Fişa suspiciunii de plagiat / Sheet of plagiarism's suspicion	Indexat la: 58/06

Opera suspicionată (OS)	Opera autentică (OA)
Suspicious work	Authentic work

OS	Dragoi, D.D., Besleaga, C., The generals consideration about the ferrofluids and their abilitty in nanotehnology, In: Modelling and Optimization in the Machines Building Field (MOCM) 14, Vol.2, 2008 pp.75-78.
OA	McHale, M., Nanotechnology: ferrofluids and liquid crystals, 2008, Disponibil la: http :// cnx . org / content / m15532 / 1 . 1 / .

Incidența minimă a suspiciunii / Minimum incidence of suspicion	
p.75:5 – p.75:10; p.75:13 – p.75:16	p.01:17 – p.01:20
p.75:19 – p.75:32	p.01:23 – p.02: 04
p.76:Figure 1	p.02:Figure 1
p.76:01 – p.76:06	p.02:05 – p.02:10
p.77:02 – p.77:14	p.03:01 – p.03:13
Fişa întocmită pentru includerea suspiciunii în Indexul Operelor Plagiate în România de la www.plagiate.ro	

Nanotechnology: Ferrofluids and Liquid Crystals

Version 1.10: Nov 6, 2008 4:55 pm US/Central

Mary McHale

1 Nanotechnology: Ferrofluids and Liquid Crystals

1.1 Objective

- To synthesize an aqueous ferrofluid (magnetite) and observe its properties.
- To understand how nanotechnology affects everyday life.
- To learn about surfactants and how they work.

1.2 Grading

- Pre-Lab (10%)
- Lab Report Form (80%)
- TA Points (10%)

1.3 Background Information

Nanotechnology is the science of controlling matter with dimensions between 1 and 100 nanometers. This includes manipulating individual molecules. It is a multidisciplinary field consisting of physics, biology, chemistry, medicine, engineering, and nearly any other applied science. The prefix nano- means ten to the minus ninth power, or one billionth. There have been great advances in nanotechnology in recent years, and scientists routinely make materials that are only a few nanometers in size, or about 1/80,000 the diameter of a human hair. See Figure 1 to notice how small a nanometer is compared to other common materials.

Materials at the nanoscale exhibit interesting optical, electronic, physical, and chemical properties due to their small size. For example, catalysis chemical reactions occur at the surface of bulk material so as particles become smaller, the ratio of the surface area to the volume of the particles increases, thereby making a volume of nanoparticle catalysts more reactive than an equal volume of bulk catalyst. Optical properties of bulk materials are not size dependant, that is no matter what the size of a piece of bulk material it will have the same optical properties. This is not the case for nanomaterials. As you will see in the instructor demo, different sizes of gold nanoparticles exhibit very different colors.

In the 1960s NASA Research Centers discovered fluids that could be controlled through the application of a magnetic field. These fluids were developed to confine liquids in space. These nanoparticle fluids are commonly known as ferrofluids and they are still an active area of research.

Ferrofluids have many current industrial applications. They are used to dampen vibration in audio loudspeakers, they can behave as liquid O-rings in rotating shaft seals, and they are used in high-speed computer disk drives to eliminate impurities. They also have many potential applications in biomedical, environmental, and engineering fields.

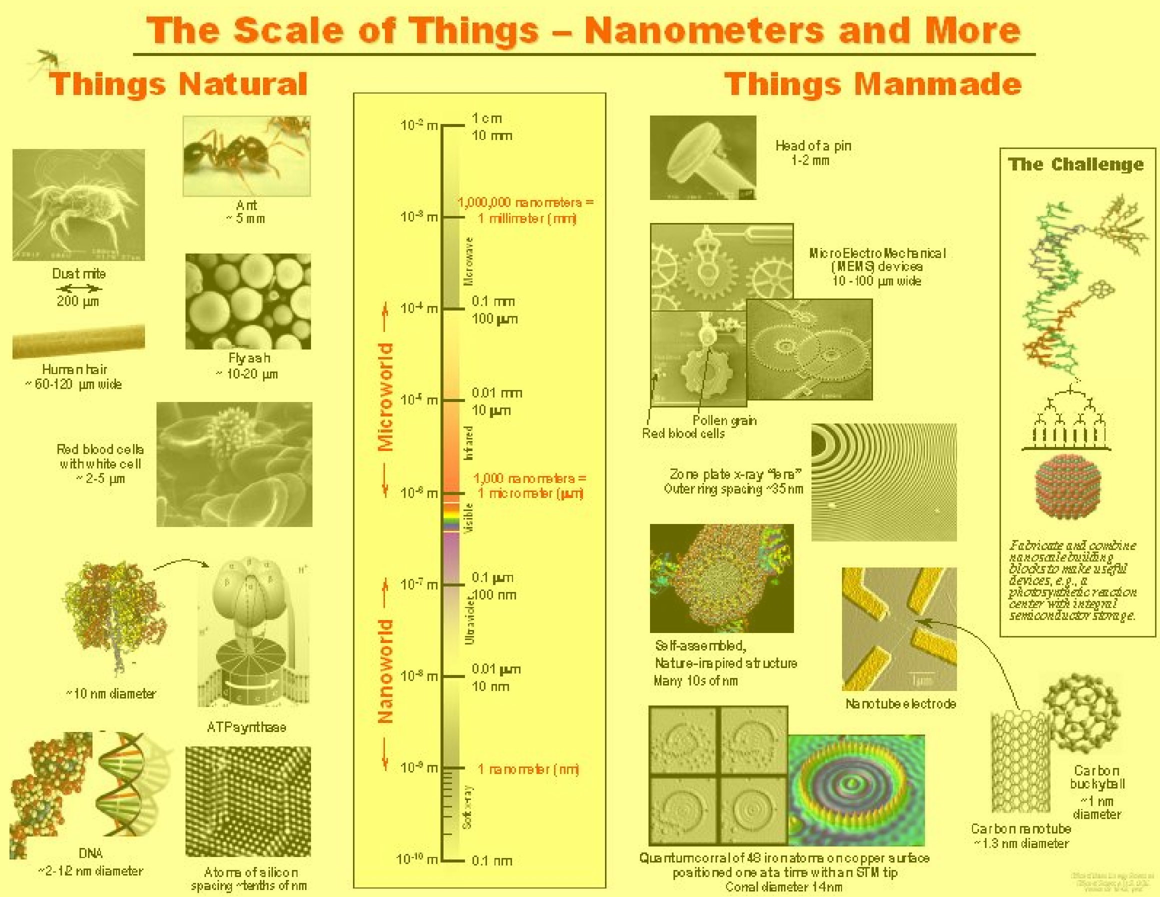

Figure 1

Figure 1-Obtained from Office of Basic Energy Sciences, US Department of Energy

A ferrofluid is a stable colloid suspension of magnetic nanoparticles in a liquid carrier. The nanoparticles are suspended throughout the liquid and have an average size of ~10 nm. It is critical that the nanoparticles are coated with surfactant to prevent the particles from aggregating together. The surfactants must be strong enough to prevent agglomeration even when a magnetic field is applied and they must overcome the intermolecular forces between the nanoparticles. For this reason, a typical ferrofluid contains 5% magnetic nanoparticles, 10% surfactant, and 85% carrier fluid by volume.

Image not finished

Figure 2

There are two basic steps in creating a ferrofluid: synthesis of the magnetic solid, magnetite (Fe_3O_4), and suspension in water with the aid of a surfactant. The magnetic particles must be very small on the order of 10 nm (100 Å) in diameter, so that the thermal energy of the particles is large enough to overcome the magnetic interactions between particles. If the particles are too large, magnetic interactions will dominate and the particles will agglomerate. The magnetite will be synthesized by a precipitation reaction that occurs upon mixing $FeCl_2$ and $FeCl_3$ with ammonium hydroxide (an aqueous solution of ammonia, NH_3). The unbalanced equation for this reaction is as follows:

$$\_\_FeCl_3 + \_\_FeCl_2 + \_\_NH_3 + \_\_H_2O \rightarrow \_\_Fe_3O_4 + \_\_NH_4Cl \quad (1)$$

The surfactant used in this synthesis is tetramethylammonium hydroxide ($N(CH_3)_4OH$). The hydroxide (OH^-) ions formed in solution tend to bind to the iron sites on the magnetite particles, creating a net negative charge on each particle. The positively-charged tetramethylammonium ions will then associate with the negatively-charged magnetite particles, forming a kind of shell around each magnetite particle. This charged shell raises the energy required for the particles to agglomerate, stabilizing the suspension.

Changing the subject to liquid crystals: with the help of nanotechnology, liquid crystal displays have become very popular in recent years. Liquid crystal displays (LCD) were first produced by RCA in 1971 and are composed of two glass plates with a liquid crystal material between them. The liquid crystal material is an organic compound that is in a state between a liquid and a solid. Their viscosities are similar to those of liquids and their light scattering and reflection properties are similar to solid crystals. Liquid crystals must be geometrically highly

anisotropic (having different optical properties in different directions)-usually long and narrow -but also become an isotropic liquid (same optical properties in all directions) through a stimulus such as a magnetic field, electric field, temperature, or pressure.

Liquid crystals have several common phases. The simplest liquid crystal phase is called the nematic phase where the molecules spontaneously order with long axes roughly parallel. It is characterized by a high degree of long range orientational order but no translational order. An uniformly aligned nematic has a preferred direction, often described in terms of a unit vector called the director. The type of phase that a liquid crystal possesses ultimately determines its applications.

A subclass of nematic phases that will be investigated in this lab due to its pressure and temperature sensitive properties is the cholestric phase. The distance over which the director rotates to equal $360°$ is referred to as the chiral pitch and is normally on the order of a few hundred nanometers, or precisely the wavelength of visible light. This allows liquid crystals to selectively reflect light of wavelengths equal to the pitch length, so that a color will be reflected when the pitch is equal to the corresponding wavelength of light in the visible spectrum. Changes in the director orientation between successive layers modifies the pitch length resulting in an alteration of the wavelength of reflected light according to the temperature. The angle at which the director changes can be made larger, and thus tighten the pitch, by increasing the temperature of the molecules, hence giving them more thermal energy. Similarly, decreasing the temperature of the molecules increases the pitch length of the chiral nematic liquid crystal. This makes it possible to build a liquid crystal thermometer that displays the temperature of its environment by the reflected color.

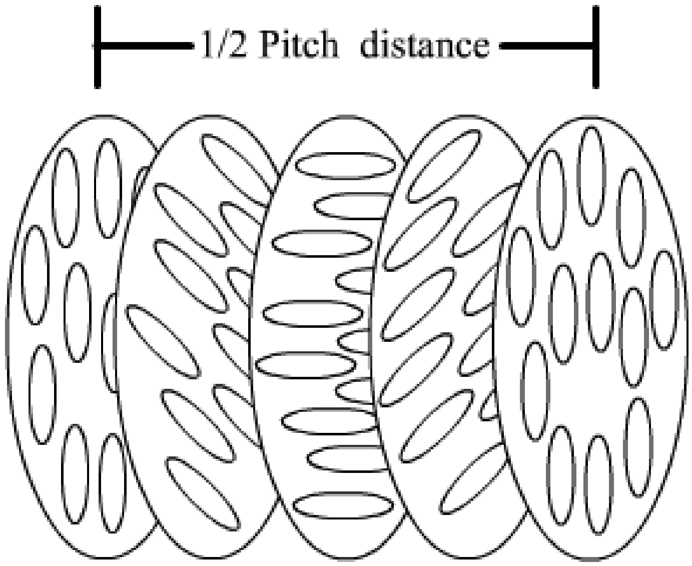

Figure 3

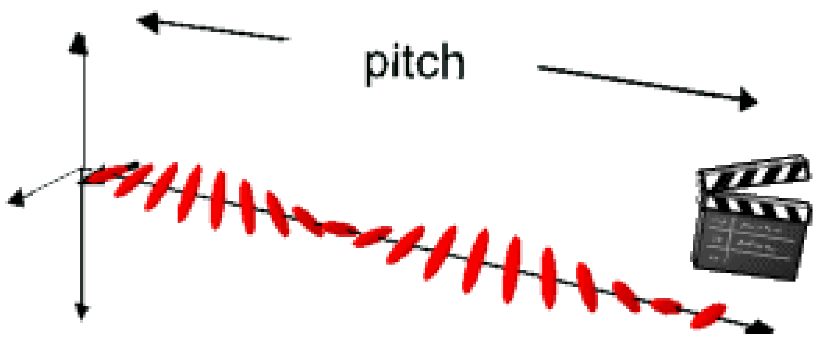

Figure 4

1.4 Experimental Synthesis

1.4.1 Part I. Synthesis of Gold Nanoparticles (DEMO)

Chemicals
1.0 mM $HAuCl_4$ (stored in amber bottle)

- 1% trisodium citrate dihydrate solution

1.4.2 Nanoparticle Synthesis

- Add 20 mL of 1.0 mM $HAuCl_4$ to a 50 mL Erlenmeyer flask on a stirring hot plate. Add a magnetic stir bar and bring the solution to a boil.
- Add 2 mL of 1% trisodium citrate dihydrate solution and observe the properties.

1.4.3 Part II. Synthesis of the Aqueous Ferrofluid (Procedure modified from J. Chem. Edu. 1999, 76, 943-948.)

2 Chemicals

1 M $FeCl_3$ in 2 M HCl Solution:
2 M $FeCl_2$ in 2 M HCl Solution

- 25% tetramethylammonium hydroxide in water

1.0 M NH_3 Solution: Dilute at least 200 mL of concentrated ammonium hydroxide with water to 3.0 L). Open containers of ammonia are odorous and their concentration will decrease over periods of time.

CAUTION: Ferrofluids can be messy. This particular ferrofluid will permanently stain almost all fabrics. Also DO NOT LET THE MAGNETITES TOUCH THE SURFACE OF THE MAGNET DIRECTLY.

2.1 Magnetite Synthesis

- In a hood, place 4.0 mL of 1M $FeCl_3$ and 1.0 mL of 2M $FeCl_2$ solution into a 100 mL beaker. Stir on a magnetic stir plate.
- While stirring, slowly add 50 mL of 1.0 M aqueous NH_3 solution over a 5 minute period using a buret. Initially a brown precipitate will form followed by a black precipitate, which is magnetite.
- CAUTION: Even though 1M NH_3 is fairly dilute, NH_3 is a strong base.
- Remove from stirring and immediately use a strong magnet to work the stir bar up the walls of the beaker. Remove the stir bar with a gloved hand being careful not to let it touch the magnet.
- Allow the magnetite to settle, then decant off the clear liquid into a waste beaker without losing a large amount of precipitate. The settling process can be expedited by placing a strong magnet below the beaker.
- Transfer the solid to a plastic weighing boat. Rinse out the beaker with a wash bottle.
- Use a strong magnet to attract the ferrofluid to the bottom of the weigh boat. Carefully decant as much clear liquid as possible into the waste beaker. Rinse again with water from the wash bottle and decant. Repeat the rinsing process a third time. What are you removing by rinsing?
- Add 1-2 mL of 25% tetramethylammonium hydroxide. Gently stir the solution with a glass stir rod for at least a minute to suspend the solid in the liquid. Use a strong magnet to attract the ferrofluid to the bottom of the weigh boat. Pour off and discard the dark liquid. Move the strong magnet around and again pour off any liquid. If the ferrofluid does not produce spikes, continue to move the strong magnet around, pouring off any liquid.

2.2 Ferrrofluid Properties

1. Hold a magnet underneath the weigh boat that contains the ferrofluid. Move the magnet around the underside of the weigh boat. Move the magnet close to and far from the weigh boat. Record your observations
2. Add a couple of drops of ferrofluid to a small piece of clean paper. Let the solution dry. Once it is dry, bring a strong magnet close to the paper. What happens?
3. Use several different magnets to observe the properties of the ferrofluid and record your observations in your notebook.

2.3 Part III. Synthesis of Cholesteryl Ester Liquid Crystals

2.4 Chemicals

- Cholesteryl oleyl carbonate
- Cholesteryl pelargonate

- Cholesteryl benzoate
- Vials
- Heat gun

2.5 Liquid Crystal Synthesis

1. Place 0.65 g cholesteryl oleyl carbonate, 0.25 g cholesteryl pelargonate, and 0.10 g cholesteryl benzoate in a vial.
2. In a hood, with the cap off, melt the solid in with a heat gun.
3. While the mixture is still a liquid, divide it into separate vials using a disposable pipette. Put the caps back on the vials. Allow the vials to cool and observe their properties.
4. Clean up your bench area.
5. Listed below is a chart of the different ratios that produce liquid crystals with different transition temperatures. Placing liquid crystals with different transition temperatures next to each other on a clear piece of contact paper makes it possible to make a thermometer.

Cholesteryl oleyl carbonate (g)	Cholesteryl pelargonate (g)	Cholesteryl benzoate (g)	Transition range, degrees C
0.65	0.25	0.10	17-23
0.70	0.10	0.20	20-25
0.45	0.45	0.10	26.5-30.5
0.43	0.47	0.10	29-32
0.44	0.46	0.10	30-33
0.42	0.48	0.10	31-34
0.40	0.50	0.10	32-35
0.38	0.52	0.10	33-36
0.36	0.54	0.10	34-37
0.34	0.56	0.10	35-38
0.32	0.58	0.10	36-39

continued on next page

0.30	0.60	0.10	37-40