Some very small interparticle forces can create some very big powder and bulk solids headaches. These forces can cause high pressure drops and plug our pneumatic conveying lines.¹ When polyolefin (polyethylene and polypropylene) powders collect into sheets and crash down into our fluidized bed reactors, or agglomerates and caking make our granulation and tabulation more difficult, or cohesion inhibits hopper emptying, these forces are at work.

Yet, these interparticle forces aren’t always evil. They’re useful when we need to powder coat our automobiles or deposit toner on our printed copies. Indeed, these forces are even responsible for the early stages of planet formation. In this column, we’ll take a look at the nature and constraints of interparticle forces to better understand how they can plague or enhance your process. [Editor’s note: For information on obtaining previous “Particle Professor” columns, see “For further reading” later in this article.]

The most common types of interparticle forces in particle technology are: van der Waals, coulombic, and capillary forces. These forces are very different from each other in terms of strength, range of interaction, and sensitivity to the composition material.

**Van der Waals forces**

Named after the Dutch scientist Johannes Diderik van der Waals, this force was at one time attributed to any repulsive or attractive force that couldn’t be explained by covalent bonds, hydrogen bonds, coulombic forces, or capillary forces. Later, this definition was more formalized as the force between two permanent, instantaneous or induced dipoles (including Keesom, Debye, and London forces). The van der Waals force is weaker than covalent bonding, has no directional dependency, always exists, and can’t be saturated or diminished.²

A gecko’s toes provide a good example of the van der Waals force. A gecko can climb smooth glass surfaces because its toes have a large surface area to maximize the contact between the gecko and the glass surface.³ Originally, capillary forces were thought to be at play here, but that hypothesis was discounted a few years ago.⁴ The large surface area of the gecko’s toes provide abundant local curvatures that provide the induced dipoles needed for the van der Waals force.

The van der Waals force’s attractive or repulsive range is very short, just a couple nanometers for particles.⁵ As a result, particle-to-particle attraction due to the van der Waals force is only possible when the particles are in close proximity to each other. Furthermore, the strength of this interaction is relatively weak for particle systems, so particles larger than 100 microns are more likely to be controlled by gravitational or hydrodynamic forces than by van der Waals forces.⁶ Even particles around 10 microns in size tend not to exhibit strong van der Waals forces. This is because gravitational force is proportional to the cube of the particle diameter, and van der Waals forces are linear with the particle diameter.

Nanoparticles, however, are susceptible to van der Waals forces on a level that could impact your process. These forces initiate clustering in carbon black and fume silica. As a result, both materials tend to be easy to fluidize, convey, and classify even though the particles themselves are small and cohesive. With van der Waals forces, these small particles cluster together without creating agglomerates or sinter into a more manageable size. If van der Waals forces weren’t limited to a very short range, these materials would cake instead of forming manageable particles.

Managing van der Waals forces can be challenging. They’re omnidirectional, can’t be saturated or diminished, and always exist. Particle properties, rather than the environment, need to be managed, and changing the particle size or surface morphology is a good first step.

**Coulombic forces**

Coulombic (or electrostatic) forces involve the exchange of electrons or ions from one surface to another. For small particles in close proximity, van der Waals forces can be stronger than coulombic forces. However, coulombic forces are much more far-reaching so are more prevalent and problematic than van der Waals forces.

We’ve all experienced coulombic forces in action. Polyethylene or polypropylene pellets are difficult to manage because of their electrostatic forces. Opening and placing a trash bag in a trash bin demonstrates this difficulty. Electrostatic precipitators use these same coulombic forces to collect fine particulate over a relatively large distance.

The nature of coulombic forces
makes sense when considering the interaction of two different materials. Rub a rubber rod along fur and the rod becomes more positively charged while the fur becomes more negatively charged. This is because one material is more of an insulator than the other. Yet, why does this happen when considering just one material? In other words, why is a bed of pellets of the same material subject to coulombic forces?

Some hypotheses have stated that this behavior is due to the combination of asymmetry between two contacting surfaces, which results in the tunneling of trapped electrons. The surface with more curvature can trap more electrons. So in a bed of particles of the same material, particle collisions will result in smaller particles capturing electrons and becoming more negatively charged, while larger particles will become more positively charged because of electron depletion. Particles of unlike charges are now attracting each other, leading to particle cluster formation and possible agglomeration. After such particle collisions, particles with no previous attraction to equipment may now have an affinity to stick to the walls.

Surface morphology plays an important role here. If particles are rough enough and have lots of surface curvatures, the charge disparity remains on the particles, and the electrons are less likely to move to the smaller particles. This was demonstrated and explained by Professor Heinrich Jaegar and a group of researchers at the University of Chicago in the journal *Nature*. The group performed powder drop experiments and found that similarly sized glass beads formed clusters while copper ones didn’t. Artificially roughing the surface of the glass beads with fumed silica resulted in the glass beads no longer clustering.

The group also found that electron charge transfer alone doesn’t always explain the attractive and repulsive behavior in particle systems. The exchange of ions also can be a significant factor. The most common ions are hydroxyl groups on particle surfaces, usually due to the presence of water. Water can quickly coat a particle’s entire surface as a monolayer (or a one-molecule-thick layer) of hydroxyl groups and should be considered to be everywhere, so coulombic forces can happen in the most unexpected places.

Unlike van der Waals forces, coulombic forces can be managed through the environment. Adding antistatics can often help reduce particle clustering, agglomeration, and buildup. Quaternary salts such as some ammonia, amides, phosphate esters, or ethoxylated amine salts provide a conductive tunnel between particles to dissipate electron buildup on smaller particles. Grounding also may help but usually only for smaller systems. Adding small nanoparticles such as carbon black or fumed silica may work well for your application. As previously noted, these materials artificially roughen particle surfaces. Humidification also works, provided the correct amount is used. Too little humidification may just add more hydroxyl groups, depending on the particles, and too much humidification may cause capillary forces to take hold.

Traditionally, capillary forces are thought of as liquid bridging between two surfaces. That’s certainly the case when caking is an issue. However, capillary forces can happen with a lot less liquid than what’s needed for bridging. Water molecules only a monolayer thick on a surface can be the attractive conduit between two particles through hydrogen bonding. Recent work from MIT suggests that an additional intermolecular force may be at play with liquid—solid interfaces. This additional force, although miniscule, can affect the hydrodynamics when a large number of liquid—solid interfaces are involved.

Capillary forces operate on a larger scale than van der Waals and coulombic forces and can be adjusted by the amount of available “liquid” (including monolayers) and that liquid’s properties, such as surface tension and viscosity. Additives that decrease the surface tension or viscosity could reduce caking or agglomeration. Such additives for a wet particulate system could be an alcohol or a surfactant. For ionic liquids the pH adjustment could have an impact.

### Capillary forces

Capillary forces are those where surface tension and bonding, or both (hydrogen bonding for instance), result in particle-to-particle attraction. Unlike van der Waals and coulombic forces, capillary forces are only attractive forces. This is the attractive force that allows liquid to move against gravity up a small straw or wet a surface above the liquid layer the surface is immersed in. Trees and plants use capillary forces to move water from the ground up to the leaves.

Capillary forces can be significant and stronger than van der Waals or coulombic forces. However, capillary forces aren’t as far-reaching as coulombic forces, and particles typically need to be within close proximity — if not touching — before capillary forces take hold.

### Solutions

If interparticle forces are causing too much or not enough clustering, agglomeration, sintering, sheeting, or caking in your process, understanding the force, or forces, responsible for such behavior may help you find a solution. However, this isn’t always easy. More often than not one must resort to trial-and-error. Using the scientific method, try the following experiments to see what’s best for managing your interparticle forces:

- Add smaller particles of the same material,
- Add nanoparticles of a different material such as carbon black or fumed silica,
- Narrow or broaden the particle size distribution,
- Roughen particle surfaces using a chemical etching agent,
- Add an antistatic agent such as a quaternary salt.
Try humidification. (Relative humidities of 40 to 60 percent are typical.)

Add a surfactant or polar solvent or change the material’s pH.

For further reading

Find more information on this topic in articles listed under “Particle analysis” in Powder and Bulk Engineering’s article index in the December 2014 issue and in the Article Archive on PBE’s website. (All articles in the archive are available for free download to registered users.)

References


