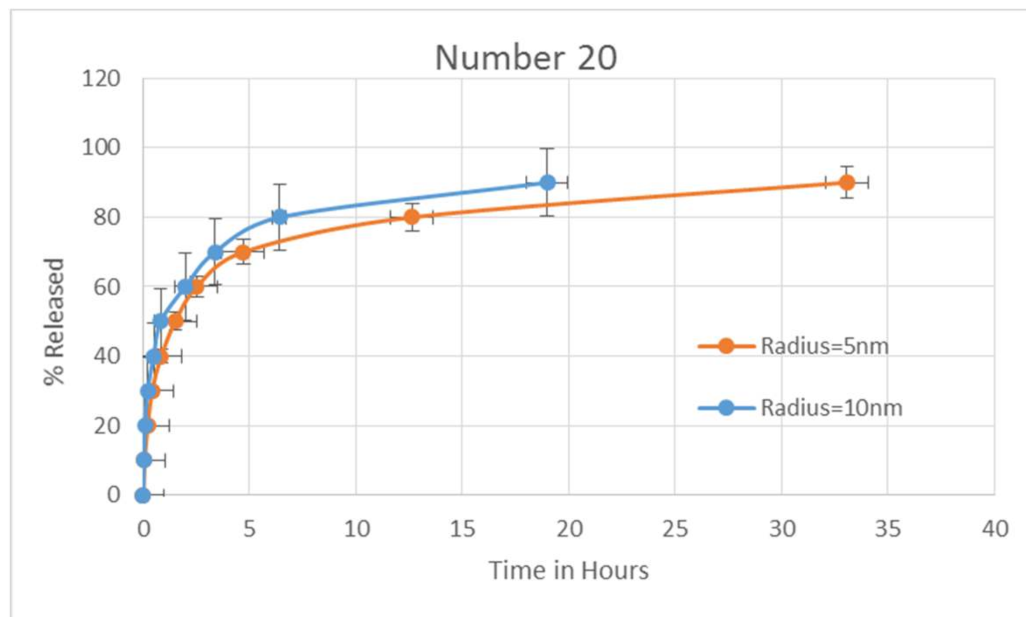






Comparison of the Release profiles for 20, 50 , 100, 1000+ ~ 1 nm charged particles from Halloysite nanotubes of 2 different radii 5 nm and 10 nm





Conclusions

- This is a viable alternative to the computationally intensive Molecular Dynamics approach.
- Diffusion in the cases studied occurs in two distinct phases with an initial burst phase, followed by a longer slower saturation phase.
- In all the cases studies during this project the interaction between the molecules and the nanotube walls was attractive.
- Simulations for nanotubes with radius 10 nm scale better than those for nanotube with radius 5 nm.
- The convergence of the release profiles for(tubes with radius=10nm) is evident specially in the saturation phase.
- The nonconformity can be explained by the significant disparity in the initial burst phase. The initial burst is highly concentration dependent.
- The data we gathered is insufficient and we need more data to better understand how the release profiles scale for nanotubes of different radii.

Papers Read

- [1] T. a Hilder, D. Gordon, and S.-H. Chung, “Computational modeling of transport in synthetic nanotubes.,” *Nanomedicine*, vol. 7, no. 6, pp. 702–9, Dec. 2011.
- [2] M. Abidian, D. Kim, and D. Martin, “Conducting-Polymer Nanotubes for Controlled Drug Release,” *Adv. Mater.*, vol. 18, no. 4, pp. 405–409, 2006.
- [3] D. Rawtani and Y. Agrawal, “Multifarious applications of halloysite nano tubes: a review,” *Rev. Adv. Mater. Sci.*, vol. 30, pp. 282–295, 2012.
- [4] R. Kamble, M. Ghag, S. Gaikawad, and B. Panda, “Halloysite Nanotubes and Applications: A Review.,” *J. Adv. Sci. Res.*, vol. 3, no. 2, pp. 25–29, 2012.
- [5] R. A. Siegel and M. J. Rathbone, “Overview of Controlled Release Mechanisms,” J. Siepmann, R. A. Siegel, and M. J. Rathbone, Eds. Boston, MA: Springer US, 2012, pp. 19–44.
- [6] V. Vergaro, E. Abdullayev, Y. M. Lvov, A. Zeitoun, R. Cingolani, R. Rinaldi, and S. Leporatti, “Cytocompatibility and uptake of halloysite clay nanotubes.,” *Biomacromolecules*, vol. 11, no. 3, pp. 820–6, Mar. 2010.
- [7] “Dexamethasone.” 2011. Material On Physical Chemical and Pharmaceutical properties and uses of Dexamethasone.

Taking My “New” Knowledge Back to the Classroom

“The Big Question”

GLE’s chosen represent those used in my activity and which could be used in an extension activity or related or lab

Grade-Level Expectations:

Grade 6, 7, & 8

1. Science as Inquiry: The Abilities Necessary to Do Scientific Inquiry (Several)

2. Understanding Scientific Inquiry (Several)

Grade 6 & 8 Physical Science

Properties and Changes of Properties in Matter

6. Draw or model the movement of atoms in solid, liquid, and gaseous states (PS-MA4)

7. Simulate how atoms and molecules have kinetic energy exhibited by constant motion(PS-M-A4)

Grades 6 & 8 Transformation of Energy

39. Describe how electricity can be produced from other types of energy (e.g., magnetism, solar, mechanical) (PS-M-C6)

40. Identify heat energy gains and losses during exothermic and endothermic chemical reactions (PS-M-C7)

Grades 6, 7 & 8 Science and the Environment

43. Explain how the use of different energy resources affects the environment and the economy (SE-M-A6)

7th Grade Life Science

Structure and Function in Living Systems

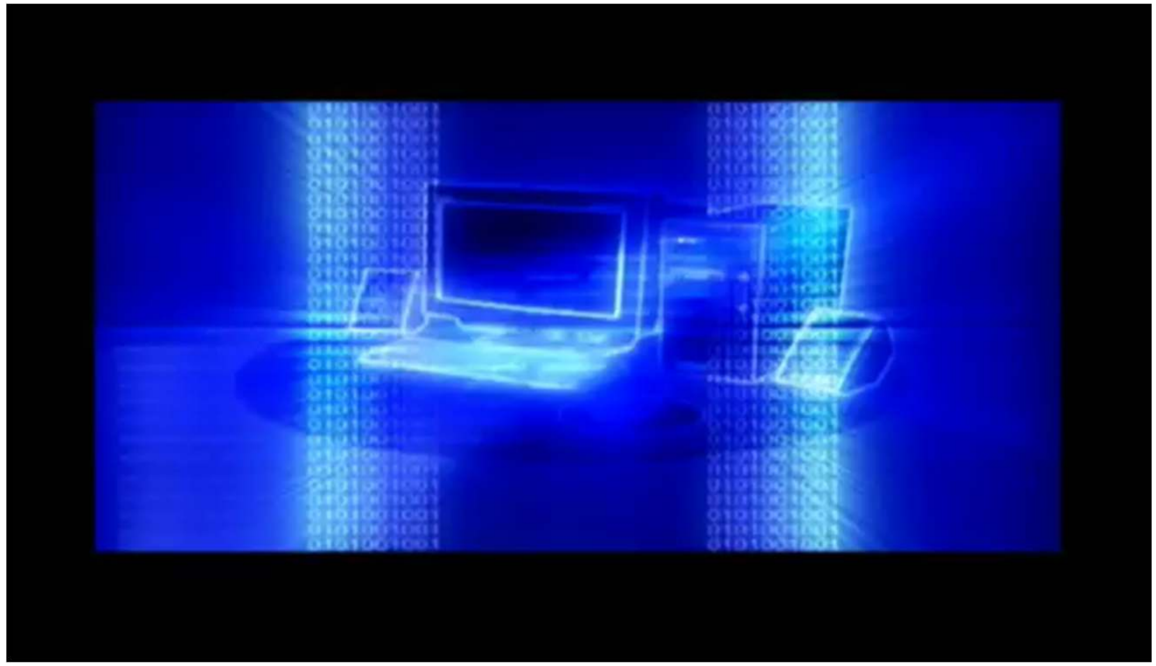
2. Illustrate and demonstrate osmosis and diffusion in cells (LS-M-A1)

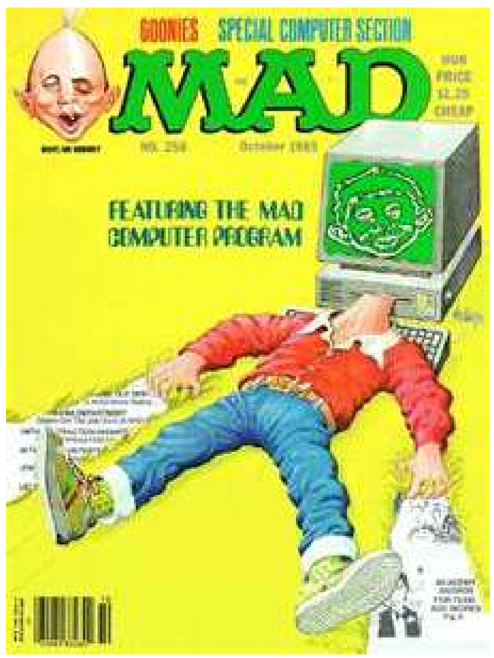
8th Grade Earth & Space Science

The Structure of Earth

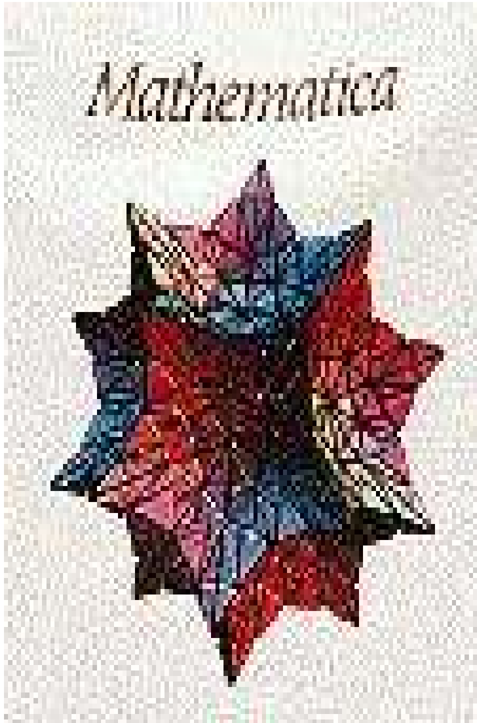
16. Compare the physical characteristics of rock and mineral specimens to observe that a rock is a mixture of minerals (ESS-M-A5) (Clay nanotubes)

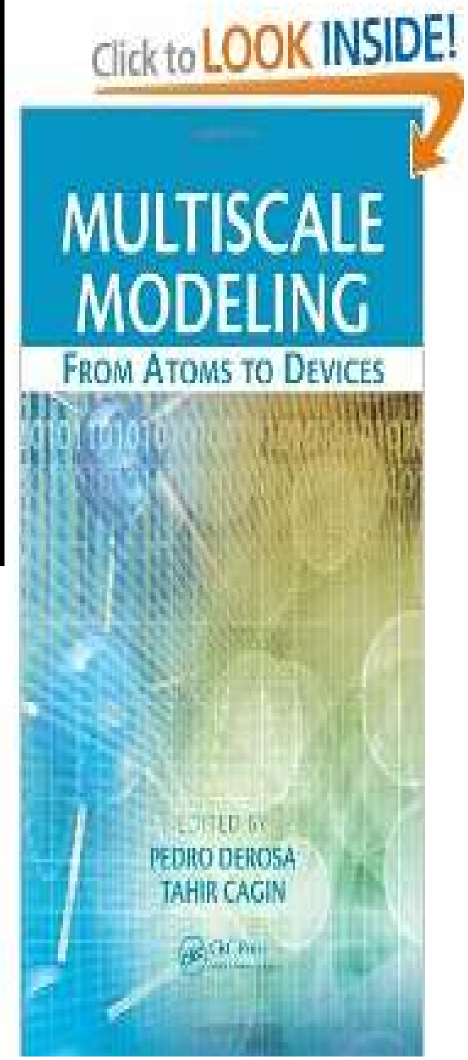
What is Computer Programming?

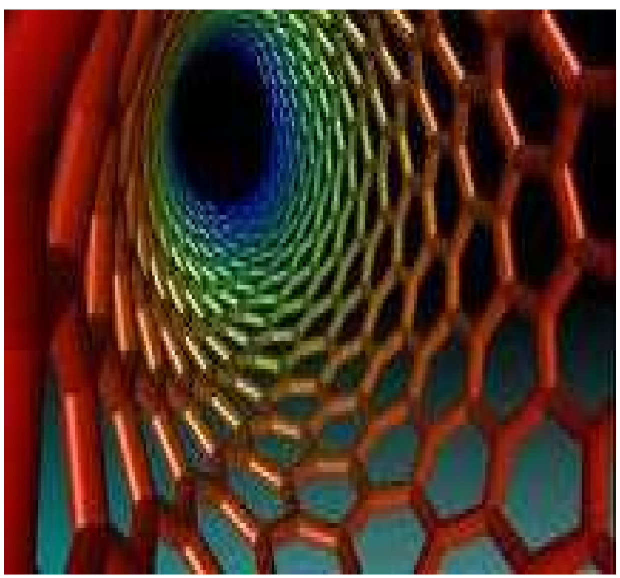


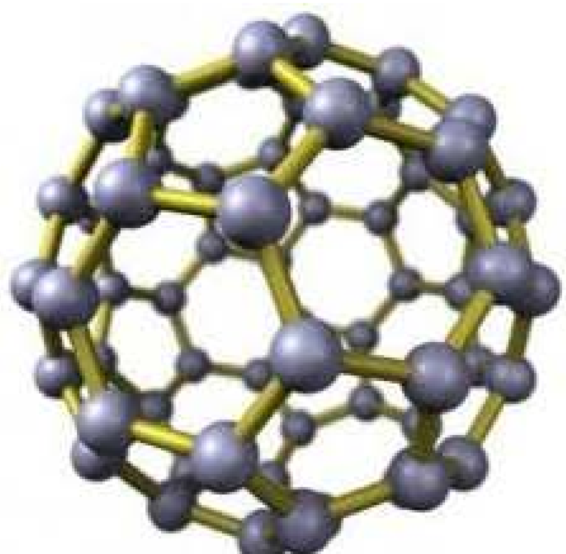


What is Material Science?









TEACH Engineering Resources for K-12

Lesson: Physical Science Grades 6-9

Contributed by: Integrated Teaching and Learning Program, College of Engineering, University of Colorado at Boulder http://www.teachengineering.org/

Next Generation Science Standards: Science [2013]

- Motion and Stability: Forces and Interactions ...more
  (Grades 9 - 12)

Current Standard

- Students who demonstrate understanding can:
  (Grades 9 - 12)

Standard's Subset

Analyze data to support the claim that Newton\'s second law of motion describes the mathematical relationship among the net force on a macroscopic object, its mass, and its acceleration. ...more

(Grades 9 - 12)

Apply scientific and engineering ideas to design, evaluate, and refine a device that minimizes the force on a macroscopic object during a collision. ...more

(Grades 9 - 12)

Explicitly Aligned Communicate scientific and technical information about why the molecular-level structure is important in the functioning of designed materials. ...more

(Grades 9 - 12)

Explicitly Aligned Plan and conduct an investigation to provide evidence that an electric current can produce a magnetic field and that a changing magnetic field can produce an electric current. ...more

(Grades 9 - 12)

Use mathematical representations of Newton\'s Law of Gravitation and Coulomb\'s Law to describe and predict the gravitational and electrostatic forces between objects. ...more

(Grades 9 - 12)

Explicitly Aligned Use mathematical representations to support the claim that the total momentum of a system of objects is conserved when there is no net force on the system. ...more

(Grades 9 – 12)

Explicitly Aligned Standard has one or more explicit curriculum alignments info
CAT Aligned Standard has one or more CAT-based curriculum alignments
SAT Aligned Standard has one or more SAT-based curriculum alignments

Acknowledgements

- DR. PE RO DEROSA
- DIVYA LUMALAI
- DR. AMACHAN RAN
- DR. DANIELA AINAR I
- DR. JIM AUL ING
- DR. WILLIAM DEESE
- LICIA BOR EAUX
- DR. URI VOV
- RA UATE AN N ERGRA UATE STU ENTS IN DR. DEROSA'S A .
- LL THE (TEACHERS), AN (STU ENTS)

LA-SiGMA

Louisiana Alliance for Simulation-Guided Materials Applications