

Advanced Thermodynamics
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Lecture – 7
Intermolecular Forces and Non-Ideal Behaviour

Welcome to the MOOCs course advanced thermodynamics. The title of this lecture is intermolecular forces and non-ideal behavior. So, we will be discussing both about the intermolecular forces and then how they are going to display a kind of or induce a kind of a non-ideality in the system that is what we are going to see. So, but before going into the intermolecular forces, we will be discussing few basic important things about the ideal gas behavior.

Then what are the forces in general act in the molecular level those kind of things we are going to discuss before going into the details of intermolecular forces.

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• Intensive properties that can be experimentally measured are

- Pressure
- Temperature
- Molar volume
- Composition

• For pure species, only two intensive properties are independent

• Constitutive equations relating these measured variables by fitting experimental data are known as Equation of State $\rightarrow f(T, P, v) = 0$

• E.O.S. can be explicit in pressure as $P = f(T, v)$
or it can be explicit in molar volume as $v = f(T, P)$ |
or in terms of dimensionless compressibility factor as

$$z = \frac{Pv}{RT} = f(T, v) \text{ or } z = \frac{Pv}{RT} = f(T, P)$$

In general, we know that intensive properties that can be experimentally measured are pressure, temperature, molar volume and composition. Let us say if you have a pure system out of these 4, the composition will not come into the picture and then since 3 intensive variables should be there in the pure system, maximum one can have two intensive variables as a kind of independent variables, okay? Now, constitutive equations relating these measurable variables by fitting experimental data is in general known as equation of state.

These equations of state are represented as function of temperature, pressure, and volume. They can be presented in different form then P is function of temperature and molar volume then molar volume = function of temperature and pressure. Then in terms of dimensionless compressibility factor also, these equations of state are represented that is $z = \frac{Pv}{RT}$ and then that again can be function of temperature and molar volume or temperature and pressure, okay?

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The slide is titled "EoS of Ideal Gases: $Pv = RT$ ". It contains the following text:

- This is derived directly from the kinetic theory of gases and valid for a gas consisting of molecules that are
 - Infinitesimally small
 - Hard round spheres that occupy negligible volume
 - Exert forces upon each other only through collisions
 - Exert no intermolecular forces
- In the absence of intermolecular forces, that internal energy is independent of pressure and function of only temperature, that is, the molecular kinetic energy of molecules:

$$u_{ideal\ gas} = f(T)$$
- As $P \rightarrow 0$, all gases approach ideal gas behaviour
- Then if intermolecular forces are included what other E.O.S can arise

Handwritten notes include "Intermolecular forces" with an arrow pointing to the last bullet point, and a diagram in the top right corner showing a coordinate system with axes labeled r and γ .

Now, we see equation of state for an ideal gas. For an ideal gas, we already know that the equation of state is nothing but $Pv = RT$ that means compressibility factor $\frac{Pv}{RT} = 1$, okay? So, ideal gas behavior in the sense the molecules occupy very small volume, negligible volume and they are far from each other. They do not exert any kind of intermolecular forces. There is no force between these 2 molecules or any 2 molecules that you take or between molecules of ideal gas there are no forces acting, right?

That means, let us say if you have a kind of pictorially if you or graphically if you wanted to represent let us say you have a intermolecular forces or intermolecular potential let us say gamma versus r, the distance between the molecules if you take, it is always 0. That is this horizontal line whatever is there, that is the graph picture, and really that is how we can represent, okay? This point is gamma = 0, okay? So that means if you have a non-ideal system, there is a kind of intermolecular force.

So how these intermolecular forces can be divided and evaluated those kinds of things we have to see, but we will see a few details of ideal gas though we already know all of them. This

equation of state for ideal gas is directly derived from kinetic theory of gases and valid for gas containing of molecules that are infinitesimally small, hard round spheres that occupy negligible volume, exert forces upon each other only through collisions exerts no intermolecular forces.

In the absence of intermolecular forces, that internal energy is independent of pressure and function of temperature only that is the reason you know the molecular kinetic energy of molecules that we can say, that you know, function of temperature. So, in this case we have only molecular kinetic energy, we do not have a molecular potential energy because potential energy comes because of the relative distance between the molecules and then that related distance when these molecules come close to each other, then this intermolecular potential develops.

But in the case of you know ideal gases, there is no such kind of intermolecular force. So then we have only molecular kinetic energy and then obviously it is a function of temperature only, it is not a function of pressure. That is in other words as P tends to 0, all gases approach ideal gas behavior because if there is no pressure that means only temperature is going to play a role, and then with increasing the temperature molecular behavior is going to become more and more random and then the gas is going to become a kind of ideal gas, okay?

Then if intermolecular forces are included what other kinds of equations of state can arise, right? So, what are these equations of state other than ideal gas behavior? When we include this intermolecular forces, then possible that we may have several equations of state that depends on the type of intermolecular forces. Several different types of forces may be acting, in some case one type of force may be dominant and in other case other type of force may be dominant.

So, we cannot have a kind of one general kind of equation of states for non-ideal system like we have for ideal systems, okay? So, depending on system to system, there we may have n number of equations of state for non-ideal systems but however, before answering these questions, what kind of other equations of states can arise because of this intermolecular forces, it is very much essential to understand what are these intermolecular forces first, okay?

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Intermolecular forces

- There are many different types of intermolecular forces
- Some of those which are relevant to the present topic of non-ideal systems are:
 - Internal (molecular) energy
 - Attractive forces
 - Intermolecular potential functions and repulsive forces

So, intermolecular forces. There are many different types of intermolecular forces in general, but we will be discussing only which are relevant to the present topic of non-ideal systems, so which include internal molecular energy, attractive forces, intermolecular potential functions and repulsive forces, okay? We are going to see a few details of each of these types of forces.

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Internal Energy

- Internal (molecular) energy can be divided into two:
- Molecular kinetic energy:
 - Because of translational, rotational and vibrational motion of molecules
 - It manifests itself by velocities of molecules and is directly related to measurable variable, **temperature**, via Maxwell-Boltzmann statistics
- Molecular potential energy:
 - Results from position of one molecule relative to others in the system
 - This also referred to as "intermolecular potential energy"
 - Since this intermolecular potential energy depends on position, it can be directly related to measurable variable, **pressure**

ϕ_i f_{puni}

Let us start with the internal energy or internal molecular energy. We know that internal molecular energy can be divided into 2. One is the molecular kinetic energy, okay? So because of translational, rotational and vibrational motion of molecules this molecular kinetic energy exists, because these molecules, what happens? These molecules even when there are no external forces are existing, sometimes what happens, this translate, they may be translating from one position to other position, they may be rotating, they may be vibrating as well.

So, because of such kind of translational, rotational or vibrational kind of motion on this molecule, we can have a kind of molecular kinetic energy. Please be careful these kinetic energy are the molecular kinetic energy that is the kinetic energy associated with the molecules at molecular transport level only, okay? Not because of the bulk motions. It manifests itself by velocities of molecules and is directly related to the measurable property, temperature according to Maxwell-Boltzmann equation or Maxwell-Boltzmann statistics, okay?

So, that is kinetic energy is function of temperature directly. Then other one is the molecular potential energy. It is also associated with the relative motion between the molecules. So, at the molecular level it results from possession of one molecule related to the others in the system, this also referred to as intermolecular potential, right? When the molecules, let us say in ideal gas system, molecules are far away from each other like this, right?

But when you increase the pressure, these molecules obviously will come close to each other and then when they come close to each other, because of the relative position you know intermolecular potential will be developed. Since this intermolecular potential energy depends on position, it can be really related to measurable variable pressure. Obviously, when the molecules are far away, one is here, another one is here, when you pressurize them, it is obviously that they may come close.

So, they are coming closer because of the pressure in the system. So, that is the reason this intermolecular potential depends on position, it can be directly related to measurable variables. And then we now understand the non-ideality in the system is because of the intermolecular potentials, intermolecular forces, those intermolecular forces causing because of the intermolecular potentials, right? So, these are now dependent on or directly related to the pressure of the system, okay?

That is the reason the fugacity calculations, I repeat, the generalized expression for the fugacity coefficient or the fugacity of pure component i etc., those we have derived at constant temperature and composition. If you remember in the previous lecture whatever the derivations we have done, right? Because pressure we cannot take constant if you wanted to bring into the system the effect of non-ideality or if you wanted to establish the non-ideality due to the measurable variables and then measurable variable is nothing but pressure in the case of molecular potential energy.

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- There are no intermolecular forces in the case of ideal gases
 - Thus the position of molecules relative to others does not matter
 - Internal energy of ideal gas is independent of pressure and depends only on temperature
- At constant temperature, as the pressure increases the average distance between molecules decreases and thus
 - Their positions relative to others get closer
 - Role of intermolecular forces start becoming predominant with increasing pressure
 - Induces non-ideality in the system *
 - It is important to develop more general EoS by including intermolecular forces

So, there are no intermolecular forces in the case of ideal gases, obviously. Thus, the position of molecules relative to others does not matter. Internal energy of ideal gas is independent of pressure and depends only on temperature as we have already seen. But at constant temperature as the pressure increases, the average distance between the molecules gradually decrease. If you increase pressure more and more, they may come very much close to each other and then obviously when the average distance between these molecules decreases. Then what happens now, the molecule start experience the intermolecular forces, okay?

Thus, their relative positions, when you increase the pressure, their positions relative to others get closer. Role of intermolecular forces start becoming predominant with increasing the pressure and then thus it induces non-ideality in the system, okay? So, pressure is the one, or increasing pressure or going pressure beyond $P \rightarrow 0$, larger the pressure, you go to the larger pressure site or gradually increase pressure you know, this non-ideal behavior gradually increases, okay?

If you decrease the pressure and go towards $P \rightarrow 0$, gradually non-ideality decreases and then you eventually end up to coming to ideal gas behavior where molecules are free from each other. There is no intermolecular collision, intermolecular potential, etc. Thus, it is important to develop more general equations of state by including intermolecular forces, okay?

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 - Their positions relative to others get closer
 - Role of intermolecular forces start becoming predominant with increasing pressure
 - Induces non-ideality in the system *
 - It is important to develop more general EoS by including intermolecular forces

Now, for developing more realistic equations of state by including intermolecular forces, what is it required? It is required to establish functional relationship for internal energy of the system as function of distance between 2 molecules and their orientations also. When you increase the pressure, what happens? The molecules may be coming closer to each other and then there is a kind of relative orientation. These molecules also translate, rotate and then vibrate, so they may be moving here and there, different orientations may be there.

Let us say one molecule is here, another molecule is initially here, so it may go like this, it may come like this, it may come like this and then it may go like this, any orientations it may take, so the orientation also important factor along with the relative distance between the molecules for which we are trying to establish the intermolecular forces. So, that is what we have to understand. What is the functional relationship for internal energy of the system as function of relative distance between the molecules as well as their orientation as well?

So, now there may be n number of orientations are possible, n number of relative distances are possible within which you know there is a kind of intermolecular force. Obviously, there is a range like you know in this certain range, there may be intermolecular potential. After that if the molecules go farther away, then intermolecular forces gradually decreases and then it becomes 0 at some distance. After that distance, we are not worried about it, but within the distance between the 2 molecules, there is intermolecular force.

Then if you decrease this distance further, so what happens? It is the intermolecular forces which increases. Further if you decrease, it may further increase, like that it may be there and

then likewise n number of orientations of these molecules are also possible. So, when you wanted to know the overall intermolecular potential for any kind of system, then what you have to do? You have to average over all possible orientation and all possible relative distance between 2 molecules for which there exist intermolecular potential.

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- For developing more realistic EoS by including intermolecular forces, it is required to
 - Establish functional relationship for internal energy of the system as function of distance between molecules and their orientations
 - Improve understanding of intermolecular potential energy which contributes to the non-ideality of the system
- Intermolecular interactions between species arise from electronic and quantum nature of atoms
- When a molecule is in close enough proximity to another molecule, electrically charged structure of its atom can lead to attractive or repulsive forces
- Attractive forces include
 - electrostatic forces between point charges or permanent dipoles, induction forces and dispersion forces

Further, you need to improve understanding of intermolecular potential which contributes to the non-ideal system. So, what is this intermolecular potential? This is what, topic of the day for us, okay? Intermolecular interactions between species arise from electronic and quantum nature of atoms and then we know when a molecule is in close enough proximity to another molecule, electrically charged structure of its atoms can lead to either attractive or repulsive forces.

In general if the molecules of same nature, similar molecules, then where these are touching each other, there will be repulsive forces, but as you move away slightly what happens gradually you know, this repulsive forces decreases and at a certain distance, what happens you know, there will be no repulsive force or no attractive force, but further if you increase what happens you know, it will start attracting, attractive force. So, when they come close to each other, they repel each other, but when they start going from each other after a certain point, they will try to attract each other.

These kind of things will happen, and then if you further gradually go increase the distance between the molecules, attractive forces decreases and then eventually at certain distance far away from this molecule, there will not be any intermolecular potential. So, we are going to

see a few of the attractive forces because we realize that attractive forces are very much essential because they are acting in the long range, right?

Repulsive forces are there only in the short range that is when r is close to 0 or when the molecules are touching each other or slightly away from each other, for that range only these repulsive forces are there, but you know what happens as the distance increases, the attractive force is developing and this attractive forces are there. Initially, they increase and then gradually they decrease, but they are there for longer range that is the reason attractive forces are much more essential in discussing this intermolecular potentials.

So, that is the reason first we discuss about the attractive forces, okay? So, what are the attractive forces? In general, electrostatic forces between point charges are permanent dipoles, induction forces, and dispersion forces because of a kind of attractive forces between the molecules, right?

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- Since intermolecular interactions result from electronic nature of atoms, it becomes important to understand "electric field"
- Electric field intensity (\vec{E}) is defined as force per unit charge exerted on a +ve test charge Q , in the field.
- It is related to negative gradient of molecular potential energy " Γ " by: $\vec{E} = \frac{F}{Q} = -\frac{\nabla\Gamma}{Q}$
 - If in r -direction only then $F = -\nabla\Gamma = -\frac{d\Gamma}{dr}$
- From above eq., the electric field intensity (\vec{E}) is related to intermolecular forces F and to the intermolecular potential energy Γ
- Negative of the potential energy, i.e., $-\Gamma(r)$ is the work which must be done to separate two molecules from the intermolecular separation distance " r " to " ∞ " separation
- There is no direct quantitative relationship between molecular physics and classical thermodynamics except in very simple systems

So, since intermolecular interactions result from electronic nature of atoms it becomes important to understand electric field. What is electric field? Electric field intensity is defined as force per unit charge exerted on positive test search Q in the field that is, it is related to negative gradient of molecular potential energy gamma by this expression. Electric field intensity \vec{E} is nothing but force by positive test charge Q that is that force is nothing but $-\Delta\Gamma$ that is gradient of intermolecular potential.

This $\Delta\Gamma$ is nothing but gradient, gradient of molecular potential energy or intermolecular potential, okay? So, now, we introduce this gamma intermolecular potential and then in most of this lecture we are going to establish what kind of relation are existing for gamma depending on the nature of the molecules, etc.. Those things we are going to see because now we understand this gamma is the one causing a kind of non-ideality in the system, right? And then it is a function of relative position between the molecules and the orientation of those modules, okay?

So, this gamma as function of relative position as well as the relative orientation of these molecules, those things we are going to see in detail and then write a few expressions for this gamma for different types of molecules. If in r-direction only orientation if you take, I mean if you take the relative position or the distance between 2 molecules in only r-direction, then $F = -\frac{d\Gamma}{dr}$, okay? We can understand that electric field \bar{E} is now related to the intermolecular force F and intermolecular potential gamma, okay?

Negative of the potential energy that is $-\Gamma r$ is the work, what is it mean? By whatever this - gamma function of r is there, that negative of Γr what it is? What does it indicate? It indicates the work that must be done to separate 2 molecules from the intermolecular separation distance or to infinity separation distance because this gamma is active for that separation distance r, right? This r maybe 0 to certain r, between this limit only this gamma is acting that is intermolecular potential is there, but you know if you go beyond r and then go towards the $r = \infty$, there will not be intermolecular force.

So, when you take 2 molecules, there is gamma that is intermolecular potential is there, okay? So, how much work should be done in order to separate these molecules beyond r and to infinity distance so that there should not be any gamma that is what, there should not any intermolecular force, so that work, this indicate that work. That much work must be done to separate 2 molecules from the intermolecular separation distance or to infinity separation.

There is no direct quantitative relationship between molecular physics and classical thermodynamics except in very simple cases but most of these details are evaluated or developed on the basis of molecular physics and then this equation of states, etc. or intermolecular potential that we are going to see, all of them are developed based on the

molecular physics, they are not part of thermodynamics to be frank, but thermodynamic properties are being affected by this non-ideality of the system.

So, we have to understand why this non-ideality is coming to the picture. That is the reason though these topics are more related to the molecular physics, we are discussing so that we have a kind of understanding why the system behave as a kind of non-ideal system in the presence of intermolecular forces, okay?

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• Then why should we study molecular physics?

- To strengthen the intuition about non-ideal behavior and to judge about what EoS to use
- To understand why some EoS work better than others
- Relation between molecular physics and classical thermodynamics can be realized
 - by the help of computers and techniques such as density functional theory and Monte Carlo simulations,
- To develop mixing rules for how thermodynamic properties of a mixture depend on composition

$a = a_1 y_1^2 + 2A_{12} y_1 y_2 + a_2 y_2^2$
 $b = b_1 y_1 + b_2 y_2$

So, then why should we study the molecular physics? Because to strengthen the intuition about the non-ideal behavior and judge about what equation of state to be used for a given application for a given system, okay? For that also we need to have some kind of basics about the molecular physics. Then to understand why some of the equations of state work better than the others, like let us say, we have taken Van der Waal's equations and Redlich-Kwong equation in some of previous lectures.

Then we developed you know fugacity of component i generalized expressions, we developed generalized fugacity expression and then for this Van der Waal's equations and Redlich-Kwong equation, what are the fugacity expressions or the fugacity of component i in a mixture which is described by equation of state or Redlich-Kwong equations those things we have seen but when you take the experimental information, okay? Experimentally you find out the fugacity of a system.

Then under the same conditions you use these equations of state, Redlich-Kwong equation of state or the Van der Waal's equation of state and then using those generalized fugacity expressions, you obtain the fugacities when these 2 equations of states are obeyed. So, which one is matching better with the experimental results. Possible that both may be matching better depending on the system, possible both may not be matching better, possible that one of them may be matching better another may not be matching depending on the system.

So, if you wanted to understand further which system, which equation of state is going to work better without doing much experimental study or without going to much details of thermodynamics, how can you develop that understanding? That understanding you can develop through molecular physics. Let us say if you have a kind of a non-polar system. Then what are the intermolecular potentials those are available for non-polar system and then which equation of state has incorporated the information about non-polar system or the non-polar nature of the system?

Then, obviously if you know that information, that equation of state which is having information about the non-polar nature, then that must be obviously giving better results that kind of understanding you may be having, right? You may be gaining if you understand, if you have some kind of basics about the molecular physics, though it is not relevant to the main course of advanced thermodynamics.

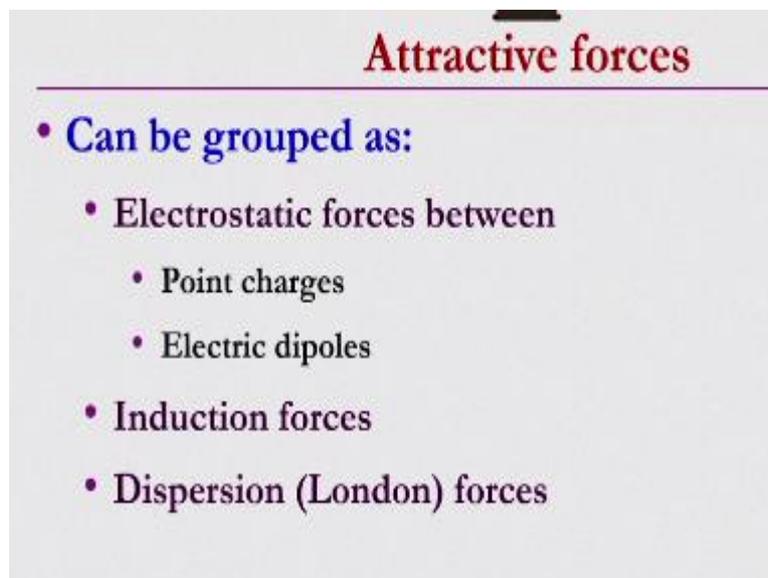
Though it may not be directly related to the present course of thermodynamics of non-ideal systems, we are estimating the thermodynamic properties and then finding out the phase equilibrium composition when the system obeys non-ideal behavior, but you know these kinds of basic understanding is required. Then further to understand relation between molecular physics and in classical thermodynamics, though there is no directly quantitative relationship except very few systems.

It is possible to develop relation between molecular physics and classical thermodynamics using the advanced computational techniques like you know molecular simulations, density functional theory, etc. These kind of computational techniques are available nowadays. So, using those techniques, one can develop relation between molecular physics and classical thermodynamics. For that reason also, it is necessary to know a few details about the molecular physics.

Then finally, this is most important actually to develop mixing rules for how thermodynamic properties of a mixture depend on composition. We have already seen in one of the previous lecture, let us say Van der Waal's equation of state we have taken, so there are constant a and b, right? And these constants are dependent on the composition when we were finding out the fugacity of component one in a binary mixture, so this a and b are required for the mixture, which were in general not available for any binary mixture.

These a and b constants are available only for individual pure gases, these kind of mixing rules also we have seen. So, this actually if you wanted to develop, then also you need to know a few basics of molecular physics, okay?

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Attractive forces

- **Can be grouped as:**
 - **Electrostatic forces between**
 - Point charges
 - Electric dipoles
 - **Induction forces**
 - **Dispersion (London) forces**

So, now let us start discussing about the attractive forces. They can be grouped as electrostatic forces between point charges or between electric dipoles and then induction forces and then dispersion forces or London forces. So, we see each of them in detail so that to understand how these are going to bring in some kind of intermolecular potential and because of that one, how the system is going to behave non-ideal that we can understand.

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Electrostatic forces

- Electrostatic phenomena arise from the forces that static or slowly moving (without acceleration) electric charges exert on each other
- Consider two point electric charges of magnitude q_i & q_j
- These charges are separated by distance r
- Then force between them is given by Coulomb's law: $F = \frac{q_i q_j}{4\pi\epsilon_0 r^2}$
- where F = force (Newton),
 q = charge (Coulomb, C),
 r = separation distance (meter)
 ϵ_0 = dielectric permittivity of vacuum and is given by
 $8.854 \times 10^{-12} \text{ C}^2/\text{Jm}$

So, electrostatic forces. Coulomb's law, we all of us know, but however, we need to have a kind of information and then these electrostatic forces are very much important and then much stronger than any other kind of attractive forces that we are going to study in this lecture especially, right? So, how we are going to see by example also. Electrostatic phenomena arise from the forces that static or slowly moving electric charges that exert some kind of force on to each other and then if you consider 2 electric point charges q_i , q_j . q_i and q_j are the magnitudes of these point charges.

So, we are not taking $-q + q$ like that, okay? They are magnitude of point charges and these are separated by a separation distance r . Then what is the force acting between them? That we can know through Coulomb's law that is $F = \frac{q_i q_j}{4\pi\epsilon_0 r^2}$. What we understand? It is inversely proportional to r^2 , okay? So, this is one of the important thing to observe in the subsequent lecture also.

Whether the intermolecular potential or if you write in terms of force, how it is related to the radial distance or the relative position between 2 molecules or relative distance between 2 molecules because we understand this intermolecular potential is function of relative position of the molecules as well as their orientation, okay? Now we are taking fixed charges q_i , q_j that is the reason we are not taking any orientation in this Coulomb's law, okay?

Here F is force in Newton, q is charge in Coulomb, r is separation distance in meter, ϵ_0 is dielectric permittivity of vacuum and is given by 8.854×10^{-12} Coulomb square per Joule meter, okay?

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• Thus potential energy is: $\Gamma(r) = - \int F(r) dr \Rightarrow \Gamma_{ij}(r) = - \int \frac{q_i q_j}{4\pi\epsilon_0 r^2} dr$
 $\Rightarrow \Gamma_{ij}(r) = \frac{q_i q_j}{4\pi\epsilon_0 r} + \text{constant}$

• No forces act at infinite separation distance of charges, i.e.,
 At $r = \infty \rightarrow \Gamma = 0 \rightarrow \text{constant} = 0$

$$\Gamma_{ij}(r) = \frac{q_i q_j}{4\pi\epsilon_0 r} *$$

• For charged molecules (i.e., ions), q_i & q_j are integral multiple of unit charge e ; thus the potential energy between two ions is:

$$* \Gamma_{ij} = \frac{z_i z_j e^2}{4\pi\epsilon_0 r} *$$

Where z_i, z_j are ionic valences and $e = 1.60218 \times 10^{-19} \text{C}$

Thus, potential energy if you wanted to know, we know that $F = \frac{d\Gamma}{dr}$ that means $\Gamma(r) = - \int F(r) dr$. So, whatever this F of r that we had just now by Coulomb's law that you substitute here and then integrate. Now here in place of F of r, F function of r substitute $\frac{q_i q_j}{4\pi\epsilon_0 r^2}$ according to Coulomb's law. Then $\Gamma_{ij}(r)$ we will get $\frac{q_i q_j}{4\pi\epsilon_0 r} + \text{constant}$, right?

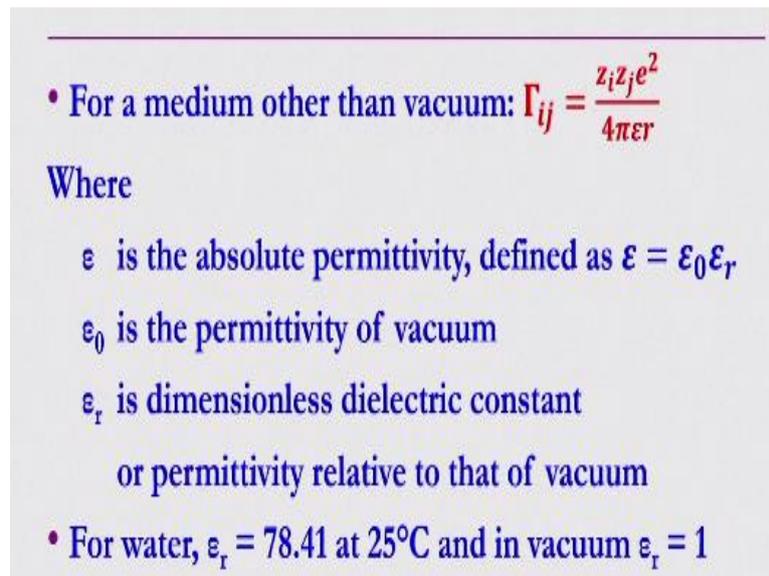
Then we know this is again Γ_{ij} that is intermolecular potential, F is the force between 2 molecules where this Γ_{ij} is the intermolecular potential energy between these 2 molecules. It is inversely proportional to r, okay? And that is the separation distance, okay? Now we know it is inversely proportional, so obviously, when these molecules move away from each other at infinite distance, there will not be any force acting amongst them. They will be independent of each other, there will not be any force or intermolecular positional between these 2 molecules.

That means at r tends to infinity, gamma tends to 0 that means constant is 0. That means, finally between 2 point charges, the intermolecular potential Γ_{ij} is nothing but $\frac{q_i q_j}{4\pi\epsilon_0 r}$. For charged molecules that is for ions, q_i and q_j are integral multiple of unit charge e and thus potential

energy between 2 ions is nothing but $\Gamma_{ij} = \frac{z_i z_j e^2}{4\pi\epsilon r}$ where z_i, z_j are ionic valences and then e is nothing but 1.60218×10^{-19} Coulomb, okay?

So, from this expression we can understand how much it is significant intermolecular potential between point charges due to the electrostatic phenomena, okay? So, we can much better understand the same thing by an example, we will do that one as well.

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• For a medium other than vacuum: $\Gamma_{ij} = \frac{z_i z_j e^2}{4\pi\epsilon r}$

Where

- ϵ is the absolute permittivity, defined as $\epsilon = \epsilon_0 \epsilon_r$
- ϵ_0 is the permittivity of vacuum
- ϵ_r is dimensionless dielectric constant or permittivity relative to that of vacuum

• For water, $\epsilon_r = 78.41$ at 25°C and in vacuum $\epsilon_r = 1$

So, for a medium other than vacuum $\Gamma_{ij} = \frac{z_i z_j e^2}{4\pi\epsilon r}$, okay? Where the ϵ is the absolute permittivity defined as $\epsilon = \epsilon_0 \epsilon_r$. ϵ_0 we already know it as permittivity of vacuum, ϵ_r is dimensionless dielectric constant or permittivity related to that of vacuum and it is 78.41 at 25 degrees centigrade for water, whereas for vacuum it is nothing but equals to 1 so that in the vacuum ϵ should become equal to ϵ_0 . Now, we take an example and understand how significant or how much important this electrostatic forces between two ions.

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Example - 1

- Calculate potential energy between two isolated ions Na^+ and Cl^- separated at a distance 2.76\AA

• Solution: $\Gamma_{ij} = \frac{z_i z_j e^2}{4\pi\epsilon_0 r} = \frac{(-1)(+1)(1.60218 \times 10^{-19})^2}{4\pi(8.854 \times 10^{-12})(2.76 \times 10^{-10})} = \underline{-8.36 \times 10^{-19} \text{ J}}$ ↙ attractive forces

- Thermal energy at room temperature

→ $kT = 1.38 \times 10^{-23} \left(\frac{\text{J}}{\text{K}}\right) \times 300\text{K} = \underline{0.0414 \times 10^{-19} \text{ J}}$ (here k is Boltzmann constant)

- Thus compared to other intermolecular energies such as thermal energy (kT), magnitude of Coulomb energy is large and of large range
- In other words, when two ions are about 560\AA far apart from each other then only coulomb energy will be equal to thermal energy

i.e., $2.76 \times \frac{8.36 \times 10^{-19}}{0.0414 \times 10^{-19}} = 557.3 \approx \underline{560 \text{ \AA}}$

- These electrostatic forces make dominant contribution to the configurational energy of salt crystals and are responsible for very high melting points of salts

Calculate potential energy between 2 isolated ions Na^+ and Cl^- separated at a distance 2.76\AA , okay? So, 2 ions are given, that is z_i, z_j are given. So, z_i is + 1, z_j is - 1, okay? So, electronic valences are + 1 and - 1 for these two. Then we know this Γ_{ij} is nothing but $\frac{z_i z_j e^2}{4\pi\epsilon_0 r}$. So, vacuum we are taking because nothing has been mentioned. So, z_i is - 1, $z_j = + 1$, e is 1.60218×10^{-19} , ϵ_0 is 8.854×10^{-12} , and then separation distance is 2.76\AA that is 2.76×10^{-10} meters.

When you substitute these numbers, then you will understand this Γ_{ij} is nothing but - 8.36×10^{-19} joules. So, this - as I already mentioned, the - indicate attractive forces. So, what we understand? When these 2, Na^+ and Cl^- ions are 2.76\AA distance apart from each other, there exist an attractive force between these 2 and the magnitude of that attractive force is nothing but 8.36×10^{-19} joules, okay? Now, this number we got.

Two things we got, the nature of force whether it is attractive or repulsive that we understood, another one thing what is the magnitude of the force that we understand, but we can understand much better about this one when we compare this one to the other kind of forces, okay? Let us say thermal energy at room temperature that is 300 Kelvin if you calculate, it is nothing but kT , k is Boltzmann constant, so that is 1.38×10^{-23} , temperature is 300 Kelvin if you take roughly, then it comes out to be 0.0414×10^{-19} joules, right?

So, now, this order of 10^{19} intentionally kept like this, so that we can understand. Now, we see here the electrostatic forces, the intermolecular potential due to the electrostatic behavior of these 2 ions is 8.36×10^{-19} joules of attractive force, whereas the thermal energy is only 0.0414×10^{-19} joules. So, that means such high magnitude of electrostatic forces are there, okay? Thus

compared to other intermolecular energy such as thermal energy, the magnitude of Coulomb energy is larger.

Obviously magnitude wise, we can see and is of large range. What does it mean by large range? At 2.76\AA , we have attractive force of 8.36×10^{-19} joules, right? But if you increase this distance, gradually what happens, this gradually decreases, it decreases but it will be still there for long distance that is what means by long range. How much long, that relative to thermal energy we can calculate. Let us say if you divide this Coulomb energy divided by the thermal energy and multiply by 2.76 whatever the distance is there.

So, that distance approximately 560\AA you are getting. That means when this Na^+ and Cl^- ions when they are 2.76\AA distance only that is very small distance between these two, right? So, there is an attractive force of 8.39×10^{-19} joules, but if you increase the distance, how much you increase, you increase to 560\AA , very large distance, but despite of this distance, there is a kind of intermolecular potential between these 2 and that intermolecular potential is equal to thermal energy.

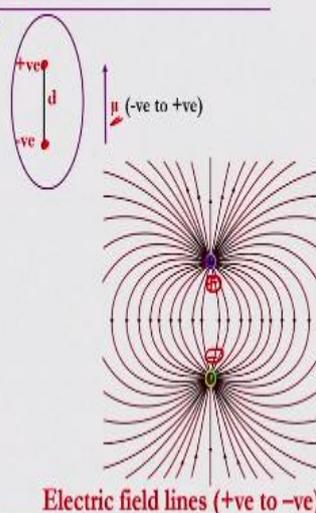
So, that is what mean by long range, okay? So, they are existing at longer separation distance that is what it means. These electrostatic forces now we can understand this Na^+ and Cl^- , the attractive force is so strong, so high because of that one in general we know that ionic molecules whatever are there, you know the salt like NaCl which dissociate as Na^+ and Cl^- you know, therefore the attractive force is so strong and then it is there for the long run.

Because of this reason what happens you know, melting of such salt requires very high energy that is reason melting point of this salt is very a large. So, that is how we can understand how significant the force between 2 ions or 2 molecules is and then we can later on relate that one to the non-ideal systems.

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Electric dipoles

- Electrostatic forces can arise even for those particles that do not have a net electric charge
- Consider a particle having two electric charges of same magnitude " e " but of opposite sign (thus net charge is zero) and are held a distance " d " apart
- Such particle has an electric couple or permanent dipole moment μ defined by $\mu = e \times d$
- Strength of dipole is characterized by dipole moment (μ), a vector that points from $-ve$ charge to $+ve$ charge
- Unit of the dipole moment is debye (D) and it is equal to 3.33569×10^{-30} C.m
- Dipole moment of a pair of charges $+e$ and $-e$ separated by 0.1nm is $\mu = 1.60218 \times 10^{-19}\text{C} \times 10^{-10}\text{m} = 1.60218 \times 10^{-29}\text{C.m} = 4.8\text{D}$



So, next one is the electrostatic force due to the electric dipoles. What happens even when there is no net electric charge, then also it is possible that electrostatic forces may exist, right? So, how does it happen that is what we are going to see? We know in general, consider a particle having two electric charges of same magnitude, e but opposite sign that is one is having $+$ sign and another one is the $-$ sign and separated at a distance d apart from each other.

Then such particle has an electric couple or permanent dipole moment μ defined as $e \cdot d$. Dipole moment $\mu = e \cdot d$. So, how does it occur? Because then even though net charge is 0, there is no net charge, what happens? Some kind of electric field is developed in some molecules, right? Because of that electric field, this dipole moment is developed, okay? So, we will see that one. Strength of dipole is characterized by dipole moment μ that is a vector that moves or points from negatives sign or negative charge to the positive charge.

Units of the dipole moment is Debye and it is equal to 3.33569×10^{-30} Coulomb meter. Dipole moment of a pair of charges $+e$ and $-e$ separated by 0.1 nanometer is nothing but $\mu = 1.603218 \times 10^{-19}$ Coulombs that is e multiplied by 0.1 nanometer that is 10^{-10} meters distance apart from each other. So, that comes out to be 1.60218×10^{-29} Coulomb meters, but 33569×10^{-30} Coulomb meter is one Debye. So, if you convert this one into the Debye, you will get 4.8 Debye, right?

So, pictorially let us say this is a negative charge here, we have a positive charge here. So, then because of some kind of arrangement, what we can say that there is a covalent bond existing sharing of electrons are taking place. So, then under such conditions, it is possible that one of

the molecules may be more electronegative compared to the other one. So, because of that one though the overall net charge is 0, there will be a kind of electric field.

Because of that electric field, there will be kind of a permanent dipole moment μ and then that points from - negative point to the positive + point, right? Under such conditions electric fields, but obviously they are pointing from + charge to - charge, okay? Now the charges one + charge, one - charge is you know balanced, but still there is a kind of electric field is developed.

Because of this developed electric field, you know what happens? Permanent dipole moment may be there even for the things where there is no net charge, okay? We take an example and see.

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Dipole moments realization at molecular level is required

- When sharing of electrons in a covalent bond is unequal,
 - an atom can gain electron density at expense of the atom to which it is bonded
- For ex., consider HCl molecule with Lewis dot structure as shown in figure 
- Bond is formed by sharing of one electron from each molecule
- However, chlorine is highly electronegative since it needs an electron to complete its outer shell
 - Thus it pulls electron from H much more strongly than H pulls electron from Cl
- In other words, electrons are not shared equally rather
 - lone hydrogen electron spends more time close to Cl atom than the shared Cl electron does next to H

So, dipole moment realization at molecular level is obviously required because when sharing of electrons in a covalent bond is unequal, an atom can gain electron density at expense of the atom to which it is bonded. For example, if you take HCl molecule with Lewis dot structure as shown here. So, this dots are shown for the valence electron of Cl and then cross is shown for the valence electron of the H. Now, the chlorine is more electronegative, we can see 7 electrons are there in the valence.

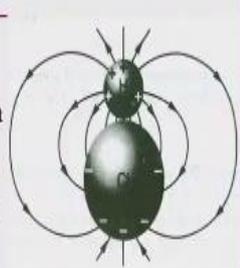
It needs only 1 electron to complete the valence electrons and become stable, right? Whereas the hydrogen also it is having only 1 electron. If it can get 1 more electron, its outer shell balance would be fulfilled with the 2 electrons nearest one, so that can also be stable. So then,

what they do? They share electron with each other, but you know this Cl⁻ it is more electronegative, so what happens? It pulls the electron of hydrogen towards it most strongly than hydrogen pulls the electron of chlorine towards it, okay?

So, there is an imbalance, though they are sharing, they are being shared unequally. Because of this unequal sharing, a kind of charge will be developed. Because of that on, electric field will be developed. Bond is formed by sharing of 1 electron from each molecule. However, chlorine is highly electronegative since it needs an electron to complete its outer shell. Thus, it pulls electron from H much more strongly than H pulls electron from Cl.

In other words, electrons are not shared equally, rather lone hydrogen electron spends more time close to the Cl atom than the shared Cl electron does next to H atom, right? Because of this one, what happens?

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- This results net charge separation with chlorine obtaining a net negative charge and H obtaining a net positive charge
 - This separation of charge leads to permanent dipole moment
- For HCl, magnitude of dipole moment (μ) is around 1.08D
- Diatomic molecules with electronegative (such as F, Cl, etc.) and electropositive (such as Li, Na, etc.) atoms have large dipole moments
- Diatomic molecules with dissimilar atoms such as HCl will always exhibit some degree of charge separation; however, it may be small
 - Thus these molecules will have permanent dipoles
- Polyatomic molecules with more than two atoms, it is required to check the molecular structure to see whether a dipole exists

This results in net charge separation with chlorine obtaining a net negative charge and hydrogen obtaining a net positive charge and this separation of charge leads to permanent dipole moment. Then for HCl, magnitude of dipole moment is nothing but 1.08 D. If you know the bond length or the separation distance between this H⁺ and Cl⁻, then you multiply by e, so then you will get 1.08 Debye, okay? So, diatomic molecules with electronegative like fluorine, chlorine, etc or electropositive such as you know lithium, sodium, etc., atoms how large dipole moments in general.

Diatomic molecules with dissimilar atoms such as HCl, H and Cl are dissimilar to each other, will always exhibit some degree of charge separation, however, it may be small. Thus these molecules will have permanent dipoles and then pictorially if you see for H and Cl⁻, we can see H is smaller and Cl is bigger one and then Cl is more electronegative than the H. So, because of that one, the electric field is developed and then that electric field induce the dipole moment and that dipole moment may be causing some amount of non-linearity or non-ideality in the system.

For the polyatomic molecules with more than 2 atoms, it is required to check the molecular structure to see whether a dipole is existing or not? So, it is difficult to say for polyatomic molecules directly like this. Let us say in HCl only 2 molecules are there, we can see valence electrons, etc., and then we can understand what kind of charge is going to develop or the electric field is going to develop or not. Because of this, is there any dipole moment going to it exist or not that we can understand but if more than 2 molecules are there, it is difficult to say directly and one has to see the molecular structure and then understand.

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- Dipole moments are caused by non-symmetric distributions of electron cloud in the molecule
 - Thus symmetric molecules does not have dipole moment
- Greater the asymmetry, greater the dipole moment
- For example, electron cloud in CH₃Cl is pulled strongly to electronegative Cl and exhibits a dipole of 1.87D
- A few more examples of molecules having dipole moment are:

H₂O (1.85D), HIF (1.91D), IIBr (0.8D), HI (0.42D), H₂S (0.9D),
 CH₃OH (1.7D), NH₃ (1.47D), NO (0.2D), N₂O (0.2D), SO₂ (1.63D),
 CH₃Cl(1.87D), CH₂Cl₂(1.8D), CHCl₃(1.1D), CO (0.12D), C₆H₅Cl (1.69D)
- A few examples of molecules having “zero dipole moment” are:

H₂, He, N₂, O₂, Ne, Cl₂, Ar, Kr, Xe, SF₆, CH₄, CF₄, CO₂, CS₂, C₂H₆, C₂H₄,
 C₂H₂, C₃H₈, C₆H₆

So, dipole moments are caused by non-symmetric distribution of electron cloud in the molecule that is what we understand. So, thus symmetric molecules does not have any dipole moment because whatever the non-equivalent sharing of electron cloud is there, that is because of the non-symmetric distribution, okay? That is non-symmetric molecules because of that one is there. So, obviously, that means symmetric molecules will not have any kind of dipole moment. Greater the asymmetry, greater the dipole moment.

For example, electron cloud in CH_3Cl is pulled strongly to electronegative Cl and it exhibits a dipole of 1.87 Debye, okay? So, a few more examples of molecules having dipole moment along with the magnitude of dipole moment are given here. In the parenthesis, magnitude of dipole moment is given, how much is the dipole moment. A few examples of molecules having 0 dipole moment that is which are not having any dipole moment, they are also given here.

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- Interaction of one dipole with a neighboring dipole is known as a dipole-dipole interaction
- Such interactions also lead to deviation from ideal gas behavior
- Potential energy of two permanent dipoles i and j is obtained by considering coulombic forces between four charges
- Potential energy of such interactions depend on distance between dipole centers and on relative orientations of dipoles
- To relate this type of electrostatic force to macroscopic behavior, one must average over all possible orientations

Now, interaction of one dipole with a neighboring dipole is known as a dipole-dipole interaction. Such interactions also lead to deviation from ideal gas behavior. So, 2 charges, one is positive charge and another one is negative charge, though that is they are balancing each other, there is no net charge, but despite of that one, there is an electric field. So, there is a dipole moment between two charges of opposite sign, okay? So there is a $1/r$ dipole, like that there may be another dipole.

So there may be interaction between 2 different dipoles and then because of that interaction between the dipoles or whatever the intermolecular forces is there that is known as the dipole-dipole interaction and then that also induces some kind of non-ideality in the system or deviation from the ideal gas behavior. Potential energy of 2 permanent dipoles i and j is obtained by considering coulombic forces between 4 charges.

Potential energy of such interactions depend obviously on the distance between dipoles centers and on relative orientations of dipoles exactly similar way like you know electrostatic forces between 2 point charges. Here also, it depends between the relative distance between the center

of 2 dipoles and then relative orientation of dipoles. If I wanted to relate this type of electrostatic force to macroscopic behavior, one must average over all possible orientation, okay?

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• If dipole separation distance r is larger than d_i (separation distance between charges of dipole i) and d_j (separation distance between charges of dipole j) then

$$\Gamma_{ij} = -\frac{\mu_i \mu_j}{4\pi\epsilon_0 r^3} [2\cos\theta_i \cos\theta_j - \sin\theta_i \sin\theta_j \cos(\phi_i - \phi_j)]$$

• If dipoles are in the same straight line and same charges of two dipoles facing each other

- then potential energy is maximum

• If opposite charges of two dipoles facing each other

So, let us say we have one negative charge here, another positive charge is here. So, the balance is 0, there is no net charge, right? They are at separation distance d_i from each other, okay? And there exists to kind of dipole moment let us say μ_i . Similarly, there is a positive charge here and there is a negative charge here, okay? They are a distance d_j apart from each other, okay? Obviously, between these 2 charges, there is a dipole moment μ_j , okay?

These dipoles, let us say either ends of these two charges are there, so they may be orientating different orientation, any different possible orientations are possible, right? Even sometimes distance also may change, but let us take a distance d_j constant. So, these orientations are there. So, these orientations let us say if you take this is the horizontal line. So, one orientation let us say if you take θ_i for first dipole moment μ_i , similarly other dipole μ_j the one orientation angle you take θ_j .

Like that several θ_i and θ_j are possible and then you align them along one straight line like this. So, at this end one dipole moment, at this another dipole moment is there. So, this dipole moment may be rotating here and there and then like this or like this, different orientations are possible. So, there is an angle between this dipole, this horizontal line and then orientation of this particular dipole. Like that other dipole also different orientations are there. So, these angles let us say ϕ_i, ϕ_j how they are rotating along the same horizontal line.

So, like this, few orientations are taken and then you can obtain the dipole-dipole interaction for each orientation and then each rotational angle, etc., and then you can do such kind of calculation for all possible orientations and then you can do a kind of average. So, free rotation of a dipole, let us say if I show the charge it can be like this as well. So, now if dipole separation distance r , so these 2 dipoles whatever the dipole moments μ_i, μ_j are there, so they are separated by distance r and this r is larger than d_i or d_j .

Then the average potential, whatever the potential is there, that for this orientation shown here the intermolecular potential $\Gamma_{ij} = -\frac{\mu_i \mu_j}{4\pi\epsilon_0 r^3} [2\cos\theta_i \cos\theta_j - \sin\theta_i \sin\theta_j \cos(\phi_i - \phi_j)]$. This is what we have, okay? So, these things actually we are not deriving because they are derived and they are of important from a molecular physics course point of view but that is not primary aim of this course, so that we are not deriving all these kind of derivations, we are just adopting them.

If dipoles are in the same straight line and charges of 2 dipoles facing each other let us say here and the different orientations are shown, okay? They are aligned in the same straight line, but different orientations, angles, etc. are shown, but when they are aligned in the same line but there same charges like negative-negative charges, similar charges, here negative here negative, they are facing each other, then the potential whatever is there that is going to be largest one, okay?

But if these charges are opposite charges, they are still in the aligned in the same straight line but the opposite charges, here +, here - or you know facing each other, then whatever this potential is there that is going to be lowest one, that one can get from this expression anyway by appropriately taking what is the θ_i, θ_j .

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- In an assembly of polar molecules, relative orientation of these molecules depend on the interplay of two factors
 - Electric field set up by polar molecules tends to line up the dipoles
 - Kinetic (thermal) energy of molecules tends to toss them about in a random manner
 - Thus as temperature rises
 - Orientations become more random until in the limit of very high temperature the average potential energy due to polarity becomes vanishingly small
 - and it is experimentally proved
 - But at low and moderate temperatures, behavior of polar gases is remarkably different from that of nonpolar gases

So, in an assembly of polar molecules, relative orientation of these molecules depend on the interplay of 2 factors, what are these factors? First one is the electric field set up by polar molecules tends to line up the dipoles, whereas the kinetic or thermal energy of molecules is the other one which tends to toss them about in a random manner. So, that means if you increase the temperature what happens? These orientations become more and more random until in the limit of very high temperature, the average potential energy due to polarity becomes vanishingly small.

So, that is the reason we say that that at high temperature usually we may not have any kind of intermolecular potentials and then system behaves as a kind of ideal gas that is at very, very high temperatures and it is experimentally proved as well. But at low and moderate temperatures, the behavior of polar gases is remarkably different from that of non-polar gases okay and this difference tends to disappear as temperature increases.

So, let us say whatever the dipole moment for the polar molecules that we have seen though the net charge is 0, there is a kind of electric field developed because of the imbalance or unequal sharing of the electrons, right? And then because of that one, there is a dipole moment is existing, and if the dipole moment is existing, then we can say those molecules as a kind of polar molecules. If they are not existing, then we can say non-polar molecules.

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- Average potential energy between two dipoles in vacuum at a fixed separation r can be found by
 - Averaging all orientations with each orientation weighted according to its Boltzmann factor
 - For dipole-dipole interactions, it is given by

$$\bar{V}_{ij} = -\frac{2}{3} \frac{\mu_i^2 \mu_j^2}{(4\pi\epsilon_0)^2 kT r^6} + \dots \text{ (i.e., expanded in power of } kT \text{)}$$
 - According to this eq., for a pure polar substance ($i = j$), potential energy varies as 4th power of dipole moment
 - i.e., a small change in dipole moment can produce a large change in potential energy due to permanent dipole forces *
 - On the other hand, contribution of polar forces to the potential energy is small for molecules having dipole moment of 1D or less
 - This contribution becomes increasingly significant for small molecules having large dipole moments

Average potential energy between 2 dipoles in a vacuum at fixed separation r can be found by averaging all orientation with each orientation weighted according to its Boltzmann factor and let us say for dipole-dipole interaction it is given by $\bar{V}_{ij} = -\frac{2}{3} \frac{\mu_i^2 \mu_j^2}{(4\pi\epsilon_0)^2 kT r^6} + \dots$. This is a series in terms of expanded in power of kT , but we are taking only 1 kT power that is, first term only, okay? So, according to this equation for pure polar substance that is if $i = j$, then potential energy what happens?

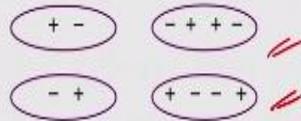
It becomes like μ_i^4 . That is potential energy varies as fourth power of dipole moment if $i = j$. So, it indicates a small change in dipole moment can produce a large change in potential energy due to permanent dipole forces. This indicates how much important to consider this you know permanent dipole moments while calculating intermolecular potentials of a given system, okay? On the other hand, contribution of polar forces to the potential energy is small for molecules having dipole moment of 1 Debye or less.

Otherwise this contribution becomes increasingly significant for small molecules having larger dipole moments. Since, as the way that we have a dipole moment between 2 point charges, though there is a kind of net charges 0, so it is also possible to have a kind of quadrupole moment that is between 4 charges though the net charge is 0.

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Quadrupole moment

- It is possible to have quadrupole moments due to concentration of electric charge at four separate points in the molecule



- For example, CO_2 does not have dipole moment
 - But its quadrupole moment is sufficiently strong to affect its thermodynamic properties that are different from those of other nonpolar molecules of similar size and molecular weight
- For the simplest case of a linear molecule, quadrupole moment Q is defined by sum of second moments of the charges as: $Q = \sum_i e_i d_i^2$
 - where the charge e_i is located at a point a distance d_i away from some arbitrary origin and where all charges are on the same straight line

It is possible to have a quadrupole moment due to concentration of electric charge at 4 separate points in the molecules. Let us say dipole moment + - charges are aligned like this in general, it can be other way also, orientations I am not showing or it can be like this. So, if you turn one of them to 180 degrees, then you will get the other dipole here, okay? The orientation + -, - + it will become other way around, okay? So, likewise if you have a quadrupole like this - +, + - or + - - + like this, you cannot get the other one by whatever the degree you rotate it, okay?

So, when you have such kind of 4 charges at 4 separate points in the molecule, then also it is possible to have a quadrupole moment. For example CO_2 does not have any dipole moment, but its quadrupole moment is sufficiently strong to affect its thermodynamic properties that are different from those of other non-polar molecules of similar size and molecular weight. For the simplest case of linear molecule, quadrupole moment Q is defined by sum of second moments of the charge as $Q = \sum_i e_i d_i^2$, where the charge e_i is located at a point, a distance d_i away from some arbitrary origin where all charges are on the same straight line, okay?

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- Potential energy between a quadrupole and a dipole; or between a quadrupole and another quadrupole is a function of

- separation distance and angles of mutual orientations

- Average potential found by averaging over all orientations; each orientation is weighted according to its Boltzmann factor kT

- For dipole i – quadrupole j: $\bar{\Gamma}_{ij} = -\frac{\mu_i^2 Q_j^2}{(4\pi\epsilon_0)^2 kT r^8} + \dots$

- For quadrupole i – quadrupole j: $\bar{\Gamma}_{ij} = -\frac{7}{40} \frac{Q_i^2 Q_j^2}{(4\pi\epsilon_0)^2 kT r^{10}} + \dots$

So, the potential energy between a quadrupole and a dipole or between quadrupole and another quadrupole is function of obviously separation distance and angles of mutual orientation here also. Average potential found by averaging over all orientations, each orientation is weighted according to Boltzmann factor kT , then for 1 dipole i and then 1 quadrupole j, the average potential energy $\bar{\Gamma}_{ij}$, bar indicates average, is nothing but $-\frac{\mu_i^2 Q_j^2}{(4\pi\epsilon_0)^2 kT r^8}$.

Here we can see it is r power 8, inversely proportional to r power 8. If we have one quadrupole i and another quadrupole j, then average potential energy because of the interaction between these 2 quadrupoles i and j is $\bar{\Gamma}_{ij}$ bar that is $-\frac{7}{40} \frac{Q_i^2 Q_j^2}{(4\pi\epsilon_0)^2 kT r^{10}}$. Here, you can see it is r^{10} , inversely proportional to r^{10} , okay? r is the separation distance.

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- Experimental and theoretical information on dipole moment is extensive
- But very less is known about quadrupole moments and even little work has been done on higher multipoles
- Effect of quadrupole moments on thermodynamic properties is
 - much less than that of dipole moments; and the effect of higher multipoles is usually negligible
- Intermolecular forces due to multipoles are of extremely short range than dipoles

Experimental and theoretical information on dipole moment is very extensive, but very less is known about the quadrupole moments and even little work has been done on higher multipoles. Effect of quadrupole moments on thermodynamic properties is much less than that of dipole moments and the effect of higher multipoles is usually negligible. Intermolecular forces due to multipoles are of extremely short range than dipoles that means whatever the intermolecular forces are there because of the quadrupole or higher multipoles you know what happens?

They exist only for small distance. If the molecules go slightly away from each other, they become very small that they can be negligible, they can be neglected without any difficulty. So, in the subsequent lecture, what we will be discussing, we will be discussing other types of attractive forces such as induction forces and then dispersion forces.

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The references for this lecture are given here. Engineering and Chemical Thermodynamics by Koretsky. Molecular Thermodynamics of Fluid Phase Equilibrium by Prausnitz et al. Chemical Biochemical and Engineering Thermodynamics by Sandler. Introduction to Chemical Engineering Thermodynamics by Smith et al. So, but most of the details presented in this lecture are taken from these 2 books that is Prausnitz et al and Koretsky.

Thank you.