Lecture 34  Review of things missed recently

Announcements
• Of course exam tomorrow and Wednesday. This means, by the way, that I can’t begin
grading until after I get back from Thanksgiving (along with lots of genchem). So, you
probably won’t be getting them back until mid to late of that last week.
• No work over Thanksgiving for you. Remember one last HW set that last week that won’t be
graded, but will cover material for quiz portion of final exam.

Outline:

Van der Waals equation
Poisson equation
Radial distribution functions

Review:
Pair potential figure – should be able to sketch

\[ U(r) = 4\varepsilon \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^{6} \]
repulsion is exponential, \( e^{-r} \sim r^{-12} \). dispersion (attraction) is \( r^{-6} \) (instantaneous-dipole
induced-dipole, same dist. dependance as induced-dipole induced-dipole)

Chemical bonds \( \sim 100 \text{ kJ/mol} \)
strong e-statics (NaCl) \( \sim 100 \text{ kJ/mol} \)
weak e-statics (H-bonding, salt bridges in proteins) \( \sim 10 \text{ kJ/mol} \)
dispersion forces \( \sim 1 \text{ kJ/mol} \)
\( k_B T \) at room temp \( \sim 1 \) (actually 2.5) kJ/mol

Van der Waals gasses
Van der Waals equation uses physical insight to account for non-ideal behavior.

\[ \left( P + \frac{a}{V^2} \right)(V - b) = RT \]
\[ P = \frac{RT}{V - b} - \frac{a}{V^2} \]

Compare to ideal gas law \( P_{\text{ideal}} \frac{V_{\text{ideal}}}{V} = RT \)
Actual $P$ is less than ideal (attraction) and actual $V$ is greater than ideal (repulsion).

Why is $V^2$ in the denominator rather than just $V$? Attractive forces reduce both force and number of collisions.

There are many other equations of state. Two of the most common are the Redlich-Kwon and the Peng-Robinson. They are more accurate than vdW, but less physically intuitive. All of these specific ones are cubic equations of state, meaning $P(V^3)$ as described in the Misovitch seminar.

All of these non-ideal equations of state account for transition to condensed phase. As also described in misovitch seminar.

**Poisson Equation**

What if we have a ridiculously complicated set of charges. Well, we could keep many terms in our multipole expansion. Or, we could do something a bit more clever.

Remember Gauss’s Law that we had previously (I think I left out the $D$):

$$\int_{\text{surface}} D\vec{E} \cdot d\vec{s} = \int_{\text{volume}} \frac{\rho}{\varepsilon_0} dV$$

If we compare this to Gauss’s more general Theory:

$$\int_{\text{surface}} D\vec{E} \cdot d\vec{s} = \int_{\text{volume}} D\vec{\nabla} \cdot E dV$$

We see that:

$$D\vec{\nabla} \cdot \vec{E} = \frac{\rho}{\varepsilon_0} \quad \text{or} \quad \vec{\nabla} \cdot \vec{E} = \frac{\rho}{D\varepsilon_0}$$

You may recognize this as one of Maxwell’s equations (quite different than Maxwell’s relations) though you may never have seen the differential form before. We can also restate this equation in terms of the potential which is often more useful:

$$\vec{E} = -\nabla \psi$$
so
\[ \nabla^2 \psi = -\frac{\rho}{D\varepsilon_0} \]

This is Poisson’s equation. Big stuff. It gives us an easy way to solve for
the potential even if we have a really complicated set of charges that sit
within different media with varying dielectric constants. Note that if we
have just point charges surrounded by a uniform dielectric, then Poisson’s
equation reduces to Coulomb’s law.

Let’s do a quick example  (just like 21.6 in the text)
We have a sphere of dielectric D with charge on the surface (total \( q \)),
also surrounded by dielectric D
What is the potential at all points in space
\[ \nabla^2 \psi = -\frac{\rho}{D\varepsilon_0} \]
What is the Laplacian in spherical coordinates (look it up table 17.1
p.313)?
fortunately for us \( \frac{d\psi}{d\phi} = \frac{d\psi}{d\theta} = 0 \)
\[ \nabla^2 \psi = \frac{1}{r^2} \left( \frac{d}{dr} \left( \frac{r^2}{r^2} \frac{d\psi}{dr} \right) \right) = \frac{1}{r} \frac{d^2(r\psi)}{dr^2} = -\frac{\rho}{D\varepsilon_0} \]
inside and outside the sphere, \( \rho = 0 \)  so
\[ \frac{d}{dr} \left( r^2 \frac{d\psi}{dr} \right) = 0 \]
\[ r^2 \frac{d\psi}{dr} = A' \]  (integrate once to get a constant)
\[ \frac{d\psi}{dr} = A'r^{-2} \]
\[ \psi = -A'r^{-1} + A_z \]  (integrate again to get a second constant)
\[ \psi = \frac{A_1}{r} + A_z \]

Now let’s think about what things look like outside the sphere. Gauss’s law
tells us that the field depends only on the total charge enclosed.
\[ E(r > a) = -\frac{q_{\text{tot}}}{4\pi D\varepsilon_0 r^2} \]
We can integrate to get the potential
\[ \psi(r > a) = \frac{q_{\text{tot}}}{4\pi D\varepsilon_0 r} + C \]
But, we know that $\psi \to 0$ as $r \to \infty$ so $C = 0$.

Equating this with what we got before tells us that outside the sphere

$$A_1 = -\frac{q_{\text{tot}}}{4\pi \varepsilon_0} \quad A_2 = 0$$

Taking this same approach inside the sphere tells us that

$\psi_{\text{in}} = \text{constant}$

Of course, $\psi_{\text{in}}$ must equal $\psi_{\text{out}}$ at the surface of the sphere. Let’s call the radius $a$. $\psi_{\text{in}}(a) = C = \psi_{\text{out}}(a) = \frac{q_{\text{tot}}}{4\pi \varepsilon_0 a}$

So, inside the sphere, $\psi_{\text{in}} = \frac{q_{\text{tot}}}{4\pi \varepsilon_0 a}$ \hspace{1cm} $\psi_{\text{out}}(r) = \frac{q_{\text{tot}}}{4\pi \varepsilon_0 r}$

Note that there is no charge inside the sphere, so the field is zero, but the potential is not… just constant. Constant potential means no force though. This is why a charged (conducting) sphere shuts out RF interference (Dr. Chase’s lab)

Note that Poisson’s equation is critical in lots of current computational applications. For example, implicit solvent models use a variation on Poisson’s equation to estimate the electrostatic contribution to the free energy of solvation.

One critical step here is that when we are talking about electrostatic work

$$\Delta G_{\text{el}} = w_{\text{el}}$$

$$w_{\text{el}} = \frac{1}{2} \sum_i q_i \psi_i$$

(This is the work needed to assemble a bunch of charges, $q_i$ in the potential $\psi_i$)

Or if we want to know about the DG of going from vacuum to water – the electrostatic contribution to the solvation energy, then:

$$w_{\text{el}} = \frac{1}{2} \sum_i q_i \Delta \psi_i = \frac{1}{2} \sum_i q_i \left( \psi_i^{\text{water}} - \psi_i^{\text{vacuum}} \right)$$
This is exactly the kind of treatment we use to calculate solvation energy of a protein.

We could also do a second example... lets say a charge \( q \) at the center of a protein \( D = 2 \) within a vacuum \( (D=1) \) compared to within water \( (D=80) \).

\[
E(r) = -\frac{q}{4\pi \varepsilon_0 D r^2} \hat{r}
\]

\[
\psi(r) = \frac{q}{4\pi \varepsilon_0 D r} + A
\]

So, except for \( D \) and \( A \), both regions are the same.

Let's look at \( r > a \)

Since \( \psi \to 0 \) as \( r \to \infty \) then \( A = 0 \)

\( D=80 \) here so

\[
\psi(r > a) = \frac{q}{320\pi \varepsilon_0 r}
\]

Now what about \( r < a \).

\[
\psi(r < a) = \frac{q}{8\pi \varepsilon_0 r} + A
\]

How do we find the constant? Boundary conditions.  at \( r=a \) the two potentials must be equal.

\[
\psi(a) = \frac{q}{8\pi \varepsilon_0 a} + A = \psi(a) = \frac{q}{320\pi \varepsilon_0 a}
\]

\[
\frac{40q}{320\pi \varepsilon_0 a} + A = \frac{q}{320\pi \varepsilon_0 a}
\]

\[
A = -\frac{39q}{320\pi \varepsilon_0 a}
\]

So, then

\[
\psi(r) = \frac{q}{8\pi \varepsilon_0 r} - \frac{39q}{320\pi \varepsilon_0 a}
\]

Notice that the presence of the external dielectric decreases the potential within the protein.  This is because the dielectric serves as negative charge.
**Radial distribution function**

Remember we are talking about intermolecular interactions. These are the things that lead to liquid behavior. (That’s what makes liquid behavior so interesting and condensed phase spectroscopy the most noble of all pursuits.) One good descriptor of liquid behavior is the radial distribution function, or the pair correlation function.

Remember that we saw correlation functions before when we were looking at diffusion. Then we looked at how velocity of one particle compares to its velocity at an earlier time.

Now we are talking about the structure of the liquid, so our correlation function tells us the density of the liquid (or solid or gas) as a function of distance from some test particle – \( g(r) \).

Starts at zero because there can’t be another particle on top of our test particle. In a solid we have a regular repeating structure.

In a liquid we have the same kind of thing, but because the long-range structure is not regular everything washes out and eventually we get a flat line at 1 (the value of the average density)