Forcing Chemistry: Comparing Intermolecular Forces of Molecules

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1   Abstract

Molecules come in varying shapes, sizes, and compositions. Consequently, different molecules will exercise different properties. One of the most interesting properties of molecules is the intermolecular forces between molecules of the same type and how they govern the behavior of large groups of these molecules.

This project is aimed at comparing the behavior of two molecules that are similar in structure but have different properties. We use a model in VPython to accomplish this. Comparing these forces with great volumes of molecules is incredibly difficult and complex, so this program seeks to show the energy of the intermolecular forces between just two molecules.

2   Background

The largest molecules known of have diameters around 100 nm. Despite its size, it would take over 14.3 million billion of such large molecules to fill a pint glass. What this means is that in order for molecules to aggregate and become recognizable in solid or liquid form, the molecules have to bind together in groups. The forces that are exercised between molecules are called intermolecular forces; those inside of a molecule are intramolecular forces. The intramolecular forces do not affect the intermolecular forces of a molecule. There are a variety of intermolecular forces employed between molecules. This project will only be exploring two very different ones: forces between molecules which have dipole moments (dipole-dipole) and forces between those molecules that do not have dipole moments (induced dipole-induced dipole). Before that, dipole moments have to be analyzed.

2.1 Dipole Moment

Not all molecules have an absolute charge on them like ions do. For example, the molecule methane has no more or less electrons than a typical methane molecule so it does not have an absolute charge. This is different than a sodium ion, which has one less electron than a normal sodium atom. Consequently, it has a permanent positive charge. However, because of the difference in the electronegativity of atoms in a molecule, dipole moments can arise. The equation for calculating dipole moments is as follows:

$$\hat{\mu} = \delta \hat{r} \tag{1}$$

where $\hat{\mu}$ is the dipole moment vector, δ is the partial charge on each atom, and $\hat{r}$ is the distance between the two atoms.[1] Electronegativity is the tendency for an atom to want to hold onto electrons. As a result, atoms in a molecule can develop partial charges on them. Replacing all of the hydrogens in a methane fluorines, which are more electronegative negative atoms, creates diffferent bond polarities in the molecule. However, because the bonds in methane are all equally spread out, these dipole moments in the direction of each of the bonds cancels out and there is not dipole moment on the molecule. However, when only one of the hydrogens in methane is replaced with a fluorine (a fluoromethane molecule), a dipole moment for the whole molecule arises. A dipole moment causes one part of the molecule to have a partial negative charge and the opposite part of the molecule to have a partial positive charge. This is because the dipole moment for the carbon-hydrogen bonds is different than the dipole moment of the carbon-fluorine bond.

2.2 Attractive Forces

The first type of intermolecular force we are looking at is dipole-dipole interactions. Molecules that have dipole moments employ this force. The charge differentials across a molecule causes similar molecules to only align is specific ways; the positive end of a polar molecule will align with the negative end of a polar molecule by Coulomb's Law. This energy from this force follows an inverse distance like the ion-ion intermolecular interactions in Coulomb's Law, but is still different. The following is the relation:

$$V = -\frac{2\mu^2}{4\pi\epsilon_0 r^3} \tag{2}$$

where μ is the magnitude of the calculated dipole moment of the molecules interacting. The constants in the bottom of the expression are proportionality constants and help make the final answer into the correct

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[1] "Dipole Moments." UC Davis - Chemwiki. N.p., n.d. Web. 04 Dec. 2014. ¡http://chemwiki.ucdavis.edu/Physical_Chemistry/Atomic_Theory/Dipole_Moments¿.

units. As aforementioned, fluoromethane exercises this type of force between its molecules. There is also a special type of dipole-dipole interaction called hydrogen bonding, but we will not be exploring this as there is no much mathematical basis therein.[2]

The other type of force being explored in this project is that of induced dipole-induced dipole. This force occurs in all molecules but is the primary force exercised in molecules that do not have a charge or dipole momentum. Normally, it would not make sense that objects that have no charge to them could be attracted, but due to the phenomenon of polarizability, molecules develop induced dipole moments that cause attraction between molecules. Polarizability is the tendency of electrons to move around in a molecule or atom. Electrons are constantly moving around, so there are moments where one side of a molecule can retain a higher electron density (and therefore a partial negative charge) for a moment. In this moment, this molecule has an induced dipole moment which can attract other molecules with dipole moments. Because the fluctuations are random and the induced dipoles are typically weak and momentary, the induced dipole-induced dipole force is weaker than dipole-dipole forces. The equation governing the energy from these forces is as follows:

$$V = -\frac{3\alpha^2 I}{4r^6} \tag{3}$$

where α is the polarizability of the molecule and I is the first ionization energy of the molecule. The first ionization energy is the amount of energy needed to remove one electron from a molecule.[3]

2.3   Repulsive Forces

When molecules get too close together, potential energy approaches negative infinity:

$$\lim_{r \to 0} V \propto -\frac{1}{r^n} = -\infty \tag{4}$$

Because the distance between molecules is zero, the energy becomes negative infinite. Molecules tend to occupy states that are at the lowest energy (by the Aufbau Principle) so all molecules would tend to want to maintain zero separation. However, this is impossible. When the bond distance is less than the sum of the radii of two molecules, then the two molecules aren't just touching but are in fact physically overlapping. This is like trying to push two blocks into each other, it just doesn't work because the laws of physics prohibit it. Therefore, a repulsion factor needs to be integrated into the potential energy equation. The repulsion

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[2] "Dipole-Dipole   Interactions."   *UC   Davis   -   Chemwiki.*   N.p.,   n.d.   Web.   04   Dec.   2014. ¡http://chemwiki.ucdavis.edu/Physical_Chemistry/Intermolecular_Forces/Dipole-Dipole_Interactions¿.

[3] "Polarizability."   *UC   Davis   -   Chemwiki.*   N.p.,   n.d.   Web.   04   Dec.   2014. ¡http://chemwiki.ucdavis.edu/Physical_Chemistry/Intermolecular_Forces/Polarizability¿.

can be approximated using the Lennard-Jones potential equation:

$$V_{LJ} = \epsilon \left[(\frac{r_{min}}{r})^{12} - 2(\frac{r_{min}}{r})^6 \right] \tag{5}$$

In this equation, r_{min} is the distance at which the bond energy is the most negative and therefore most ideal. ϵ represents the depth of the potential well, or the energy at r_{min}. This model is typically used to approximate the repulsive forces between molecules that do not have dipole moments; however, for the molecule that does have a dipole moment, the dipole-dipole energy equation will be added to this to make the expression for the energy of the intermolecular forces of the dipole molecule. In this equation, the term with the 12 exponent is the repulsive component and the term with the 6 exponent is the induced dipole-induced dipole term. So by using the Lennard-Jones potential, we know have the equation governing the forces in our molecules.[4] Generally, repulsions between molecules not due to electronics result from the overlapping of molecular orbitals on neighboring molecules.[5]

3 The Math

3.1 Creating the Molecules

The molecules were attempted to be constructed as realistically as possible using experimental data that discovered the bond length and angles in methane and bromomethane. The following table gives the data pertinent for constructing the molecules:

Category	Representative Variable	Value
C—H bond length	r_1	1.08 Å
C—Br bond length	r_2	1.94 Å
H—C—H bond angle	θ_1	109.5° methane, 111.2° bromomethane
Br—C—H bond angle	θ_2	107.7°

The easiest way to create the molecules in VPython was to place as many of the objects onto the axes of the xyz space as possible. The central atom of each molecule, carbon, was placed at the origin. The principle atom in each molecule (any hydrogen in methane, the bromine in bromomethane) was placed on the positive y-axis. The next carbon substituent atom was placed on the xy plane, and the other two molecules were rotated around the y-axis so that the three identical substituents were equidistant and equiangular about

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[4] "Lennard-Jones Potenial." *Wikipedia.* Wikimedia Foundation, n.d. Web. 04 Dec. 2014. http://en.wikipedia.org/wiki/Lennard-Jones_potential.

[5] Atkins, P.; Jones, L. *Chemical Principles: The Quest for Insight, 5th Edition*; W.H. Freeman and Company: New York, NY. 2010. p.172-178.

and around the y-axis. This led to following for the positions of each atom within a frame to create methane:

$$C = (0, 0, 0)$$

$$H_1 = (0, r_1, 0)$$

$$H_2 = (r_1 \cos(\theta_1 - 90°), r_1 \sin(90° - \theta_1), 0)$$

$$H_3 = (r_1 \cos(\theta_1 - 90°) \cos(120°), r_1 \sin(90° - \theta_1), r_1 \cos(\theta_1 - 90°) \sin(120°))$$

$$H_4 = (r_1 \cos(\theta_1 - 90°) \cos(240°), r_1 \sin(90° - \theta_1), r_1 \cos(\theta_1 - 90°) \sin(240°))$$

The following atom positions are for bromomethane:

$$C = (0, 0, 0)$$

$$Br = (0, r_2, 0)$$

$$H_2 = (r_1 \cos(\theta_2 - 90°), r_1 \sin(90° - \theta_2), 0)$$

$$H_3 = (r_1 \cos(\theta_2 - 90°) \cos(120°), r_1 \sin(90° - \theta_2), r_1 \cos(\theta_2 - 90°) \sin(120°))$$

$$H_4 = (r_1 \cos(\theta_2 - 90°) \cos(240°), r_1 \sin(90° - \theta_2), r_1 \cos(\theta_2 - 90°) \sin(240°))$$

Accordingly, the atoms were constructed. During construction, it was found that halving the found bond distances created the most accurate molecular representations; however, the reason behind this was not discovered.

3.2   Potential Energies

The two molecules that are being compared in this project are methane and methyl bromide/bromomethane. The relevant information for the two molecules in terms of their input values for the potential equations are given in the following table[6][7]:

Category	Methane	Bromomethane
Formula	CH_4	CH_3Br
α ($\mathring{A}^3$)	2.448	5.610
μ (Debye)	0	1.810
I (eV)	12.6	10.5
r_{min} ($\mathring{A}$)	2.08	2.40

[6]NIST Computational Chemistry Comparison and Benchmark Database. NIST Standard Reference Database Number 101. Release 16a, August 2013, Editor: Russell D. Johnson III. http://cccbdb.nist.gov/

[7]r_{min} of bromomethane approximated from values of similar molecules

Because bromomethane has a dipole moment, its potential energy will include a dipole-dipole energy term. The well depths of each molecule were discovered by equating the polarizability term from the Lennard-Jones potential equation to the general equation discovered for polarizability. The following is the well depth equation for methane:

$$\epsilon_{methane}\left[-2(r_{min})^6\right] = -\frac{3\alpha^2 I}{4} \tag{6}$$

$$\epsilon_{methane}\left[-2(2.08\times10^{-10}\text{Å})^6\right] = -\frac{3\left((2.448\times10^{-10}\text{Å})^3\right)^2\left(12.6eV * 1.6\times10^{-19}\frac{J}{eV}\right)}{4} \tag{7}$$

$$\epsilon_{methane} = 2.01\times10^{-18}J \tag{8}$$

The following is the well depth for bromomethane:

$$\epsilon_{bromomethane}\left[-2(r_{min})^6\right] = -\frac{3\alpha^2 I}{4} \tag{9}$$

$$\epsilon_{bromomethane}\left[-2(2.40\times10^{-10}\text{Å})^6\right] = -\frac{3\left((5.610\times10^{-10}\text{Å})^3\right)^2\left(10.5eV * 1.6\times10^{-19}\frac{J}{eV}\right)}{4} \tag{10}$$

$$\epsilon_{bromomethane} = 1.04\times10^{-16}J \tag{11}$$

One problem that arises from using the Lennard-Jones potential to help approximate the energy of the intermolecular forces is that it attributes most of the energy to the r^{-6} term, which was not planned. However, the final result still shows the bromomethane intermolecular bond in stronger than the methane intermolecular bond:

$$\frac{\epsilon_{bromomethane}}{\epsilon_{methane}} = \frac{1.04\times10^{-16}}{2.01\times10^{-18}} \approx 51.6 \tag{12}$$

This is only an approximation because the dipole-dipole energy term for bromomethane has not been factored into this equation. However, the term is negligible:

$$V_{dipole} = -\frac{2\mu^2}{4\pi\epsilon_0 r_{min}^3} = -\frac{2(6.04\times10^{-30})^2}{4\pi\epsilon_0(2.40\times10^{-10})^3} = -4.74\times10^{-20}J \tag{13}$$

as it is about 2000 times weaker than the energy approximated from the Lennard-Jones potential equation at r_{min}.

4 The Programs

Both programs were attempted to be combined into one program; however, the program would not run when they were combined for whatever reason, so they were kept separate.

4.1   Software & Hardware

Both RTICAs can be executed using of VPython with the visual, visual.graph, __future__, and math python libraries. The files were written in Python 2.7, so compatible versions would most likely be necessary for running. A functioning keyboard is necessary to move the molecules, stop the molecules, and print the potential energy of the molecules.

4.2   Running the Programs

Both programs showed two molecules separated by the equivalent of 8 angstroms (8×10^{-10} meters). One of the molecules can move closer and further from the other molecule. As the molecule moves, a graph traces the values of the potential energy of the intermolecular interaction of the two molecules for each distance traced. Also, as the molecule moves, an arrow changes in magnitude (and direction for positive versus negative values) to mimic the change in potential energy. However, the arrow has to be scaled because it is too small to be seen without scaling. The following sections show the particulars for the each of the RTICAs. The potential energy at the current separation can be printed with the press of a key.

5   Conclusions

This program showed that for this example, the more polar molecule had stronger intermolecular forces. It did not work out exactly as planned because over 99% of the energy of the intermolecular interaction is consequent from the polarizability portion of the equation, which was unintended. This may be due to the fact that the Lennard-Jones potential was used to approximate the repulsion factor towards zero distance. If this program were done again, methane would have likely been replaced with an ethane (CH_3CH_3) molecule, a more suitable partner to compare bromomethane to, considering they have more comparable sizes and polarizabilities. Nonetheless, the product was a success and a lot was learned; all goals were accomplished.