

## CHAPTER 2 | Three-Dimensional Geometry, Intermolecular Interactions, and Physical Properties

Chapter 2 reviews VSEPR theory, net dipoles, and dipole moments—concepts that students encountered in general chemistry. The polarity of molecules is used to explain intermolecular attraction (intermolecular forces), and the understanding of intermolecular attraction is then applied to melting points, boiling points, and solubility. In addition to those topics, the chapter explains dash–wedge notation (which students have seen in general chemistry but may not have been asked to use correctly), introduces protic and aprotic solvents, and describes the structures and functions of soaps and detergents.

### HEADS UP!

Although this chapter may seem like the same simple general chemistry review (with an organic twist) that one sees in many textbooks, in several places Karty has introduced information now that many books wait until later to talk about in depth. For example, Karty explicitly defines protic and aprotic solvents for the first time here, providing discussions and pictures involving solubility, not just as an example of ion–dipole interactions but as a direct lead-in to mechanistic discussions later in the text. This chapter also emphasizes visualization, encouraging students not only to think in 3D but also to start looking at partial charges on a molecule (again with a view to reactivity in later chapters). Taking the time to set up a good foundation here makes later chapters easier.

### COMMENTS BY SECTION

#### 2.1. Valence Shell Electron Pair Repulsion (VSEPR) Theory: Three-Dimensional Geometry

VSEPR theory is introduced in general chemistry, and students should be familiar with it. The presentation in organic chemistry is simpler, much to the relief of students, because we can ignore trigonal bipyramidal and octahedral arrangements.

*The term to describe the arrangement of electron pairs around a central atom is electron geometry; the term for the arrangement of atoms is molecular geometry. The designations vary from one text to another, so you may wish to be consistent with those terms or introduce synonymous ones that your students learned in general chemistry.*

Table 2-2 summarizes electron geometry, and Table 2-3 summarizes the possible molecular geometries for each electron geometry. Section 2.1b introduces angle strain (in the context of ring strain). That concept will reappear in the discussion of stabilities and conformations of cycloalkanes in Sections 4.4 and 4.5.

In a lecture presentation or discussion, some simplifications can make discussing VSEPR less wordy. For example, you can define atoms attached to a central atom and lone pairs around a central atom as “things.” You can then ask students to determine the number of “things” and explain how that number determines the electron geometry. You can also simplify electron geometry to *geometry* and molecular geometry to *shape*. That approach simplifies a discussion of water, for example: How many “things” are around the oxygen? If there are four things, its geometry is tetrahedral. And its shape? Bent!

Tetrahedral arrangements are harder to illustrate and harder for students to visualize. A colleague gave me the best illustration I’ve found: a tetrahedron made of drinking straws and tape. It allows me to point to the center of the tetrahedron or actually put a model of methane inside it to point out the relationship between the molecule and the tetrahedron. It also clarifies the fact that the central atom is at the center of the tetrahedron.

The value for the bond angles in a tetrahedral arrangement also is not intuitively obvious. I tell students that the law of cosines or vector algebra would allow us to calculate the value. (See the “Resources” section for a relevant reference.) One year, I had a student who used the law of cosines to prove the value of  $109.5^\circ$  for extra credit.

#### 2.2. Dash–Wedge Notation

This section describes dash–wedge (or dagger) notation explicitly. It describes the “V” formed by the normal lines and its orientation with respect to the V formed by the dash and wedge. It is important to start emphasizing dash–wedge notation, and 3-D visualization, in this chapter; the sooner students become comfortable with that notation, the easier the concepts will come to them.

I use my model kits (both a ball-and-stick model kit and a Darling model kit, see the “Resources” section for that reference) and draw a structure similar to the artwork from Figure 2-5. I hold both models directly up to the

drawing on the board, emphasizing which bonds are in the plane of the chalkboard (paper) to try to make the model kit and the drawing match in the students' eyes.

### 2.3. Strategies for Success: The Molecular Modeling Kit

The “Strategies for Success” sections do not have to be taught in class. They are generally either exercises that students can pursue outside class or methods that can be integrated into the lecture for the other sections (which is how I approach this section; I weave it throughout the chapter). The skills taught in those sections are important. Section 2.3 requires students to convert dash–wedge drawings into models, rotate the model, and then draw the correct dash–wedge representation of the model in its new position. That practice will help students learn to interchange two-dimensional and three-dimensional representations.

### 2.4. Net Molecular Dipoles and Dipole Moments

This section begins with the net dipole of a diatomic molecule (HF) and then defines a dipole moment. A discussion of vector algebra is followed by a qualitative assessment of net dipoles in linear and tetrahedral arrangements of atoms and lone pairs. Students need to leave this section with an understanding not only of direction but also of magnitude of the dipole.

### 2.5. Physical Properties, Functional Groups, and Intermolecular Interactions

Table 2-4 contains the physical properties of molecules of similar sizes but different functional groups. That context leads to a discussion of the difference in distribution of charge in various functional groups and the introduction of five types of intermolecular interactions:

1. Ion–ion interactions
2. Dipole–dipole interactions
3. Hydrogen bonding
4. Induced dipole–induced dipole interactions
5. Ion–dipole interactions

I confess that I organize those intermolecular interactions slightly differently because approaching hydrogen bonding first—oversimplifying it as a “special kind” of dipole–dipole interaction—has led to less confusion regarding hydrogen bonding's being an intermolecular interaction rather than an actual bond.

Regardless of what order you present the information in, Table 2-4 is an excellent start for discussing intermolecular interactions. *Note the box in the section summarizing the differences in those attractions:* “All else being equal, the greater the concentrations of charge that are involved in an intermolecular interaction, the stronger is the resulting attraction.”

### 2.6. Melting Points, Boiling Points, and Intermolecular Interactions

This section begins by contrasting solids, liquids, and gases and discusses the correlation between intermolecular interactions and melting/boiling points.

The discussion of intermolecular interactions continues, going from strongest to weakest:

1. Ion–ion interactions (ionic bonds; Section 2.6a)
2. Dipole–dipole interactions (Section 2.6b)
3. Induced dipole–induced dipole interactions (London dispersion forces; Section 2.6d)

Hydrogen bonding is discussed as a special form of dipole–dipole interaction in Section 2.6c. That section introduces hydrogen bond acceptors and donors.

Section 2.6d discusses the role of polarizability and surface area of molecules, something students often find challenging. Drawing long molecules on the board with a “squishy” electron cloud around them sometimes helps, as does an analogy of trying to squeeze into a bus seat next to another passenger. If both passengers are wearing big,

bulky fluffy coats and carrying large bags, rearranging to fit comfortably next to each other is easier (move the bags to each side, squish the coats) than if both passengers are trying to squeeze together in a small space and are wearing only shorts.

## 2.7. Solubility

This section introduces and elaborates on “like dissolves like,” discussing entropy’s role as a driving force. It also discusses ion–dipole interactions and how hydrocarbon groups affect solubility. *Note the highlighted box in Section 2.7a that relates the strength of ion–dipole interactions to the magnitude of the dipole moment.*

The differences among the motions and arrangements of molecules in solids, liquids, and gases can be explained by using John Fortman’s analogies of a military unit, a reunion party, and a soccer game, respectively:

Solids (Military Unit)	Liquids (Reunion Party)	Gases (Soccer Game)
Short distance between molecules	Short distance between molecules	Long distance between molecules
Rigid	Flowing	Diffusion
No disorder	Much disorder	Much disorder
No random motion	Some random motion	Much random motion

(See the “Resources” section for reference.)

*Intermolecular interactions* are synonymous with *intermolecular forces* (IMFs), which may be the term that your students learned in general chemistry.

Ion–ion interactions are not, technically, intermolecular interactions because neutral molecules are not involved. You may wish to explain to students that ion–ion interactions are discussed here because of their relevance.

## 2.8. Strategies for Success: Ranking Boiling Points and Solubilities of Structurally Similar Compounds

As mentioned, this section can be assigned for out-of-class reading. It presents a detailed example in which students evaluate intermolecular attractions and use them to assign relative boiling points.

The excellent worked example thoroughly discusses a complex problem. I recommend requiring students to read and understand this section before class and then giving an in-class exercise to assess their understanding.

## 2.9. Protic and Aprotic Solvents

This section introduces the differences in solubility of ionic compounds in protic and aprotic solvents by comparing the solubility of NaCl in water and DMSO. Table 2-7 lists common protic and aprotic solvents and introduces abbreviations such as *DMSO* and *DMF*. *The difference between protic and aprotic solvents is presented here so that students will understand the role of solvents in substitution and elimination reactions. The higher solubility of ionic compounds in polar protic solvents serves as an easy introduction to the role that those solvents will play in facilitating the dissociation (heterolysis) of alkyl halides and other substrates in  $S_N1$  and  $E1$  reactions.*

This section introduces abbreviations for common solvents (DMSO and DMF). You may wish to discuss the prevalent use of abbreviations in organic chemistry and tell students whether you expect them to identify a specific abbreviation with the full name, structure, or both. To understand most problems (and for the American Chemical Society final exam in the second semester), students typically need to know DMSO, DMF, and THF.

## 2.10. Soaps and Detergents

This section discusses the structure and action of soaps and detergents. (Section 20.3 covers the synthesis of soap.) The discussion introduces and defines the terms *hydrophilic*, *hydrophobic*, *ionic head group*, *hydrocarbon tail*, *micelle*, *emulsify*, and *detergent*. The section also discusses hard water, precipitation of soap scum, and how detergents address the problem of soap scum.

Although most texts place that discussion with saponification of esters, the topic fits well with the coverage of intermolecular interactions. The discussion also introduces terms that allow students to better understand the structure and function of phospholipids, which are discussed in Section 2.11b.

## 2.11. An Introduction to Lipids

Because lipids are defined by their relative insolubility in water (or solubility in ether), this chapter is a logical place to introduce them. The section includes four subsections:

- 2.11a. Fats, Oils, and Fatty Acids
- 2.11b. Phospholipids and Cell Membranes
- 2.11c. Steroids, Terpenes, and Terpenoids
- 2.11d. Waxes

## STUDENTS' PERSPECTIVES

This chapter is all about introducing new ways of viewing molecules and setting up good habits; with any luck, those visualization tools (dash-wedge notation, model kits) will become second nature. Introducing dash-wedge notation here, early, and forcing students to use it repeatedly seems to help them master the skill.

I agree with Joel Karty's blog post ("Molecular Model Kits," posted October 9, 2012, at teachthemechanism.com) about students' reluctance to use molecular model kits. Students need the time in the class periods to see not only how to use them but also how useful they are in solving certain types of problems. Karty has incorporated several of those lessons into the textbook sections marked "Strategies for Success." One such section shows how molecular models can be used to arrive at various dash-wedge representations of the same molecule.

Intermolecular attractions are, historically, hard for students to grasp. The difficulty arises from several sources.

First, we are trying to simplify a complex subject. For example, most organic chemistry texts omit the factors arising from crystallinity that affect melting points.

Second, students often think of *polar/nonpolar* and *soluble/insoluble* as discrete variables (i.e., yes-no) instead of continuous variables. That is, a compound is not actually inherently polar or nonpolar; it is polar or nonpolar in relation to another compound. For example, the solvents benzene and toluene are less nonpolar than acetone; however, toluene is more polar than benzene. Getting students to a point at which they can explain that relationship is challenging. Similarly, all organic compounds are soluble to some extent in water.

Third, the terminology can be confusing. *Hydrogen bonding*, for example, opens the door to confusion of intermolecular attractions with covalent and ionic bonds. Students often use the term *bonds* inaccurately in their descriptions and in their cartoon drawings. In addition, the multiple terms that may be (or may not be, according to some) synonymous (*London forces*, *dispersion forces*, *van der Waals attractions*) add confusion. Finally, *ion-ion attractions* and *ion-dipole attractions* cause a problem because they technically do not involve attractions between molecules. The terms logically fall with intermolecular attractions but contradict the strict definition of that term.

The study of intermolecular attractions requires students to visualize what is happening at a molecular level, and that presents a challenge. Using model kits early in the semester, and focusing on 3-D representations of molecules early in the semester, does help, as does asking conceptual questions (explain this, draw that) rather than simple identification questions (rank by boiling point).

## RESOURCES

For a discussion of how to determine the  $109.5^\circ$  bond angle in a tetrahedral arrangement of atoms, see "Employing Vector Algebra to Obtain the Tetrahedral Bond Angle" by George H. Duffey. *J. Chem. Educ.* **1990**, *67*, 35. doi:10.1021/ed067p35.

For a history of dash-wedge notation, see "The Historical Origins of Stereochemical Line and Wedge Symbolism" by William B. Jensen. *J. Chem. Educ.* **2013**, *90*, 676–677. doi:10.1021/ed200177u.

Many instructors have their own preferences for which modeling kit their students use. I have found the most useful sets to be the ones produced by Steve Darling (www.darlingmodels.com) because the geometry is built into the structure. Students do need some instruction in how to assemble them correctly, however, and be careful to help students perceive the difference between trigonal planar carbon and tetrahedral carbon.

For details describing an analogy that compares solids, liquids, and gases to a military unit, a reunion party, and

a soccer game, respectively, see “Pictorial Analogies I: States of Matter” by John J. Fortman, *J. Chem. Educ.* **1993**, *70*, 56. doi:10.1021/ed070p56.

*Napoleon’s Buttons: 17 Molecules That Changed History* by Penny Le Couteur and Jay Burreson (New York: Jeremy P. Tarcher/Penguin, 2004) has a chapter titled “Oleic Acid.” The chapter discusses the history of soap, the structure of fatty acids and triglycerides, saponification, and how soap functions.

The following classroom demonstration allows you to discuss intermolecular interactions, including the effect of alkyl chain length.

1. Combine approximately 10 mL of hexanes and 10 mL of methanol in a large test tube. At this point, the students will see two layers, although not of equal volume.
2. Add approximately 10 mL of 1-butanol and mix. The students will see that the contents of the tube are homogeneous.
3. Add approximately 10 mL of water and mix. A top layer of hexanes, approximately one-fourth of the total volume, will form at the top of the tube.

After each step, you can ask students to use IMFs to explain what they observe. The results in step 2 allow you to discuss the different roles of the hydroxyl group and the alkyl chain in 1-butanol.

In a follow-up activity, you can have students draw the intermolecular attractions at each step to explain what they observed. That activity, combined with the demonstration, allows for a discussion of IMFs that is based on experimental observation and asks students to depict what occurs at the molecular level.

### Suggested Clicker Questions

The following clicker questions have been selected from the Chapter 2 Clicker Question PowerPoints available on [wwnorton.com/instructors](http://wwnorton.com/instructors). More questions for each chapter are available at the website.

#### 2.4. Net Molecular Dipoles and Dipole Moments

“How many of the following molecules are polar? (Consider 3-D geometry.)”

That question forces students to think in 3-D and involves substituted cyclobutane. As a bonus, the problem is much easier to solve if students use their model kits.

#### 2.6. Melting Points, Boiling Points, and Intermolecular Interactions

“Which of the following compounds has the highest boiling point?”

That question deals with hydrogen bonding in a series of nitrogen-containing cyclic compounds.

“Which of the following compounds has the highest boiling point?”

That question has students compare symmetric systems and asks them to rely on size/polarizability to determine the molecule with the greatest IMFs.