Chem 163, Lecture 18

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11/22/2022

1 Misc. Announcements

Thus far we have restricted our discussion to non-interacting particles, possibly in the presence of an externally imposed potential. Indeed, there are still a great many more things we could discuss considering only the Brownian motion of non-interacting particles. But in real-life there are many interactions. These interactions make life interesting and considerably more complicated.

Today we will take a whirlwind tour of the ways in which molecules in solution push and pull on each other. This is a truly fascinating area, and could be the subject of an entire course. It is one of the few areas in which an effect obtained in fourth order perturbation theory in quantum electrodynamics, taking into account the zero-point energy of the vacuum, has important biological consequences. We'll get to that in a bit. Some important effects (electrostatic screening and polymeric forces) will have to wait until we cover those topics separately.

I've put on the website the first chapter of a book by Henry Margenau on the theory of intermolecular forces. This chapter is a fascinating historical overview of how people thought about intermolecular forces going all the way back to the Ancient Greeks. If you read it, you'll see that people were pretty clever even before they knew quantum mechanics. I highly recommend reading it.

2 What the ancients knew

It has long been appreciated that some mysterious forces hold the constituents of matter together. These forces seem to act only over a very short range, but to be capable of being quite strong (try breaking a rock in half). From the time of Newton until the mid 19th century, people hoped to find a universal law of cohesion, akin to Newton's universal law of gravitation. People knew that it had to be a very short-range law because cohesion seems to play no role for any macroscopically sensible separation between objects. In fact, Gauss, who had no knowledge of electrostatics or quantum mechanics, derived that these forces had to fall off with distance at least as fast as $1/r^6$. We're going to go through the argument because it is so simple and elegant.

Consider two blobs of material. If the forces between each element of blob 1 and each element of blob 2 are additive (that is the outer skin of the material does not shield the interactions due to deeper components), then we can expect the total interaction energy to be proportional to the product of the volumes of the two masses (or equivalently to the product of their masses). Let's say that the interaction energy varies as $1/r^n$. Then we can guess that the interaction energy will have the form:

$$U = U_0 \frac{V_1 V_2}{r^n}. \tag{1}$$

Now suppose we scale all the dimensions in our system by some amount k. Then, as a function of k, the interaction energy is:

$$U(k) = U_0 \frac{V_1 V_2 k^6}{r^n k^n}. \tag{2}$$

Here is the part where we have to apply some physical intuition. We know that intermolecular forces are significant for microscopic bodies, but not for macroscopic ones. This means that if we scale all dimensions in the system by a factor k, we want the net interaction energy to decrease as k increases. Since $U \propto k^{6-n}$, we require $n > 6$.

This is an amazing result: we have inferred the long-range form of the retarded van der Waals-Casimir interaction from purely geometric arguments.

Now we're going to catalog some of the intermolecular forces found in nature. We'll see that many of them vary as $1/r^n$ with $n = 6$. The contradiction between this result and the requirement $n > 6$ that we just derived wasn't resolved until Casimir and Polder introduced the zero-point energy of the vacuum into the calculations in 1948.

Note that electrostatic forces, which fall off like $1/r$ are allowed by a loophole in the above argument: we assumed that the forces all had the same sign. Electrostatic forces come in two varieties, attractive and repulsive, leading to a complete cancelation for neutral objects–even though the component forces are long-ranged.

3 Coulombic forces, torques

If you have two charged bodies with charge distributions $\rho_1(\mathbf{r})$ and $\rho_2(\mathbf{r})$, their mutual electrostatic energy of interaction is:

$$U = \frac{1}{4\pi\epsilon} \int d\mathbf{r}_1 \int d\mathbf{r}_2 \frac{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|}, \tag{3}$$

That is, each piece of charge density in body one interacts with each piece of charge density in body two, and all of these interaction energies add. The above equation is all you need if you're trying to calculate electrostatic intermolecular forces on a computer. But when thinking about things it's often useful to have approximation schemes.

3.1 Multipole expansion

The multipole expansion is the most convenient approximation scheme. Here is how it works. I'll simply state without proof, that the potential of a bounded charge distribution can be rewritten as:

$$V(\mathbf{R}) = \frac{1}{4\pi\epsilon}\sum_{n=0}^{\infty}\frac{1}{R^{(n+1)}}\int d\mathbf{r}'(r')^n P_n(\cos\theta)\rho(\mathbf{r}'), \tag{4}$$

where θ is the angle between $\mathbf{r}'$ and $\mathbf{R}$, and $P_n(x)$ is the n^{th} Legendre polynomial. The point of this expansion is that it breaks up the potential into a series of independent terms, each of which varies as $1/r^n$. So for instance a point charge experiences a $1/r$ interaction with the monopole term, $1/r^2$ with the dipole, and so on.

Now if the test body has some complicated shape, we can expand the interaction energy in powers of the local field, finding:

$$U = qV(0) - \mathbf{p}\cdot\mathbf{E}(\mathbf{0}) - \frac{1}{6}\sum_{i,j} Q_{ij}\left.\frac{\partial E_j}{\partial x_i}\right|_0 + \ldots. \tag{5}$$

That is, a charge interacts with a potential, a dipole interacts with an electric field, a quadrupole interacts with field gradients, and so on. The traceless quadrupole tensor is defined as:

$$Q_{ij} = \int (3x_i x_j - r^2\delta_{ij})\rho(\mathbf{r})d\mathbf{r}. \tag{6}$$

[SHOW CHART ON INTERMOLEC FORCES FROM ISRAELACHVILI]

4 Induced-dipole interactions

It is uncommon to have static, fixed charges in squishy system. Usually charges are tumbling and whirling around, and this makes life much more interesting. We'll start with a seemingly trivial example, and then work our way up to some interesting results.

Does a charge pull on a neutral molecule with no intrinsic dipole or multipole moments? Yes! The reason is that the charge creates a field which can *induce* an asymmetric charge distribution in the neutral species. The polarizability, α, of a molecule is defined by the relation:

$$\mathbf{p} = \alpha\mathbf{E} \tag{7}$$

where $\mathbf{p}$ is the induced dipole moment and $\mathbf{E}$ is the applied electric field. Now the electric field from a point charge is

$$\mathbf{E} = \frac{q\hat{r}}{4\pi\epsilon r^2}. \tag{8}$$

The force on a dipole is $\mathbf{F} = \mathbf{p}\cdot\nabla\mathbf{E}$, or

$$\mathbf{F} = \alpha\mathbf{E}\cdot\nabla\mathbf{E}. \tag{9}$$

But we have the mathematical identity:

$$\mathbf{E}\cdot\nabla\mathbf{E} = \frac{1}{2}\nabla\left|\mathbf{E}\right|^2. \tag{10}$$

This means that we can write the force as the gradient of something. This something has to be the negative of the interaction potential. So we have an interaction potential:

$$U = -\frac{1}{2}\alpha\left|\mathbf{E}\right|^2. \tag{11}$$

This is a broadly useful result. When **E** is due to a charged ion, this interaction energy is the main enthalpic contribution to the solubility of the ion in water: water is very polarizable, so the charge-induced dipole interaction is strong (in water the electric field near an ion can be so strong that water molecules are strongly oriented and the linear response picture used here breaks down–but the principle still applies). If **E** is an oscillating electric field, this energy is still nonzero because the time-average of $|\mathbf{E}|^2$ does not vanish. So for instance when **E** is an optical-frequency electric field due to a tightly focused laser beam, we have laser tweezers: dielectric particles are attracted to the region where $|\mathbf{E}|^2$ is greatest, which is the region of maximal light intensity. When **E** is due to a radiofrequency electric field we have dielectrophoresis, which is another technique for moving small particles around in a fluid. When **E** is due to a classical or quantum dipolar fluctuation of another nearby molecule we have the van der Waals force.

Before we plunge ahead, there's a subtlety in the above equation which bears consideration. It's the factor of 1/2 in front. Recall from the discussion of the multipole interaction that we said the interaction energy of a dipole with an electric field is $-\mathbf{p}\cdot\mathbf{E}$. Well if $\mathbf{p} = \alpha\mathbf{E}$, why couldn't we simply write:

$$U_{\text{tot}} = -\alpha\,|\mathbf{E}|^2? \tag{12}$$

Why did we go about this convoluted line of argument, calculating the force, then integrating it to get the potential? And where did that extra factor of 1/2 come from? I won't tell you the answer, but a hint is that it has to do with the fact that we're considering an *induced* dipole, not a permanent dipole. Think about it.

Let's run through two examples. If **E** is from a fixed charge q, then we have:

$$U = -\frac{q^2\alpha}{2(4\pi\epsilon)^2 r^4}. \tag{13}$$

Good. If **E** is due to a dipole, then

$$U = -\frac{p^2\alpha(1+3\cos^2\theta)}{2(4\pi\epsilon)^2 r^6}, \tag{14}$$

where θ is the angle between the dipole and the intermolecular axis. The only part of this expression that isn't totally obvious is the angular dependence, which comes out if you work all the electrostatics. I won't bore you with the derivation. Interestingly, if the dipole is freely rotating, this interaction energy *does not* average to zero.

5 Keesom forces

It is a useful mathematical fact that the average of $\cos^2\theta$ over a sphere is 1/3, to wit:

$$\begin{aligned}\langle cos^2\theta\rangle_\Omega &= \frac{1}{4\pi}\int_0^{2\pi} d\phi \int_0^{\pi} d\theta \cos^2(\theta)\sin(\theta) d\theta d\phi \\ &= \frac{1}{2}\int_{-1}^{1} x^2 dx \\ &= \frac{1}{3}.\end{aligned} \tag{15}$$

Applying this useful mathematical fact, we see that the interaction energy between a randomly tumbling dipole and a polarizable particle is:

$$\langle U\rangle_\Omega = -\frac{p^2\alpha}{(4\pi\epsilon)^2 r^6}. \tag{16}$$

Suppose we have *two* randomly tumbling dipoles. It's pretty simple to show that if you average the $1/r^3$ dipole-dipole interaction energy over all possible relative orientations of the dipoles, the energy averages to 0. But a randomly tumbling dipole has a polarizability: put it in an electric field, and its tumbling will be slightly biased in favor of orientations that have a lower interaction energy with the electric field. This bias leads to an average net dipole moment, i.e. a polarization. So the electric field of one randomly tumbling dipole slightly biases the tumbling of its neighbor. And *vice versa.* That is, the electrostatic interaction introduces a *correlation* in the random tumbling of the dipoles, which leads to a net attractive interaction. Now we'll calculate this effect by doing something tricky. Hold onto your seats.

Remember the equipartition theorem? For every degree of freedom with energy quadratic in displacement, we get $\frac{1}{2}k_BT$ of energy. It relates the linear response of a system to its spontaneous fluctuations. Well, here we've got fluctuating dipoles and we're interested in their linear response. The energy of a dipole in an electric field is $\frac{1}{2}\alpha\langle|\mathbf{E}|^2\rangle$, which we can rewrite as $\frac{1}{2\alpha}\langle|\Delta\mathbf{p}|^2\rangle$. We set this equal to $\frac{1}{2}k_BT$, from which we get:

$$\alpha_{xx} = \frac{1}{k_BT}(\langle p_x^2\rangle - \langle p_x\rangle^2), \tag{17}$$

where α_{xx} relates the x-component of the induced polarization to the x-component of the applied electric field, and p_x is the x-component of the molecule's dipole moment. For a freely rotating dipole in the absence of an electric field, $\langle p_x\rangle = 0$ and $\langle p_x^2\rangle = \frac{1}{3}p^2$ (recall the average of $\cos^2(\theta)$ over a sphere). Thus we have the useful result:

$$\alpha_{xx} = \frac{p^2}{3k_BT}. \tag{18}$$

Incidentally, the same result applies to the magnetic susceptibility of a freely tumbling magnetic dipole in a magnetic field. And we saw when we did the Freely Jointed Chain model of polymers how the same argument yields an analogous formula for the force-extension curve.

Plugging the above result into the formula for the interaction energy of a dipole with a polarizable particle we get:

$$U = -\frac{p_1^2 p_2^2}{3(4\pi\epsilon)^2 k_BT r^6}. \tag{19}$$

This energy is called the Keesom energy and is the classical analog of the van der Waals force. The Keesom energy was known long before quantum theory was established. Using the FDT we can rewrite the Keesom energy in a more suggestive way:

$$U = -\frac{3\alpha_1\alpha_2 k_BT}{(4\pi\epsilon)^2 r^6}. \tag{20}$$

One way to think about this is that a thermal fluctuation induces a dipole moment in particle 1. This dipole then generates an electric field at particle 2 and polarizes particle 2. Then the thermally induced and electrically induced dipoles interact to generate a force. The $1/r^6$ dependence arises because the dipole field has to travel the intermolecular distance twice: once to polarize the second particle, and once to interact with the polarized second particle.

Another way to think about the Keesom force is to start with the formula for the interaction energy of two dipoles with fixed orientations:

$$U = \frac{3(\mathbf{p}_1 \cdot \hat{\mathbf{n}})(\mathbf{p}_2 \cdot \hat{\mathbf{n}}) - \mathbf{p}_1 \cdot \mathbf{p}_2}{4\pi\epsilon_0 r^3}, \tag{21}$$

where $\hat{\mathbf{n}}$ is the unit vector along the line joining the two molecules. To see that this energy is zero if the two dipoles are rotating completely freely, note that $\langle \mathbf{p}_1 \cdot \hat{\mathbf{n}} \rangle = 0$ and $\langle \mathbf{p}_1 \rangle \cdot \langle \mathbf{p_2} \rangle = 0$ (We factored the expectation values *because* we assumed $\mathbf{p}_1$ and $\mathbf{p}_2$ were fluctuating independently). However, we know that even if two quantities individually have zero expectation value, their product need not have zero expectation value. Due to the electrostatic interaction, the fluctuation of the two molecules becomes coupled, and we get the expression for the energy given above.

The result as expressed here applies more generally than just to tumbling dipoles. Any polarizable particle experiences this classical form of the van der Waals force when it is at finite temperature.

6 van der Waals forces

So far we have considered only classical contributions to the intermolecular force. There are important quantum contributions too. The essential idea is that quantum fluctuations can become correlated just as can classical fluctuations. Even for a molecule with no net dipole moment, the dipole *operator* is a fluctuating quantity. This is because the dipole operator does not commute with the Hamiltonian. Thus if the molecule is in its ground electronic state, successive measurements of the dipole moment yield different answers. Thus even though the expectation of the dipole operator $\langle \hat{\mathbf{p}} \rangle = 0$, it is usually the case that $\langle \hat{\mathbf{p}}^2 \rangle \neq 0$.

I will state, without derivation, the London dispersion energy:

$$U = -\frac{3}{4}\frac{\hbar\omega\alpha_1\alpha_2}{(4\pi\epsilon)^2 r^6}. \tag{22}$$

You see here that the energy is again related to the polarizabilities of both particles, in a symmetric way. The energy source leading to the spontaneous fluctuations is $\hbar\omega$, where ω is a characteristic electronic absorption frequency. For most non-dipolar molecules $\hbar\omega \gg k_B T$, so the quantum term actually dominates.

There are some beautiful formulas that interpolate smoothly between the quantum and classical limits, which I'm happy to discuss with you outside of class.

7 Retardation

Now I will discuss in a qualitative sense how Casimir and Polder found that intermolecular forces should fall off *faster* that $1/r^6$. The basic idea is that we have been assuming that the electromagnetic signal propagates instantaneously from one molecule to the other. In fact, the signal propagates at the speed of light. The timescale of the fluctuations is the period of the electronic oscillations of the molecule. During one oscillation of the electrons, light propagates a distance equal to one wavelength. So the analysis we have used applies only when the separation between the particles is $\ll \lambda$. In the opposite limit, we have to take into account not only the finite propagation delay of the electromagnetic field, but the fact that light is subject to quantum mechanics too. Namely, in a pure vacuum, at absolute zero, in the dark, we have $\langle \hat{\mathbf{E}} \rangle = 0$, but $\langle |\hat{\mathbf{E}}|^2 \rangle \neq 0$. This fluctuating zero-point field simultaneously induces dipole moments in both atoms. The resulting induced dipoles interact with each other. This interaction leads to a potential:

$$U = -\frac{23\alpha_1\alpha_2\hbar c}{4\pi(4\pi\epsilon)^2 r^7} \tag{23}$$

While they seem spooky, zero-point electromagnetic fields have numerous measurable consequences. Just one example is the attraction of parallel mirrors in vacuum.

[INSERT DRAWING OF TWO PARALLEL MIRRORS]

Only certain vacuum modes are allowed in between the mirrors because the mirrors enforce the boundary condition that the tangential electric field has to be zero on their surface. Meanwhile, everywhere else the vacuum experiences its continuum of radiation modes. The zero-point fluctuations exert a “radiation pressure” on all surfaces. But in the gap between the mirrors, this pressure is reduced because there are fewer modes than in the continuum. A consequence of this is that the mirrors experience and attractive force that scales as $1/d^4$.

There are classical analogs of the Casimir effect that occur in complex fluids (e.g. liquid crystals, solutions near a phase transition, polymer solutions, etc.) where the presence of boundaries modifies the number of states available to the system. In quantum systems you have a zero-point energy of $\frac{1}{2}\hbar\omega$ available per coordinate; in thermal systems you have $\frac{1}{2}k_BT$. In either case, changing the density of states can lead to forces.

8 Entropically mediated forces

We’ve seen how thermal fluctuations can lead to fluctuating dipole moments which, when correlated via electrostatic couplings, attract each other. Thermal fluctuations can also lead to numerous other subtle forces in solution. There are a host of subtle forces that arise between bodies because the approach of the bodies changes the volume of phase space available to the system. This changes the entropic contribution to the free energy, and thus leads to a force. There are two particularly important examples of this, namely double-layer overlap and polymeric forces. Those two examples are sufficiently complicated that we’ll discuss them separately when we talk about electrokinetics, and polymers, respectively. Today we’ll discuss another important effect: molecular crowding.

8.1 Displacement forces

Consider a solution containing a mixture of big particles and little particles. These might be proteins and sugar molecules, or plastic beads of different sizes.

The little particles exert an osmotic pressure:

$$\Pi = CN_A k_B T, \tag{24}$$

where C is the concentration of the little guys and N_A is Avogadro's number. For a big particle in the middle of the solution, it is constantly bombarded by little particles from all sides, so it feels no net force. But now consider what happens if one of the big guys approaches one of the walls of the container (the same reasoning will apply if he approaches another big particle). Once the spacing between the big particle and the wall becomes smaller than the diameter of the little particles, the little particles become excluded from the region between the big particle and the wall. Now the little particles exert osmotic pressure on the back side of the big particle, but not on the front side. Thus the big particle feels an effective attraction towards the wall.

We can estimate the functional form for this attraction as follows. Near the point of contact with the wall, the height of the big particle follows

$$h(r) \approx \frac{1}{2}\frac{r^2}{R}, \tag{25}$$

where R is the radius of the big particle. If the little particles have diameter d, the excluded region has area

$$A = 2\pi d R. \tag{26}$$

From this we see that the the force holding the big guy to the wall is:

$$F = 2\pi d R C N_A k_B T. \tag{27}$$

If the big particle is to be held against the wall, then the effective potential it experiences must be deeper than $k_B T$. The force F is applied over a characteristic distance d, so for the big particle to be trapped we require:

$$2\pi d^2 R C N_A > 1. \tag{28}$$

The precise numerical factors depend on the details of the geometry: a brick shape excludes more particles than does a sphere, and a sphere against a wall excludes more particles than do two spheres in contact. Nonetheless we can look at the scaling. Let's call the particle number-density $CN_A \equiv \nu$. Let's call the volume of space excluded to little particles V_{excl}. Then little particles will cause condensation of big particles *at any temperature* if $V_{\text{excl}}\nu > 1$, i.e. if on average there would have been more than one little particle within that excluded volume.

This displacement effect is qualitatively similar to the Casimir effect. In the displacement effect, two closely spaced surfaces exclude small particles, so these particles cannot exert osmotic pressure keeping the plates apart. In the Casimir effect, two closely spaced surfaces exclude zero-point vacuum fluctuations, so these fluctuations cannot exert radiation pressure keeping the plates apart.

9 Hydrophobic effect

The hydrophobic effect is not very well understood. Qualitatively this effect has to do with the preference of water to adhere to itself (due to hydrogen bonds) than to non-polar surfaces. If you calculate the change in surface area of the water-hydrophobic interface as a consequence of two hydrophobic particles coming together, and multiply by the surface tension of water ($\gamma_{H_2O} = 77$ mN/m), you can get a fairly accurate estimate of hydrophobic interaction energies.

The distance over which the hydrophobic effect acts is a matter of intense debate, but the answer probably is just a few molecular diameters, corresponding to the distance over which order persists in water.