

Learning Materials Science Via the Web Using Nanospheres and Scanning Probe Microscopes

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ABSTRACT

The Interactive Nano-Visualization for Science and Engineering Education (IN-VSEE) project at Arizona State University (ASU) has developed a remotely operable scanning probe microscope (SPM), a visualization gallery of images, and a number of educational modules with materials themes. It exploits the incredible potential of materials science for teaching at the high school and college level about fundamental concepts that cross traditionally separated disciplines. The packing of spheres is a topic that is ideal for linking together the different science and engineering disciplines because of the ubiquity and relevance of spheres in the materials world and the universality of the rules that govern their packing over a large range of sizes. Students can perform a number of discovery-based learning activities, over the web by simultaneously using IN-VSEE's web-accessible module (e.g., The Music of Spheres) and its remotely operable SPM for experimenting with nanosphere samples that they prepare. With these resources students can pose materials questions and are empowered to design their experiments to increase their understanding of real materials. The fundamental concepts (e.g., packing geometry, density, surface composition, long-range/short-range ordering, intermolecular forces, etc.) they learn through these materials science experiments are applicable to many other curricular, research, and technology areas.

INTRODUCTION

The rapidly emerging fields of nanoscience and nano-engineering, critical for the successful development of nanotechnology, will underpin the next industrial revolution. The preparation of a new generation of scientists and engineers for these rapidly growing fields is essential. The following quote captures the urgency required in education and training of a new generation of scientists and engineers:

“Finally, in order for the field of nanostructure science and technology to truly reach fruition, it is an absolute necessity to create a new breed of researchers who can work across traditional disciplines and think ‘outside the box.’ Educating this new breed of researchers, who will either work across disciplines or know how to work with others in the interfaces between disciplines, is vital to the future of nanostructure science and technology. People must start thinking in unconventional ways if we are

to take full advantage of the opportunities in this new and revolutionary field.”

- from the Nanostructure Science & Technology: A Worldwide Study under the guidance of National Science and Technology Council (NTSC), 1999.

The integration of nano-science and technology concepts into the curricula of upper-division high school and lower-division college levels, which are critical transition points in a student's educational career, requires innovative educational approaches that will help students understand the structures and properties of matter on a scale below 100 nanometers (0.1 micrometers), i.e., the nanoscale. Important vehicles for training these students, include the integration of advanced telecommunication technology and analytical instrumentation with materials education, and employment of interactive and discovery-based educational experience [1-3].

Nanospheres provide an ideal gateway for teaching students about fundamental concepts important to the understanding of the nanoworld. They can be used to illustrate the rules used in Self-Assembly, the effect of Van der Waals forces, crystallization and crystalline unit cell, substrate-adsorbate vs adsorbate-adsorbate interactions, crystal defects on “real” surfaces, epitaxy and size calibration of biomaterial structures. Experimental projects using nanospheres are relevant due to the ubiquity of spherical objects and their packing schemes found in natural and synthetic substances, e.g., paints, foundation used in makeup, protein particles, ball bearings.

This paper describes some experimental results from a series of student independent projects that used IN-VSEE web-accessible resources, namely, “The Music of Sphere” educational module, Visualization Gallery, and remote SPM experiments using nanosphere samples to help students understand the behavior of materials at the nanoscale.

The goals of the IN-VSEE approach are to

- Educate students in the principles, execution, interpretation, and rational design of experiments.
- Increased student understanding of structure, composition, and properties of materials across size scales.
- Reinforce fundamental concepts appearing in beginning level college curriculum through the integration of examples from nanoscience and nanotechnology research.

EXPERIMENTAL

Remote SPM microscopy was performed using a Topometrix ExplorerTM instrument. Web-based control of this instrument is facilitated by software interface developed by the IN-VSEE project [4-6] in collaboration with University of North Carolina's Nanomanipulator project (<http://www.cs.unc.edu/Research/nano/>). The remote operator accesses the instrument with an assigned password. Remote observers, on the other hand can freely view and participate in the live experiments.

Polystyrene nanospheres of various sizes, suspended in an aqueous medium were procured from Polyscience, Inc. or Duke Scientific. Suspensions containing single or multiple sized spheres were diluted to appropriate concentrations with deionized water. Described in this

paper are three examples of experiments and their sample preparation protocols that allow students to explore how nanospheres self-assemble to form different packing schemes.

DISCUSSION

Summary of the Music of Sphere module

The “Music of Spheres” module was developed and made web-accessible by the IN-VSEE project. It has been used to supplement one of six core laboratory experiments used in a multidisciplinary SPM laboratory course for undergraduate students, at ASU to help prepare them for the imminent revolution in nano-science, engineering and technology.

This module uses conventional text segment and still images from photographs, electron microscopes, and scanning probe microscopes, and video clips of spheres in the process of packing [courtesy Vega Science Trust (<http://www.vega.org.uk/>)] to convey the technical information. The concepts within the module were further reinforced using measuring, modeling, and calculator activities, developed using Java Applet and JavaScript codes. Students can test their understanding of the material and hypothesize new packing scenarios by learning from these activities. Users can obtain additional related images showing the packing nanospheres from the IN-VSEE Visualization Gallery. Also included are macroscopic examples such as marbles and coins that pack under similar sets of rules. The module also provides several, stand-alone focused lesson plans on fundamental materials science concepts that can be adapted/adopted by a teacher into the classroom. They include:

- Packing rules and patterns of same and different sized spheres in 2-D and 3-D
- Order, symmetry and the crystalline unit cell
- Concept of crystalline unit cells, point defects and dislocations
- The action of intermolecular forces, and underlying concepts of adhesion and self-assembly
- Thermodynamics and kinetics of self-assembling systems
- Application of mathematics concepts and techniques

The module can be accessed through the IN-VSEE website (<http://invsee.asu.edu>) under the heading of “Modules”.

Remote Experimentation

After reviewing the contents of the “Music of Sphere” module users can design experiments to enhance their understanding and test hypotheses about the packing of spheres at the micro- and nanoscale. Institutions that need access to scanning probe microscopes can perform Remote SPM experiments through IN-VSEE’s instrument over the Web through the project’s website under the “SPM Live” heading on navigation bar. Remote operators with assigned passwords can control the area of the sample that the SPM will scan, the scan rate of the SPM probe, two-dimensional (2D) or three-dimensional (3D) display of the sample surface, and operation of the IN-VSEE webcam.

The impact of such remote experiments can be broadened by the participation of many remote observers through the remote observer webpage. Live image broadcasted over the web from the IN-VSEE remote SPM microscope can be shown as a 2D or 3D on the remote Observer page [4,5]. The area of the sample that is being explored by the SPM scope is also displayed. A webcam allows the users to see the microscope. Users can communicate with each other during a remote session via the text-based chat. Other resources such as the Visualization Gallery,

educational modules, etc. are also accessible through this page. Users can also take snapshots of the remote session's images and store them on their local computers

Ideas for Student Exploration

The packing of polystyrene nanospheres can serve as analogies to the self-assembly of atoms and molecules of materials, spherical proteins, etc. Experiments like those described in this paper can be easily modified to test a student's hypotheses about material systems and yield astonishing packing arrangements that can be imaged with an SPM. They can also stimulate discovery-based learning about materials science and mathematics.

Exp #1-Objective: In this experiment, students are encouraged to (1) describe the patterns they observe in terms of common geometric systems, e.g., triangular or hexagonal patterns, and relate these to idealized packing arrangements used to describe crystals, e.g., cubic, hexagonal arrangements. (2) look for periodicity and symmetries to construct crystal unit cells, as well as observe domains, point defects such as vacancies, line defects like dislocations, and determine packing density of spheres. The protocol for this experiment is- deposit polystyrene micro- and nanospheres of uniform size on freshly peeled mica by spreading a suspension of appropriate concentration and allow the sample to dry. The image in Figure 1 was obtained when a student prepared a sample in accordance to the above protocol. The image shows the self-assembly of 269 nm nanospheres. Note that domains of hexagonally closed packed spheres form. This surface is similar to arrangement of metal atoms along the $\langle 111 \rangle$ direction of many face-centered cubic metals. The domains are separated by line defects that can be analogous to grain boundaries or dislocations. Vacancies are also observed. The top layer appears to be more defective probably due to imperfect registry between it and the bottom layer. The upper portion of this image also shows the formation of an island. This experiment illustrates some of the mechanisms that control the formation of thin-films that are important to the coating and semiconductor industry.

Exp #2-Objective: In this experiment, students are encouraged to explore the effects of thermodynamic and kinetic parameters on the ordering of spheres. The students may also investigate how non-equilibrium conditions may affect packing configurations, especially at the lower temperatures and faster rates of evaporation.

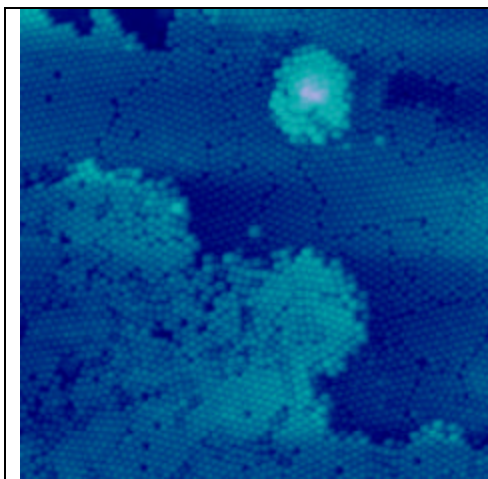


Figure 1. 16 μm x 16 μm image of packing spheres from experiment 1.

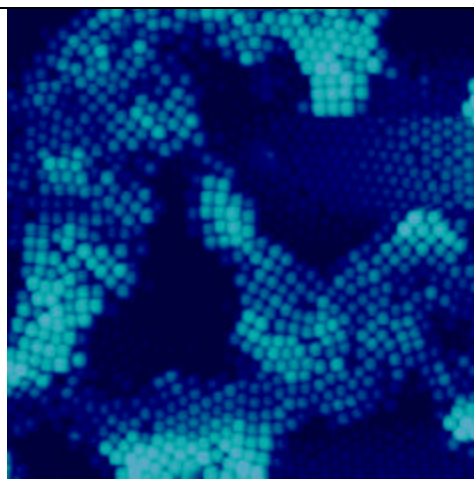


Figure 2. 10 μm x 10 μm image of packing spheres from experiment 2.

This system can simulate the packing of atoms and molecules in an annealed versus a quenched material. The relative stability of various packing configurations can be estimated by counting their population and using thermodynamic quantities. The protocol for this experiment is – deposit nanospheres on freshly peeled mica by spreading a suspension of appropriate concentration and allow the sample to dry at different temperatures and/or at different humidities. The image in Figure 2 was obtained when a student prepared a sample in accordance to the protocol of experiment #2 with 269 nm nanospheres. In addition to the features observed from experiment #1, the rapid drying (quenching) resulted in the formation of the metastable square packing arrangement that have a lower packing density than those in the hexagonal packing (hcp) scheme. The relative stabilities of the spheres in hcp packing, spheres in square packing, vacancies, and line defects can be estimated by counting their population per unit area. Students can get a visual appreciation of thermodynamics in relation to relative stability of a configuration and population of a configuration from this experiment.

Exp #3-Objective: In this experiment, students are encouraged to explore how relative differences in diameter between two spheres affect their coordination shells. The students can explore how certain relative sphere ratios (e.g., critical radius ratios) affect the ordering of the compare the packing structures obtained with those predicted by mathematical models developed. Students can also observe that clusters of spheres with certain coordination numbers cannot have long-range ordering over a surface. The protocol for this experiment is- deposit nanospheres of two different sizes both co-deposited from a suspension of a mixture or sequential depositions of pure size spheres onto freshly peeled mica and allow to dry. The image in Figure 3 was obtained when nanospheres of two different sizes (200 nm and 100 nm) were co-deposited. Packing models based on rigid spheres, as described in the module, predicted that spheres with diameters of 2:1 pack together to form square patterns with the smaller sphere in the center surrounded by 4 larger spheres and spheres of identical size pack together to form hexagons where a central sphere has six closest neighbors. A number of both these arrangements can be found throughout the image. Even though the spheres are slightly deformable they seem to follow the rigid sphere prediction. This can be analogous to the formation of molecules from atoms, formation of solvation complexes between a solute species with solvent molecules, or the alloying of metals. The image in Figure 4 was obtained when nanospheres of two different sizes (200 nm and 100 nm) were deposited sequentially, with the larger spheres on the bottom and the smaller on top.

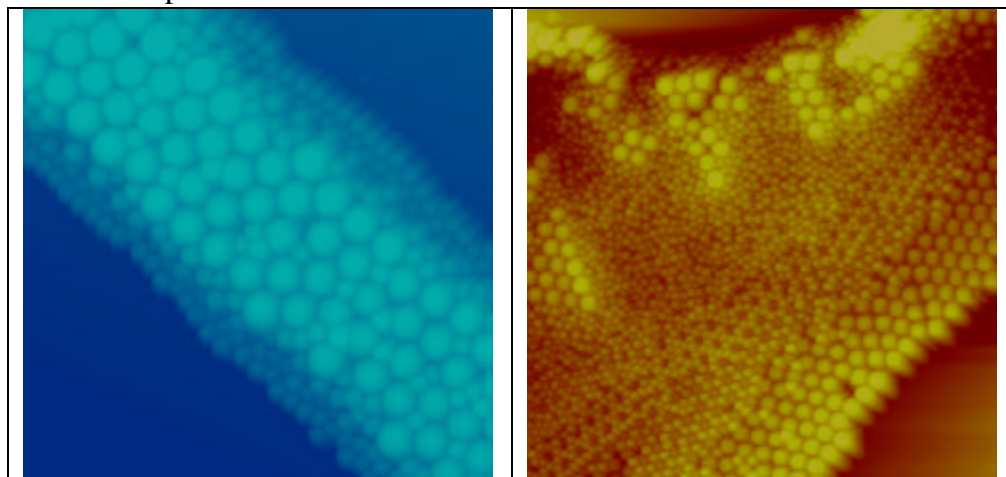


Figure 3. 8 μm x 8 μm image of packed spheres from experiment 3.

Figure 4. 16 μm x 16 μm image of packed spheres from experiment 3.

Note the fading in and out of two different semi-ordered mixed “phase” followed by disorder. This “phase” cannot extend indefinitely because some the groups have a 7-fold rotation axis. This situation can be analogous to the adsorption of molecules and atoms onto crystalline surfaces where registry to the surface is controlled by adsorbate-adsorbate forces competing with adsorbate-substrate forces and surface topography.

Samples from these experiments and also from extensions of these studies can be investigated by other techniques such as Optical Microscopy, Scanning Electron Microscopy, and Near-Field Optical Microscopy. The resulting images can be posted onto the IN-VSEE website and compared with the SPM images, allowing the student to get a more comprehensive picture of their samples.

CONCLUSIONS

This “Music of Spheres” module explores why spheres, that are so ubiquitous in nature, spanning vast range of size scales and diverse physical systems, pack together in definite geometric patterns to form interesting structures. The principles learned in this module and reinforced by remote SPM exploration apply broadly across diverse material systems. These can range from fundamental unit cell structures, such as crystals, to everyday, real-world examples such as the film formation by latex-based paints, the micro-texture of cosmetics, assembly of biological structure, to the optimum packing of fruits at the grocery store.

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