Worksheet #3 - Non-Bonded & Intermolecular Interactions

Team #: _______  Manager:  mpm
Class Period:  1/18/06  Recorder: 
Resources:  Cramer 2.2, Jensen 2.2  Speaker:
Stone Ch. 1 excerpt  Analyst:
Leach Sec. 4.8

1. Based on the normal boiling point of CCl₄, \( T_b = 77.6 \, ^\circ C \), estimate the depth of the attractive well (\( \varepsilon \)) between two CCl₄ molecules à la Stone. Provide results in units of Kelvin and kJ/mol. (1-digit accuracy is sufficient here.)

Stone suggests that \( \frac{\varepsilon}{k_B} \approx \frac{20}{T_b} \) where \( T_b \) is the boiling point and \( n \) the # nearest neighbors in the liquid. Assuming \( n \approx 12 \) (like CCl₄ or Xe) \( \frac{\varepsilon}{k_B} \approx \frac{20(173+78)}{12} \approx 505K \quad \varepsilon \approx 4.9 \text{ kJ/mol} \)

(b) How might you estimate the size parameter \( \sigma \) for the interaction between two CCl₄ molecules in an equally simple manner?

- use the mass of CCl₄ and the mass density of CCl₄ (e)

or CCl₄(s) and some simple assumption about the packing.

For example, if simple cubic packing (1molecule per cube of length \( L \)),

\[ \ln \sigma\text{, for CCl}_4\text{, } MW=154 \text{ g/mol}, \text{ } d=1.58 \text{ g/cm}^3 \text{, molar volume is} \]

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\[ \ln \sigma = \frac{154 \text{ g/mol}}{1.58 \text{ g/cm}^3} = 97.5 \text{ cm}^3 \text{ mol}^{-1} \rightarrow 162 \text{ Å}^3 \text{ molecule}^{-1} \frac{1}{2} \rightarrow \ln \sigma \approx 5.4 \text{ Å} \]

(accurate value is 5.2 Å)

2. With the exception of small, highly polar molecules like water, the largest contribution to the attractive energy between molecules results from dispersion interactions. Dispersion interactions are universally present and are responsible for the fact that all molecules condense at sufficiently low temperatures.

(a) Describe the origin of dispersion interactions.

Dispersion interactions result from the coupled motion of electrons which give rise to an instantaneous dipole - instantaneous dipole interaction. The effect is purely quantum mechanical in nature.

\[ \begin{array}{c}
\begin{array}{c}
\vdots
\end{array}
\end{array} \]

(see Jensen, bottom of p. 18, Corme (P28))
(b) At the right is a plot of the depth of the pair potentials between like rare-gas atoms. How might you rationalize the dependence on \( Z \) shown here?

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as the number of electrons increases the polarizability increases which enables much more correlated electron motion and thereby greater dispersion interactions
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3. Both the interactions between two molecules and the interactions between remote (as defined below) parts of the same molecule are called "non-bonded" interactions in the language of MM. Within a single molecule, non-bonded terms are included in evaluating the energy only between atoms that are separated by more than 3 bonds. In some FFs the magnitude of the nonbonded interactions between 1-4 pairs of atoms are reduced by a factor of \( \frac{1}{2} \) whereas in other FFs the full interaction is used.

(a) Why are non-bonded interactions not included for 1-3 atom pairs? Why are they always included for 1-5 atom pairs? Why is there some variability in the treatment of 1-4 pairs?

- The relative configurations that can be adopted by atoms connected in a 1-3 manner are already strongly constrained by the 1-2, 2-3 stretching and 1-2-3 bending portions of the potential. Non-bonding terms are relatively small in comparison to the latter terms and are not needed.
- 1-4 atoms are similarly constrained by 1-2-3-4 torsional terms but these terms are comparable to non-bonded torsional terms so it is best to include the latter interactions and so it is best to include the latter.
- For 1-5+ there aren't other terms in the FF and it is therefore critical to include nonbonded terms.

To avoid overlap. (see Jenne p25)
(b) Use the numbering scheme provided to enumerate all of the pairs of atoms that interact via non-bonded interactions in urea $\text{CH}_4\text{N}_2\text{O}$.

$$
\begin{align*}
2-5, 2-6, 2-7, 3-8, 4-7, 4-8
\end{align*}
$$

4. In the context of MM FFs and the expression $E_{\text{FF}} = E_{\text{str}} + E_{\text{bnd}} + E_{\text{tors}} + E_{\text{vdw}} + E_{\text{el}} + E_{\text{cross}}$, what is meant by “van der Waals” interactions?

All non-bonded interactions not included in the electrostatic term are called van der Waals terms. What is included are repulsion and dispersion, usually parameterized in the form of a Lennard-Jones function.

(b) If Lennard-Jones functions are used to represent $E_{\text{vdw}}$ between two interacting urea molecules, how many distinct parameters are required and what are they?

For two distinct urea molecules, each type $j$ atom $\{C, O, H, N\}$ would interact with all others. The number of distinct types of atom pairs is $10$.

$$
\begin{align*}
&\{C+C, C+O, C+H, C+N, O+O, O+H, O+N, \\
&H+H, H+N, N+N\}
\end{align*}
$$

The number of parameters would be $20$ ($\epsilon_j, \sigma_j$ for each pair).

5. Combining rules are important for limiting the number of independent parameters that need to be determined in a force field.

(a) Give two examples of combining rules that might be used for $\epsilon$.

Most common is: $E_{\text{AB}} = (\epsilon_{AA} \cdot \epsilon_{BB})^{1/2}$ (geometric mean)

Other possibilities are $E_{\text{AB}} = \frac{1}{2}(\epsilon_{AA} + \epsilon_{BB})$; $E_{\text{AB}} = \left(\frac{1}{\epsilon_{AA}} + \frac{1}{\epsilon_{BB}}\right)^{-1}$

(b) How many Lennard-Jones parameters are required to specify the van der Waals portion of a FF having 100 distinct atom types both without and with the use of combining rules?

For $N$ atom types in the absence of combining rules there are $N(N+1)/2$ unique pairs so $N(N+1)$ parameters would be needed ($\epsilon_j$ for each pair). Using combining rules reduces the number down to $2N$ (Cramer p35). Here $N=100$

so $w/o.$ $= 10,100$ is with $= 200$ (big difference)
6. The simplest description of the charge distribution of a molecule is provided by its multipole moments, i.e. its charge, dipole moment, quadrupole moment, etc. At distances of more than a few molecular diameters, the electrostatic interactions between two molecules can be calculated based solely on the interaction between the lowest-order non-zero multipole moments of the molecules. In typical cases "dipole – dipole" interactions are the dominant electrostatic interaction.

Representations of the electrostatic potentials ("ESPs") \( \Phi(\vec{r}) \) resulting from point dipole, quadrupole, and octopole moments are shown below:

![Figure 1. Equipotential contours of ideal multipoles. The innermost contour level that is drawn is the same in each plot and corresponds to a unit test charge having an interaction energy of 18 000 \( \text{cm}^{-1} \). The step from one contour level to the next is the same throughout (2000 \( \text{cm}^{-1} \) for a unit test charge). Contours for higher equipotentials have not been drawn to avoid congestion of lines. The multipoles are at the centers of these 8-Å \( \times \) 8-Å grids and are oriented along the horizontal axis of each plot: (a) an ideal dipole of 1.0 au, (b) an ideal quadrupole of 1.0 au, and (c) an ideal octopole of 1.0 au. For comparison, if the same potential contours were drawn about a unit charge or zeroth order multipole, the first (i.e., at 18 000 \( \text{cm}^{-1} \)) would be a circle outside the 8-Å \( \times \) 8-Å grid.](image)

Note that dashed curves are used to represent negative values of the potential.

1 au dipole moment = 2.54 D


(a) What is the electrostatic interaction energy between a point charge \( q \) and a potential \( \Phi(\vec{r}) \)?

\[
E_{el}(\vec{r}) = q \Phi(\vec{r})
\]
(b) Estimate the interaction energy between a unit point charge and these unit multipoles when the charge is placed at the coordinates (3.0, 0.0). Express your answer in units of kJ/mol using the conversion factor $10^3$ cm$^{-1}$ "= 12 kJ/mol.

\[
\begin{array}{ccc}
E/10^3 \text{ cm}^{-1} & \text{dipole} & \text{quadrupole} & \text{octapole} \\
& 0 & 2.5 & \sim 1 \\
E/\text{kJ mol}^{-1} & 72 & 30 & 12
\end{array}
\]

(c) Give examples of molecules whose lowest-order non-zero multipole moment is: (i) a dipole, (ii) a quadrupole, and (ii) an octapole.

\[
\begin{array}{ccc}
\text{dipole} & \text{quadrupole} & \text{octapole} \\
\text{H} & \text{C} & \text{Cl}_4
\end{array}
\]

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#7 is to be done as homework. Feel free to discuss it among your team if there is time, but turn your answer individually in on a separate piece of paper next Monday (1/23). There is a PowerPoint copy of this figure on the Worksheet page of the course web site that you might find useful.

7. On the following page are electrostatic potentials of the water molecule as determined from accurate electronic structure calculations and as represented by atom-centered point charges and bond-centered point dipoles. (The latter representations are the sort used in the OPLS and MM2 FFs, respectively.)

(a) How do all of these potentials differ from that of an ideal point dipole?

(b) Describe and explain the origins of some of the differences between the "true" ESP in Fig. 2(a) and the model versions in Figs. 2 (f) and (c).

(c) FF models of water often treat the van der Waals part of the water-water intermolecular interaction using a single Lennard-Jones potential centered at the O nucleus and having a value of $\sigma$ of $\sim 3$ Å. (Note that the spatial coordinates in Fig. 2 are in atomic units, $a_0=0.529$ Å.) Because the interaction energy rises very steeply (as $r^{-12}$) for O-O separations larger than $\sigma$, the representation of $\Phi$ does not have to be accurate for smaller separations in order to provide a good representation of intermolecular interaction energies. Keeping this fact in mind, comment on the relative quality of the point charge and bond dipole representations used here.

(d) Would an interaction model using the van der Waals interaction described in part (c) and the point charge or bond dipole representations in Figs. 2(f) and (c) include hydrogen bonding? Explain.
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(a) In the plane of the molecule (left-hand panels) the contours in the vicinity of the H atoms are flattened in the horizontal direction compared to the ideal dipole. On the O side of the molecule the contours are closer to the dipolar shape, especially in the case of (f) and (c). In the plane bisecting the H-O-H angle (right-hand panels) The shapes of the contours in (f) and (c) are very similar to those of the point dipole. However, the sizes of the positive and negative lobes is very dissimilar near to the nuclei.

(b) In the immediate vicinity of the nuclei the potentials are quite different because of the different nature of the charge distributions. The real charge distribution in (a) comes from point charges at the nuclear positions (+1 at H and +8 at O) covered by a cloud of negative electronic charge. At high positive potentials the contours possess the “shape of the molecule”. These contours lie just beneath the skin of the electron density surface where the positive nuclear charges are almost but not quite completely screened, leaving the potential positive (but only slightly so compared to what happens when the nuclei are approached more closely). In the case of the model charge distributions, when one is “within” the molecule in this way the potential is not uniformly positive. Rather here the potential changes sign along the O-H bonds either because there is are point charges at the atoms or point dipoles at the bond centers.

The real charge distribution also shows evidence for the presence of lone-pair electron density in the form of subtle lobes above and below the molecular plane in the right-hand panel of (a). These features are not present in the model distributions because these charge distributions are purely planar.

(c) The cartoon at the right illustrates the closest approach of two water molecules. The red shaded region centered on the first molecule is not typically sampled by a pair of water molecules and it is therefore not necessary that the representation of the electrical potential be accurate in this region. On the following page I’ve reproduced Fig. 2 with this unimportant region shaded out. I’ve also colored in the contours at ±6000 cm⁻¹. Looking only at the regions outside of this shaded region, the electrical potentials of the different charge distributions look more similar. Both model charge distributions do a reasonable job representing the real charge distribution in the plane of the molecule, especially on the positive (H-atom) end. Both models fare less well in the plane of the HOH bisector.

(d) Yes, to the extent that hydrogen bonding is largely electrostatic in nature the combination of $E_{vdw} + E_{el}$ in most force fields account for hydrogen bonding without adding additional terms. (See Cramer p. 33, Jensen p. 23) For example, the “OPLS” model in (f) is parameterized, among other things, to reproduce the enthalpy of vaporization of liquid water. This enthalpy and many other properties of water are dominated by hydrogen bonding. If the model didn’t do a decent job of representing the hydrogen bonding in liquid water it would not be of much value.
Figure 2. Electrostatic equipotential contours for the water molecule. On the left are contours in the plane of the water molecule, and on the right are contours in the plane perpendicular to the molecular plane that includes the symmetry axis. The contour spacing is the same as in Figure 1, and the distance units for the horizontal and vertical axes are atomic units (au): (a) The electrostatic