

Engineering Materials

A Study of Nanomaterials, Biomaterials, and Smart materials

United States Military Academy

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Engineering Materials: A Study of Nanomaterials, Biomaterials, and Smart Materials

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Nanotechnology

Nanomaterials

4.1 BACKGROUND: MATTER MATTERS

It matters to nanotechnology for the same reasons it matters to every other field of engineering: people make stuff out of matter. We use it. Matter that can be used for something has its own name: material. Gold veins buried inside a mountain and carbon floating around in the air are not immediately useful. To be useful, material must be collected. Then we bang on it, or melt it, or attach it to other material, or rearrange it until it meets our needs. The study of materials is the study of matter *for the purpose of using it*.

As human beings, we cannot help but be awed by the stunning symmetry of atoms in a crystal. But as engineers and scientists we are interested in matter for more pragmatic reasons. We have to ask how it might be useful as an ingredient in something we make. Can we use materials in new ways if they are in smaller pieces? The short answer is yes, and hence a chapter on nanomaterials. The longer answer follows.

4.2 BONDING ATOMS TO MAKE MOLECULES AND SOLIDS

Put a few of atoms together and they become a molecule. Pack a lot of atoms together in a pattern and you get a solid. All atoms can form solids (with the lone exception of helium). Interatomic forces serve as the mortar, holding the atoms together. This is the case at the nanoscale, and all the way on up to the macroscale. The reason your body will not just vaporize and drift away into the ether is that the atoms that comprise you are stable where they are, held together by interatomic forces.

When two atoms are “infinitely” far apart (which to an atom might just be a micron), there is no force between them. When they are brought closer together, attractive and repulsive electrostatic forces (caused by electric charge held by the atoms) act on the atoms.

The interaction of two atoms to form a molecule, and later a solid, is a matter of conserving energy—a fundamental principle of the universe. Shown in Figure 4.1 is a general plot of the potential energy of two atoms separated by a distance, x . On the plot, negative energy corresponds to a net attractive force that pulls the atoms together. Positive energy corresponds to a net repulsive force that pushes the atoms apart. We can see that the net

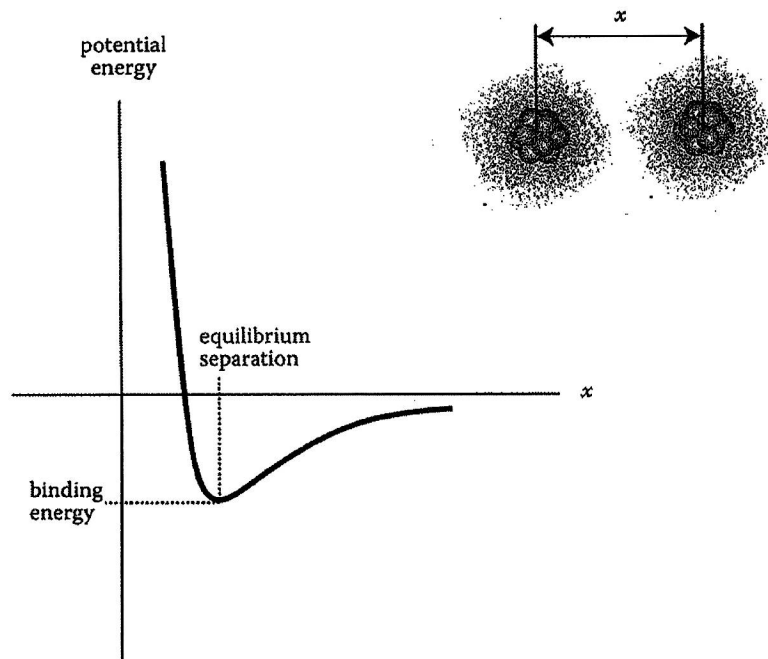


FIGURE 4.1 Total potential energy of a pair of atoms as a function of separation distance. At large separation distances, attractive forces pull the atoms toward one another, toward the equilibrium separation distance. At small separations, repulsive forces dominate.

force is attractive when the atoms first begin to interact, pulling them toward one another. This net attraction increases until the atoms reach an equilibrium separation—the lowest energy level on the plot. This is the distance at which the attractive and repulsive forces balance for a net force of zero.

When atoms are separated by this equilibrium distance, energy is required to move them closer together or to move them further apart. Unless energy is added, the atoms are content to exist where they are. When enough energy is added to drive them together, they become molecules. Repeat the process a few thousand times, and you get a nanoparticle. Repeat it a trillion *trillion* times (10^{24}) and you will get a baseball, a calculator, or even your hand.

The mechanisms by which these forces bond molecules and solids together are complex. There are three main kinds of bonds that hold together molecules: (1) ionic bonds, (2) covalent bonds, and (3) van der Waals bonds (Table 4.1). These three kinds of bonds are also what hold together the more complex, large-scale crystalline formations of atoms within solids, as well as nanoscale materials. Metals are one exception. A special arrangement of atoms and electrons known as the metallic bond holds solid metal together. We will discuss these bonding types now.

4.2.1 Ionic Bonding

When an atom loses or gains extra electrons, it becomes either positively or negatively charged. The sodium atom, Na, tends to give up its highest energy electron to become the

TABLE 4.1 Main Types of Bonding

Bonding	Among Atoms and Molecules	Within Solids
Ionic	Oppositely charged atoms are attracted to one another to make molecules Example: Na ⁺ and Cl ⁻ make the NaCl molecule.	Crystal structure is formed by an array of atoms held together by opposing charges Example: magnesium oxide, a crystal formed by O ²⁻ (and Mg ²⁺) molecules.
Covalent	Two atoms share electrons; their atomic orbitals overlap to make a molecular orbital Example: two hydrogen atoms make the H ₂ molecule	Crystal structure is formed by an array of atoms sharing electron orbitals Example: diamond, made from C atoms each sharing electrons with four other C atoms.
Van der Waals (three types)	Two atoms are attracted to one another by weak electrostatic forces Example: polar H ₂ O molecules cling to one another, endowing water with unique characteristics.	Atoms already organized as a solid are still subject to weak interaction forces with other atoms Example: covalently bonded layers of carbon in graphite stack like paper with weak van der Waals forces; layers can slide, making graphite soft (see Figure 4.8).
Metallic	The same as "Within solids."	Metal atoms are held together by a "sea" or "gas" of electrons; these electrons can move freely among the atoms, making metals conductive Example: copper atoms in a telephone wire.

Note: These bonding mechanisms are what enable atoms to form molecules as well as solids. Much about the way matter behaves can be explained by the way in which the atoms are held together.

positively charged ion, Na⁺; whereas the chlorine atom, Cl, tends to pick up a spare electron to fill out its electronic configuration, thereby forming Cl⁻. Negative and positive ions are drawn together (by Coulomb attraction) and we obtain NaCl (table salt).

The Coulomb attraction energy, E , that drives ionic bonding is given by:

$$E = \frac{z_1 z_2 e^2}{4\pi\epsilon_0 \epsilon x} \quad (4.1)$$

Here, x is the distance between the ions, ϵ_0 is the permittivity of free space, and ϵ is the dielectric constant of the medium between the ions (or the relative permittivity). The magnitude and sign of the two ions are given in terms of e , the elementary charge ($e = 1.602 \times 10^{-19}$ C), multiplied by the valence state of the ions, z_1 and z_2 . In the case of Na⁺, for example, $z = +1$; for Cl⁻, $z = -1$. An ion such as Ca²⁺ has $z = +2$, and so on.

Back-of-the-Envelope 4.1

How much energy and how big a force hold the NaCl molecule together?

First we need to know the separation distance x . We know Na has an atomic radius of 186 pm. However, when the Na atom loses an electron, it shrinks; Na^+ has a radius of 97 pm. The opposite is true of Cl, which upon acquiring an extra electron grows in radius from 99 to 181 pm. The sum of these two ionic radii is 0.278 nm. The dielectric constant of air is 1. The binding energy is therefore:

$$E = \frac{(1)(-1)(1.602 \times 10^{-19} \text{C})^2}{4\pi(0.278 \times 10^{-12} \text{C}^2 \text{N}^{-1} \text{m}^{-2})(1)} = -8.3 \times 10^{-19} \text{J}$$

This energy is attractive. The binding force is:

$$F = \frac{(1)(-1)(1.602 \times 10^{-19} \text{C})^2}{4\pi(0.278 \times 10^{-9} \text{m})^2(8.854 \times 10^{-12} \text{C}^2 \text{N}^{-1} \text{m}^{-2})(1)} = -8.3 \times 10^{-19} \text{J}$$

As a quick review, energy is a force applied over a distance. Taking the negative derivative of the energy equation with respect to distance, or $-dE/dx$, gives us the force, F , between the atoms. Here, negative forces and energies are considered attractive and positive forces and energies are considered repulsive. The Coulomb force, F , is therefore given by:

$$F = -\frac{dE}{dx} = \frac{z_1 z_2 e^2}{4x^2 \pi \epsilon_0 \epsilon} \quad (4.2)$$

When *numerous* ions come together to form a solid, the ionic interactions become more complex. In the case of NaCl, the positive sodium ions self-arrange so as to minimize the repulsion between one another and maximize the attraction to the negative chlorine atoms, thereby achieving an equilibrium where breaking apart the crystal structure thus formed would require more energy than maintaining it. Each sodium ion is surrounded by six chlorine ions, and each chlorine ion is surrounded by six sodium ions, as shown in Figure 4.2.

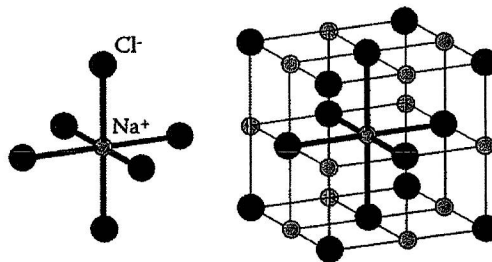


FIGURE 4.2 Crystal structure of table salt. Each sodium atom is attracted to six neighboring chlorine atoms, and vice versa. NaCl is an example of ionic bonding. The length of the cube edge is 563 pm.

More than 200 compounds assume the same crystal structure as NaCl, one of many ionic crystal structures. Ionic crystals tend to be stable, hard crystals with poor electrical conductivity because they lack free electrons. They have high vaporization temperatures and are especially soluble in water (or any polar liquid) because the permanently dipolar H_2O molecules tug at the charged ions in the crystal, breaking the bonds and dissolving the solid. Typically, ionic crystals are transparent to radiation in the visible range, but absorb radiation in the infrared range. The heavy ions in the crystal have low natural frequencies and therefore tend to absorb low-energy (lower frequency) photons from the infrared region of the spectrum.

4.2.2 Covalent Bonding

Two atoms share electrons in a covalent bond. The atoms' individual orbitals overlap to form a mutual molecular orbital. This happens with hydrogen: two hydrogen atoms bond covalently as H_2 , each atom sharing its one electron so that the molecule has two shared electrons. This effectively elongates the spherical orbital shape of a single hydrogen atom into more of a pill shape where the probability of finding one of the shared electrons is highest in the region between the two nuclei. The H_2 molecule is represented in Figure 4.3. Covalent bonds are very stable and hold together such molecules as F_2 , CO_2 , CO , H_2O , and CH_4 .

Solids held together by covalent bonding are, like covalent molecules, highly stable. Covalent forces are of very short range, on the order of interatomic separations (100 to 200

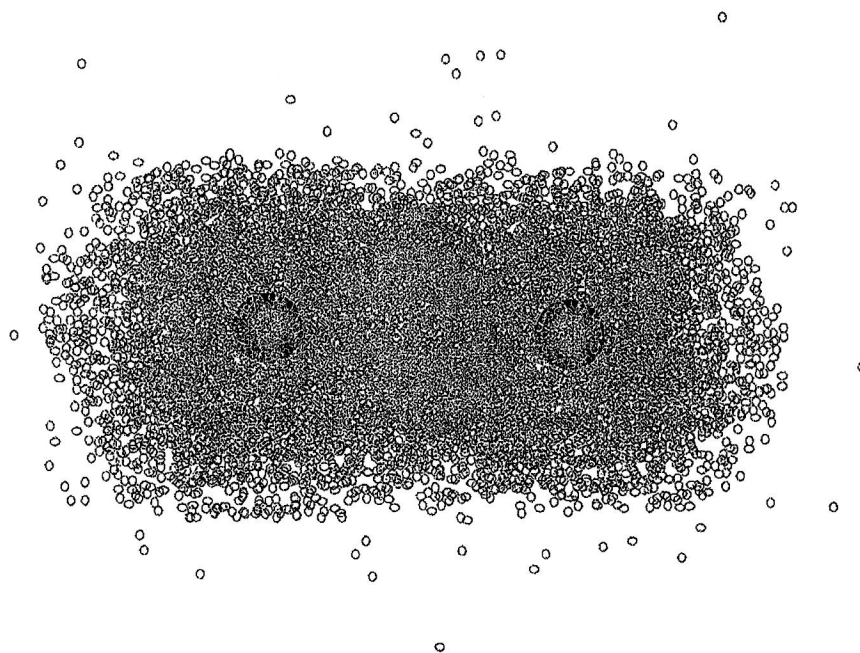


FIGURE 4.3 A covalent bond between hydrogen atoms. The probability of finding an electron in the H_2 molecule is highest in the region between the two nuclei.

pm), with typical binding energies from 4×10^{-19} to 1×10^{-18} J per bond. For example, the oxygen–hydrogen bond in a water molecule has a strength of 7.6×10^{-19} J.

Diamond is formed entirely from covalent carbon atoms—each sharing electrons with four neighbors, all 0.154 nm away, in what is known as a “giant molecule” throughout the solid crystal. Silicon and germanium both crystallize in the same pattern as diamond. Covalent crystals can be extremely hard due to the cohesiveness of covalent bonds, which can also make for very high melting temperatures (4000 K in the case of diamond) and poor conductivity.

4.2.3 Metallic Bonding

About two thirds of the elements in the Periodic Table are metals. Many of the physical properties we associate with metals, including their luster, malleability, and high electrical and thermal conductivity, result from metallic bonding. When metal atoms organize into solid form, the electrons in their outermost orbitals (known as valence electrons) disassociate from the atoms. These newly free electrons form a “sea” that can flow in and around the lattice of positive ions. This is similar to covalent bonding in that the electrons in both cases are shared among two or more atoms; the discreteness of the atoms is lost.

The metallic bond is nondirectional. It does not lead to structures quite like those in ionic and covalent crystals. Although it is difficult to separate metal atoms in a solid, it is somewhat easier to move them around, as long as they stay in contact with each other. Because of this, metal atoms can be dissolved in other types of metals to form alloys, with customizable metal-to-metal ratios. One particular ratio might improve tensile strength, another corrosion resistance.

The energy binding the “sea” of shared electrons to the atoms in a metal is about the same amount of energy carried by photons of visible radiation (1 to 3 eV). Thus, light interacts strongly with metal electrons and is absorbed and re-emitted near a metal’s surface instead of being completely absorbed; hence, metals’ shiny appearance. The free “sea” of electrons is what conducts heat and electricity so well.

4.2.4 Walking through Waals: van der Waals Forces

Dutch scientist Johannes Diderik van der Waals (Figure 4.4) did not like the fact that real gases did not obey the ideal gas law. So he rewrote it. He pursued the idea that there were attractive forces between the molecules in a gas, forces the ideal gas law ignored, and added terms to the equation to account for them. Granted, the very concept of a “molecule” was still in its infancy, a topic of hot debate. And van der Waals could not quite explain how these attractive forces worked, but his pioneering studies were nonetheless worthy of the 1910 Nobel Prize in Physics.

The unique set of forces that bear his name are better understood now. They are short-range in nature and lead to weak bonds among atoms and molecules. Although weaker than covalent, metallic, and ionic forces, van der Waals forces have a significant impact on the physical properties and behavior of all matter, and are especially relevant at the nanoscale.

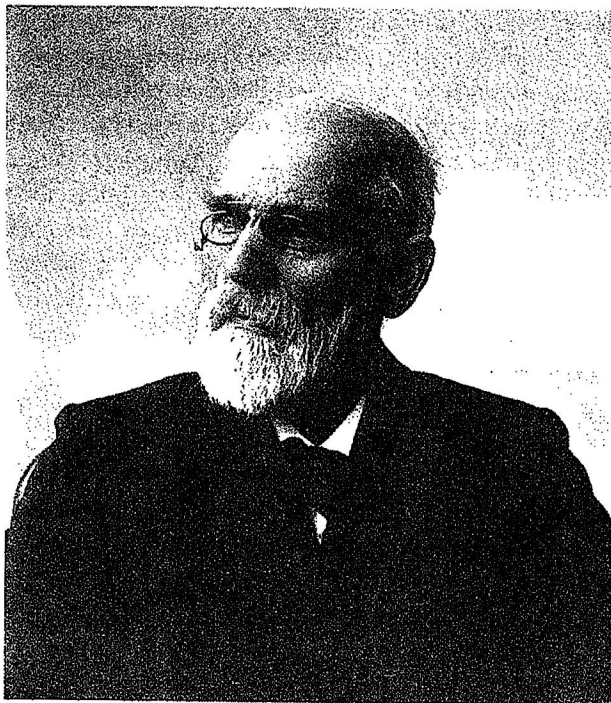


FIGURE 4.4 Johannes Diderik van der Waals (1837–1923). (Photo courtesy of Smithsonian Institution Libraries, Washington, D.C.)

Some people simply say “van der Waals forces” when referring to *all* the weak interaction forces between nonbonded molecules. There are three types of van der Waals forces, and, as you will see below, the many names given over the years to these three types seem to justify the practice of just calling them “van der Waals forces” for simplicity’s sake. Keep in mind that, at any moment, more than one type of van der Waals force can be at work between atoms.

First, there is the *dipole–dipole force* (sometimes called the *orientation* or *Keesom force*). This force occurs between polar molecules such as HCl and H_2O . Polar molecules have an unequal distribution of electrons, making one side of the molecule more positive, the other more negative. When polar molecules are near one another, they favor an orientation where the positive portion of one molecule aligns with the negative portion of its neighbor, like a pair of bar magnets.

Such is the case for a particularly important type of dipole–dipole interaction known as hydrogen bonding. In the case of water, the attraction created by hydrogen bonding is what keeps H_2O in liquid form at more temperatures than any other molecule its size (instead of separating into individual vapor molecules). Since the hydrogen bonds require extra energy to break, water is a good place to store heat. Animals store excess heat in the water in their bodies. When the water has absorbed as much heat as possible, it evaporates away from the body and takes heat with it. Hydrogen bonding is what endows water with a

high surface tension—the reason you can fill a glass with water slightly above the rim and it does not spill out. A network of hydrogen bonds enables water molecules to bind together as an ice crystal and is the reason why water is less dense as a solid than as a liquid, a rarity among substances. A hydrogen bond has only about 1/20 the strength of a covalent bond.

The next van der Waals force is the *dipole—induced-dipole force* (sometimes called the *induction* or *Debye force*). This weak force arises when a polar molecule brings about the polarization of a nonpolar molecule nearby. An example of a nonpolar molecule is the noble gas argon, which has a homogeneous distribution of electrons around its nucleus. When in close proximity to a polar molecule such as HCl, argon's electron distribution is distorted to one side of the nucleus. This is an induced dipole and it causes the molecules to be attracted toward each other.

Finally, there is the *dispersion force* (sometimes called the *London force*, *charge-fluctuation force*, *electrodynamic force*, or *induced-dipole—induced-dipole force*). This force is probably the most important of the van der Waals forces, as it plays a role in many phenomena: adhesion; adsorption; surface tension; wetting; the properties of gases, liquids, and thin films; the strengths of solids; and the structures of proteins and polymers. Let's discuss it in more detail.

4.2.4.1 The Dispersion Force

Like the force of gravity, the dispersion force acts on *all* atoms and molecules. This sets the dispersion force apart from solely electrostatic forces, which require charged or dipolar molecules. In fact, even nonpolar molecules can be made into dipoles, and this is the basis of the dispersion force. This force can act as a “long-range” force between molecules separated by up to 10 nm, but it also acts at interatomic spacings (~200 pm).

To understand how the dispersion force works, we will use the simplest kind of molecule there is: a single atom. We have learned that as electrons move around the atom's nucleus, they are like particles appearing here and there—on one side of the nucleus or another. Think about taking a snapshot of hydrogen: wherever the single electron is at that instant is, in essence, a very short-lived pole. Take another picture, the electron has moved and the pole has moved with it. The same is true of larger atoms and larger molecules. This rapidly fluctuating dipole, created by electrons as they move about the atom, creates momentary pockets of charge density called finite dipole moments.

When two molecules, in this case two atoms, come near one other, the one with the stronger fluctuating pole induces a synchronous, although opposite, fluctuating pole in the other. The molecules are attracted by the pole of their neighbor. *This tug is the dispersive force.* The larger the molecule, the larger the possible dipoles, and the larger the dispersive force. This is why larger molecules tend to have higher boiling points: because they can have larger fluctuating dipoles, larger molecules can be “stickier.” In other words, they are more difficult to pry away from neighboring molecules into a vapor form.

4.2.4.2 Repulsive Forces

There is one final component of the van der Waals interaction between molecules; this component is repulsive. Repulsion dominates the interaction of molecules as soon as they are

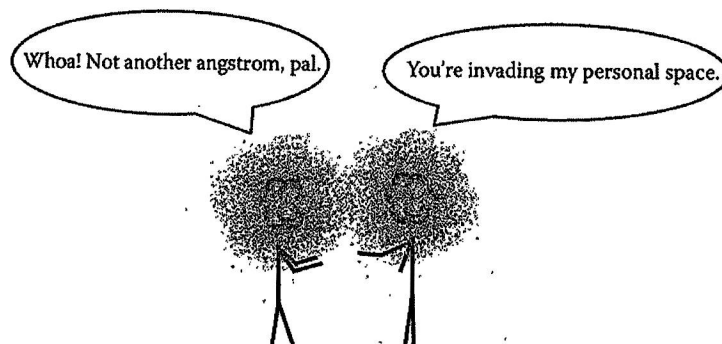


FIGURE 4.5 Some “hard core” repulsion.

too close together—when their electronic orbitals begin to overlap. These repulsive forces are quantum mechanical in nature and referred to by many names—*exchange repulsion*, *hard core repulsion* (Figure 4.5), *steric repulsion*, and, in the case of ions, *Born repulsion*.

The Pauli Exclusion Principle governs this phenomenon. According to this principle, there can never be more than two electrons at a time in any one orbital. This means that if two atoms or molecules get close enough to one another, their electron distributions can overlap only if the electrons are promoted to higher, unoccupied energy levels. Therefore, extra energy is necessary if two atoms or molecules are to be pushed any closer to each other than the equilibrium distance.

Repulsive forces play a role in how molecules pack together in solids—how closely and “comfortably” they can remain in proximity. If the molecules cannot pack together in a stable lattice, the melting point of the solid will be low. Meanwhile, higher melting points tend to correspond to better packing.

4.2.4.3 The van der Waals Force versus Gravity

Gravity makes home runs and slam dunks difficult. Gravitational forces give us the ocean tides and the orbits of the planets. However, the force of gravity at the nanoscale is negligible. It equals the acceleration of gravity ($g = 9.8 \text{ m/s}^2$ on Earth) multiplied by the object’s mass. At the nanoscale, the masses are so minute that other forces such as van der Waals forces become the dominant forces. This is among the more difficult concepts for us to grasp, subject as we are to Earth’s constant tug on our bodies.

To get a feel for the relative magnitude of these forces, we start with the Lennard-Jones potential and model the interaction energy, E , of a pair of atoms separated by a distance x . This is a good way to approximate the van der Waals interaction. The Lennard-Jones potential equation is used often in simulating molecular dynamics. In the case of two of the same type of atom, it can be written as:

$$E(x) = \epsilon \left[\left(\frac{2r_{vdw}}{x} \right)^{12} - 2 \left(\frac{2r_{vdw}}{x} \right)^6 \right] \quad (4.3)$$

In this equation, ϵ is known as the well depth and r_{vdw} as the van der Waals radius (or hard sphere radius). We can see both the attractive van der Waals interaction (which varies with the inverse-sixth power of the separation distance) and the repulsive interaction (which tends to vary by roughly the inverse-twelfth power of the distance). The parameters ϵ and r_{vdw} vary by atom. This relation is shown graphically in Figure 4.6.

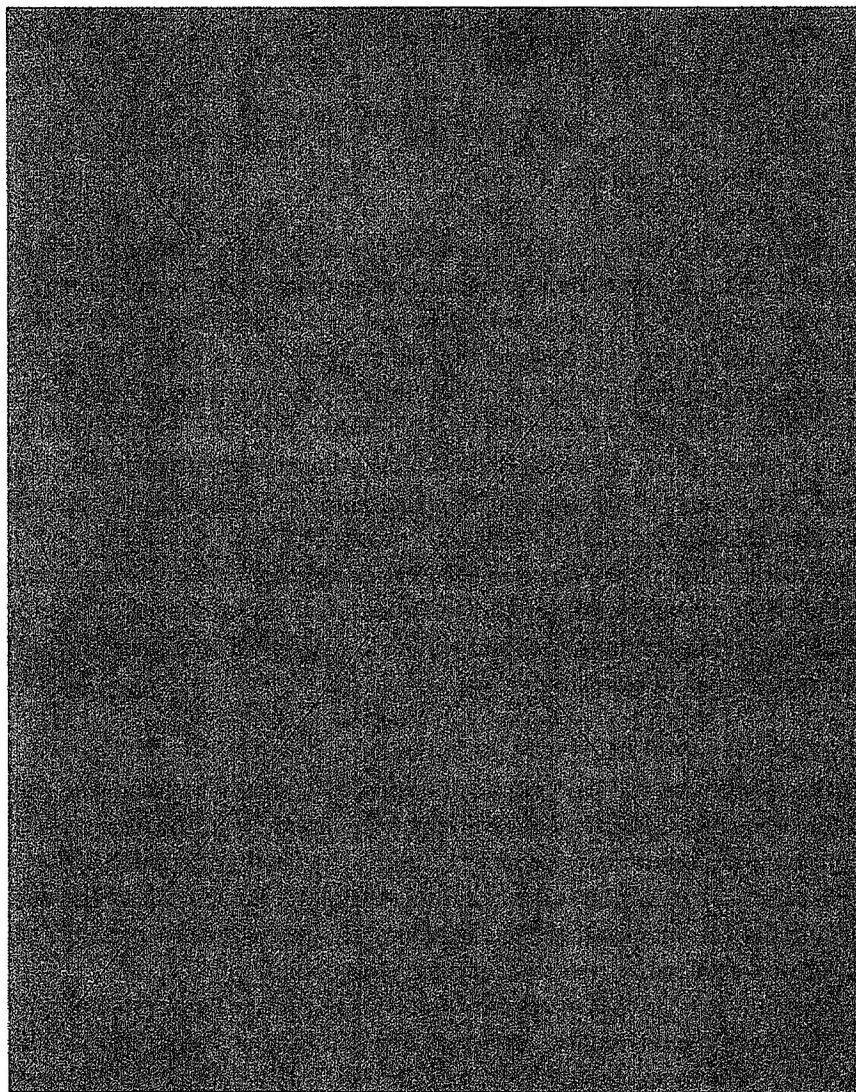


FIGURE 4.6 The van der Waals interaction. The graph shows the van der Waals forces between two molecules separated by a distance, x . The attractive forces, proportional to $1/x^6$, dominate at larger separation distances, but the repulsive force, which scales as $1/x^{12}$, dominates at closer range—separation distances of about twice the molecular radius, r_m , if both molecules are the same. The combination of these repulsive and attractive forces (shown as dotted lines) governs the van der Waals force interaction (thick gray line).