Introduction to Nanoengineering

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Dedications

To Dina and Cora.

Darren J. Lipomi

In loving memory of Dr André Minor.

Robert S. Ramji

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Preface

When I (Darren) was a student majoring in chemistry, I could not understand why chemistry was called “the central science” and why it was told to me that chemistry was fundamental to everyday life. The content I was learning, although interesting, seemed unimportant. Balancing chemical equations, solving Lewis dot structures, and performing acid–base titrations in the lab seemed very far from things I could touch or see, and which affected the way my world worked. Even when I joined a research laboratory in organic chemistry as an undergraduate, where I made molecules of purported value to medicine and pharmaceuticals, the real-world relevance of what I was doing was not apparent to me. While this feeling was most likely born of inexperience, along with perhaps an unfounded lack of faith in the importance of fundamental research, the feeling was inescapable. After all, we considered it a success when we obtained a measly 10 milligrams of the product! (Enough to get a spectrum to prove that we made what we thought we made). Ten milligrams—about the mass of a few grains of sand—after 18 months and 16 painstaking synthetic steps! Ultimately, I knew that the knowledge I created would be of at least a little value to medicinal chemists working at pharmaceutical companies to develop drugs to treat life-threatening diseases. However, I wanted my research to generate results that I could see and feel, and which could lead to fundamentally new advancements in science and technology.

One of the benefits of starting research as an undergraduate (as I would encourage you all to explore!) was the ability to present my work at conferences. At these venues, attended by some of the top scientists in the world, I learned that my experience—not yet

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expertise—in making molecules was directly applicable to materials science, in particular the flavor of materials science where control over the nanostructure enabled the discovery of new, apparently magical, properties. After all, the reason I entered into science and technology was not for its practice, which involves the meticulous collection of data, but for the fact that it was the only legitimate route to magic and the fantasy world of Star Trek and Star Wars. Thus, it wasn't until later into my undergraduate studies that I came to understand how phenomena and materials that occurred on the nanometer scale that gave rise to much of what motivated me to pursue a degree (and a life) in science and engineering.

Indeed, as we will see, phenomena that occur on the nanometer scale are the basis for all of modern computation, imaging, and human-machine interfaces; chemical catalysis, fuels, and materials manufacturing; drug delivery and tissue engineering; and technologies for the conversion and storage of energy (*i.e.*, solar cells and batteries). These real-world applications are enabled by the physics that comes into play when objects become so small that their properties are dominated by atoms at their surfaces, or when electrons are confined to small spaces. With such small structures separated by even smaller gaps, seemingly insignificant forces arising from van der Waals interactions can challenge the strengths of the strongest bodybuilders.

At the intersection of physics, chemistry, and several sub-disciplines of engineering, nanoengineering is the manipulation or design of materials and phenomena that occur on the scale of roughly 1–100 nm to accomplish useful tasks. So, when in 2012, I got an offer to become an assistant professor in the Department of NanoEngineering at UC San Diego, I was home at last. Finally, a chance to do research and teaching at the very nexus of all that fascinated me as a student and researcher in my previous life! One of the purposes of this book is for me to share some of my excitement with you.

This book can be used to accompany either a one quarter (ten week) or one semester (fifteen week) introductory undergraduate course in nanoengineering. Such a course might be a core requirement of degree programs in nanoengineering, chemical engineering, or materials science, or as an elective in mechanical engineering, electrical engineering, or bioengineering. It can also be used in courses which teach wide-ranging STEM topics to non-STEM majors. Indeed, when I was a graduate student at Harvard, I served as the lead teaching assistant for such a course, Core Science A50: Invisible Worlds, taught by George Whitesides and Mara Prentiss. While such courses taught to freshmen are usually surveys of the broad application areas of nanoengineering with not much time for depth, I attempted to provide enough detail—enough to be "dangerous"—for the motivated students to dig deeper on their own. If survey courses present material in a form which is "a mile wide and an inch deep," I hope that this course maintains a depth of at least several inches at most places. Thus, attention is paid to fundamental concepts that underlie all phenomena and applications. While concepts such as force, energy, entropy, electrostatics, quantum mechanics, and intermolecular forces play key roles, no prior knowledge or prerequisites beyond ordinary high school courses in chemistry, physics, biology, and math are required for the motivated students to develop a working knowledge of these topics.

A note to students: to achieve success in this or any course, it is essential to do some pre-reading before coming to class. A note to instructors: ideally, class time would be used to reinforce concepts using individual and team-based problems, multi-day design challenges, and discussion—the so called "active learning" or "flipped-classroom" approach. To read effectively, you should have a notebook to extract the main points and concepts and make bulleted lists where you summarize and connect concepts. Try to invent your own mnemonics or semantic associations (associate terms with people, places, objects, and events from your own life…or movie characters, songs, food items, *etc.*) for terms that are difficult to remember. Some students—including myself—like to put these notes on index cards (*i.e.*, flash cards), which can be taken along on the bus or trolley. While I have tried to make the content accessible to the widest range of preparation possible, it is impossible to anticipate the depths of past courses taken by every student. Thus, if you see an unfamiliar term, feel free to look it up online or ask the teaching staff. I would encourage the use of generative AI (*e.g.*, ChatGPT) to help you, but at the time of this writing, it provides lot of incorrect information on science topics, so it is crucial to cross-reference explanations with the book, other sources, or your own understanding.

While you read, be sure to write down every question you have. You can use these questions as the basis for "reading as detective work." Sometimes the questions will be answered later in the book, and some questions will be best answered by discussing them with your study groups or by asking the teaching staff. It is best to focus your effort outside of class with an approach that is characterized by the activity of learning—which is an active process—as opposed to studying. The word studying often conjures a picture of a student staring at the book passively with an elbow perched on the desk with their hair clutched in their hand, in deep though, or—more likely—frustration. That is, aim to learn the concepts so that you can teach it to others in your class, rather than simply studying the material by staring at the pages.

This book is a product of my 22 years of work as a student, researcher, and educator in higher education in chemistry, engineering, and nanotechnology. The collection of topics in this book is idiosyncratic; another nanotechnology researcher/educator would have chosen a somewhat different collection of topics. My coauthor, Robert, a rising expert in the field of computational nanoscience, coauthored every chapter. He revised my drafts of Chapters 1–14 with an eye toward the best way to explain these concepts to first-time learners. He knows from experience as both a first-time learner and later as a teacher of this material: the first time I taught this class to undergraduates in the winter of 2017, Robert was in my class. Since then, he has served as a teaching assistant, and has nearly as many years of experience in applying and explaining the concepts in this book as I do. Robert also took the lead on writing Chapter 15, on computational nanoscience. As a non-expert in this area, I took the role of revising through the lens of a first-time learner.

You will notice that the "Further Reading" section at the end of each chapter is focused on only a few key entries per chapter. Its brevity arises in part because much of the knowledge in this book was synthesized by our experiences as professional researchers (and researchers in training) and from nearly 100 courses the two of us have taken and taught (as well as the two of us collectively having fallen into many thousands of rabbit holes on Science YouTube, Wikipedia, and ChatGPT). Nevertheless, there are some key books and articles which played a key role in shaping our intuition of many topics. We have highlighted these sources and also provided descriptions of where to find the relevant information within them and/or why we found them so valuable.

Finally, we tried to write the book that we would have wanted to read. We enjoyed writing it, and at times it felt autobiographical. To a great extent, it reflects the processes, mnemonics, and personifications of inanimate objects that led use to our own understanding of each topic. Ultimately, we hope that this book is interesting and inspires you to find your passion within the wide and fascinating field of nanoengineering.

Yours in Nano,

Darren J. Lipomi, Robert S. Ramji
San Diego, California

Symbols

Δ	Indicator of difference or change in a variable, often used to represent a finite increment in mathematics and in physical sciences to denote a change in state or condition.
δ	Partial derivative or infinitesimal difference symbol, often used in calculus to denote a small change in a variable. In equations, it indicates that the derivative is taken with respect to one variable while holding others constant. May also refer to chemical shift in NMR measurements
α	Total polarizability of an atom or molecule
α_0	Electronic polarizability of a molecule or atom
α_{dip}	Dipolar polarizability of a molecule
ε	Dielectric constant, aka relative permittivity of a material with respect to the permittivity of vacuum. ε may also be used to refer to engineering strain, the fractional increase in length from a starting length, L_0
ε_0	Absolute dielectric permittivity of vacuum, $\varepsilon_0 \approx 8.854 \times 10^{-12}\ \mathrm{F\,m^{-1}}$
u	Permanent dipole moment of a molecule
u_{ind}	Induced dipole moment of a molecule or atom
z	Atomic number of an atom: number of protons in the atomic nucleus
k	Boltzmann's constant, also written as k_{B}, $1.380649 \times 10^{-23}\ \mathrm{J\,K^{-1}}$. May also refer to the spring constant, a measure of the stiffness of a spring, indicating the force required to displace the spring by a unit length.

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kT	Thermal energy at temperature T, a useful value for contextualizing covalent and noncovalent interactions at the nanoscale. At room temperature, $kT = 4.01 \times 10^{-21}$ J
I	Ionization energy, the energy required to eject the most loosely held electron from the atom or molecule under consideration
C	Constant, used as a general form to represent larger expressions, particularly for components of the van der Waals force, *e.g.*, C_{VDW} represents the total van der Waals constant, $C_{\mathrm{dip-dip}}$ represents the dipole–dipole component of the van der Waals constant, *etc.*
σ	The van der Waals diameter of an atom, 2× the van der Waals radius
$\mathrm{p}K_{\mathrm{a}}$	A measure of the acidity of a substance, specifically the negative logarithm of the acid dissociation constant K_{a}. It indicates the tendency of a molecule to lose a proton H^+ in a solution. Lower $\mathrm{p}K_{\mathrm{a}}$ values correspond to stronger acids.
A	LJ attractive coefficient for van der Waals energy; it controls the depth of the potential well
B	LJ repulsive coefficient for van der Waals energy; it controls how hard particles repel each other at close distances
a	Attractive parameter in van der Waals equation of state; it represents corrections to the ideal gas equation due to intermolecular attraction
b	Repulsive parameter in van der Waals equation of state; it represents corrections to the ideal gas equation due to finite size of molecules
Q	Electrostatic charge, which is a property of matter that gives rise to electrostatic force
z	Valency of an ion, indicating the number of charges gained or missing from an atom to form the ion
e	Charge of one electron, approximately -1.6×10^{-19} Coulombs
r	Interparticle separation, typically refers to the center-to-center distance between two particles
R	Distance between macroscopic surfaces, commonly used in continuum mechanics. May also refer to an arbitrary linear dimension that characterizes the size of an object
N_{A}	Avogadro's number, approximately 6.022×10^{23} molecules per mole

ρ_{mass}	Mass density of a material, generally expressed in terms of $\text{kg}\,\text{m}^{-3}$
ρ_{number}	Number density of a material, generally expressed in terms of $N_{\text{particles}}\,\text{m}^{-3}$, where the particles maybe atoms or molecules depending on the material
γ_{LG}	Surface tension, also referred to as γ, the energy required to increase the surface area of a liquid by a unit area, typically measured in $\text{mN}\,\text{m}^{-1}$ or $\text{dyne}\,\text{cm}^{-1}$
γ_{SL}	Surface energy of a solid–liquid interface
γ_{GS}	Surface energy of a gas–solid interface
I	The imbibition parameter, or "thirsty parameter". If I is greater than 0, liquid will rise in a capillary tube
g	Gravitational constant, the acceleration due to gravity near the surface of Earth, approximately 9.81 $\text{m}\,\text{s}^{-2}$
M_{n}	Number-average molecular weight, the arithmetic mean of molecular weights of individual chains in a polymer sample
M_{w}	Weight-average molecular weight; a "weighted" mean of molecular weights that takes into account not only the size of each molecular species but also its relative abundance by mass in the sample
$Đ$	Dispersity, a dimensionless measure of the distribution of molecular mass in a given polymer sample, defined as the ratio $Đ = \frac{M_w}{M_n}$
R_{g}	Radius of gyration, a measure of the size of an object, like a polymer chain or a colloidal particle, in a way that takes into account its shape and mass distribution. For a polymer, it provides an average distance of the monomer units from the center of mass of the polymer chain.
T_{m}	Melting temperature; the temperature at which a material transitions from a solid to a liquid, during which it loses its ordered structure.
T_{b}	Boiling temperature; the temperature at which a material transitions from a liquid to a gas
T_{g}	Glass transition temperature in polymers; the temperature at which the polymer transitions from a hard, glassy material to a soft, rubbery material, marking the onset of segmental motion in the polymer chain.
T_{c}	Crystallization temperature in polymers; the temperature between T_{g} and T_{m} where the crystallization degree of a polymer is maximum

h	Planck's constant, a fundamental constant that sets the scale of quantum effects, $6.62607015 \times 10^{-34}$, $\mathrm{m^2\,kg\,s^{-1}}$.
ν	Frequency of a wave, often measured in hertz (Hz).
c	Speed of light in vacuum, exactly 299, 792, 458, $\mathrm{m\,s^{-1}}$.
λ	Wavelength of a wave, often measured in meters (m) or nanometers (nm). May also refer to the skin depth, the distance into the bulk to which the loss of multibody effects impacts the properties of the material
$\hbar$	Reduced Planck's constant, defined as $h/(2\pi)$, where h is Planck's constant. It is a fundamental constant that appears in quantum mechanics, $1.0545718 \times 10^{-34}$, $\mathrm{m^2\,kg\,s^{-1}}$.
ψ	Wavefunction in quantum mechanics, a complex-valued function that encodes the probability amplitude distribution of a quantum system. The square of its magnitude, $\lvert\psi\rvert^2$, gives the probability density for finding a particle at a given position and time.
$\omega(\sigma)$	The intermolecular pair potential for atoms or molecules of the substance at contact
T_R	Melting temperature of a nanoparticle, which is reduced from the bulk melting temperature due to scaling laws
γ_R	Surface tension or energy of a nanoscale droplet or particle, which is reduced from the bulk value due to scaling laws
ΔG	Gibbs free energy change, indicating the thermodynamic potential for a process to occur spontaneously at constant pressure and temperature
E_a	Activation energy, the minimum energy required for a chemical reaction to proceed
A	Pre-exponential factor in the Arrhenius equation, which is a measure of the rate of a reaction without the energy barrier
l_free	Mean free path, the average distance a particle travels between successive collisions
X	Concentration, the amount of a component in a mixture or solution, often expressed in moles per liter, weight percent, *etc.*
ϕ	Work function, the minimum energy required to remove an electron from the surface of a material into a vacuum.
E_f	Fermi level; the energy level below which all electronic states are filled and above which all states are empty at absolute zero temperature.

E_{cb}	Energy of the conduction band; the lowest energy level that is free to move and conduct electricity in a material.
E_{vb}	Energy of the valence band; the highest energy level that is normally filled with electrons in a material.
E_{g}	Bandgap energy; the energy difference between the top of the valence band and the bottom of the conduction band, indicating the energy required to move an electron from the valence band to the conduction band.
d	Interplanar spacing in Bragg's law; the distance between crystal planes that results in constructive interference of X-rays scattered off those planes.

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Part I: Introduction to Introduction to Nanoengineering

1 Nanoengineering: At the Center of It All

All areas of learning are interconnected. You cannot have chemistry without physics, and you cannot have biology without chemistry. Although nanoengineering is a new field, it stands at the intersection of several disciplines that we are already familiar with. The significance of learning about nanoengineering early—or really at any point—in your education is that it allows you to visualize how the knowledge acquired in other classes manifests in the real world. It also represents the forefront of nearly all fields of engineering. Moreover, a considerable portion of the discoveries in basic sciences that result in commercially viable products achieve this through some form of nanoengineering application. For example, information processing using microchips with transistors made on the nanoscale, drug delivery vehicles for vaccination and cancer therapy based on nanoparticles, composite materials for ultralightweight aircraft that incorporate nanofibers, and new materials for batteries and solar cells can only be understood through the "nano" perspective. For a video primer to this chapter, visit https://youtu.be/Rzm8gqknP70 or scan the QR code:

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1.1 Introduction

When I was in high school, my beat-up, loaner textbook which belonged to the school was titled *Chemistry: The Central Science*. "Central," I wondered, relative to what? Apparently, central, in relation to physics on one side and biology on the other. That is, physics—with its focus on atoms, electrons, photons, and thermodynamics—underlies the rules of chemistry, just as chemistry—with its focus on bonding, reactivity, and interactions between molecules—provides the basis for biology.

The biologist Edward O. Wilson described such connectedness between areas of science as *consilience*. Consilience literally means the "jumping together"—or ultimately the *unity*—of knowledge. The chain of relatedness of scientific fields is often discussed in terms of a *discipline* and an *antediscipline*. An *antediscipline* is the discipline that "comes before," that is, the field of learning that provides the foundation for the next field. For example, physics is the antediscipline of chemistry, and chemistry is the antediscipline of biology.

Given that few universities offer degrees in nanoengineering, what is the relationship between nanoengineering and other, more established, fields? Which fields provide the basis for nanoengineering, and which fields, in turn, does nanoengineering provide the basis for? How is nanoengineering related to the natural sciences and engineering? And, what is the difference between the similar-sounding words of *nanoengineering*, *nanoscience*, and *nanotechnology*?

The antedisciplines of nanoengineering are certainly each of the "big three" of the natural sciences: physics, chemistry, and biology.[†] However, the relationship between nanoengineering and the other engineering disciplines is different. It is not a linear relationship but rather a convergence based on the scale of the physical system. See Figure 1.1.

So, I no longer believe that chemistry can be considered the "central science."[‡] I have instead come to believe that the field that is truly at the center of everything is nanoengineering. Nanoengineering is the understanding and use of materials and phenomena that occur on the scale of around 100 nm or less. Implicit in the word "engineering" is the use of these structures for the benefit of society. Nanoengineered products appear in microelectronics (integrated circuits), medicine (nanoparticles for drug delivery), energy

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[†] The "natural sciences" as differentiated from the "social sciences"—sociology, psychology, linguistics, economics, *etc.*—and from engineering. The "physical sciences," traditionally physics, chemistry, and sometimes math, are a subset of the "natural sciences."

[‡] Blasphemy for someone who holds all their degrees in chemistry!

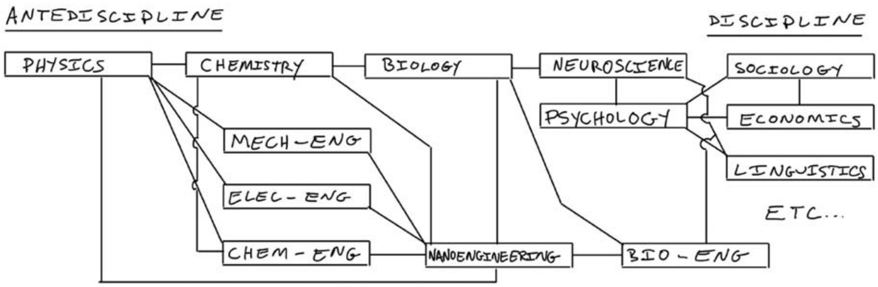

Figure 1.1 The authors' view of the relationships between fields in science and engineering. Would you construct the map the same way?

conversion (solar cells) and storage (lithium ion batteries), and chemical manufacturing and environmental remediation (in the form of catalysts).

Nanoengineering exists at the frontiers of most traditional engineering disciplines—certainly chemical, mechanical, electrical, and biomedical engineering—in two distinct senses. The first sense pertains to the size scale: when structures considered by these kinds of engineers are shrunken to dimensions of 100 nm or less, they are best viewed through the lens of nanoengineering. The second sense involves the exploitation of new physical effects to solve problems in the real world. Classical engineering, based on the laws of Newton, work effectively when treating objects as if they have no internal structure. Consider a block on an inclined plane from high school physics. In this scenario, the simplification of the block and the plane as solid objects with no internal structure works very well for objects that you can see with your eyes. Indeed, much of what needs to be known about mechanics and materials science to produce "macroscopic goods" (*e.g.*, bridges, automobile engines, dishwashers, and radar antennae) is already known. On the other hand, the frontier of research in these areas—which are likely to uncover new physical effects and thus technologies that could transform everyday life—lie at the nanoscale.

1.2 Nanoengineering, Nanoscience, and Nanotechnology

There is often some confusion among students (and professors) regarding the terms *nanoengineering*, *nanoscience*, and *nanotechnology*. Our working definition of *nanoengineering* is *the development and use of materials and systems whose properties are derived from physical effects that occur when matter is constrained in one or more dimensions to*

100 nm or less. The study of these physical effects, driven not necessarily by application but by curiosity, is *nanoscience*. Finally, devices and commercially sold systems that are the products of engineering are examples of *nanotechnology*. We regret if there are likely instances of these terms in this very book which do not align very closely with these definitions. For such instances, we are sorry.[§]

1.2.1 Nanoengineering in a Flask *vs.* Nanoengineering on a Wafer

Now is as good a time as any to admit how controversial the above definitions of "nano" are, even among people who work in "nano" throughout their day. Indeed, words with this prefix mean different things to different people. These differences have led to some comical interactions in my journeys as a professional nanoengineer. For example, it is very common for professors to make a few trips per year to different universities to give talks about their research. During this type of trip, the speaker visits with multiple faculty members in their offices to discuss research or education, or merely to reminisce about old times. During one such visit several years ago, a professor I had never met was adamant that nanoengineering was simply *colloid science*[¶] with a new name. Furthermore, they asserted that there was nothing novel about nanoengineering, and that it was merely a form of "marketing," designed to recruit students and to attract research funding. I found this point of view unsettling and bizarrely confrontational.[‖]

My interrogator was correct that colloid science describes the forces between suspensions of nanoparticles, such as those found in paint, fat globules in milk, and nanoparticles containing mRNA vaccines.[**] However, colloid science, as venerable and as important a field as it is, is only a part of nanoengineering. You see, my exposure to nanoengineering came from a completely different perspective. In my PhD research, I developed some techniques to make arrays of nanostructures with controlled dimensions. These structures were made on flat, two-dimensional surfaces for applications in chemical sensors, light filters, and solar cells. In this respect, my work was more akin to the fabrication of microchips than it was to colloid science. Nevertheless, I was so taken aback by the stridency of my interrogator

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[§] But only a little.

[¶] The study of small particles suspended in liquids.

[‖] Them's fightin' words!

[**] In fact, the excellent—though advanced—textbook *Colloids and Interfaces*, by Prof. John C. Berg of University of Washington, acknowledges the connection to nanoengineering in its subtitle: *A Bridge to Nanoscience*.

that I could not articulate my views. Having served as a professional professor in a nanoengineering department for more than a decade, I now have a better idea of how I would have responded to my inquisitor, who was so sure that there was only *one* kind of “nano.”

In fact, there are two kinds of “nano”: “nano” in a flask and “nano” on a wafer, see Figure 1.2. “Nano” in a flask is synonymous with colloid science, while “nano” on a wafer is akin to microelectronics. “Flask nano” is also closely related to chemistry. That is, in chemistry, you synthesize things in a flask. Chemistry becomes colloid science when the substances you synthesized assemble into particles and arrangements of particles in a solution. “Wafer nano,” on the other hand, is closely associated with electrical engineering. You start with a silicon wafer, pattern your transistors, capacitors, and conductive traces, and dice it up into microchips. The other way to think about this type of application is to take a circuit board and shrink it down to nanoscale dimensions.

Flask nano produces structures in random locations in a flask or reactor but it does so at a high volume. In contrast, wafer nano produces structures in precise locations but it does so at a low volume.

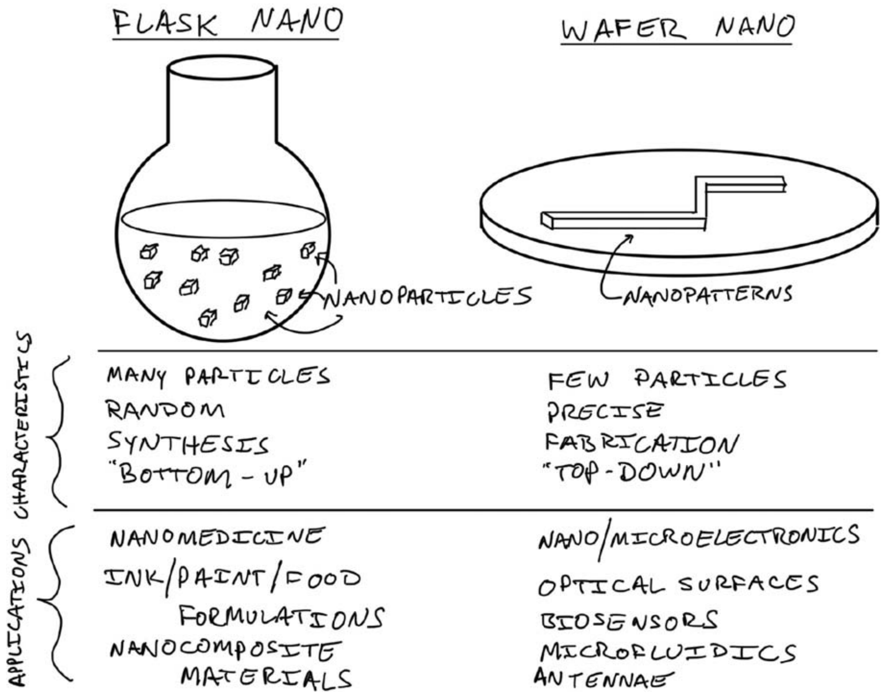

Figure 1.2 Illustration of what we mean by “flask nano” and “wafer nano.” Listed are the characteristics of such systems along with applications for which they are used.

That is, in flask nano you can generate copious amounts of stuff in a three-dimensional “soup” made of chemical reagents (the ingredients) in a solvent medium (the broth). Usually, such particles are used “as-is,” in this liquid environment. That is, they are used *in suspension*: as in milk, a bucket of paint, or a formulation of vaccine. However, if you want to deposit the particles you have made onto a surface, it is very difficult to arrange them into precise geometries (doing so is often called “deterministic assembly”). In other words, you have very little control over where the final particles are arranged on a 2D substrate.

In wafer nano, in contrast, you can make almost any type of 2D pattern on a flat surface, like silicon (think microchips) or glass. It is also possible to make 3D structures by building up layer upon layer of 2D structures, like laying bricks to make a house. Such control can be achieved with outstanding precision using a process called *photolithography*. Photolithography, in our opinion, is the most sophisticated process ever employed for the manufacturing of commercial devices.[††]

The products of flask nano and wafer nano are quite different in appearance, but the rules which govern their behavior are the same. For example, electrostatic forces, including *van der Waals forces*, partially determine whether you get a stable suspension of particles or a solid clump. At the same time, these forces are responsible for the stickiness of metals, ceramics, and semiconductors to each other in solid, planar devices. Moreover, the optical and electronic effects of confining materials to nanoscale dimensions are equally applicable to both “flask” and “wafer” forms of nanotechnology. For example, the nanoscale processes responsible for the fluorescence of semiconducting nanocrystals in a flask (or perhaps some day in the bloodstream) are the same as what happens in the diffuser panels in quantum LED (“QLED”) high-definition TVs. Finally, the physical effects of size confinement are ubiquitous. We will find many consequences of the fact that when the critical dimensions of an object approach the atomic scale, materials have a significantly larger proportion of their atoms on the surface. That is, as objects shrink, the fraction of atoms on the surface increases.[‡‡]

The consequences of size confinement are profound. Consider the example of chemical reactivity. In solid catalysts with nanoscale

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[††] Such sophistication comes at a cost: A new semiconductor manufacturing facility, called a *fab*, has a cost in the billions of dollars!

[‡‡] Consider a cubic nanoparticle consisting of 3 atoms on each edge, or 27 nanoparticles total. Exactly 26 atoms are on the surface and only one is in the bulk (the one in the center). If you shrink the cube to 2 atoms along each edge, there are 8 atoms total, and every single one of them is on the surface!

dimensions, there are many more active sites for chemical transformation than there would be if the catalyst were a big chunk with smooth sides. For applications in sensing, chemical and biochemical analytes can attach and detatch more quickly from the surface of the sensing material if it has a lot of surface area relative to its mass or volume. Moreover, the signals arising from the binding and de-binding of the analytes to the sensor material are produced more strongly and more immediately. All of these effects are common to materials produced through both flask nano and wafer nano, and thus all fit under the umbrella term of *nanotechnology*, understood by *nanoscience*, and produced by *nanoengineering*.

1.3 Engineering Across Traditional Boundaries

Nanoengineering draws inspiration from—and has an effect on—essentially all areas of science and engineering.[§§] By learning about nanoengineering as an independent discipline and your native "STEM language," you get to learn about the good stuff first. That is, you get to take a supersonic journey directly to the frontiers of science and technology, without the need to retrace the steps of centuries of work carried out by generations of scientists and engineers. For example, what required mechanical, chemical, and electrical engineers decades to incorporate into world-transforming technologies—*e.g.*, the strength of carbon nanotubes, the biocompatibility of lipid-based nanoparticles for drug delivery, and light emission from quantum dots—serves as the starting point for nanoengineers. Purists will say "you have to learn the fundamentals first!" And you will learn them. But asking a nanoengineer to get all the way through a physics, chemistry, or engineering degree before learning the good stuff would be like asking a sociologist to first learn everything about neuroscience and psychology before the first semester of sociology course, which is normally undertaken during the first year of undergraduate studies.

1.3.1 All Roads Lead to Nano

When we started the Department of NanoEngineering at UC San Diego in 2007, we recognized that the frontiers of most engineering fields lay in nanostructured materials. Consider a few examples: microprocessors in which the transistors have dimensions of less

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[§§] Except maybe cosmology?

than 10 nm; composite materials for aircraft which incorporate nanocarbon fibers; lipid nanoparticles for the delivery of mRNA vaccines; and display technologies utilizing semiconductor nanocrystals—*i.e.*, *quantum dots*—for increased vibrancy of the images. Ask yourself, at what point in an undergraduate curriculum did the individuals who engineered these marvels of technology learn how to do this? The answer is nowhere. They learned how to accomplish these feats on the job, or by accident. In this book, we will teach you how to "skip to the end." That is, learn how to arrive at the frontier of science and engineering without having to earn a degree in a discipline which is only somewhat related to what you want to do after graduation. That is the power of nanoengineering that we are going to share with you.

1.4 Traditional Science Disciplines

The traditional science disciplines, sometimes called the *natural sciences*,[¶¶] include physics, chemistry, and biology. Just as biology is linked to physics through chemistry, nanoengineering is a product of chemistry, understood using physics, and often has applications in biology, or at least the biomedical sciences.

1.4.1 Physics and Nanoengineering

Nanomaterials derive their unique properties from their small sizes and the physical effects that result from this confinement. These effects often arise from the fact that a material sample with nanoscale dimensions has a large fraction of its atoms on its surface. The atoms at the surface have *unsatisfied valencies*, or bonds that they could form or would like to form, but have not done so. Visualize molecules at the surface of a thin puddle of water. When these surface molecules look up, toward the air, they find that they lack *stabilizing electrostatic interactions* with other molecules like them. That is, they are deprived of around half the "bonds" that are experienced by atoms deeper in the bulk of the material.[‖‖] Effects arising from the missing interactions of atoms or molecules near the surface give rise to several

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[¶¶] Other science areas outside of the natural sciences are the social sciences and engineering.

[‖‖] The word "bonds" is in quotation marks because we are talking about two kinds of bonds: "real," or covalent, bonds which involve sharing of electrons, and weaker—but still really important—bonds that arise from electrostatic interactions. These electrostatic interactions include dipole–dipole, dipole-induced dipole, and London dispersion effects, which you may have heard about in your high school chemistry class and which we will describe in a lot of detail in Chapter 2.

properties of nanoscale materials. Such surface-associated properties include greater chemical reactivity, lower surface tension (for liquids only), reduced melting points (for solids only), and other effects. Collections of nanoparticles also organize themselves into dynamic systems based on principles of electrostatics and entropy. For example, nanoparticles—just like gas molecules in a container—like to spread out. These *osmotic* or entropic forces give rise to a range of important physical effects that occur on the nanoscale but have consequences that can be measured on the *macroscopic* scale.***

1.4.1.1 Matter, Energy, and Force

Matter is the substance of which all things are made. In turn, matter is made of atoms and molecules, and can be found in one of the three basic phases (*i.e.*, solids, liquids, and gases), along with a few other kinds that are important for various reasons (*e.g.*, plasmas and supercritical fluids). The properties of matter depend not only on the properties of atoms and molecules (size, charge, *etc.*), but also on the way in which these atoms and molecules interact.

Forces between atoms and molecules—the so-called interatomic or intermolecular forces—are hugely important. These non-covalent bonds[†††] are interactions that underlie biology, materials science, and everyday phenomena (see Chapters 2 and 3). For example, the strength of these intermolecular forces determines whether the molecules in a given substance will form a solid, liquid, or gas, at a given temperature and pressure. Intermolecular forces, in turn, can be predicted by understanding the potential energies with which the atoms or molecules interact, but *only if we know how this potential energy changes as the atoms, molecules, or nanoparticles get closer together or move farther apart*. To illustrate with a familiar example, we know that the gravitational force is attractive because your potential energy *increases* as you climb a hill, and *decreases* as you climb down. Indeed, we will learn that the numerical value of the energy of the system holds no physical significance except in its relationship to a reference state (see Figure 1.3). In the case of the gravitational potential energy of a system comprising you and the earth, the energy of the reference state (you standing on the ground) is set to zero, by convention. In other systems, like those consisting of atoms, molecules, or nanoparticles, the reference state is chosen such that the interacting objects are as far apart as possible.

*** Meaning you can see it with your eyes.

[†††] Meaning they do not share electrons, as in a chemical bond.

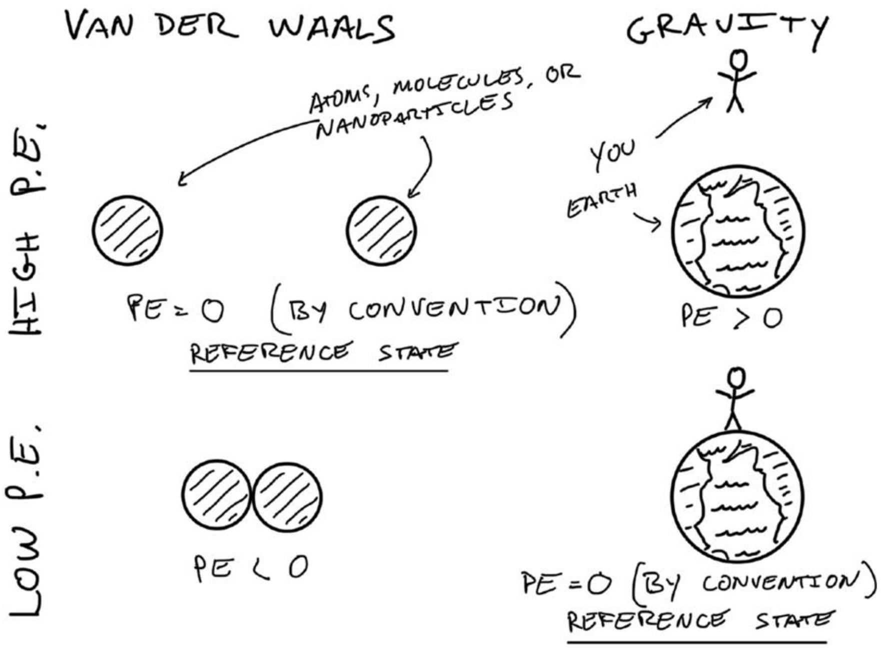

Figure 1.3 Two examples of reference states used in calculations of potential energies: a van der Waals interaction between atoms, molecules, and nanoparticles (left) and a gravitational interaction between you and the earth. Regardless of the reference state chosen for a potential energy of zero (large separation for particles or objects in contact for gravity), we may always say that the force is attractive if the potential energy decreases, or becomes more negative, as the objects get closer together.

In other words, the amount of force between molecules, nanoparticles, and objects is equal to the rate of change of the potential energy between them. Thus, to say that the potential energy of a system is <0 or negative—usually treated as favorable—does not mean anything unless we know what the energy was before that state emerged. That is, the “before” state: the state with all the atoms held apart at infinite separation, at the farthest corners of the universe. This artificial reference state ensures that there is no energy of interaction at all—*i.e.*, the potential energy of interaction is zero. Thus, by convention, this arrangement means that when objects are stuck together, their potential energy of interaction is a large negative number.

1.4.1.2 Light and Waves

One of the defining features of materials with nanoscale dimensions is that they interact with light differently than do materials with macroscopic dimensions. Such properties of matter at the nanoscale are a consequence of the physical confinement of *electronic states*, or the “places” an electron either lives or is allowed to live. In other words, the available energy levels and/or the physical locations which an electron may occupy when confined within a nanoscale structure. Interactions between light and matter are dictated by a branch of physics called *quantum mechanics*. *Quantum* in this case just means that quantities like energy, wavelength, frequency, momentum, and so forth can only have certain values and not others. This property is called *quantization* and means that properties can have only discrete values and not a continuous range of values.

The interaction of light and nanoparticles is a branch of nanoscience called *nanophotonics*, which is the basis of many fields of physics and modern technology. For example, optical signals confined to optical fibers under the oceans mediate much of the transfer of digital information, globally. Light–matter interactions can also be used to glean the properties, shapes, and energies of particles of matter: when a photon—a tiny particle of light—strikes a molecule, nanoparticle, or surface, one of many different things can happen. The photon may be scattered or absorbed by the particle, or it may pass directly through the particle. To a large extent, the fate of the photon which interacts with a particle of matter depends on the energy of the photon and the size of the particle. For one thing, as stated above, the size of the particle determines the energy that electrons which reside in the particle can have. The energies of photons that can be absorbed often correspond to the *energy gaps* between these energy levels for electrons. Absorption occurs when an electron gets *promoted* from a lower energy state to a higher energy state. Photons—which consist of oscillating *electromagnetic waves*—can transfer energy to these electrons. The size of the particles determines the allowable energies of electrons, and thus which photons can be absorbed. When an electron falls from a higher energy state to a lower energy state, a photon may be *emitted*. This process, *emission*, can be either *fluorescent*, which is usually bright and instantaneous, or *phosphorescent*, which is usually dim and occurs over a long time (think glow-in-the-dark stars or stickers, possibly on the walls of your childhood bedroom).

For nanoparticles made of metal, there is a special type of phenomenon called *localized surface plasmon resonance (LSPR)*. The LSPR involves the periodic oscillation (sloshing back and forth) of the loosely held conduction electrons at the surface of the particle. Particles that are highly symmetric like cubes and spheres exhibit

LSPR at only one frequency. However, those with oblong shapes (*e.g.*, like cylinders or grains of rice) exhibit two distinct LSPRs: one for the long dimension and another for the short one.[‡‡‡] Thus, if you can collect and analyze the absorbed, scattered, and emitted photons, and plot the intensity as a function of energy (or equivalently as a function of wavelength or frequency), you can learn a lot about the size, shape and composition of a nanoparticle. This group of techniques, collectively called *spectroscopy*, is among the most powerful types of research tools available to a nanoengineer (or chemist, materials scientist, or astronomer). The power of spectroscopy is that it reveals aspects of the structure and the composition of a material, even if the sample is too small to see using a microscope. In this book, we will discuss many examples of the use of spectroscopy to elucidate (shed light on, pun intended) the structures of nanoparticles.

1.4.2 Chemistry and Nanoengineering

In order to engineer nanostructured materials, the initial step is to have the capability to make them. The ability to synthesize materials, including nanomaterials, is the realm of chemistry. That is why chemistry forms the basis of a significant portion of nanoengineering.[§§§] For example, semiconductor nanocrystals (quantum dots), metallic nanoparticles, and polymer nanoparticles are all synthesized using techniques common to chemistry. In fact, the manufacturing of microprocessors using techniques such as photolithography was enabled by chemical inventions such as *chemically amplified photoresists*.[¶¶¶]

1.4.2.1 Molecules

A molecule is a collection of atoms which are bound to each other in a precise 3D arrangement. The bonds between these atoms are covalent, meaning that they share electrons. What differentiates a molecule from any old material is that a molecule has finite extent and size (a few tens of nanometers, maximum). Moreover, every other molecule of the same type has exactly the same structure, and is

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[‡‡‡] A spherical particle is called *isotropic*, while one with unequal dimensions is called *anisotropic*. These words appear in many other contexts, such as liquid crystals, which derive their most interesting properties from phases which exhibit alignment of molecules along a single axis with a high degree of *anisotropy*.

[§§§] At the time of this writing, around one third of the faculty in the Department of NanoEngineering at UC San Diego have degrees in chemistry.

[¶¶¶] A photoresist is a light-sensitive polymer on which one can project images to modify the silicon wafer or other substrate beneath, as in the fabrication of computer chips.

therefore interchangeable. Due to the unique bonding properties of carbon and the ways in which it can bond with itself, the skeletal structures of molecules mainly consist of carbon atoms. Thus, the chemistry of molecules is synonymous with *organic chemistry*. Organic—*i.e.*, carbon-based—structures are named so because they are the basic building blocks of life: proteins, nucleic acids, carbohydrates, fats, and other molecules like hormones and neurotransmitters are all organic molecules. Synthetic compounds like fuels and other combustibles, some pharmaceuticals, and plastics represent extremely important areas of industrial manufacturing and engineering.[‖‖‖]

Organic structures, specifically organic nanostructures, are everywhere. Look around you, particularly the objects and surfaces of objects in your current environment. Whether you are in an office, classroom, library, desert, or beach, it would be challenging to find any object that is not made of or covered with organic or molecular materials. Even desert sand and rocks have a surface microbiome (the "biocrust") made of many types of microorganisms, lichens, and fungi. As you are likely indoors, consider that the window, although its bulk structure is silicon dioxide glass, is covered with either polymeric coatings or adventitiously (not inherent to the material, accidentally) absorbed organic substances from the air—possibly even from your breath! Thus, the ability to engineer materials at the nanoscale requires, at the very least, a functional understanding of molecular species.

1.4.2.2 Reactivity

Like all forms of matter, nanostructures are made of atoms and molecules, and thus have the potential for reactivity. Thus, they are subject to change and can also be engineered to bring about changes in their environments. In the field of catalysis, which often uses nanoparticles or nanostructured surfaces of larger samples to induce chemical changes, reactivity is their primary function. However, sometimes it is necessary to create a nanoparticle and suppress its reactivity. For example, you would not want a nanoengineered drug delivery system to damage cells or internal organs. Knowledge of chemical reactivity also plays a role in the synthesis of nanostructures

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[‖‖‖] We fully realize that the word "organic chemistry" scares a lot of people, but all that "organic" really means is that it is derived from carbon. Perhaps a more suitable name would be "molecular chemistry," or "the chemistry of molecules." We think this substitution could be made without losing any precision whatsoever.

in a flask. Many tried-and-true methods for the synthesis of nanoparticles made from semiconductors (*e.g.*, silicon, cadium telluride, lead sulfide, *etc.*) and metals (*e.g.*, gold, silver, copper, palladium, platinum, *etc.*) exist in the literature with procedures that are relatively easy to follow. Like the wheel or the multiplication table, such methods do not need to be invented again. While this book will not cover chemical reactivity to the same extent a course in organic or inorganic chemistry, it is important nonetheless to know some key aspects. Such instances will be covered in this book where appropriate, for example, in the sections on catalysis and the synthesis of nanoparticles. However, there will not be a separate section on reactivity.

1.4.3 Biology and Nanoengineering

Some of the most exciting potential applications of nanoengineering are found in biology or biomedical technology. One only needs to consider the success of the mRNA vaccines against the coronavirus that causes COVID-19 to realize the impact of, in this case, nanoscale organic vehicles that deliver mRNA. Nanoscale drug-delivery vehicles have been around for decades, but their sophistication is rapidly increasing. In the case of delivering mRNA molecules, the justification for using nanoparticles is manifold. For one thing, mRNA vaccines cannot function without a vehicle to deliver them into the bloodstream and to the cells of the host. One reason is that mRNA molecules are unstable and would be hydrolyzed instantly in the bloodstream if not encapsulated. Moreover, if they were encapsulated in some random particle, the immune system would recognize them immediately and destroy them. So, structures called *lipid nanoparticles* or *liposomes*, which have polymeric or molecular components, were engineered so as to both encapsulate the mRNA molecules and to target them to the appropriate cells.

1.4.3.1 Biology: A Natural Proof of Principle

Nanoengineers often draw inspiration from biology. Biological systems are full of examples of functional nanostructures. For example, molecular motors spin bacterial flagella, viruses are quasi-living nanoparticles, and geckos stick to walls using a mechanism that arises inherently from nanoscale phenomena. Although there was much hype in the 1980s and 1990s about hypothesized "molecular assemblers"—little robots that put molecules together atom by atom—biology already accomplishes this. For example, enzymes and ribozymes are basically automated nanoscale robots. These automatons can affect chemical reactions to generate molecular and nanostructures from simpler components. Engineers often attempt to borrow from the design principles that permit such exquisite control over molecular structures by these *natural* molecular assemblers.

1.5 Engineering Disciplines

Engineering is the use of scientific principles and physical effects to solve problems. My whole life, I have been interested in science fiction. I loved *Star Trek* and *Star Wars*,**** and the magic of other worldly devices: the transporter, warp speed, and light sabers. Who, among those reading this book, has not been inspired by sci-fi and fantasy fiction? However, it was not until I started majoring in science that I learned that science itself—the process of pure discovery for its own sake—involved much more patience and bookkeeping than I could handle. Moreover, the products of science I wanted to help create—light sabers and the rest—would not come directly as a result of scientific discovery but due to a closely related realm of human learning, engineering.

Unlike many professional scientists and engineers, I do not make a sharp distinction between science and engineering. For example, there is no engineering without science, and you cannot do good science without tools created by engineering. Moreover, inventing a new material or device or algorithm—*i.e.*, engineering—only gets you so far if you do not know how it works. So to learn how your invention works, you again need science. So, while there may be a dictionary difference, most of us working in technical research are at some level practicing both science and engineering. We pass between one frame of mind and the other, without even thinking about it. In any case, engineering, just like science, comes in many different flavors with broad zones of overlap. Below, I briefly mention how nanoengineering learns from and contributes to the most common fields of engineering.

1.5.1 Materials Science, Materials Engineering, and Nanoengineering

In a way, all nanoengineering is materials science, because nanoscale systems are, of course, made of materials. However, the two fields

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****Yes, it is possible to love both *Star* things.

have different intellectual roots. Historically, materials science arose from *metallurgy*: the production of metals from oxidized minerals by *smelting*, and subsequent *casting*, *forging*, or *machining* of the base metal into useful parts. In particular, how these processes lead to the internal structure that determines the properties (*e.g.*, hardness, strength, flexibility, *etc.*) of the finished object. Thus, the arrangement of atoms, sizes of grains, kinetics of processes, and thermodynamics of phase changes, are the bread and butter of materials science. These structures and processes are probed with X-ray diffraction techniques, electron microscopy, and calorimetry. To be sure, nanoengineering uses many of the same tools. However, broadly speaking, compared to materials science, nanoengineering is often concerned with the *surfaces* of such structures and the properties which emerge from size confinement. Nevertheless, you will still find materials scientists doing nanoengineering, and *vice versa*. It is not that there is no overlap, rather, the center of the bullseye is somewhat different for the two fields.

1.5.1.1 Hard and Soft Materials

One major point of divergence, however, between classical materials science and nanoengineering is how they treat soft materials—polymers, gels, biological tissue, and self-assembled structures like micelles and liposomes. Indeed, materials science did not subsume the study of polymeric materials until relatively recently. Polymers, however, play a central role within nanoengineering, given the criticality of *photolithography*[††††] and *photoresist*[‡‡‡‡] chemistry as the central technique of manufacturing on the nanoscale. Moreover, organic molecules of the type that form micelles and lipid nanoparticles are the basic building blocks of solution-based nanotechnology.

1.5.2 Chemical Engineering and Nanoengineering

When I was a student, I used to think that chemical engineering was a synonym for chemical manufacturing. I realized much later in my academic career that while chemical engineers are employed in chemical manufacturing, the design of large-scale chemical synthetic

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[††††] The process by which patterns are created in metals and semiconductors using a light-sensitive polymer called a *photoresist*.

[‡‡‡‡] The light-sensitive polymer into which patterns are etched with light and subsequent chemical processing. Layers of photoresist serve as “stencil masks” through which the underlying substrate—*e.g.*, a silicon wafer—can be modified and eventually formed into a microchip.

sequences is indeed still carried out by chemists.[§§§§] Chemical engineers, in contrast, are concerned first and foremost with the continuum properties of fluid media[¶¶¶¶] that may or may not have reactions going on within them. That is, how to induce a chemical change on the large scale while making it as safe and as profitable as possible. While chemical engineering has matured, the frontier of research in the field has gone from phenomena that occur on a continuum scale—*i.e.*, where you can ignore molecular details—to the molecular scale—where you cannot. Chemical engineering interfaces with nanoengineering in many areas, but especially in polymer science. Not only is the manufacturing of polymers a hugely important area for chemical manufacturing, but polymers themselves are a highly important intermediate in other manufacturing processes.[‖‖‖‖]

1.5.2.1 Fluid Flow and Transport

Transport phenomena—including the transport of heat and mass—are the bedrock of chemical engineering, and many of the tools used to treat these phenomena on the macroscopic scale also apply to the nanoscale. Indeed, nanoscale processes are subject to heat transfer by convection, conduction, and radiation, and more or less follow the rules of continuum fluid mechanics. One example of an effect of size confinement is the greater probability of *laminar flow*[*****] between adjacent layers in a *microfluidic channel.*[†††††] Indeed, the field of *microfluidics*[‡‡‡‡‡] involves a suite of tools and techniques for transporting liquids and generating droplets and even nanoparticles. Often, such *lab-on-a-chip* type devices are used in analysis of small samples or generating particles for therapies. The lipid nanoparticles used as delivery vehicles for mRNA vaccines and chemotherapeutic agents are famous examples. We will find that the transport of nanoparticles is often driven by *entropic* or *osmotic* effects. Namely, gradients in concentration or differences in the number of available *statistical microstates* between one state and another. The entropic or osmotic driving force propels the system to evolve in a manner that maximizes the number of states available under given conditions.

[§§§§] Specifically, *process chemists*.

[¶¶¶¶] That is, liquids and gases.

[‖‖‖‖] Consider the centrality of polymer photoresists in microelectronics manufacturing, see Chapter 12.

[*****] Laminar flow is flow with no mixing between adjacent layers, or lamellae.

[†††††] A microfluidic channel has cross-sectional dimensions of less than approximately 1 mm.

[‡‡‡‡‡] Microfluidics is the field which attempts to understand and exploit transport of fluids using small channels.

1.5.2.2 Separations

Separations comprise a range of industrial processes, from distillation of ethanol in the production of whisky to water purification by reverse osmosis. A key technology which enables separations in fluids is a often a nanoporous *membrane*, and thus the design and synthesis of such membranes involve nanoengineering. At the very least, they involve the use of a polymeric structure whose system of pores may allow for the transmission of some types of molecules but the exclusion of others. Separation is most often carried out on the basis of size, but could also be based on charge or chemical functionality. Consider the case of dialysis bags used in management of kidney disease.

1.5.2.3 Catalysis

Catalysts are chemical species that speed up a reaction but which are not part of the reactants or products. They work by lowering the *activation barrier*—or the *potential energy*—embodied by the *transition state*, which is a short-lived molecule halfway between reactants and products. If the barrier (hill) is lowered by the involvement of a catalyst, the reactants can get over the hill much, much more quickly. In fact, many reactions do not occur within any reasonable time frame because there is no catalyst present. Catalysts thus make the impossible possible. They are used ubiquitously (everywhere) in the manufacturing of chemicals, materials, and fuels.

Examples of catalysts are small organic molecules, metal atoms or ions surrounded by organic *ligands*,[§§§§§] biological enzymes, and surfaces. When we say "surfaces" we are usually talking about surfaces that have some kind of nanoscale features, often roughened or having pores throughout their bulk (like a type of mineral known as *zeolite*). Alternatively, catalysts can exist in the particulate form. The advantage of using surfaces and particles as catalysts is that they can be easily removed from the reaction mixture and reused later. The importance of catalysts has turned them into a lucrative industry: the market for catalysts is in the tens of billions of dollars annually, while the value of chemical manufacturing enabled by catalysts is many trillions, worldwide.

1.5.3 Mechanical Engineering and Nanoengineering

The purview of mechanical engineering is the forces, movements, heat flow and energy flow, usually within or between solid

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[§§§§§] In this context, a ligand is an organic molecule that stabilizes a metal atom or ion by binding to it.

structures.[¶¶¶¶¶] Most of the time, classically, mechanical engineers treat such processes using continuum theories. Continuum theories ignore the atoms and molecules of which matter is made. That is, such theories lack granularity. Classically, for most systems obeying Newton's laws of motion, atoms, electrons, and molecules can be ignored. However, as the frontiers of mechanical engineering have touched on kinetics, heat flow, kinematics, and forces in more sophisticated, modern systems, it has become impossible to ignore molecular effects. A good example is the theory surrounding *microelectromechanical systems (MEMS)*. In such systems, the effects of size confinement are ever-present. Moreover, it is not uncommon to find mechanical engineers at work in explicitly the nanoscale domain. Indeed, one does not even need to consider the existence of atoms and molecules to arrive at one of the most prevalent or striking consequences of size confinement, that is, *scaling laws*.

1.5.3.1 Scaling Laws

Some of the most import consequences that result from shrinking the dimensions of materials comes not from any quantum phenomenon but simply from math. That is, *scaling laws*. Scaling laws refer to the fact that certain dimensions or aspects of a block of material become larger or smaller relative to others as the system shrinks. For example, consider the ratio of surface area to volume of a sphere. The volume of the sphere, $V = \frac{4}{3}\pi R^3$, scales with the cube of the radius. Its surface area, $A_{\text{surface}} = 4\pi R^2$, however, scales with its square. Thus, as a sphere shrinks, the surface area shrinks less slowly than does the volume. To put it differently, the surface area scales with volume in proportion to $\frac{1}{R}$. Small R values give you a big surface area, relative to the volume.

Scaling laws such as the relationship between the surface area and volume are true whether we are talking about objects the size of planets or of tennis balls. But, the physical effects of downscaling do not really become profound until you reach sizes of micrometers ("microns") and less. One example from the field of nanomedicine (see Chapter 13), is the concept of *burst release* (Figure 1.4). Consider the problem of encapsulating drug molecules inside a spherical

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[¶¶¶¶¶] In one conception of the difference between chemical engineering and mechanical engineering, both are branches of engineering dealing with continuum mechanics. However, chemical engineering usually deals with fluids and mechanical engineering usually deals with solids.

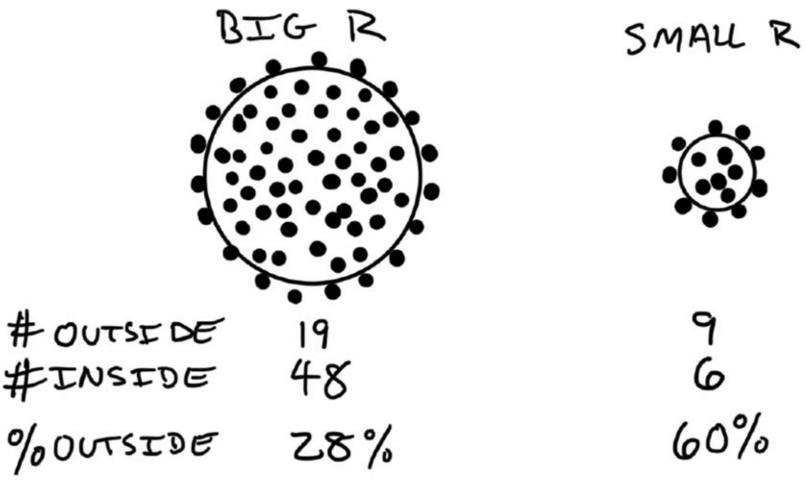

Figure 1.4 Illustration of burst release. As particles get smaller, the ratio of the surface area to volume becomes larger, and more molecules as a percentage of the total molecules are adsorbed to the surface as opposed to those encapsulated in the bulk. Note that in the image, we have drawn circles (2D) instead of spheres (3D). In any case, the scaling is the same: the circumference (surface area) scales with $\frac{1}{R}$ with the interior area (volume).

nanoparticle. The maximum achievable loading will depend on the interior volume of the nanoparticle, along with the drug's solubility. However, given the strength of van der Waals forces on the small scale, you can also expect some fraction of the drug molecules to stick to the surface of the nanoparticles. These molecules will be the first to escape into the bloodstream as soon as the nanoparticles are injected. The smaller the nanoparticles, the greater the surface area compared to the volume, and thus the greater proportion of drug molecules would be released in such a "burst" mechanism. Therefore, one must carefully engineer the nanoparticles system, such that the appropriate amount of drug is released at the appropriate time.

Scaling effects occur whenever you shrink an object, whether or not you consider the atomic structure of the material specimen. However, the existence of atoms and molecules leads to a new set of phenomena that are also a consequence of scaling. For example, in the field of catalysis, it is often the case that atoms closest to the surface are the ones that are the most reactive. Remember, these surface atoms have unfilled capacity to bond to other atoms, whether they are of the same kind in the bulk, or atoms of reactants. Moreover, the smaller the catalytic particle gets—considering the particle as a whole or as bumps on a catalytic surface—the more atoms we have at the surfaces and edges, the more effective the catalytic process. In contrast, a very large sphere, when zoomed in, appears to have atoms arranged in a two dimensional sheet without significant opportunity for molecules to bind and react at the catalyst surface.

The unusual properties of surface atoms do not stop with those located exactly at the surface. In fact, the bonding of a an atom in a solid or liquid usually extends a few layers beyond those in which it is in physical contact. For example, consider a thin film of liquid with nanoscale dimensions. Say that the liquid film is about 5 nanometers thick. As we will find in Chapter 4, the surface tension of the liquid arises due to the difference in potential energy of a molecule at the surface compared to the energy of the same type molecule deeper in the bulk. If you shrink a liquid sample down to molecular dimensions, there is less of a difference in energy between a molecule on the surface compared to a molecule in the bulk, and thus the overall surface tension is reduced. The examples of surface reactivity, burst release, and surface tension are just three examples of size surface to volume effects that have significant effects which can be used in nanoengineered systems.

1.5.4 Electrical Engineering and Nanoengineering

Perhaps no field has benefited more from advances in nanoengineering than the fields of electrical and computer engineering. All of modern microelectronics and thus all of modern information technology is based on nanoscale systems and devices. These devices—microprocessors, integrated circuits, graphics processing units (GPUs), memory chips, *etc.*—are made using fabrication and manufacturing methodologies that are by definition nanoengineering. For example, every integrated circuit in the phone or laptop on which you may be reading the e-version of this book was made by a process called *photolithography*. Photolithography—meaning, literally, writing in stone with light—is the most sophisticated manufacturing process ever devised for a commercial product. It involves chemical processing, manufacturing engineering, chemistry and polymer engineering, and optical physics. The result of this sophisticated process is to make devices such as transistors and capacitors on silicon microchips. The structures on these chips can be made routinely with sizes significantly less than 10 nanometers. While microchips have had dimensions of less than 1 micrometer (or “micron”) for decades, the process of making these devices has always been called *micro*fabrication. Notwithstanding, the prefix "micro" is a misnomer. Indeed, the features on microprocessors are as "nano" as things get.

1.5.4.1 Moore's Law

No concept in technology is more closely associated with the miniaturization of microelectronic devices than *Moore's Law*. Moore's law, named after Gordon Moore, the co-founder and CEO of Intel during much of its rise, noticed that the density of transistors on a microchip doubles approximately every 18 to 24 months. There are several other formulations of Moore's law, with some suggesting that the cost of computation approximately halves every 18 months or the sizes of transistors shrink by half every 18 months, but the overall effect is clear: computational power has been on an exponential rise for decades. Moreover, this growth is enabled by advances in nanoengineering. Indeed, essentially all of the processes we will talk about in this book have played a role in this unprecedented technological development.

1.5.4.2 Microfabrication

Processes of mass production by replicating patterns on 2D surfaces are now centuries old. For example, the Gutenberg Bible, the first book manufactured by the printing press, ushered in a cultural transformation. After this invention, it became possible, if not to read the minds of the authors, then to come as close as possible. The printing press used to operate by first creating large metal sheets with raised features—"boilerplates"—that when inked could be pressed into paper over and over again to make many copies of words on a page. Nanofabrication engineering, in the service of microelectronics manufacturing, has taken these basic concepts and elevated them to completely new heights.[‖‖‖] Instead of boilerplates, modern techniques of replicating nanoscale patterns use transparency masks made of quartz and covered with an opaque layer of chromium with apertures that let light through. These nanoscopic holes can be etched into the metal using a process that starts with a technique known as *electron beam lithography*.[******] This mask is akin to a photographic

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[‖‖‖] Or reduced them to completely new levels of tininess.

[******] Electron-beam lithography, which will be discussed in detail in Chapter 12, is a process which uses a focused beam of electrons to create patterns into a polymer film which is sensitive to beams of electrons. This pattern can be transferred into the chromium film using a chemical etchant.

"negative," a strip of film that contains the image from which the photographic prints are created in a dark room. In nanofabrication processes, we use a modern type of darkroom, called a *cleanroom*.[††††††] The room must be clean, because a grain of dust could be orders of magnitude larger than the devices you are trying to make. If this dust came between the mask and the substrate, it might ruin the entire chip.

1.5.4.3 Optoelectronics of Nanoscale Materials

Electrical engineers at consumer electronics companies like Sony, Samsung, LG, and Philips are doing a lot of nanoengineering. Modern day consumer electronic devices use a wide range of materials which derive their properties from nanoscale phenomena. Take display technologies as an example. Organic light-emitting displays (OLEDs) use molecular semiconductors to emit colored light with high efficiency and with high contrast between adjacent pixels. These nanoscale molecules emit light at particular visible wavelengths which are partly determined by the manner in which their electrons are confined. Even a conventional *liquid crystal display (LCD)* uses rod-like molecules to increase or decrease the brightness of white light that passes through a red, green, or blue color filter. Moreover, *quantum-dot* enabled panels ("QLED" displays) use fluorescent light coming from a sheet of *semiconductor nanocrystals* to generate a color gamut that is warmer[‡‡‡‡‡‡] and more pleasing to the eye. The exploitation of new optical phenomena arising from nanostructured materials like molecular semiconductors, liquid crystals, and quantum dots is the very essence of nanoengineering.

1.5.5 Bioengineering and Nanoengineering

Compared to the ancient core disciplines of mechanical, electrical, and chemical engineering, bioengineering is a relative newcomer.[§§§§§§] Bioengineering is a vast area comprising disparate fields such as

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[††††††] The degree of cleanliness depends on the number of particles of a certain size permitted in the air. For example, a class-100 cleanroom, under the typical definition permits no more than 100 particles with sizes of 500 nm or bigger per cubic foot of air. The people who came up with the system apparently have no qualms about mixing SI and imperial units.

[‡‡‡‡‡‡] Warmer means more red and cooler means more blue; ironically the cooler light is composed of higher energy photons than the warmer light.

[§§§§§§] The fields of "bioengineering," "biological engineering," and "biomedical engineering" have some differences among their practitioners but have large enough overlap that we can group them together here.

biotechnology (including protein engineering), and *biomedical imaging* (which has a lot of overlap with electrical engineering), *bioinformatics* (which involves a lot of computer science), and engineering of orthopedic structures (which shares overlap with mechanical engineering). Like nanoengineering, it is so broad that it can be hard to define, but advances in various areas within bioengineering have already led to marked improvements in human life. As with many of the connections between disciplines we have explored in this chapter, the boundaries between what qualifies as bioengineering and nanoengineering—or even *bionanoengineering*—are not always distinct. The two examples that I will discuss below, tissue engineering and drug delivery, could just as well be discussed in a book on applications of chemical engineering in the medical sciences. Nevertheless, the nano-centered perspective yields some important insights.

1.5.5.1 Tissue Engineering

The design and synthesis of implantable scaffolds for wound repair, bone regeneration, and constructs that control the release of drugs is known as *tissue engineering*.[¶¶¶¶¶¶] When applied in biomedical technology, the use of scaffolds, usually polymers or hydrogels mixed with host-derived cells such as stem cells, is known as *regenerative medicine*. For these cells to adher to these implantable synthetic scaffolds, such constructs must necessarily have nanoscale features. The constructs must also have a porous internal structure that blends in with the physiology of the host, so that it is not rejected by the immune system. That is to say, a material that enabled the creation of new blood vessels in this artificial milieu must be engineered on the nanoscale.

1.5.5.2 Drug Delivery

Perhaps the defining application of the field of nanomedicine is the delivery of drugs using nanoengineered vehicles. The advantages of confining drugs to nanostructures prior to delivery into the bloodstream have been known and exploited for decades. There are many reasons. First of all, naked, unencapsulated drug molecules often have low solubility in the bloodstream. Moreover, they do not always

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[¶¶¶¶¶¶] Some technologists dream that work on tissue engineering and *artificial skin* might pave the way for the creation of android-like creatures like Lieutenant Commander Data from *Star Trek: The Next Generation* or Bishop from *Alien*, or any of the sentient androids from *Westworld*.

reach the diseased tissue, and have adverse effects when they interact with healthy tissue. Nowhere is this unwanted cellular toxicity more problematic than in cancer therapy. Indeed, tumors are human cells, and thus most chemical agents that kill tumor cells can also kill healthy ones.

Thus, nanoscale particles that serve as delivery vehicles for such drugs which can target the cancer cells have been the subject of intense research for decades. In fact, rudimentary forms of nanoparticles in the form of micelles and liposomes have been used to deliver drugs in chemotherapy infusions since the 1970s. If you or someone you know has undergone chemotherapy, it is very likely that the infusion involved some kind of nanoscale vehicle which delivered the drug. Other functions of such particles include evasion of detection by the host's immune system and also localization to the site of the cancer tissue. At the time of writing, the COVID-19 pandemic is receding significantly because of the advent of nanoparticle delivery agents. In particular, mRNA molecules used to encode the spike protein of the coronavirus would be broken apart quickly after entering the bloodstream. Thus, nanoparticles based on lipid (fat) molecules, polymers, and detergent-like *surfactant* molecules are used to encapsulate the mRNA. For these reasons and others that we will discuss in Chapter 13, nanoengineering is expected to continue to increase the power of therapeutics with profound benefits for human health.

1.6 Outlook

Nanoengineering derives its intellectual strength from decades—or even centuries—of learning in the basic sciences. Moreover, we would argue that many of the most exciting challenges in traditional engineering disciplines fall into the category of nanoengineering. While most practitioners in academic and industrial research and development are trained in one of these traditional disciplines, they must learn the principles of nanoengineering on the job. Our goal is to allow you to "skip to the point" and start your education as a nano-minded individual exactly where the action is. Along the way, you will learn deep physical principles—from this course and others—that actually provide a frame of reference for future learning in disciplines which have a more established intellectual history. That is, physics, chemistry, biology, and all the flavors of engineering. This kind of study will be more fun, make more sense, and be highly motivating.

We are excited to share our knowledge with you in the next fourteen chapters.

1.7 Problems

Problem 1

Reflect on what excites you about nanoengineering? Why did you take this course? What do you hope to learn? If you are taking it because "it is required for my degree," then write a few words as to why you chose this degree program.

Problem 2

How big is a nanometer? How many nanometers thick is a red blood cell? A human hair? A cat's hair? An optical fiber? A transistor on a microchip?

Problem 3

Give three examples of products around your space right now that were manufactured using nanoengineering.

Problem 4

Consider an enzyme, which is a protein which evolved in biological systems to catalyze a type of reaction. The enzyme contains a pocket called the *active site*, which binds one or more substrates. Do you suppose that the shape of the active site is most complementary to the shapes of the reactants, the products, or the transition state that resembles the conversion from reactants to products? Why?

Problem 5

Describe at least two consequences of size confinement. These effects can be physical, chemical, or biological.

Problem 6

What are some consequences of the increasing surface-to-volume ratio as objects approach the nanoscale? Consider both mathematically smooth surfaces along with "real" matter consisting of atoms.

Problem 7

In what ways does the field of biology serve as an inspiration for sophisticated nanoengineered systems?

Problem 8

Why are nanoparticles useful as vehicles for drug delivery?

Problem 9

Some people say that the field of nanoengineering began with the speech by Caltech professor Richard Feynman "There's Plenty of Room at the Bottom." Look up the text of this speech. What is your reaction? Which of his predictions have come true?

Problem 10

What is your favorite example of nanotechnology or miniaturization from fiction? In what way is it plausible and in what way is it implausible?

1.8 Solutions

Answer to Problem 1

What excites us about nanoengineering is its central role in essentially all of modern technology. Moreover, its foundations are derived from every area of the basic sciences, from physics and chemistry to biology. From the nanoscale tools used to design and manufacture microprocessors for information technology and artificial intelligence systems to nanoscale carriers used to deliver vaccines and other drugs, nanostructured materials are everywhere, and they are transforming the world. We are excited to be able to contribute to research and education in this field, and to share our passion with you.

Answer to Problem 2

One nanometer (1 nm) is 1 billionth of a meter, or 1×10^{-9} m. A red blood cell is around 2 μm thick, or 2000 nm. A human hair is around 100 μm or 100 000 nm. On average, a cat hair is at most half the diameter of a human hair, or 50 000 nm. A typical multimodal optical fiber is about the thickness of a human hair, including the inner glass core (where the light actually travels) and outer glass cladding. The minimum feature size that can be patterned through photolithography on a microchip is less than 10 nm, although the actual size of a transistor is somewhat larger than this.

Answer to Problem 3

The physical products of nanoengineering are everywhere. Objects that have nanoscale dimensions in one dimension only include myriad thin films of various compositions: metals, ceramics, polymers, and inks. For example, the wrapper on the protein bar I am eating has a shiny aluminum coating that was probably deposited by *sputter deposition*, as well as multiple layers of polymers engineered for various purposes (protective films, adhesion promotors, ink, *etc.*). I am looking through eyeglasses that have many coatings, such as anti-reflective polymers. My phone has a layer of a fluorine-decorated polymer that is only one molecule thick! (The purpose is to make it slipperier for scrolling and writing texts without taking your thumb off the screen, and for making it easier to clean.) My computer, phone, and tablet have dozens of integrated circuits each, all of which have nanoscopic circuit elements like transistors, resistors, vias (conductors that travel up and down through the layers), and other conductive traces, all with dimensions in the tens of nanometers. These structures were all manufactured using *photolithography*, the primary “top-down” tool used for nanoengineering.

Answer to Problem 4

The active site is the place in an enzyme where the reaction takes place. A significant portion of the rest of the structure of an enzyme serves to stabilize and/or define the shape of this active site. In order to affect the reaction as rapidly as possible, the active site should have a shape that is *complementary to the transition state*. A snug fit with the transition state will lower the overall potential energy of the state in which the enzyme and substrate are in physical contact. If the active site of the enzyme were instead designed to fit the reactant(s) instead of the transition state between reactants and products, then the reactants would just sit in the active site like a lazy person watching TV on the couch, with no reason to move toward becoming products. If the active site had a shape which was complementary to the products, the reactants probably would not even bind, and there would be no reaction.

Answer to Problem 5

There are many effects or properties of nanostructures that arise from confining matter to one or more dimensions. In the realm of physical size confinement, the ratio of surface area to volume increases as particles become smaller. This effect is purely mathematical; that is, it happens whether or not we consider the fact that matter is made of molecules! Also, when electrons are confined to small particles of semiconductors and metals, such objects exhibit optical absorbance and fluorescence (*e.g.*, in semiconductor quantum dots) and localized surface plasmon resonances (*e.g.*, in metallic nanoparticles) that do not occur in larger samples of these materials. In the realm of chemical effects of size confinement, the increase in surface area relative to volume places a larger fraction of atoms and molecules near the surface, which can lead to increased catalytic activity.

Physical effects of the size confinement also include the fact that relatively weak forces can have large effects on small particles. That is, small particles are also much more likely to be under the influence of relatively weak forces like van der Waals forces, which do not have a much effect on macroscopic objects compared to the effects of, for example, gravity. For biological systems, the effects of size confinement are related to the fact that cells are small, viruses are small, bacteria are small, and biological macromolecules are small. For example, drug molecules that are encapsulated in nanoparticles drug delivery vehicles can easily sluice through holes in leaky vasculature—*i.e.*, blood vessels—for delivering particles to tumor tissue. Moreover, nanoparticle-based agents can be used in radiology and medical imaging to enhance contrast. Such particles often have strong optical absorption or fluorescence. Such materials include small structures like quantum dots and metallic nanoparticles, which can be injected into the bloodstream and can thus find their way into tight places. Additionally, some organisms have developed the ability to manipulate the surface energy and/or adhesion of their skin. Such abilities make it possible for certain species of lizards, such as geckos, to either walk on water—*e.g.*, the Brazilian pygmy gecko—or upside down on ceilings—*e.g.*, many other species of gecko.

Answer to Problem 6

There are many ways in which the properties of materials change as we approach as we approach the nanoscale. These effects occur whether or not we consider the fact that real material is made of atoms and molecules. For example, the strength of the leg of an elephant scales with the cross-section of its legs, while the weight of an elephant scales with its volume. Also, consider a cube of a catalytic nanoparticle. It has more surface area relative to its linear dimension—independent of its atomic structure—if you scale it down, than does a larger cube. Chemically, what you have with the smaller cube is a greater fraction of its total number of atoms on the surface compared to the bulk. In terms of reactivity, the smaller cube will be more reactive, but its physical properties will also change. For example, the forces between atoms will be decreased because atoms on the surface have fewer van der Waals interactions with other atoms. Thus, the cohesive energy density will be decreased, as will the melting point. These examples point to two kinds of effects that arise from size confinement: (1) effects arising from simple geometry (*i.e.*, math), and (2) effects arising from the fact that the object is made of atoms.

Answer to Problem 7

Biological systems serve as a wonderful inspiration for engineers, particularly nanoengineers. The concept of the *nanoscale assembler*, popularized by K. Eric Drexler, with which atoms can be arranged in precise ways and in large quantities, is already in some sense a reality. That is, biological systems made of macromolecules already perform these sophisticated tasks, particularly the action of metabolism and enzymatic biosynthesis. Also, there are examples of energy dissipating systems in biology that can perform complex, machine-like tasks. These tasks include the action of a ribosome, which can receive instructions from messenger RNA (mRNA) and convert it into protein. Other great examples are in the realm of biological motors, such as the flagella of microorganisms and sperm cells.

Answer to Problem 8

There are a number of advantages of nanoparticles as delivery vehicles for drugs. The first advantage is solubility. Many drug molecules are hydrophobic and do not dissolve in the bloodstream, or they dissolve in very low concentrations in the bloodstream. Moreover, a poorly soluble drug molecule can aggregate with itself. The resulting precipitate can form an embolus—a solid particle which circulates in the blood vessels—that can occlude (block) the healthy flow of blood. The second advantage is the ability to precisely target diseased tissue. In the field of anticancer therapeutics, it is the case that drug molecules that kill cancer cells may also be harmful to healthy cells. Thus, a method of administering the drug that reaches all tissue equally well can be highly toxic. For example, it is often the chemotherapy that makes cancer patients feel sick, not just the cancer itself. The third advantage of nanoparticle drug delivery vehicles (from this admittedly incomplete list) is the ability to encapsulate drug molecules. Thus, a nanoengineer has the ability to control the release of a drug molecule over time. Too large of a release all at once could have toxic effects or could not have the kind of sustained therapeutic power as if the drug molecule were slowly released into the system at a controlled rate.

Answer to Problem 9

There are many people who believe that the advent of nanotechnology was signaled by the physicist Richard Feynman's famous lecture delivered in 1959, "There's Plenty of Room at the Bottom." In this talk, Feynman made predictions about what might be achievable in a future world based on nanotechnology. For example, a motor with a dimension of a very small fraction of an inch, as well as the prediction that it would be possible to fit a very large amount of information in the form of the text of *The Encylcopædia Brittanica* on the head of a pin, with a size reduction of $\frac{1}{25\,000}$. Both of these achievements were achieved by scientists and engineers during this time. For example, the motor was made through a very painstaking assembly of mechanical parts using very fine tools, which, although being very difficult, did not really require any nanoengineering. Writing text on a pinhead took longer but was eventually accomplished by means of writing with an electron beam. Although the entire text of the encyclopedia was not achieved, an equivalent information density was achieved by writing the first page of Dickens' *A Tale of Two Cities*.

Answer to Problem 10

Darren's favorites nanotechnology or miniaturization technology comes from the TV show *Star Trek: The Next Generation*. In this show, the crew of the Enterprise encounters a species known as the Borg. The Borg are half biological, half machine beings that communicate with each other wirelessly and through *subspace* to create something called *The Borg Collective—i.e.*, a collective consciousness involving millions of beings, which can make decisions instantly and as a group, with disastrous consequences! Famously, the Borg try to "assimilate" other biological species and cultures into their collective.

In the movie *Star Trek: First Contact*, it has been revealed that the first step toward assimilation is the injection of nanobots into the bloodstream of the victim. These nanoscale terrorists co-opt the biology and metabolism—and even the thoughts!—of the victim and lay the groundwork for the future installation of electrical and mechanical prosthetic devices characteristic of the Borg's outward appearance (do an image search on Google after you are done with your homework). So, this is certainly a gloomy prediction based on fiction, but it was Darren's favorite, nonetheless. A number of technological hurdles would be required to achieve this level of sophistication for nanoengineered systems. For example, such a system of nanobots would have to have the ability to control matter, affect chemical reactions, and infiltrate cells while overcoming the effects of van der Waals forces, which are extremely sticky on the nanoscale.

1.9 Further Reading

My ideas about consilience originated from Edward O. Wilson's book of the same name. I read this book after my freshman year in college, in the summer of 2002. To this day, I consider it the most important and inspirational book of scientific philosophy I have ever read. In many ways it has guided the development of my own research trajectory, which now combines nanoengineering and chemistry, with neurobiology and human perception.

E. O. Wilson, *Consilience: The Unity of Knowledge*, Vintage, 1999, p. 384.