

Chapter 1

INTRODUCTION

The focus of this text is interfaces and colloids, and it makes the argument that this is the “bridge to nanoscience.” It often appears that finite systems, even at equilibrium, cannot be described neatly in terms the usual set of intensive and extensive variables, *i.e.*, size matters. The most basic reason for this is that all tangible material systems have boundaries, or “interfaces,” that have properties of their own. Physical, as opposed to mathematical, interfaces are nano-scale strata of material whose structure is profoundly different from that of “bulk phase material,” and as the objects of interest are made smaller and smaller, more and more of their total mass is part of “the interface,” with major consequences for their properties. Also, as the “kinetic units” are made smaller, their thermal energy assignments begin to exert influence, and ultimately one must acknowledge the corpuscular nature of matter: molecules, atoms, sub-atomic particles, etc. How do these regions blend into one another? It is the “in-between” region that is of concern in this text, and it too finds itself divided into parts. In the first, continuum concepts are retained, but a range of “new” properties and phenomena emerge, such as the influence of droplet size on vapor pressure, spontaneous clumping together of particles, Brownian motion, etc. This is the traditional domain of “colloid science,” and extrapolations from it into the nano region (down to as small as 1-10 nm) often provide valid descriptions of properties and behavior. Such extrapolations, dealt with in this text, constitute “generic nanoscience.” But one may also encounter other behavior, if continuum descriptions start to break down. Most notable are the properties attributable to quantum confinement, and it is sometimes to these kinds of systems that the term “nanoscience” is restricted. Despite their more exotic attributes, however, the objects in question are still subject to most, if not all, of the rulebook of generic nanoscience, the bridge to which is knowledge of interfaces and colloids. The following brief overview seeks to set the stage.

A. Interfaces

“Interfaces” (or “surfaces”) are the thin boundary regions separating macroscopic chunks of matter from their surroundings or from one another. “Interface” is the more general term for any phase boundary, while the word “surface” generally refers to the boundary between a condensed phase and a gas. Use of the term “interface” for all situations would be desirable because it reminds us that the properties of all boundaries depend on *both* phases.

The “surface” of a silica micro-particle in contact with air, for example, is different from its “surface” in contact with water, or in contact with an apolar solvent or *in vacuo*. While interfaces appear abrupt to the naked eye, they all have in fact a finite thickness, typically ranging from a few Ångströms to a few nanometers, as suggested in Fig. 1-1. The material in

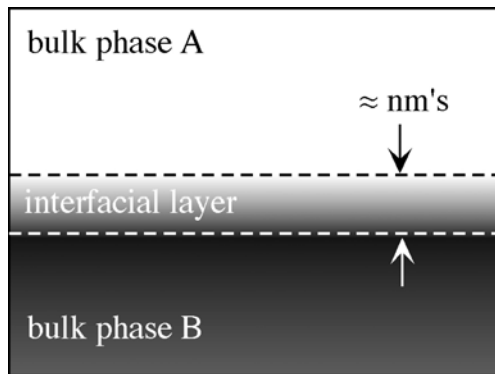


Fig. 1-1: Schematic of material interface, showing zone of inhomogeneity and adjacent bulk phases.

these thin regions is first of all inhomogeneous, and its properties differ profoundly from those of material in a bulk phase state. No system is free of the influence of its interface(s), and in many applications or situations, it is essential that one know not just the bulk properties, but the *interfacial properties* as well. For example:

- *Surface tension* determines the shape of small fluid masses or menisci.
- *Surfaces* of adjacent systems determine whether they stick to, slide over, or repel one another.
- It is often only the interaction of light with the *surfaces* of systems that we see.
- It is the dependence of *surface tension* on system composition that makes possible the formation of such unlikely liquid structures as foams or froths.
- It is often the accumulation of trace components at *surfaces*, i.e., “adsorption,” that governs the chemistry of their interaction with adjacent phases.

Consider some of the most fundamental ways in which material in interfaces differs from bulk materials. First, the state of *internal mechanical stress* in the interfacial stratum is different from that in the bulk phases. In the case of fluid interfaces, this difference is manifest as a measurable contractile tendency, *viz.*, the surface or interfacial tension. A fluid interface acts as an elastic membrane seeking a configuration of minimum area. The origin of the boundary tension can be stated in terms of local internal mechanical stresses as follows. In the interior of unstrained bulk fluid at rest, the stress at any point is given by a single scalar quantity, *viz.*, the pressure p . But in the fluid interfacial layer under the same conditions, the state of stress requires a tensor for its specification; the components pertaining to

stresses parallel to the layer are equal to one another but *less* than the component normal to the layer. It is this tangential pressure deficit in the interfacial layer that leads to boundary tension. The study of fluid interfaces is referred to as *capillarity*. Solid–fluid and solid-solid interfaces are also generally in a state of tension, although it is not readily measurable. These boundary strata have more complicated stress fields than fluid interfaces, and often are not in states of internal equilibrium. Thus they depend not just on the thermodynamic state but also on how the interface was formed, whether from the fracture of a bulk phase, from the stretching of a pre-existing surface, from precipitation out of solution, or from some other process.

The *chemical composition* of the interfacial stratum is also different from that of the bulk phases it separates. Consider, for example, the apparent interface between a piece of metal, such as iron or aluminum, and air, as shown in Fig. 1-2. Unless it is a noble metal, it will be covered with an oxide layer, which is at least partially hydroxylated from contact with water vapor in the air. The -OH groups have an acid or a base character depending on the metal. On top of this will probably be a layer of tightly bound water and possibly an additional layer of loosely bound water, depending on the relative humidity. The very top layer is likely to be an adsorbed scum of grease or other organic contaminant. The ability of interfaces of all kinds to contain components that may or may not be present in the bulk phases at the instant of interest makes their composition more complex than might be expected.

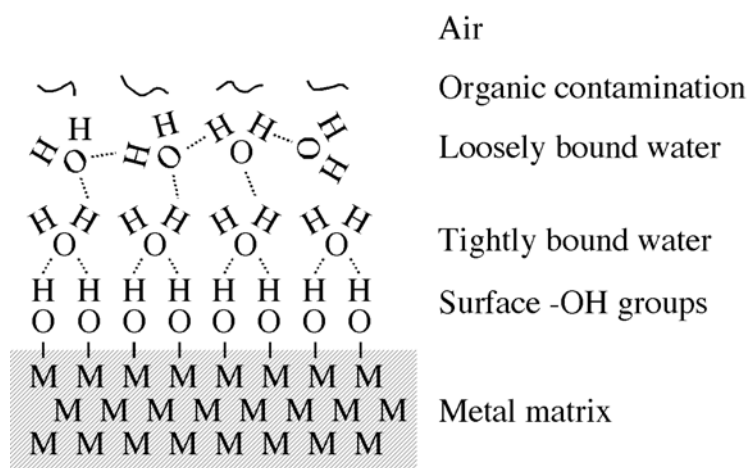


Fig. 1-2: Schematic representation of the typical chemistry at a nominal metal-air interface.

The interfacial stratum also often exhibits *electrical charge separation*. Interfaces dividing electrically neutral bulk phases may appear to bear a charge when viewed from one side or the other because positive and negative charges separate in the direction normal to the interface, leading to the formation of an “electrical double layer.” There are a number of mechanisms by which the charge separation arises, and its existence has many consequences. Particles dispersed in water, for example as shown in

Fig. 1-3, may repel one another upon close approach, due to overlap of the like-charged outer portions of the double layers at their surfaces, keeping the particles from clumping together, and when placed in an external electric field, migrate by the process of electrophoresis. Fluid interfaces with electrical charge separation in an external electric field may become unstable to wavy disturbances, such that they are distorted or even torn apart in the processes of electro-spraying or electro-emulsification.

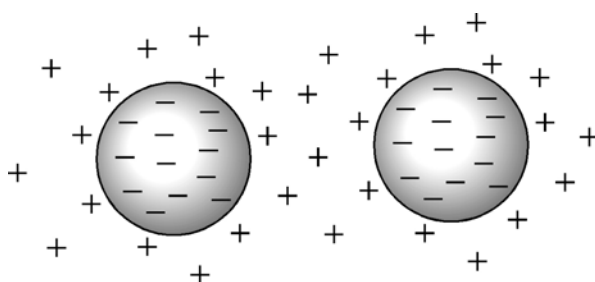


Fig. 1-3: Electrical charge separation at the interfaces of particles against their dispersion medium, water.

The unique mechanical, chemical and electrical properties of interfaces exert great and highly varied effects upon the behavior of material systems that cannot be described or explained in terms of bulk phase behavior alone. Interfacial effects reserve their greatest impact for systems with large area-to-volume ratios, such as thin films, fine fibers and small particles, or pushed to the limit: “nanofilms,” “nanowires” or “nanorods” and “nanoparticles.”

B. Colloids

“Colloids” refer to dispersions of small particles, usually with linear dimensions from 1 nanometer to 10 micrometers, thus spanning the “nano” to “micro” size range. The “particles” may be either dissolved macromolecules or macromolecular structures formed from smaller structural units, or they may constitute a separate phase, as in aerosols, powders, pigment dispersions, emulsions, micro-foams and finely pigmented plastics. The description of multiphase colloids, such as those just named, must take account of the properties of both phases as well as the interface between them, so that their investigation is a natural adjunct to the study of interfaces. Reaching down to the size of colloid particles, there are six overarching aspects that distinguish their behavior from that of their larger counterparts:

- **Mobility due to thermal kinetic energy**
- **Absence of inertial effects**
- **Negligibility of gravitational effects**
- **Inter-system molecular interactions: adhesion**
- **Size effects on thermodynamic properties, and**
- **Interaction with electromagnetic radiation**

Simple kinetic theory assigns to all objects (“kinetic units”), whether they be molecules, bowling balls or planets, a fixed amount of translational kinetic energy, viz. $3/2 kT$ on the average, where k is Boltzmann’s constant, and T is the absolute temperature. This amounts at room temperature to about 10^{-20} Joules, completely negligible for objects of macroscopic size. For molecules in a gas phase, however, it is sufficient to cause them to fly about in straight lines at velocities of several hundred m/s, colliding with each other and their confining boundaries. In an ideal gas at room temperature and atmospheric pressure, the average distance between collisions, the “mean free path,” ranges from 10-100 nm, depending on molecular size. In liquids and solids, the mean free path is of the order of one Ångström (0.1nm), and the motion of molecules resulting from their intrinsic kinetic energy resembles more closely vibration within a cage of nearest neighbors, with an occasional “escape.” For colloid particles, usually consisting of hundreds up to 10^{10} molecules or so, kinetic effects are still important. They are sufficiently small that when they are dispersed in a gas or liquid medium, any unevenness in the bombardment they receive from the surrounding molecules causes them to move about in a process is known as “Brownian motion.” Thus in contrast to macroscopic objects, colloid particles do not stay put, and the smaller the particles, the more pronounced is their *Wanderlust*. The effect of kinetic energy on other objects of colloidal dimensions, such as ultra-thin deformable films (*e.g.*, bilayer lipid membranes) or long nanowires, is also evident in the wave-like undulations these objects exhibit. The effect of intrinsic kinetic energy on fluid interfaces is manifest as microscopic waves called “riplons.”

The second consequence of smallness is the absence or near absence of inertial effects. The response of colloids to the presence of external fields (gravitational, electric, magnetic, etc.) that act on the particles to orient them, move them about and generally to concentrate them in some region of the system is effectively instantaneous. This derives from the law that Impulse = Momentum, *i.e.*, $Ft = mv$, where F is the average force acting on the object during the time interval t , m is the mass of the object, and v is velocity it attains. Since the mass of a colloid particle is so small, the time required for it to reach its steady state velocity upon application of a force is essentially nil. For example, a one-micrometer diameter sphere of density 2.0 g/cm^3 sedimenting in water reaches its terminal velocity in about 50 microseconds. The movements of small particles resulting from of an external field are termed *phoretic* processes, and may be exemplified by electrophoresis of particles with electrical double layers in an electric field, or magnetophoresis of magnetic particles in a magnetic field. The ability to “herd” colloid particles around through the control of external fields provides one of the important strategies for controlling colloidal systems. As the particles get down into the nano size range, the randomizing effects of Brownian motion may start to overtake the phoretic processes, and one must be able to deal with or perhaps even exploit the balance between the two.

The third difference between ultra-small objects and their larger counterparts is the relative unimportance of gravity compared with other forces acting on them. Gravitational forces scale with the third power of the object's linear dimensions, while many of the "colloid forces" scale with the second power of the linear dimensions, *i.e.*, they are "surface forces."

The fourth difference is the effect that intermolecular interactions have upon them. Just as molecules interact across a distance with one another through a variety of forces (dispersion, dipolar, electrostatic, etc.), objects consisting of many molecules interact with one another by virtue of the *collective* effect of these molecular interactions. Particles "feel" each other across distances up to tens of nm's or greater. Since this is much greater than the range of interaction between molecules, they are termed "long range" forces. The interaction between like particles in a given medium is always attractive, so that they are drawn together and stick, and a significant part of colloid science is the design and use of strategies to prevent such sticking. These rely on repulsive interactions, which are often the result of electrical charges or the presence of adsorbed macromolecules at the surfaces. The intervening fluid between the particle surfaces may be viewed as a film which, upon reaching a certain degree of thinness, may spontaneously thin further, re-thicken or break up into drops or bubbles. Such behavior is critical to the formation of ultra-thin coatings as well as to the drawing together (aggregation and coalescence) of colloid particles in fluid media.

The fifth distinguishing feature is that many intensive thermodynamic properties begin to change with particle size as size is reduced. For example, the vapor pressure of a tiny droplet of liquid depends on its diameter. The vapor pressure of a 1- μm droplet of water at room temperature is approximately 1% higher than the handbook value. For 100-nm droplets, it is 12% higher, while for 10-nm droplets it is higher by a factor of three. The vapor pressure enhancement is one manifestation of the effect of curvature on thermodynamic properties, known as the "Kelvin effect." Other consequences of the Kelvin effect include the condensation of vapors into small pores, crevices and capillaries at partial pressures below their vapor pressure, the enhanced solubility of small particles over larger ones, and the mechanism of phase change by nucleation. The Kelvin effect governs the process of cloud formation and ultimately their evolution into raindrops.

The sixth distinction concerns the interaction of electromagnetic radiation, in particular visible light, with small objects, an interaction dependent in part on the ratio of the particle size to the wavelength. For objects large relative to the wavelength, light is refracted or absorbed by the system, or reflected from its surface and diffracted at its edges, leading to a blurring of the edges by an amount approximating the wavelength. Thus ordinary optical microscopy produces images with a resolution no better than that wavelength (400–700 nm). Particles in the colloidal domain *scatter*

visible light, giving a colloid a turbid appearance. Turbidity is a maximum when the scattering centers (particles) are roughly comparable in size to the wavelength of visible light, while for smaller particles, falls off as the sixth power of the particle diameter. For diameters less than approximately 50 nm, they may become effectively invisible. Most sunscreens use particles that absorb ultraviolet light but are in a size range that only negligibly scatters visible light and are thus clear on the skin. In another example, nanoparticles may be incorporated into optical coatings to improve mechanical properties (scratch resistance, etc.) without compromising transparency.

It is fun to think of questions regarding the behavior of every-day systems or processes that cannot be answered without knowledge of interfaces and colloids. A few examples are listed in Table 1-1. They are posed here without answers, but all are dealt with in the text. The first question concerns the fact that one may easily “float” a needle or other dense object, such as a paper clip, on water if it gently placed on the water surface.

Table 1-1: Examples of questions that can be answered only with knowledge of interfacial and colloid science.

1. How can a metal needle (7-8 times as dense as water) be made to “float” on water?
 2. Why will a teaspoon of certain materials spread spontaneously over several acres of water surface, and then suppress both waves and evaporation?
 3. Why do liquids stick to some surfaces but not to others? How does an adhesive work?
 4. How do soaps and detergents help us to wash things?
 5. How can water remain as a liquid at temperatures more than 20°C below its freezing point?
 6. How can we make water into a froth or a foam?
 7. How can we dissolve large amounts of oil in water using just a trace of a third component?
 8. How can particles much denser than water be suspended in water almost indefinitely?
 9. How can pumping gasoline through a hose lead to a spark, and possible disaster?
 10. How does an absorbent paper towel soak up spills?
 11. Why does a liquid jet break up into droplets?
 12. How does the addition of salt to turbid water cause it to clarify?
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It is evident that factors other than gravity are involved. The second question is illustrated in the frontispiece of the pioneering monograph by Davies and Rideal: **Interfacial Phenomena**, and is reproduced in Fig. 1-4. It shows the mirror-like surface of Loch Laggan, in Scotland, resulting from the application of a small amount of hexadecanol, which spreads out into a

monolayer and damps all small wavelets. The monolayer also significantly suppresses evaporation. Question 3 addresses the everyday observation that liquids appear to stick to some surfaces, but not others. Teflon-coated cookware is designed to avoid the sticking of food; carpet fibers are surface treated with anti-soil coatings; Gore-TexTM outer garments are designed to shed water. On the other hand, liquids may be formulated to be pressure-sensitive adhesives. Question 4 notes the everyday need for soaps and detergents to facilitate the cleaning of clothes, dishes and our hands, and asks: What is it that makes the dirt come loose and disappear? Question 5 reminds us that the freezing point of water, or any liquid, found in the Handbook, does not necessarily tell us the temperature at which freezing



Fig. 1-4: A monolayer of hexadecanol spread on Loch Laggan, Scotland. From: [Davies, J.T., and Rideal, E.K., **Interfacial Phenomena**, Academic Press, New York, 1961.]

will actually be observed. If one is careful, for example, water may be chilled to nearly -40°C without freezing, but if subjected to even a small disturbance, sudden phase change occurs. Question 6 asks why water can form itself into the delicate polyhedral structure known as a froth or foam, but apparently only if the water is *dirty*. Question 7 addresses the experiment in which water containing dissolved detergent is then capable of dissolving significant amounts of an otherwise-insoluble oil, such as gasoline. Question 8 is exemplified by an unsettled dispersion of gold particles [sp. gr. 13.7] in water prepared in Michael Faraday's lab in the mid 1800's, as shown in Fig. 1-5, and which can be viewed in the British Museum in London today. Question 9 recalls a problem associated with the pumping of volatile fuels, such as during the gassing of an automobile. If the hose is not grounded, or the gasoline does not have additives giving it a certain degree of electrical

conductivity, a potential may develop along the hose great enough to produce a spark, which in the fuel-air mixture can lead to an explosion. Question 10 notes the development of absorbent products capable of imbibing many times their weight in water, and asks how this can be achieved. Question 11 addresses the fact that cylinders of liquid are unstable



Fig. 1-5: Gold sol prepared by Michael Faraday, on view in the Faraday Museum, London.

and will break up into droplets, which in jets occurs too rapidly to be seen by the naked eye. Figure 1-6 shows a flash photograph of the phenomenon. The clarification of a turbid dispersion of clay or silt in water by adding salt, as suggested in Question 12, is observed on a large scale in the formation of river deltas bordering on saltwater bodies. Looking at an atlas of maps will confirm that similar deltas do not form where rivers empty into freshwater bodies.

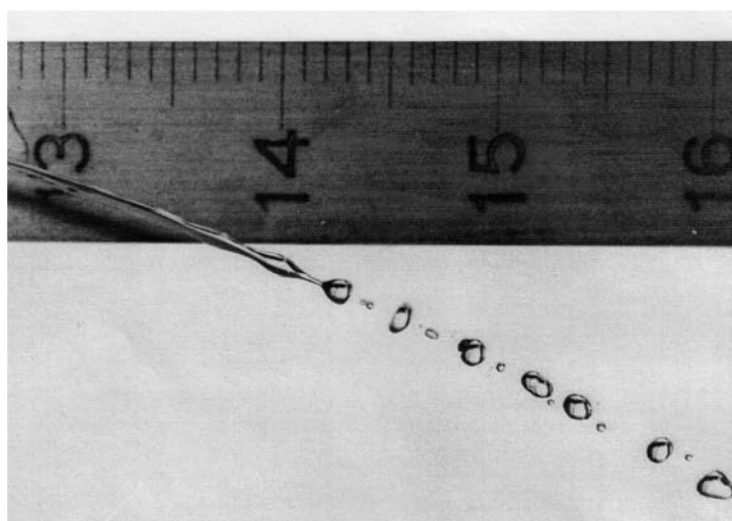


Fig. 1-6: Breakup of a capillary jet.

C. The bridge to nanoscience

1. What is “nanoscience?”

A search of amazon.com for books, using the keyword “nanoscience,” reveals 2,061 (!) titles currently (Summer, 2009) in print. The first dozen are listed in Table 1-2. Even a cursory perusal of the literature reveals the

Table 1-2: The first 12 titles listed by amazon.com with a search request of “nanoscience.”)

- **Introduction to Nanoscience** by Gabor L. Hornyak, H.F. Tibbals, Joydeep Dutta, and Anil Rao (2008)
- **Nanophysics and Nanotechnology: An Introduction to Modern Concepts in Nanoscience** by Edward L. Wolf (2006)
- **Nanoscience: Nanotechnologies and Nanophysics** by Claire Dupas, Philippe Houdy, and Marcel Lahmani (2006)
- **An Introduction to Nanosciences and Nanotechnology** by Alain Nouailhat (2008)
- **Introduction to Nanoscience and Nanotechnology** by Gabor L. Hornyak, H.F. Tibbals, and Joydeep Dutta (2008)
- **Introduction to Nanoscale Science and Technology (Nanostructure Science and Technology)** by Massimiliano Di Ventra, Stephane Evoy, and James R. Heflin (2004)
- **Nanotechnology For Dummies** by Richard D. Booker and Mr. Earl Boysen (2005)
- **Nanotechnology: A Gentle Introduction to the Next Big Idea** by Mark A. Ratner and Daniel Ratner (2002)
- **Understanding Nanotechnology by Scientific American and editors at Scientific American** (2002)
- **Handbook of Nanoscience, Engineering, and Technology, Second Edition** by William A. Goddard III, Donald W. Brenner, Sergey Edward Lyshevski, and Gerald J. Iafrate (2007)
- **Nanotechnology: Basic Science and Emerging Technologies** by Mick Wilson, Kamali Kannangara, Geoff Smith, and Michelle Simmons (2002)
- **Nanosciences: The Invisible Revolution** by Christian Joachim and Laurence Plevvert (2009)

amazing diversity and inter-disciplinary character of this emerging field, making it somewhat difficult to visualize it as a single, coherent body of knowledge. In its simplest conception, nanoscience may be defined as the study of objects with structural elements in the size range of 1–100 nm, *i.e.*, the low end of the colloidal domain. As indicated earlier, many of the size-dependent aspects of the behavior of entities in the colloidal size range may be successfully extrapolated into the nano range. The point at which continuum concepts start to break down is different for different materials and conditions, and different properties. The bulk-phase equations of state

may become inapplicable, and the phenomenological equations of transport (Fourier's Law of heat conduction, Fick's Law of species transport, Newton's Law of viscosity, Ohm's Law, etc.) begin to fail. Thus what may be required is not just new size-dependent properties, but "new physics."

Even though systems requiring "new physics" are not the focus of this text, a few examples are recounted here. One of the best known of these is the observation that the color of nanoparticles of various semiconductors (called "quantum dots") is a function of their size. The electrons in a quantum dot are confined to distinguishably discrete energy levels (quantum confinement), dependent on dot size, so that when the dot is illuminated, it emits only light of a given wavelength, dependent on the particle size and composition. Figure 1-7 shows a set of dispersions of CdSe/ZnS core-shell nanocrystals varying in size from ≈ 1.7 nm to ≈ 5 nm from left to right.

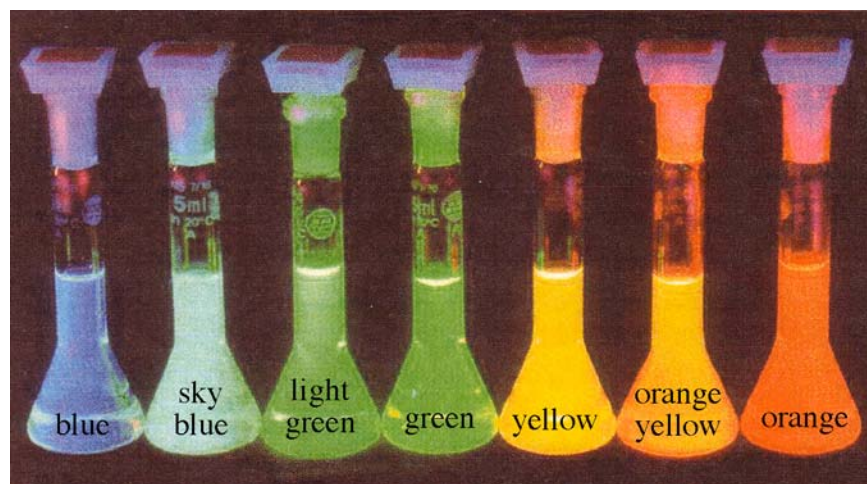


Fig. 1-7: Size-dependent change of the emission color of colloidal dispersions of CdSe/ZnS core-shell nanocrystals, varying in size from left to right: ≈ 1.7 to ≈ 5 nm. For full color, see image at: [<http://www.nanopicoftoday.org/2003Pics/QDRainbow.htm>]

This property gives rise to many potential applications, including use as biological markers. Quantum dots of a known range of size and concentration might be incorporated into a single colloidal latex particle, which in turn may be attached to a particular type of tissue using an appropriate biological targeting agent. Upon illumination, such a particle will produce a unique spectrum (a spectral bar code) characteristic of the particular collection of quantum dots, thus identifying the existence and location of the tissue in question. As another example, the transport of electricity along a nanowire or a carbon nanotube (virtually the poster child for nanotechnology) is a function of diameter and may be governed by quantum effects. This means it may be possible to construct transistors, diodes, switches, gates, as well as conductors and other components of microcircuits from such objects, leading to ultra-small electronic computer logic systems. Recent discussion has moved to the possibility of using properly designed *single molecules* for this purpose. One of the problems of using these tiny elements for controlling charge flow is the fact that

whenever they are bumped by neighboring nano objects (kinetic energy!), they are easily discharged.

Another example of the specific importance of size in the nano range concerns magnetic properties. A particle of magnetite (Fe_3O_4) in this range, for example, will retain its magnetism more effectively the larger it is, making it a better magnetic data storage medium than smaller particles, which are subject to loss of their magnetic information by being bumped by their neighbors. When it becomes too large, however, it will split into two magnetic domains of opposite polarity, and much reduced total magnetism. Thus there is an optimum single-domain magnetic nano-crystal size (called the super-paramagnetic limit, and often about 50 nm) for data storage, well known to the manufacturers of magnetic data storage media. Other examples of the special photonic, electronic and magnetic properties of nano-objects could be listed.

2. Nanostructures and assemblies

In the nano range, one often cannot refer to the objects of interest as “phases” or “particles,” but must think of them as “structures.” Sometimes nanoparticles are single molecules, or consist of a countable number of atoms or molecules, arranged in particular ways. It is useful to describe just a few of these “nano-structures” to give an idea of what is possible.

Buckyballs: As pictured in Fig. 1-8, Buckyballs are hollow spherical molecules of carbon atoms, more formally known as “Buckminsterfullerene,” in view of their resemblance to structures created by the architect and inventor, Buckminster Fuller (1895-1983). The structure first discovered in 1985 upon examining the debris formed by vaporizing graphite with a laser was C_{60} . It consists of 5-member rings isolated by 6-member rings and is approximately one nm in diameter. Since then, many other fullerenes of different numbers of carbon atom and different structures have been discovered and characterized. Furthermore, fullerene-like structures of other

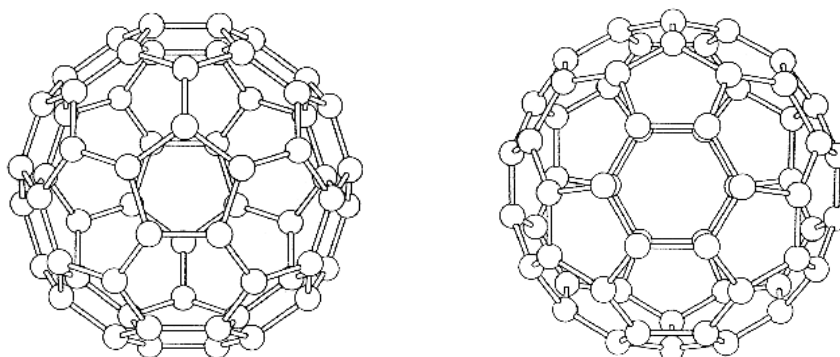


Fig. 1-8: Two views of the structure of a C_{60} “Buckyball”
From: [www.bfi.org/?q=node/351]

materials, notably tungsten and molybdenum sulfides, WS_2 and MoS_2 , have recently been made and characterized. Atoms or small molecules can be put inside these structures or attached to their exteriors. These structures have some remarkable properties. For example, when certain metal atoms are trapped inside the cages, they exhibit superconductivity.

Carbon nanotubes: As shown in Fig. 1-9, carbon nanotubes are cylinders whose walls are made from monomolecular sheets of graphite, termed *graphene*, resembling chicken wire. Graphene layers themselves, including their exfoliation from graphite and their bottom-up synthesis, are objects of current interest. The tubes may be single-walled (SWNT's), about 1.5 nm in diameter, or multi-walled nanotubes (MWNT's) of somewhat larger diameter. Different types of SWNT's are formed when the graphene

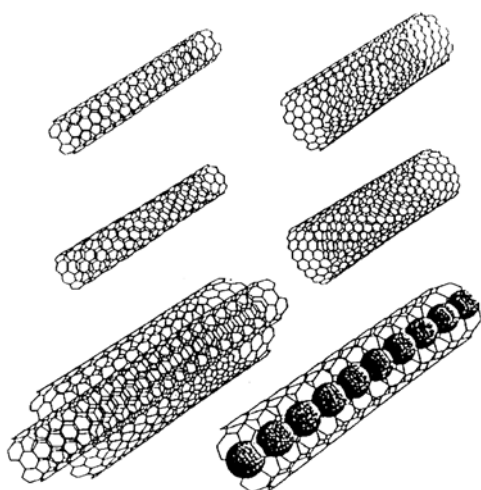


Fig. 1-9: Carbon-wall nanotubes, showing single-walled (SWNT) and multi-walled (MWNT) configurations and a tube filled with nanoparticles. From: [www.wtec.org/loyola/nano/04_03.htm]

sheet is rolled in different ways, and the different structures have different electrical properties. One type is conductive, one is semi-metallic and another is a semiconductor, with quantum confinement of electrons. They may be filled with metal or other atoms and chemically functionalized externally. Carbon nanotubes are usually formed in a plasma arcing process, although other methods of synthesis are available, and still others are under investigation. They are incredibly strong for their size and weight, and may be the basis for super reinforced nanocomposites. It has even been speculated that they may be the basis for a cable supporting a “space elevator” on which one might ride to the stratosphere. Nanotubes can also be made from other inorganic materials producing structures different from those of carbon and holding the promise of a range of new applications.

Vesicles: As shown in Fig. 1-10, vesicles are spherical bilayer structures of lipids or other surfactants, and may be single-walled or multi-walled, with an aqueous interior. They form spontaneously in water upon gentle agitation when the right monomeric species (usually di-tail surfactants or lipids) are present. Vesicles may be as small as 30 nm in diameter, or as large as one micrometer or more. The smaller ones in particular are showing promise as drug delivery vehicles, with an appropriate drug in the interior

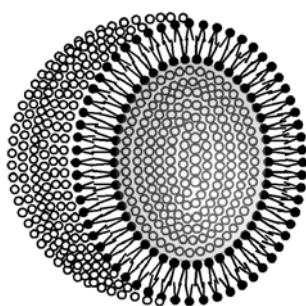


Fig. 1-10: Single-walled vesicle formed from di-tail lipid monomers.

and targeting agents attached to their outer surfaces, or nano-reactors of various sorts.

Dendrimers: As shown in Fig. 1-11, dendrimers are highly ordered, regularly branched single globular macromolecules, sometimes called starburst polymers. They are formed by the successive addition of layers (or “generations”) of chemical branches, and have reached sizes up to 100 nm. The sponginess of their structure has led to their use as impact modifiers in composite materials. These remarkable molecules can also be designed to allow the incorporation of desired guest molecules in their interiors (for applications like drug delivery) or chemical functionality of their exteriors. Their controllable chemistry and structure has led to their use as synthetic catalysts themselves, and recently a dendrimer-based method has been reported for controllably synthesizing 1-nm and subnanometer-sized metal catalyst particles containing a well-defined number of atoms. It turns out that 3-nm diameter particles show higher catalytic activity for the oxygen-reduction reaction (ORR) than either smaller or larger particles.

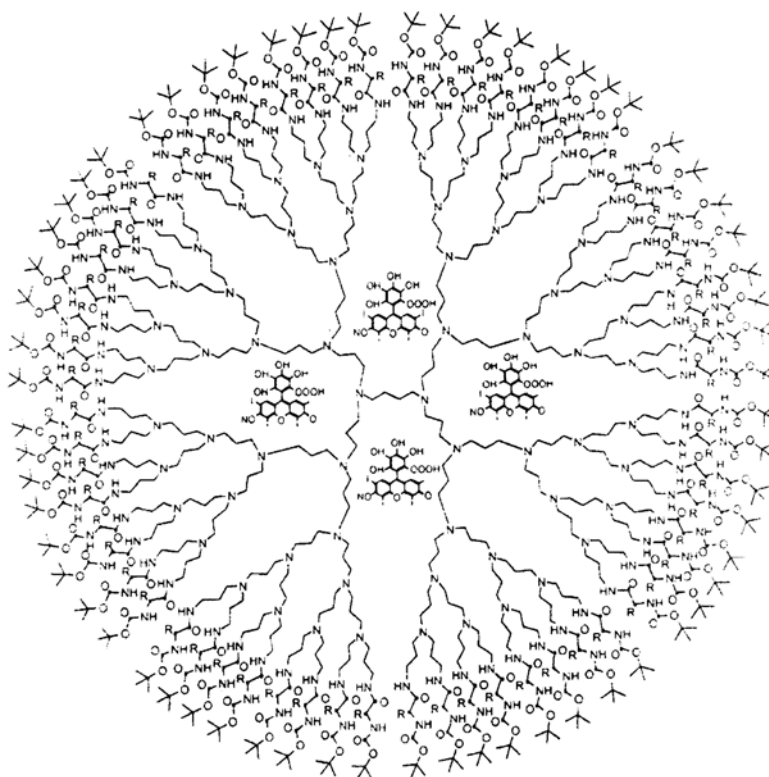


Fig. 1-11: Bengal rose encapsulation in a dendrimer center. From: [Zeng, F. and Zimmerman, S. C., *Chem. Rev.*, **97**, 1681 (1997).]

Many more nanostructures are displayed in the delightful website: “Nanopicture of the Day:” www.nanopictureoftheday.org, from which three more examples are drawn.

Nanoforests: Figure 1-12 shows a scanning electron micrograph (SEM) of a “forest” of uniform gold nanowires produced by plasma etching a polycarbonate film containing the nanowires. The loaded film had been

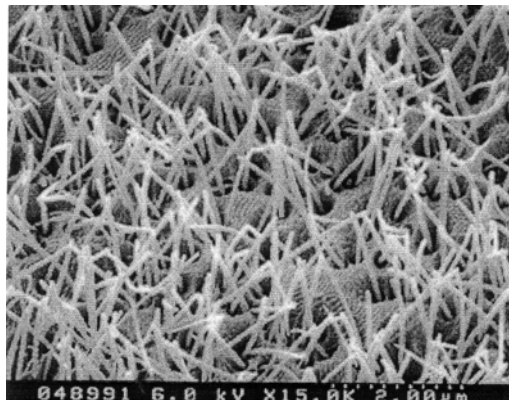


Fig. 1-12: A forest of gold nanowires produced by plasma etching a polycarbonate film containing the nanowires. From: [Yu, S., Li, N., Wharton, J., and Martin, C. R., *Nano Letters*, 3, 815 (2003).]

prepared by electrochemically filling holes that had been etched in the polycarbonate by electron beam lithography. When the nanowires-containing membranes are exposed to an O_2 plasma, the polymer at the membrane surface is selectively removed, exposing the ends of the gold nanowires. The length of the nanowires is controlled by varying the etch time. Other types of nanoforests can be constructed in other ways. Tree-like nanostructures (‘nanotrees’) can be formed through the self-assembled growth of semiconductor nanowires via a vapor–liquid–solid growth mode. This bottom-up method uses initial “seeding” by catalytic nanoparticles to form the trunk, followed by the sequential seeding of branching structures. This controlled seeding method has potential as a generic means to form complex branching structures, and may also offer opportunities for applications. One of the methods for synthesizing carbon nanotubes is by chemical vapor deposition using catalyst seeds that produce carpets of the nanotubes fibers.

Nanohelices: Figure 1-13 shows a scanning electron micrograph of nanohelices formed from single-crystal zinc piezo-electric nano-belts produced by chemical vapor deposition. They are formed in response to the electrostatic energy introduced by the spontaneous polarization across the thickness of the nanobelt, owing to the presence of large polar surfaces. The shape of the nanohelix is determined by minimizing the energy contributed by electrostatic interaction and elasticity. The piezoelectric and possibly ferroelectric nanobelts have potential as surface selective catalysts, sensors, transducers, and micro-electromechanical devices.

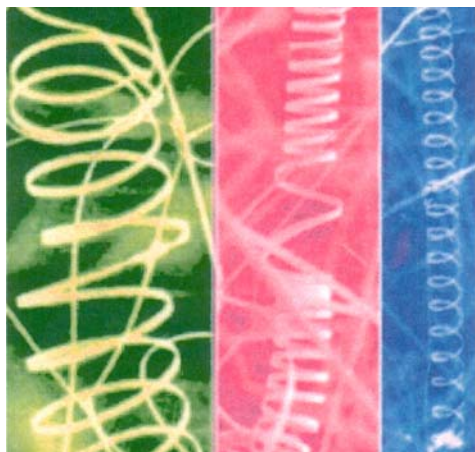


Fig. 1-13: Nanohelices.
From: [Kong, X. Y., and
Wang, Z.L., *Nano Letters*,
3, 1265 (2003).]

Nanoarrays: Figure 1-14 shows a regular array of platinum catalyst nanoparticles, 20 nm in diameter, 15 nm high and spaced 100 nm apart, as viewed by an atomic force microscope. It is found that catalytic activity often depends critically on the particle size, aspect ratio and spacing, and these features can now be controlled in the synthesis process. In the case shown, the structure was created using a template formed by a thin polymer film coated onto a smooth silicon oxide surface subsequently etched into the desired pattern by an electron beam. A platinum film was then evaporated onto the polymer, filling in the holes. Finally, the polymer film was removed, leaving the pattern shown.



Fig. 1-14: An array of
platinum catalyst
nanoparticles. From: [Gabor
Somorjai: Nano Picture of
the Day, Jan. 24, 2004]

Structures such as those described above and others may in turn be dispersed in a medium or assembled (or *self*-assembled) into mesoscopic or macroscopic superstructures (monoliths) with unique and important properties. Micro- or nano-composites may be constructed of units of these dimensions to produce materials of almost any desired properties; for example, materials with the heat resistance of ceramics and the ductility of metals, or materials with the strength of steel, but the weight of a polymer, etc. Sintered arrays may produce nano-filters or membranes, super thermal insulation materials, or storage media for liquefied gases at modest pressures. One exciting possibility is that of constructing nano-circuits from quantum dots, nanowires and other elements, put into a proper array onto some surface. Another possibility is the creation of a device for bringing chemicals together in miniscule quantities so that they may react to produce some recordable result. One may imagine an assembly of nano- or micro-sized tubes, channels, reservoirs, etc., assembled on some surface for this

purpose. These are referred to as LOC (“*lab-on-a-chip*”) configurations and may be the basis for chemical sensors more accurate than any known today and small enough to be injected into the blood stream. The motion of fluids through such a system is governed by “*micro- or nano-fluidics*,” which in the ultimate may not be able to treat the fluids as continua. Still other configurations made of nano building blocks might be motors or mechanical actuators, converting chemical energy into mechanical work or electricity with nearly 100% efficiency. These structures, known as MEMS or NEMS (“*micro- or nano-electromechanical systems*”) may someday be the molecular assembly devices for making structured nano-objects. One concept for the realization of such devices is that of harnessing the random kinetic energy of all kinetic units by devising ratchets that allow net movement to occur only in one direction, and another speculated that they could be the basis for nano-manufacturing (“*nanobots*”), perhaps even to replicate themselves.

As their potential has come into clearer view over the past decade, “nanoscience” and its application, “nanotechnology,” have become among the hottest topics for academic inquiry, government research funding and fanciful speculation. George Whitesides (Professor of Chemistry, Harvard University), in a recent (March, 2009) plenary lecture before the American Chemical Society, described nanoscience and nanotechnology as now entering late adolescence, *i.e.*, past the exaggerated expectations of infancy (self-replicating “nanobots,” space elevators, single-molecule computing, etc.) as well as the over-reaction to the inevitable disappointments, and moving into a more mature status in which the focus has returned to fundamentals, “discovery,” and “science.”

3. *Generic nanoscience*

In addition to the dazzling array of “special effects” associated with many of the objects of nanoscience, perhaps one of the most amazing observations is how many of them may be described by just properly taking into account the generic effects of smallness while extrapolating the world of interfaces and colloids into the nano domain. Despite any special properties they might have, all of these micro or nano entities must contend with the six universal aspects of smallness listed earlier, and it is to these that principal attention is given in this text. The practical issues concerning these entities are that they must be:

- *Produced*, either by somehow subdividing larger systems in so-called “top-down” procedures, or grown out of molecular or atomic media by so-called “bottom-up” procedures;
- *Characterized*, *i.e.*, one must be able to “see” or image the particles or structures and determine their mechanical, chemical, electrical, etc., properties

- *Assembled*, often into two-dimensional or three-dimensional arrays by means of flow, external fields, or by various self-assembly processes;
- *Manipulated, i.e.*, placed where they are wanted, possibly one at a time, and usually on some surface, in accord with some blueprint; and
- *Protected*, against moving out of position, becoming attached to unwanted particles, vaporizing, etc.

4. *New tools of generic nanoscience*

The recent emergence of nanoscience and nanotechnology owes as much to the development and refinement of tools for the accomplishment of the above tasks as it does to the birth of quantum dots, carbon nanotubes, and the like. Some of these new tools are listed in Table 1-3. One of the most important developments is the family of scanning probe techniques, described briefly here but in more detail in Chap. 4.M. The first to emerge was Scanning Tunneling Microscopy (STM), pictured in Fig. 4-92. When a sharp conducting tip is poised a few nanometers above a conducting surface,

Table 1-3: Some new tools for the characterization and manipulation of nanosystems.

SPM (scanning probe microscopy)
• STM (Scanning Tunneling Microscopy) • AFM (Atomic Force Microscopy) • NSOM (Nearfield Scanning Optical Microscopy)
Colloid force-distance measurement
• SFA (Surface Forces Apparatus) • MASIF (Measurement and Analysis of Surface Interactions and Forces) • TIRM (Total Internal Reflection Microscopy)
Particle manipulation
• Optical tweezers (optical trapping) • Traveling-wave dielectrophoresis

and a slight bias is imposed across the gap, electrons may tunnel directly across. It occurs when the highest occupied molecular orbital (HOMO) of the material on one side of the gap overlaps with the lowest unoccupied orbital (LUMO) of the material on the other side of the gap. The tunneling current is exponentially sensitive to the distance between the tip and the nearest atom on the surface. As the tip is rastered across the surface, it is moved up and down by a piezoelectric controller to maintain the current constant. The up-and-down motion of the controller is tracked and recorded by a computer to produce a topographical map of the surface with atomic resolution. A related device, the Atomic Force Microscope (AFM), does not

require that the tip and surface be conductive. In the simplest mode of operation, shown in Fig. 4-93, the sharp tip is held with constant force in direct contact with the surface by means of an ultra-thin cantilever beam. As the sample is rastered below the tip, the cantilever moves up and down to follow the topography. The motion of the cantilever is tracked by means of a laser reflected from its back to a photodiode system, revealing the topography of the scanned sample. The topographical resolution of STM or AFM is of the order of Ångströms, far better than that of the wavelength-limited optical microscopy. The techniques are thus ideally suited to the examination of nano features and nano structures. AFM may also be configured to map adhesion, stiffness, lubricity, and many other properties of the scanned surface, or may be operated in an intermittent contact mode to probe soft samples or in a non-contact mode (in which the tip vibrates above the surface) to probe the force fields emanating from the surface.

Another scanning probe method for overcoming the wavelength limitations of optical microscopy is that of Nearfield Scanning Optical Microscopy (NSOM), shown in Fig. 4-91, in which the object of interest is illuminated by the evanescent light which emerges a few tens of nm from the back side of a medium in which there is total internal reflection of light. Information pertaining to a spot a few nm² is captured by a sharp transparent probe tip a few nm above the spot and transmitted to a computer. Images are again built up by rastering the tip over the surface, or the sample beneath the probe.

A variety of methods have been developed for the *direct* measurement of forces of the type existing between proximate colloid particles, as described in Chap. 7 in detail. One of the most important of these devices is the Surface Forces Apparatus (SFA), pictured in Fig. 7-1, in which the force acting between a pair of approaching crossed cylinders (of radii of a few mm) attached to sensitive leaf springs. Positioning and force measurement are effected using piezo-electric positioners, and the distance of separation (with Ångström resolution) is determined interferometrically. An important breakthrough in the development of the SFA was the discovery that freshly-cleaved Muscovite mica is atomically smooth, and is thus used for the surfaces of the approaching cylinders. Other materials of interest may be coated on to these substrates. The MASIF device is similar to the SFA except that a bimorph strip (two slices of piezo-electric material sandwiched together) is used to measure the force between the approaching surfaces. TIRM (Total Internal Reflection Microscopy) monitors the level of particles suspended against gravity by repulsive forces above a surface from which an evanescent beam is emerging.

A number of methods are being developed for the manipulation of micro- or nano-particles one at a time. The AFM probe may be used to push or pull nano structures (and even single atoms!) around on a surface. In a famous image now more than a decade old, IBM researchers in Zürich

produced the company logo in this way by arranging an array of 35 individual xenon atoms on a Ni(110) surface into the letters IBM. Figure 1-15 shows AFM images of strands of DNA adsorbed onto a modified graphite surface. Manipulation was effected by bringing the AFM tip into contact with the surface and moving it using homemade hardware and software: (a) shows molecules as deposited, (b) shows two the molecules

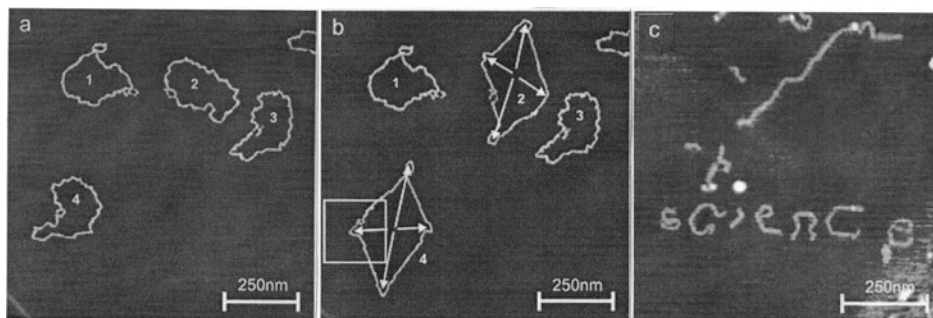


Fig. 1-15: Manipulation and overstretching of genes on a solid substrate. From: [Severin, N., Barner, J., Kalachev, A. A., and Rabe, J. P., *Nano Letters*, **4**, 577 (2004).]

stretched into diamond shapes, and (c) shows fragments drawn into the word “science.” Nano objects can also be picked up using a pair of carbon nanotubes like chopsticks attached to a cantilever tip. The tweezer-like device is closed or opened with an applied electrical bias. In a simpler way, particles can be plucked out of an array, or put down in a desired position on a surface by charging and discharging a cantilever tip.

Another technique born out of the technology of atomic force microscopy is Dip-Pen Nanolithography (DPN), a scanning probe nano-patterning technique pictured in Fig. 1-16 in which an AFM tip is used to

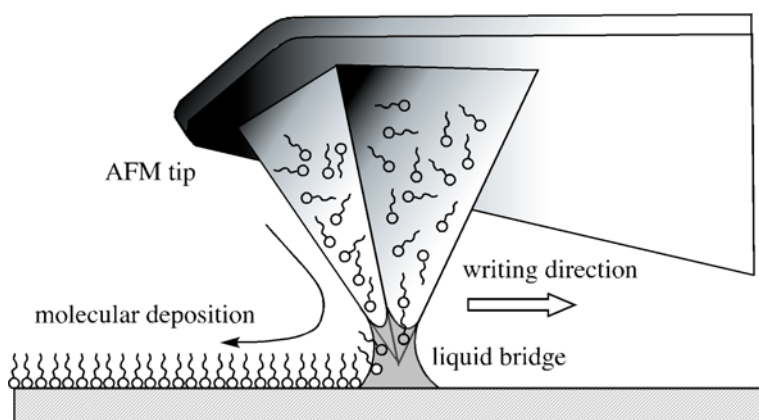


Fig. 1-16: Schematic of dip-pen nanolithography.

deliver molecules to a surface via a solvent meniscus, which naturally forms in the ambient atmosphere. This direct-write technique offers high-resolution patterning capabilities for a number of molecular and bio-molecular “inks” on a variety of substrate types such as metals, semiconductors, and monolayer functionalized surfaces. Figure 1-17 shows a paragraph from Richard Feynman’s 1959 speech: “There’s Plenty of Room at the Bottom,”

written using DPN on a 7- μm square surface. Feynman's speech¹ is regarded as the birth document of nanoscience, and the portion of it is shown in Fig. 1-17 reads:

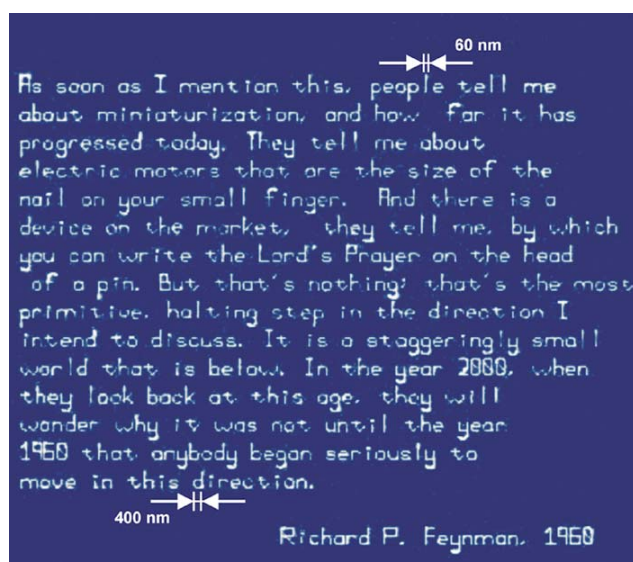


Fig. 1-17: DPN-written portion of Feynman's speech: "There's Plenty of Room at the Bottom." From: Mirkin Group, Northwestern University [http://www.nanotech-now.com/basics.htm]

"As soon as I mention this, people tell me about miniaturization, and how far it has progressed today. They tell me about electric motors that are the size of the nail on your small finger. And there is a device on the market, they tell me, by which you can write the Lord's Prayer on the head of a pin. But that's nothing; that's the most primitive, halting step in the direction I intend to discuss. It is a staggeringly small world that is below. In the year 2000, when they look back at this age, they will wonder why it was not until the year 1960 that anybody began seriously to move in this direction."

A powerful technique for positioning and holding a micro-particle at a desired position in three-dimensional space is that of "optical trapping," pictured in Fig. 6-44. A particle whose refractive index differs significantly from that of the suspending medium, and whose size is greater than the wavelength of the light, is held by photonic forces in the focused beam of a laser. The device is also referred as "laser tweezers," and may be used to assemble structures one particle at a time or several at a time into aggregates or arrays of desired structure using independently-controlled, time-shared optical traps or "holographic optical tweezers," in which a propagating laser wave front is modified by passing through a pattern of interference fringes. Laser tweezers may also be used as *in situ* force sensors as well as micromanipulators. They thus provide, in principle, an additional method for probing colloid force-distance relationships.

Another method for moving particles is that of "traveling wave dielectrophoresis," in which particles are acted upon by a traveling,

¹ Feynman, R. P., *Engineering and Science (Caltech)*, Vol. XXIII, No. 5, pp. 22-36 (1960).

sinusoidal electric field, which induces dipoles in the particles. When there is a time lag between the induced dipole and the field, a particle experiences a force, which induces motion.

5. *The plan*

The journey in this text begins with a study of fluid interfaces and the many consequences of the contractile tendency (surface or interfacial tension) they exhibit, *i.e.*, *capillarity*. Next is an explicit look at the thermodynamics of interfacial systems, particularly those that are multicomponent. Adsorption at both fluid and solid interfaces is examined, and the wondrous diversity of surfactants and their solutions is investigated. It moves on to the examination of the physical interaction between liquids and solids, and the interaction of fluid interfaces with solid surfaces. This includes wetting, coating, spreading, wicking and adhesion. It includes examination and characterization of the properties of solid surfaces: topography, surface energy, and surface chemistry. Next, the world of colloids, including nano-colloids, is explored. Their morphological, kinetic, phoretic and optical properties are described. The electrical properties of interfaces, and their many consequences, are examined next, and the following chapter deals with the interaction between colloid particles. Following a consideration of colloid system rheology, fluid phase colloids, *i.e.*, emulsions and foams, are examined, and the journey concludes with a consideration of interfacial hydrodynamics, symbolized by the image of “wine tears” on the cover.