

Chapter 1

The Behavior of Small Particles



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Introduction

We encounter objects of various sizes every day, some of which we can see with our naked eyes, while others are too small to resolve. For example, fish eggs and larvae can span sizes between 100 microns and 1 mm, placing them on the cusp of what we are able to observe visually. Even though they are too small for us to see, we know that materials such as soot, vehicle exhaust or pollen are also composed of particles, based on their characteristics and behaviors.

This book is concerned with the nature and effects that particles commonly found in paints, plastics, and paper laminates have on end-use properties. As a prerequisite to

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this, we must define precisely what, in our context, a particle is. The word “particle”, as it is commonly used, is quite general and, because of this, somewhat vague. In broad terms, we can define a particle as an object having a specific size and exhibiting both physical and chemical properties. For our purposes, we will define a particle as an object that is smaller than approximately 100 microns and will refer to materials larger than this as “macroscopic objects”. We will further divide particles into three size categories, with “large” particles being roughly 20 microns or larger, “small” particles spanning the range from 0.1 micron (100 nm) to 20 microns, and “nano” particles being smaller than this.

Our reason for dividing particles into these three groups is that many physical properties of particles are determined by their size, and the particles grouped according to these different size categories behave differently from one another in many very important ways. In our everyday life, we mainly deal with macroscopic objects—from grains of salt to carry-on luggage. In coatings, plastics, and paper laminates we deal predominantly with objects that are much smaller, with a range of characteristic sizes between roughly 0.2 and 20 microns—that is, objects that we defined as small particles in the paragraph above. Because most of our experiences are with large particles and macroscopic objects, and because the behaviors of large and small particles are very different from one another, as we will see, it is worthwhile to discuss the properties of small particles as a prelude to understanding their effects on many paints, plastics, and paper laminate properties.

Physical Laws Governing Small Particles

We are familiar with the behaviors of objects that are large enough to hold in our hands. Objects of this size, such as grains of salt or ball bearings, flow easily and independently of one another, separate easily, are significantly acted on by gravity, and pack efficiently. However, the behaviors of objects that are smaller than this—objects that we defined as “small particles”—are much different. We rarely knowingly encounter small particles in everyday life and so are not familiar with many of these differences.

We will begin our analysis of small particle behavior with a review of the important forces that act on and between these particles.

The Forces of Nature

Physicists have identified four fundamental forces from which all other forces are derived. These are the weak force, the strong force, electromagnetism¹, and gravity.

¹ As the name implies, the electromagnetic force can be split into two inter-related forces, the electrostatic force (which causes attraction and repulsion of charged species at rest) and the magnetic

Two of these forces are familiar to us in our everyday lives, and two, the weak force and the strong force, are quite foreign. We are unfamiliar with these two forces because their reach is subatomic—the strong force is important only at distances similar to those of the atomic nucleus, while the weak force operates at distances that are a small fraction (0.1%) of the size of an individual proton. The weak force is roughly a million times less intense than the strong force.

Electromagnetic forces and gravity operate over a much larger length scale than strong and weak forces. As an extreme, gravity can cause galaxies separated by distances of many millions of light-years to aggregate into galactic clusters. Both gravitational and electromagnetic forces decrease in strength as the square of distance, and the equations describing these forces are very similar:

$$F_{gravity} = G \frac{m_1 m_2}{r^2}, \text{ where } G = 6.67 \times 10^{-11} \frac{\text{Nm}^2}{\text{kg}^2} \quad (1.1)$$

$$F_{electrostatic} = k \frac{q_1 q_2}{r^2}, \text{ where } k = 8.99 \times 10^9 \frac{\text{Nm}^2}{\text{C}^2} \quad (1.2)$$

Note the large difference in the values of the constants in these equations (G and k). Although we cannot equate coulombs to kilograms, we can say that these are convenient units to describe the number of electrons and quantities of mass with which we are accustomed to interacting. The difference in magnitude of these constants—20 orders of magnitude—suggests a very large difference in the relative strengths of these two forces. This is, in fact, the case. As a point of comparison, consider two electrons separated from one another by some distance d . These electrons will be attracted to one another by gravity and repelled from one another by charge repulsion. The electrostatic force of repulsion between these electrons is a remarkable 4.17×10^{42} times stronger than the attractive force of gravity [1].

The fact that gravity is by far the weakest of the four forces may come as a surprise since gravity plays such a dominant role in our everyday lives. However, if we look carefully, we can see indications that this force is, in fact, quite weak. For example, a relatively weak 10-gram magnet can easily pull a paperclip off of a table—in the process of completely overcoming the gravitational attraction of the 5.972×10^{24} kg mass of the Earth. Similarly, when rubbed on fur, a balloon can be attached to a ceiling, again overcoming the gravitational attraction of the Earth, in this case through electrostatic, rather than magnetic, interactions.

We may wonder why, if gravity is over forty orders of magnitude weaker than the electric force, it dominates our lives. There are two reasons that, together, explain this. The first is that there are two types of electric charges, positive and negative, and the interactions among them are both attractive and repulsive, unlike gravity, which operates solely on an attractive basis. The second reason is, paradoxically, that the electrical forces are so very strong.

force (which arises from charged species in motion). These forces were united by Maxwell in the mid-nineteenth century.

The first of these reasons suggests a way that electrical forces can be minimized—charge cancellation. Because there are two opposing types of electrical charge, differently charged subatomic particles can balance one another. This is what occurs in free atoms and in molecules, where there are equal numbers of protons and electrons. Ions, on the other hand, are charged, but oppositely charged counterions are nearly always found in close proximity, again balancing the total charge of the system.

Not only can most electrical charges be balanced on a very small scale, they almost always are. This is explained by the second reason that the effect of gravitational force on Earth dominates that of the electric force. Both the attractive and repulsive forces are very strong between charged materials. The strength of the repulsive forces makes it difficult for unbalanced charges to build up in a given region of space, and the strength of the attractive forces assures that any buildup of charge will quickly be neutralized by charges of the opposing sign. The net effect is that, due to the high strength of attraction between oppositely charged materials, Nature will find a way to bring oppositely charged materials together, canceling their interactions with other materials or objects.

The net result of these factors is that the electrical charges are almost always balanced on a very small scale (on the order of a few nanometers), and so their influences do not typically extend beyond the molecular scale. Gravitational forces, on the other hand, are always attractive and so cannot be shielded or canceled in the same way as electrical forces. Gravitational forces instead always add onto one another, combining in a way that extends their influence to the galactic scale.

The Nature of Forces

We are familiar with the most obvious ways that electrical energy reveals itself—the shock we get crossing a room on a low humidity day, the benefit we get from plugging appliances into electric outlets, the light we get by turning on a switch, and so forth. However, there are also manifestations of electrical energy that are not so obvious. One of these is the attraction of small particles to one another and to surfaces. These attractions are generally referred to as van der Waals forces, a term that includes three related types of interactions:

- those between permanent dipoles—the Keesom force,
- those between a permanent dipole and an induced dipole—the Debye force, and
- those between non-polar atoms or molecules arising from instantaneous dipoles—the London dispersion force.

Note that unlike electrical forces, which decrease as the square of distance, the magnitude of van der Waals forces decreases as the sixth power of surface separation distance and so recedes quite rapidly as touching particles move away from one another. They are therefore only important at distances of no more than a few nanometers.

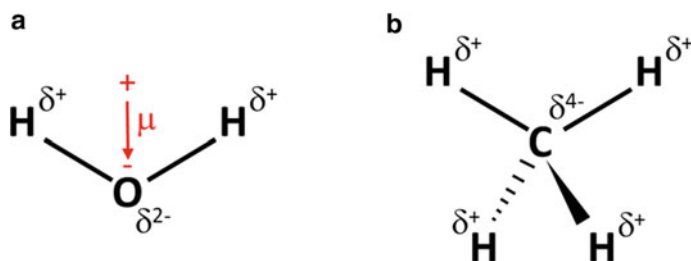


Fig. 1.1 Charge separation in molecules. δ indicates a fractional charge. **a** Water. **b** Methane. Dipole moment in **(a)** indicated by arrow

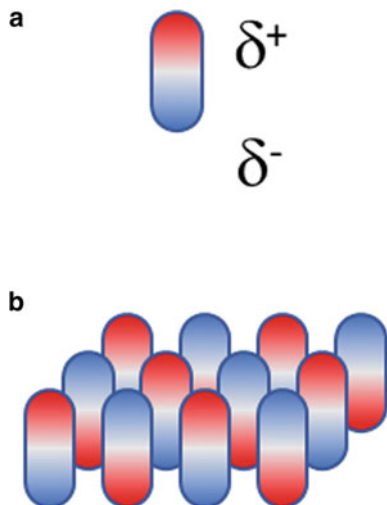
The three components of van der Waals forces arise from electric dipoles. Dipoles are atoms or molecules for which there is a slight separation of electric charge. Permanent dipoles are found in molecules when atoms of different electronegativities are bound to one another and the symmetry of the molecule is not high enough to balance these charges. For example, the hydrogen atoms in a water molecule are less electronegative than the oxygen atom. This generates a slight positive charge on the hydrogen atoms (designated as δ^+) and a negative charge double that on the oxygen atom (δ^{2-}). This is shown in Fig. 1.1a. Because the hydrogen atoms are on one side of the water molecule, and the oxygen atom on the other, there is a slight separation of electrical charges in the molecule. This separation is referred to as the dipole moment (designated as μ) and is shown in Fig. 1.1a as an arrow pointing to the negative part of the molecule. Molecules with dipoles are termed polar, and those without them are termed non-polar. As an example of the latter, there are slight charge separations in methane (CH₄), just as in water, yet methane has no net dipole moment (Fig. 1.1b). This is because of the high (tetrahedral) symmetry of this molecule, which causes all vectors of charge separation to cancel.

When polar molecules are arranged in a liquid or solid, they align themselves to maximize attractive electrostatic forces and minimize repulsive attractive forces. This means that the positive end of one molecule aligns next to the negative end of another. This is shown pictorially in Fig. 1.2. These interactions result in a net attraction between the molecules and a net stabilization when molecules with dipoles assemble.

There is also a net attraction between molecules with a dipole moment (polar molecules) and those without one (non-polar molecules). In this case, as the molecules approach one another, the positive part of the polar molecule pulls towards it the electrons in the non-polar molecule, while the negative part of the polar molecule is aligned with the remainder of the non-polar molecule. Note that this remainder is partially positively charged because some electron density flowed from it towards the positive end of the polar molecule.

The separation of charge seen in a non-polar molecule that comes in contact with a polar one is called an induced dipole. While the interactions between polar and non-polar molecules are attractive, they are not as strong as the interactions between permanent dipoles.

Fig. 1.2 Alignment of molecular dipoles **a** individual molecule. **b** Assembly of molecules. Red shading indicates areas of excess positive charge; blue shading indicates areas of excess negative charge



Finally, we have the situation where two non-polar molecules come close together. This, too, results in an attraction between them. The electrons within any molecule are in constant motion, and at any given instant they could be imbalanced—that is, there could be a net positive charge in one area of the molecule and a net negative charge in another. This charge separation occurs spontaneously and is temporary. This is referred to as an instantaneous dipole in the molecule.

When two non-polar molecules are in contact with one another, and one molecule develops an instantaneous dipole, an induced dipole is created in the second, much as occurs when a non-polar molecule is brought in contact with a polar molecule. As was the case with polar/polar and polar/non-polar interactions, instantaneous dipole moments cause an attraction between molecules. The attractions between non-polar molecules are, however, significantly weaker than the other two types of dipolar interactions.

The three ways that dipoles can align are shown in Fig. 1.3. Taken together, these forces are called the van der Waals forces, and they account for the assembly of atoms or molecules that are not chemically bound to one another (for example, they account for the liquification of methane at low temperatures).

In our discussion of Fig. 1.2, we noted that molecules in solids typically orient themselves in a way that maximizes the attractive electric forces and minimizes the repulsive forces. Because of this, the surfaces of these typically have alternating positive and negative patches. Other molecules coming into contact with these surfaces will generally align themselves according to these interactions. This explains the well-known phenomenon of the adsorption of a gas or a dissolved molecular species onto a particle surface.

This also explains the attraction particles have towards other particles. This attraction is a surface phenomenon—surface atoms act as shields and prevent the dipole

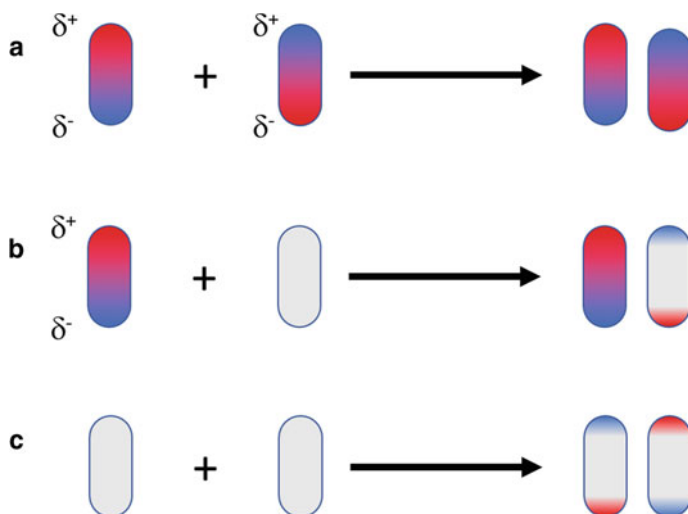


Fig. 1.3 Dipolar interactions between molecules. **a** Permanent dipole–permanent dipole (Keesom force); **b** permanent dipole–induced dipole (Debye force); **c** Instantaneous dipole–induced dipole (London force)

charges from penetrating deeply into a particle. Because of this, we find the attraction strongest for particles with high specific surface areas.² Particles that have high specific surface areas are either porous or, more commonly, quite small. A sizeable fraction of the atoms and molecules within particles that are smaller than about half a micron are located at or near the particle surface, where they can participate in particle–particle interactions. The high proportion of surface atoms and molecules, and the sharp drop in interaction strength with distance, cause small particles to be more strongly attracted to one another (and to surfaces in general) than large particles.

The Balance of Forces in Large and Small Particles

The differences in behaviors of large and small particles, on the one hand, and nanoparticles, on the other, are due to differences in the physical laws that they follow. Large and small particles follow what are considered the classical laws of physics—the laws discovered by scientists several centuries ago. As a group, we will call these Newtonian laws. These include, for example, the force law (force = mass times acceleration) and the law of gravity (see Eq. 1.1 above).

Nanoparticles, however, follow a different set of laws. These are the laws of quantum mechanics, where uncertainties in location and motion (momentum) are

² Specific surface area is the surface area of a particle divided by its weight. A collection of smaller particles has a higher specific surface area than a collection of the same weight of larger particles.

linked to one another. Quantum behavior is quite foreign to us, and the implications of quantum mechanics are difficult to perceive and understand at an intuitive level.

While nanoparticles follow quantum mechanical laws, both large and small particles follow the same laws (the Newtonian laws described above). As such we might expect their behaviors to be similar. This is not the case, however. Although large and small particles follow the same laws, the relative importance of the different laws is quite different between the two particle size regimes. As discussed above, large particles are governed primarily by gravity. Small particles, on the other hand, are governed primarily by surface forces.³ These include friction and the natural attraction of one surface to another.

Gravitational forces scale as the volume of a particle (d^3 , where d is the particle diameter), whereas surface forces depend on the surface area of a particle (d^2). The relative importance of the two for a specific particle can be described by the ratio of the forces. This ratio (d^3/d^2) changes linearly with particle size (d). For large particles (large d), gravitational forces (d^3) are dominant, whereas for small particles (small d), surface forces (d^2) are dominant (Fig. 1.4). This can also be understood by comparing the fraction of molecules (or atoms) in a particle that are near the particle surface to the fraction of those in the bulk. Those molecules (or atoms) near the surface can be influenced by other surfaces, as discussed above, while those away from the surface are affected only by gravity.

The remainder of this chapter will focus on comparing and contrasting the behaviors of large particles—behaviors that we are familiar with through our everyday lives—to those of small particles—which we rarely encounter. For many, the most common opportunity for interacting with small particles is in the kitchen, where many food staples are in powder form. These powders often exhibit small particle behavior, and an excellent point of reference for this chapter is the different behaviors of large and small particles of the same material—sugar. One can use granular sugar (a large particle) and powdered sugar⁴ (a small particle) to show the similarities and differences between these two size regimes, and readers are encouraged to confirm the observations made below for themselves by using these forms of sugar as examples. Some of these differences are also demonstrated in the video associated with Fig. 1.5.

³ There is a second distinction between large and small particles that affects certain small particle behavior. This distinction applies when particles are so small as to approach the atomic or molecular dimensions. For macroscopic objects, we can ignore the fact that material is made up of indivisible units (atoms or molecules), but we sometimes cannot do so for small particles. Brownian motion is an example of this. Random imbalances of gas or liquid molecules striking a macroscopic object are much too slight for detection, while for small particles, such as grains of pollen, the imbalance is great enough to cause the particle to move. This is manifested as the random (Brownian) motion of these materials in air or water. An explanation of Brownian motion was one of Einstein's first contributions to physics, and the fact that it arises from a discontinuity in structure (i.e., the indivisibility of atoms) was determined by Perrin and was the basis for Perrin being awarded the Nobel prize in physics in 1908.

⁴ Sometimes called confectioners' or 10X sugar. It is called icing sugar in the UK.

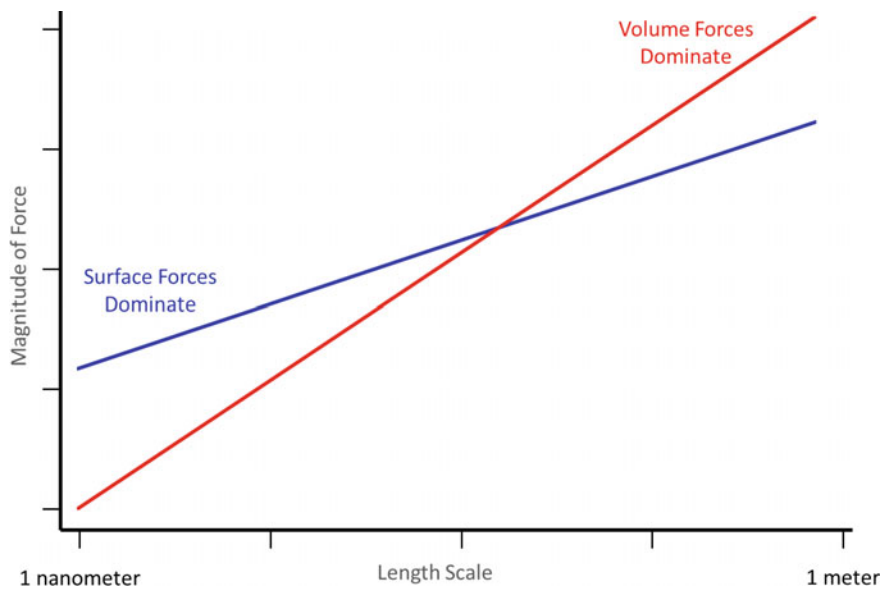


Fig. 1.4 Schematic of the relative importance of volume and surface forces as a function of particle size (both axes are logarithmic)



Fig. 1.5 Video demonstration of the behavior differences between granular and powdered sugars

Properties of Small Particles

There are many properties common to all small particles that determine, in part or in whole, their physical behaviors. These properties can be broadly divided into two groups—physical properties and chemical properties. For the most part, chemical behaviors are determined by the chemical nature of the particle surface, since atoms below the surface are not available for chemical reaction. These behaviors can be altered by modification of the particle surface, usually through the adsorption of a small molecule or ion, or by the deposition of a new solid onto the particle surface.

By contrast, physical behaviors are determined by both the surface properties and the dimensional characteristics of the particle. Here, the chemical nature or elemental composition of the particle is not as important. Instead, aspects of the particle such as size, shape, weight, density, coefficient of friction, etc., control these properties. In this sense, we are concerned with the “object” characteristics of the particle rather than the reactivity characteristics.

We will discuss many of the properties of small particles, particularly those that have relevance to coatings and plastics. Before doing so, we note that, unless otherwise specified, we will typically refer to a property on the basis of a unit weight of particles, rather than on the basis of a single particle or a set number of particles. For example, a single large particle clearly has a higher surface area than a single small particle of the same shape. However, a gram of large particles will have a smaller surface area than a gram of small particles. Our reason for defining properties on a mass basis is that particles are formulated into paints, plastics, and paper laminates on a weight or volume basis, rather than on a number basis, and so it is on this basis that we will discuss their attributes.

Shape

All particles, regardless of their size, have specific shapes. This can include roughly uniform shapes, such as a sphere, cube or block, irregular shapes, such as plates or rods, and all shapes in between. It is most convenient to classify shapes based on the number of dominant dimensions a particle has. We live in a three-dimensional world, and therefore there are three shape categories (Fig. 1.6). Three-dimensional, blocky shapes, such as a cube or a sphere, are roughly the same size in all directions. Plates can be considered two-dimensional—they extend in breadth and width but have very little thickness. Finally, needle-like or rod-shaped (acicular) particles extend in a single dimension (length), with negligible breadth and width.

Particles acquire a given shape in one of two ways. First, they can be formed with a preferred shape. This occurs when a small seed particle begins to grow. Growth typically occurs by the addition of “building blocks” to an existing particle. When building blocks are added to a growing crystal, they often do not attach to all faces equally. This is because some faces of the crystal are more energetic than others

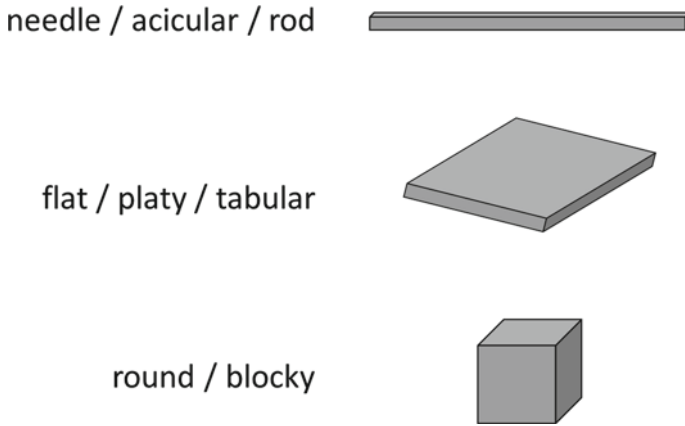


Fig. 1.6 Representative particle shapes

and so are more likely to be attached to an incoming building block. This causes crystal growth on certain faces to be more rapid than on other faces, with the result that particle growth may occur preferentially in certain directions. This leads to the formation of plates or needles.

Once a particle is formed, it can also be shaped through attrition. When particles are ground, they are broken into smaller particles. This can occur through impact or shear. The former crushes the particles, while the latter pulls them into pieces. The origin of impact forces is obvious—a material collides with the particle. Shear forces, on the other hand, are forces that vary in magnitude across a distance perpendicular to the direction of the force. When shear is applied to a particle, one part of the particle experiences a greater force than another part of the particle (Fig. 1.7).

In general, regardless of the shapes of the original particles, attrition results in the formation of particles that are blocky or spherical. We can see this in the spherical and ellipsoidal shapes of small stones polished in a river or on an ocean shore. The

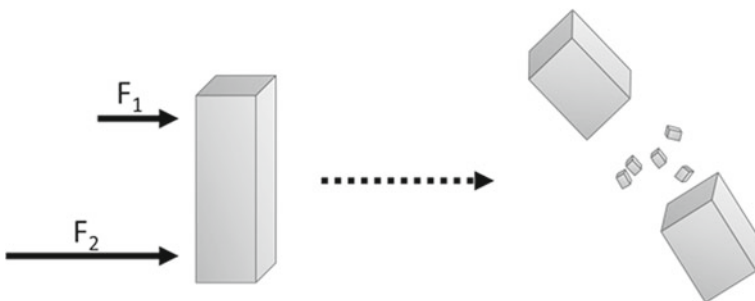


Fig. 1.7 Unbalanced (shear) forces applied to a large particle, resulting in that particle breaking into smaller particles

reason for this is that when one or two dimensions of the crystal are longer than the other(s), the shear forces are greatest between the two ends of the crystal that are the furthest apart. This is analogous to the greater ease of snapping a pencil in half perpendicular to its long axis as opposed to cleaving it in half lengthwise.⁵

Particles of all three shape types (block, plate, or needle) can be found in paints and plastics. In some cases, the shapes bring a desired property, such as those discussed below, while in other cases, the shapes are simply those that are the most convenient for the powder manufacturer to produce.

Rod-shaped particles have a positive impact on two paint film properties. First, the rods near the film surface cause surface protrusions. These protrusions enhance the adhesion between layers of paint (the so-called paint “tooth”). Second, rods within the film will reinforce it, enhancing its physical strength and resistance to abrasion. This is analogous to the incorporation of rebar in concrete.⁶

Plate-shaped particles (typically extenders) are often used to enhance the protection from water penetration that the paint provides to the substrate. Because of surface tension, platy particles will orient parallel to the film surface as the paint dries. Since water cannot penetrate through an extender, it must follow a long and tortuous path if it is to travel from the surface of the paint to the substrate. This increase in the distance that the water must travel to reach the substrate will enhance the protection of the substrate by the paint. In addition, special effects pigment particles are often platy particles that orient themselves in the paint or plastic (see Chap. 8). This causes the interactions between the pigment particles and light to have an angle dependence.

True Density and Bulking Value

There are two types of density that are important to particles: true density and bulk density. True density is the density of a solid object made of a specific material, while bulk density is the density of a collection of particles, such as a bag or container of particles. Bulk density is inevitably lower than true density because any collection of particles, no matter how tightly packed, will contain interparticle voids.

True density and its reciprocal (the bulking value, normally reported as liters per kilogram or gallons per pound) are important to the paint industry for economic reasons. Paint makers purchase their ingredients on a weight basis (e.g., dollars per kilogram) and mostly sell them on a volume basis (e.g., dollars per liter). Because of this, low-density (high bulking value) fillers have an advantage over high-density fillers since a unit weight of low-density particles has a greater volume than an equal weight of their high-density counterparts.

⁵ This can also be understood in terms of the number of bonds that must be disrupted to create the break. This number will be a function of the area of the cross section of the break. The smallest cross-sectional area will be perpendicular to the longest dimension of the particle.

⁶ The name “rebar” comes from the shortened conjunction of the words “reinforcing bar”.

The true density of a particle also is important when the particle is suspended in a liquid (i.e., in slurries and paints) because this, in part, determines the settling rate of that particle. The force by which gravity affects a particle in such situations is moderated by the difference in density between the particle and the liquid. Dense particles are therefore more prone to settling than less dense particles and this must be taken into account whenever a slurry or paint is stored.

We will discuss the bulk density of particles in detail in a later section on bulk properties.

Surface Properties

As discussed above, the sizes of particles found in paints and plastics can be small enough that a significant fraction of the individual molecules or atoms is close to the particle surface. For this reason, many of the behaviors associated with small particles are controlled by the surface of the particle. The extent to which the surface of a particle affects its behavior depends on two factors: the amount of surface (i.e., the surface area) and the chemical and physical state of the surface (i.e., the energetics of the surface atoms or the roughness of the particle surface). We will begin our discussion on surface properties with surface area.

Surface Area

Surface area is a physical property of all particles. Surface area increases when large particles are broken down into smaller particles. It is easy to see why this is the case—each time a particle is broken, two new surfaces are created. As shown in Fig. 1.8, surface area increases linearly as particle size decreases—that is, cutting a cube apart in half in all three dimensions increases the total surface area by a factor

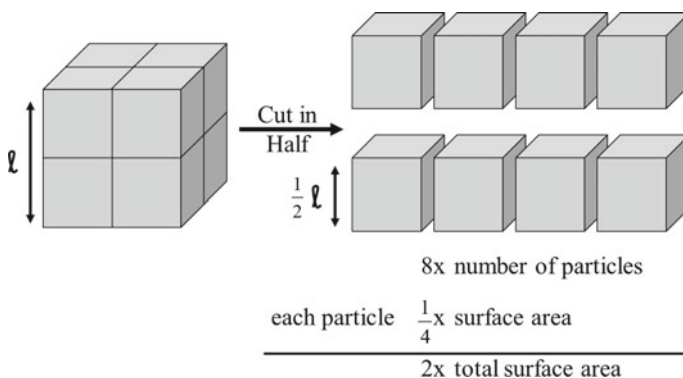


Fig. 1.8 Increase in total surface area as particle size is reduced

Table 1.1 Geometric surface area as a function of edge length of a cube

Length	Area (m ² /g)
1 mm	0.003
10 μm	0.3
1 μm	3
10 nm	300

of two (the surface area of each small particle is one quarter that of the larger particle, but there are eight small particles).⁷

For most particles found in paints and plastics, surface areas vary between 1 m²/g and 80 m²/g, although in a few exceptional cases (such as diatomaceous earth), surface areas can be much higher. Table 1.1 shows surface area values for cubes of a density of 2 g/cc (common for extender particles) as a function of the length of the cube edge. To give an appreciation for the magnitude of surface area for small particles, a tonne of pigmentary TiO₂ has a surface area of roughly 15 square kilometers.⁸

Surface Energy

In addition to area, surfaces have an energy characteristic that will vary from one type of particle to another. Surface energy is an important determinant of the bulk and handling characteristics of a powder.

To understand the origin of surface energy, consider what happens when a piece of quartz is broken. Quartz (crystalline silicon dioxide) is a network solid, meaning that there is a network of chemical bonds that link all of the atoms together (see also Chap. 14).⁹ Before breaking, each interior silicon atom is chemically bonded to four oxygen atoms, and each interior oxygen atom is bonded to two silicon atoms (Fig. 1.9a). This arrangement of the atoms maximizes chemical bonding interactions and leads to an energetically favored state.

When the quartz crystal breaks a series of Si–O bonds are disrupted (Fig. 1.9b). Some silicon atoms on the new surfaces are bonded to only two or three oxygen atoms, rather than the optimal number of four. This is a high-energy, highly reactive state for the silicon atoms. The silicon atomic orbitals that had been directed to

⁷ Recall that surface area is reported on a weight basis rather than a particle basis. On a per particle basis, surface area decreases as the square of particle diameter. On a per gram basis, it increases linearly with decrease in particle diameter, as shown here.

⁸ This includes contributions from nano-sized particles that are normally deposited on the TiO₂ particle surfaces to enhance pigment performance (see Chapter 7).

⁹ This can be compared to a telephone network. Here, a network of wires joins all of the telephones together. There are no direct lines between a given telephone and every other telephone; instead, the lines go from one telephone to the next. Similarly, in a network solid, there are no direct bonds between a single atom and every other atom. Rather, an atom is bonded to a few of its nearest neighbors, which, in turn, are bonded to other nearby atoms, and so on.

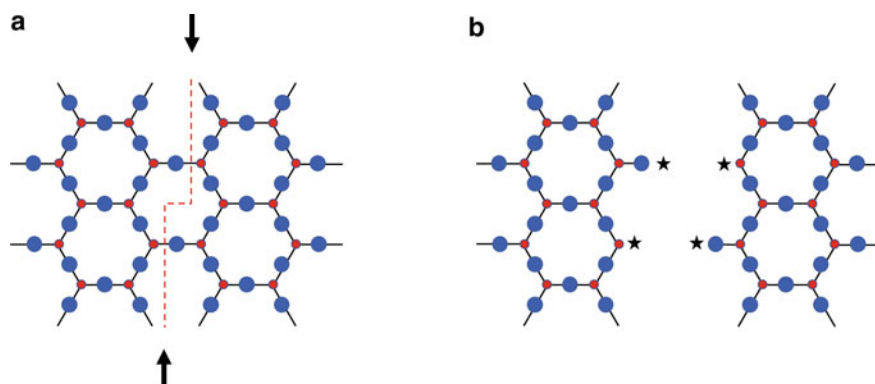


Fig. 1.9 Creation of surface energy in quartz through bond breakage. Red circles are silicon atoms and blue circles are oxygen atoms. Note that each silicon atom is bonded to one oxygen atom that is above or below the plane of the page. **a** Before breaking. The break occurs at the arrows and the dotted line shows where the new surfaces will be. **b** After breaking. Stars indicate high-energy unsaturated atoms

oxygen atoms and were a part of an energetically favorable interaction now point to empty space. In the same way, the oxygen atoms on the new surface are also in a high-energy state.¹⁰ The excess energy that the surface atoms have relative to those atoms in the bulk is called surface energy.

The amount of surface energy for any particle will depend on two factors. The first is the strength of the bonds that must be broken to create a surface—the greater the energy required to break these bonds, the greater the energy per unit area of surface (energy must be conserved and the chemical energy of the bonds is transformed into surface energy). The second parameter is simply the amount of surface—obviously the greater the surface area, the greater the surface energy. The total surface energy is the product of the energy per unit area (which depends on the chemical composition of the particle) and the total surface area of the particle (which depends on particle size and shape).

In general, nature is driven towards low energy states, which in this case means that the high-energy surface atoms are driven to react in ways that lower their energies. To some extent, the excess energy of these atoms can be lowered by relaxation of the surface—some atoms physically move, migrating to lower energy positions where they can interact with a higher number of atoms than they interacted with in their original configuration. In addition, water, oxygen, and even nitrogen from the air adsorb onto the highest energy (most reactive) sites on the surface. Water, in particular, is very effective at decreasing surface energy. The oxygen atom in a water molecule has two lone pairs of electrons that are available for bonding to silicon atoms. The hydrogen atoms in the water can hydrogen bond to the surface oxygen atoms.

¹⁰ Breaking these bonds can also lead to charge separation (e. g., SiO^- or Si^+ surface groups).

Table 1.2 Example strengths for different bonding interactions

Bond type	Example	Bond energy (kJ/mol)	Melting point (°C)	Surface energy (mJ/m ²)
Van der Waals	N ₂	3	-196	12
Hydrogen	H ₂ O	21	0	65
Covalent	Diamond	347	4027	600

The surface energy of a particle depends on the weakest set of bonds that hold it together. We can divide most chemical bonds into one of three groups. In order from weakest to strongest, they are van der Waals forces, hydrogen bonding, and covalent bonding. Examples of the bond energies of materials experiencing these different interactions are given in Table 1.2, along with their melting points, which are rough measures of the strength of the bonds holding these materials together, and their surface energies.

An additional means by which surface energies can be decreased is through contact with other surfaces. In the extreme case, this could lead to chemical bonds forming across the surfaces, which would be the reverse of breaking the particle in half. However, even in the absence of chemical bond formation, the close contact of two surfaces will decrease surface energy due to van der Waals interactions between atoms on the two surfaces. Said differently, the two particles will be held together by van der Waals forces acting between the two surfaces.

A consequence of this is that surfaces are “sticky”. While this is true for all surfaces, it is most apparent for small particles since these particles have high surface areas (so high amounts of surface energy) and low weights. We can see this by comparing the stickiness of particles against a wall. A relatively large particle, such as a grain of sand, will, if pressed against a wall and released, readily slide down the wall because the gravitational force on the particle is greater than the van der Waals forces between the particle and the wall. However, for a small particle, such as a speck of smoke, the balance between surface area (and therefore surface energy) and weight (gravitational energy) favors the adhesion of the smoke particle to the wall—the wall blackens. The small smoke particle will not slide down the wall because the gravitational force is now less than the friction generated by van der Waals forces holding the particle against the wall.

Friction

Friction is a force that acts at the junction of surfaces. It is defined as any force that hinders (or entirely prevents) touching bodies from sliding across or over one another. It is a vector quantity (i.e., it has both a magnitude and a direction), and is always in a direction parallel to the surface of contact and opposite the direction of motion or applied force if any.

The magnitude of the frictional force between two bodies is determined by two factors. The first is the strength of the force holding the bodies together. In our everyday lives, this is normally gravity. For example, the strength of friction between a book and a table on which it is placed depends on the weight of the book. However, friction can result from any applied force. For example, consider a book pressed against a wall. The book does not slide to the floor because the friction between the book and the wall,¹¹ which is created by applying a force to the book, prevents it from moving.

The second factor is the identity of the two bodies. For example, friction is higher between rubber and asphalt than between rubber and ice, and for this reason, a car can be stopped more quickly when it is on dry pavement than on icy pavement.

Because small particles have high surface areas, the importance of friction is much greater for these particles than for larger ones. This is manifested in the bulk behaviors of the particles.

Bulk Density, Bulk Flow, and Powder Compressibility

Density is simply the mass of a material that fills a unit volume. The density of a solid mass with no internal voids or porosity is termed the “true” density of that material, as discussed earlier. The true density of a material depends primarily on its composition,¹² and for any given material it is a constant that can be measured accurately and reproducibly.

The density of a collection of particles is invariably lower than that of a solid mass because of the void spaces between the particles [2]. This density is referred to as the loose bulk density of the material if the material is not under any stress. For obvious reasons, the loose bulk density is determined by both the true density of the particles themselves and the efficiency with which they pack together. For uniform macroscopic spheres, such as ball bearings, packing is generally very efficient and can approach the limit of random closest packing (approximately 54–58% solid and 42–46% void space). Particle shape can also play a role in packing efficiency—when randomly arranged, blocky particles pack the most efficiently, and acicular (rod-like) particles the least.

The packing efficiencies of small particles, in comparison to large particles or small objects (e.g., sand or salt grains), are low and are dependent on particle size and surface characteristics such as surface chemistry and surface morphology [3]. The dependence of bulk density on particle size is shown in Table 1.3 for silica particles.

In this table, we specify that the bulk density values are “loose” bulk densities. This is important because the bulk density of a sample can be changed quite easily. The

¹¹ The friction between the book and the hand applying the force is also critical.

¹² Although density can be affected by temperature (thermal expansion), this effect is small and can be easily taken into account. In addition, different crystalline phases of the same material may have different densities.

Table 1.3 Bulk density and void fraction as a function of particle size

Material	Particle size (μ)	True density (g/cc)	Loose bulk density (g/cc)	Void fraction (%)
SiO ₂ sand	1,000	2.6	1.6	38
SiO ₂ microbeads	1.5	2.6	0.88	66
Fumed SiO ₂	0.015	2.2	0.05	98

sample can be compressed, increasing the bulk density, or “loosened”, for example by shaking the particles in air. This can be understood on the basis of friction. A sample of particles will naturally settle under gravity until it reaches a certain density. During this settling, the number of particle–particle contacts increases. Settling ceases and bulk density is set, when the frictional forces between the particles are greater than the gravitational forces that act on them. Applying an outside force, such as by using a piston in a pellet press or even rapping a small sample on a tabletop, augments the gravitational force. The particles then move to a denser state, where the increased friction from additional particle–particle contacts again equals the other forces acting on the particles.

Bulk density can be measured either when the particles have been exposed only to gravitational forces (loose bulk density) or when the particles have been subjected to an additional force, in which case the bulk density is described by the nature of that force (e.g., “tapped” density).

The degree to which a given amount of additional force causes the particles to densify is referred to as the compressibility of the particles. Needless to say, compressibility is a function of the particle size, the particle surface, the strength of the additional force, and the coefficient of friction. Compressibility is greater for particles that are initially loosely packed since the degree to which the particle packing can increase is greater for loose particles than for particles that are already packed tightly.

The effect of particle size on bulk density and compressibility is shown in Fig. 1.10. The same weight of two samples of sugar has been added to two test tubes. The sugars differ in particle size (540 microns vs. 60 microns). The smaller particles, due to stronger interparticle interactions, occupy a larger volume and so have a lower bulk density. The heights of the powder beds were marked, and then the test tubes rapped sharply on a tabletop ten times. After tapping, we see that the small particles have compressed to a greater extent than the large particles (the volume of the small particles decreased by 38%, while that of the large particles by only 2%). The small particles are more compressible because these particles initially have more void volume. Despite their greater compressibility, the small particles still occupy a greater volume than the same weight of larger particles after compressing. Note that the total frictional forces resisting compression (and, roughly, the total area of contact between the particles) are the same for each bed of particles since each has been acted on by the same forces.

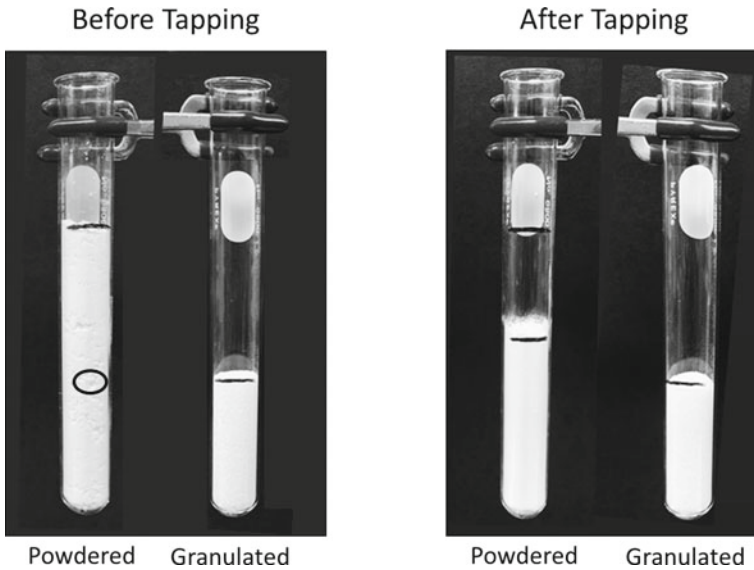


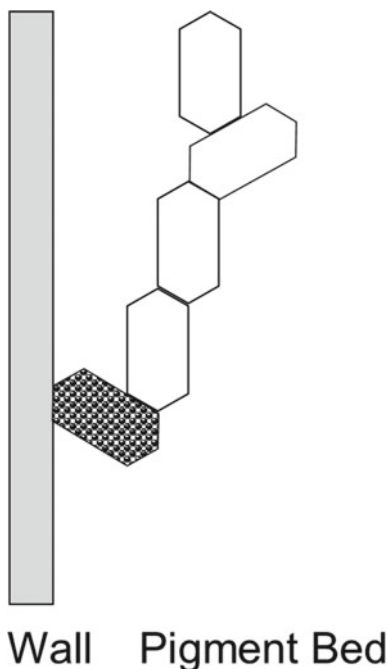
Fig. 1.10 Test tubes showing compaction of equal weights of granulated and powdered sugar. Note large void in untapped powdered sample (circled)

A second important bulk property of small particles is their flow characteristics. If put in motion, large particles will interact with one another when they collide, but otherwise move independently. On the other hand, small particles tend to move as a coherent mass—all of the particles move with respect to their surroundings, but they do not move with respect to one another. The smaller particles remain locked in place due to friction, in a manner analogous to their resistance to compression. Here, we see that the balance between the volume force (gravity) and the surface force (friction) results in very different behaviors. For large particles gravity dominates, and both the initiation and continuation of flow are more facile than with their smaller, higher surface area counterparts.

At extreme conditions, when particles are very small and the surface chemistry of the particles leads to strong interparticle forces, conveying and handling the material in pneumatic lines and storing it in silos become challenging. For dilute-phase pneumatic conveying, the particles need to be dispersed in the gas phase, and significant energy and high turbulences are required to initiate and maintain this degree of dispersion. The challenge for storage is initiating the flow of the particles from the bottom of the storage silo when removing the particles for use. Such a silo may contain several tens of tonnes of titanium dioxide, yet when the outlet at the bottom of the silo is opened, flow might not occur, even, in extreme cases, when the chute diameter approaches one meter. Instead, the particles remain “hung up” in the silo.

This observation leads to an obvious question: what is holding the weight of the titanium dioxide particles, if not the bottom of the silo where the outlet is located? It is the walls of the silo that support the load through a combination of wall friction,

Fig. 1.11 Frictional resistance to flow of a particle in contact with the wall of a bin



interparticle cohesion, and interparticle friction. Particles that touch the walls are held in place by wall friction, and these particles, in turn, hold particles that are touching them in place by internal friction (Fig. 1.11). A simple calculation shows that a single particle in contact with the wall can support the weight of as many as one million other particles. Such is the importance of friction for particles in this size regime.

Finally, we may wonder about the packing structure of small particles. For example, a sample of pigmentary TiO_2 is roughly 80% voids. How are these particles arranged? We first note that the particles cannot be distributed evenly at the single-particle scale (Fig. 1.12a). Here, there are far too few contacts to support the weight of the particle bed. This is also inconsistent with electron micrographs that show a tight packing of the particles at this length scale (Fig. 1.12b).

Instead, the particles pack in a fractal arrangement.¹³ Here particles are densely packed into small micro-clumps (Fig. 1.13, top), consistent with what is seen in the electron micrograph in Fig. 1.12b. These micro-clumps, in turn, pack together densely into meso-clumps (Fig. 1.13, middle), which in turn pack together into macro-clumps (Fig. 1.13, bottom). If we assume a packing density of 50%, then the micro-clumps are 50% void, the meso-clumps are 75% void, and the macro-clumps are 87.5% void.

¹³ A fractal is an object that appears the same at different length scales. An example is the appearance of a coastline—the general character of a coastline looks the same from orbit as it does from an airplane. This is known as the coastline paradox. This situation can be contrasted with the appearance of a tree—we can easily tell the scale at which we observe the tree by the features that we see.

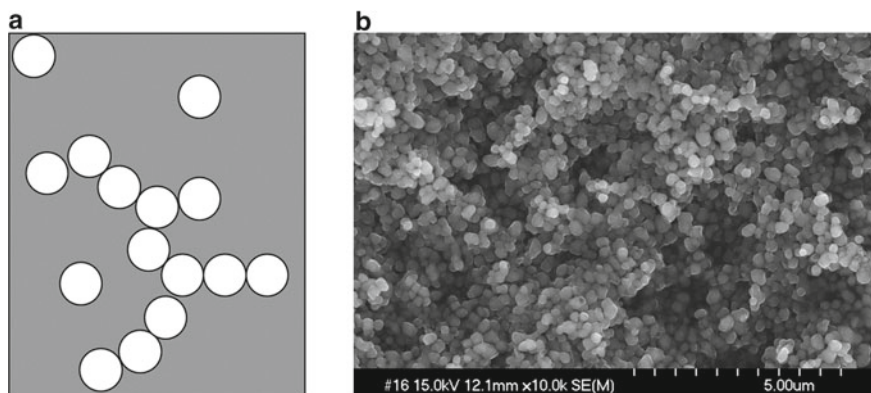


Fig. 1.12 Arrangements of small particles. **a** Even arrangement at 80% void volume. **b** Actual packing of pigmentary TiO_2 with a bulk void volume of 80%

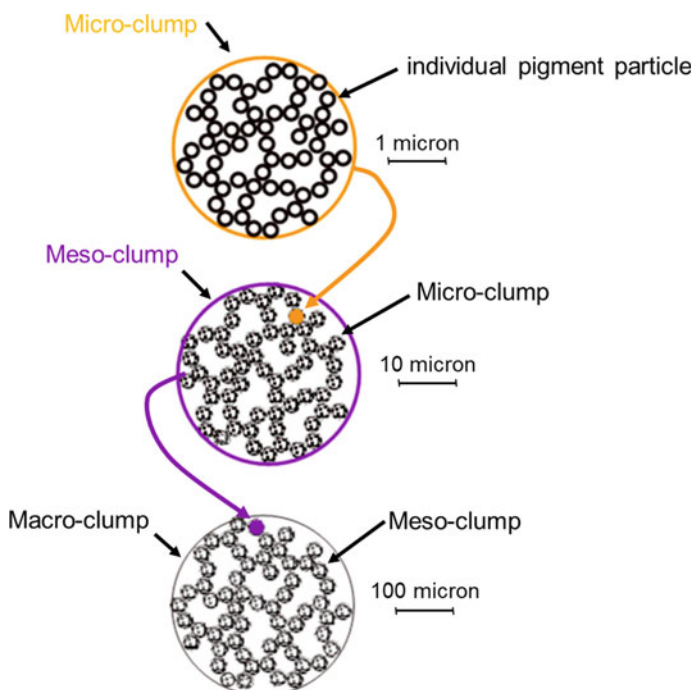


Fig. 1.13 Fractal packing arrangement of pigmentary TiO_2

Of course, the sizes of the various clumps vary continuously over a large range rather than falling into just these three categories.

Surface Charge—General

The surfaces of many materials can hold an electrical charge—either a negative charge due to an excess of electrons or surface anions or a positive charge due to a deficit of electrons or an excess of surface cations. This is true for both macro and microparticles, and in both air and in slurry. However, the origin, control, and stability of accumulated electrical charge on a surface are quite different in the wet and dry states.

Surface Charges in Dry Powders

The charges on dry particles are typically referred to as static electricity and are found when there is an excess or deficit of electrons on the particle. For energetic reasons, the extra electrons will travel to the surface of the particles where they are arranged in a way that minimizes electron–electron repulsive energy. For spherical particles, this will be an even distribution on the particle surface. For other particles, charge tends to accumulate based on surface curvature. Regions of high curvature (edges, corners, or protrusions) accumulate a greater charge than relatively flat regions.

When a charged surface approaches an electrically grounded (earthed) surface, the excess charge will travel through the air and discharge into the grounded surface as a spark. The distance over which this discharge occurs depends on the magnitude of the charge and environmental conditions (temperature, relative humidity, etc.). The surface density of the electrons controls the magnitude of the charge—as density increases, the voltage of the surface electrons increases. Charge will accumulate on the surface until the number of charges per unit area, which determines the surface voltage, exceed a threshold and the particle discharges to a grounded surface.

For small particles, the most common source of static charge is the friction generated when particles move past one another, a process known as triboelectrification. As discussed above, charges will accumulate on the surface until a certain surface density is exceeded. Obviously, the greater the surface area, the greater the number of charge units that can accumulate. For this reason, the accumulation of static electricity is greater for smaller particles than for large ones. As a consequence, considerable charge (sometimes thousands of volts relative to ground) can build up in a stream of moving small particles, and for safety reasons, it is essential that equipment through which particles are conveyed is electrically grounded.

Surface Charges in Liquid Slurries

The surfaces of slurried or suspended particles can also be charged but by a much different mechanism. As outlined in the discussion on surface energy, the surfaces of particles tend to be high energy, and therefore chemically reactive. This leads to the adsorption of molecules or ions onto suspended particle surfaces. In some cases, these absorptions occur at reactive sites on the surface, and the reactivities of these sites are dependent on the chemical state of the site, the nature of the adsorbing molecule or ion, and the identity of the liquid medium (water or organic solvent). Certain combinations of surface site and adsorbing species can be quite energetically favored, leading to strong adsorption.

Molecular salts, including acids and bases, tend to be soluble in water because the water molecule is polar. When dissolved in water, these materials dissociate into charged species, with the charges being either negative (anions such as hydroxide or chloride) or positive (cations such as protons or sodium ions). Even in the absence of foreign dissolved species, water has both anionic and cationic species within it. These are the hydroxide (OH^-) and proton (H^+) ions that spontaneously form when water molecules dissociate. The concentrations of these species change when an acid or base is dissolved in the water.

The surfaces of most inorganic oxides are covered with oxide groups, hydroxyl groups, and/or adsorbed water molecules. These groups can react with dissolved hydroxyl groups or with dissolved protons. These reactions include the removal of a proton from a surface hydroxyl or adsorbed water molecule, the addition of a hydroxide ion onto the surface, the removal of a hydroxyl group from the surface, or the adsorption of a proton onto the surface. The first two of these give the surface a net negative charge, and the last two of these give the surface a net positive charge. Note that both positively and negatively charged surface species can be present on a given surface at the same time because a surface can have more than one type of reactive site. Important aspects of surface charge formation are given in greater detail in Chap. 2.

Interactions with Light

To some degree, all particles interact with light. These interactions can take two forms: light absorption and light scattering. In principle, both types of interactions occur for all particles. However, in most cases, one or the other of these interactions dominates.

Light absorption by atoms, molecules, and particles occurs when the energy of a photon matches the energy required to affect some change in the material. This change can be an increase in the rotational rate of a molecule, an increase in the amount of a vibration between atoms in molecule or particle, or an increase in the electronic energy. These different transitions require different amounts of energy. Typically, rotational changes occur when microwave radiation is absorbed, vibrational changes

when infrared radiation is absorbed, and electronic energy changes when visible or ultraviolet radiation is absorbed. The exact frequency of light absorbed depends on the chemical identity of the absorbing species. This leads to, as an example, different visible light wavelengths being absorbed by different materials, which explains why different materials have different colors. This is discussed in greater detail in Chap. 8.

Light scattering occurs when light changes direction as the result of encountering a particle. This change in direction occurs without a change in frequency (color) or intensity (energy) of the light. The degree to which the direction of the light is changed for a particle isolated in a medium depends on four factors: the wavelength of light, the size of the scattering particle, the refractive index of the particle, and the refractive index of the surrounding medium. In general, scattering is greatest when the size of the scattering species is close to the wavelength of light being scattered and when the refractive index of the particle is very different from that of the surrounding medium. This is discussed in greater detail in Chaps. 3 and 4.

Even weak scattering, which is defined as a small change in direction for a given scattering event, can be important if there are many such events. An example of this is the blue color of the sky during the day, and the red color seen when the sun is on the horizon. The separation of blue light from red light is caused by differences in the light scattering strength of nitrogen and oxygen molecules in the air as a function of the wavelength of light. More specifically, blue light is scattered by these molecules more strongly than red light. Although each scattering event results in only a small change in direction of the light, the thickness of the atmosphere (almost 100 km) ensures that there is a multitude of such events.

Summary

Microscopic particles behave in many ways quite differently than their larger counterparts. Because our everyday experiences are mostly with macroscopic particles or objects, microscopic particle behavior can be both unexpected and foreign to us. The factor that differentiates the behavior of large and small particles is the balance between particle volume and particle surface area. On an equal weight basis, microscopic particles have a much higher surface area than macroscopic particles, and as such their behaviors are dominated by surface forces whereas the behaviors of large particles are dominated by gravitational forces.

Regardless of particle composition, there are many important characteristics that are common to all the small particles that are routinely used in the coatings and plastics industries. These include particle shape, particle size and size distribution, surface charge, light interactions, and various bulk powder properties such as bulk density, bulk flow, and compressibility.¹⁴ By understanding the source and nature of surface forces, we can understand these properties of powder samples.

¹⁴ The measurement of these properties is detailed in Chap. 2.

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