

# **Fundamentals of Statistical Thermodynamics**

**Prof. Nand Kishore**

**Department of Chemistry**

**Indian Institute of Technology, Bombay**

**Lecture – 58**

## **Radial Distribution Function**

Welcome back to the next lecture on Statistical Thermodynamics. So far we have restricted our discussion mostly to gaseous molecules and we have derived several equations. We have also discussed several applications of the those derived equations and also solved several numerical problems. Understanding the arguments to liquids and solids requires further discussion. We will not be able to go too much deep into the extension of whatever we have discussion to liquids and solid systems, but at least some background should be made. So, when we say gas liquid solid at that point we should consider the structure the arrangement of molecules in gas in liquid and in solid. The various distribution functions that we have discussed so far Maxwell Boltzmann distribution or Bose Einstein or Fermi-Dirac distribution functions we mostly restricted to the gases. Now when we talk about the solids and liquids how do we go about that? What is a solid first of all? And in solids if we further restrict to perfect crystals that means perfect crystal have well ordered structures well ordered structures. Some example is for like you know HCl molecule at absolute 0 you have HCl HCl HCl HCl kind of arrangements that is a well ordered structure and that can be called as a perfect crystal and we say that the entropy of perfectly crystalline substance is equal to 0. Next comes gases, gases mean molecules are chaotic the entropy is high.

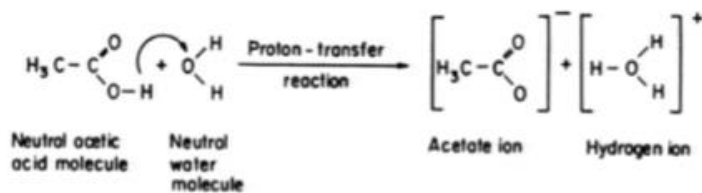
See Slide Time: 3:16

The image is a screenshot of a video player. The main content is a slide with a blue border containing three bullet points. Below the slide is a video player control bar with a progress bar, play/pause button, volume icon, and time display (3:16 / 24:12). The video player interface includes standard icons for play, volume, and settings.

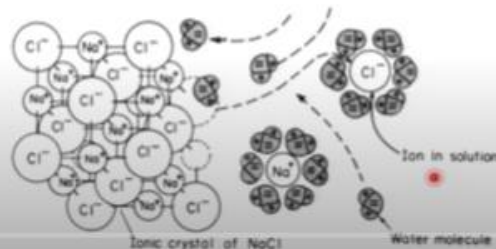
- **In solids, perfect crystals have well ordered structures**
- **Gases have totally chaotic distribution of molecules**
- **Liquids lie in-between two extremes: some short range order but little long-range order**

So, gases have totally chaotic distribution of molecules. The molecules are free to occupy any volume which is available which is true for liquids also, but for solids there is a well ordered structure. Galaxies have total chaotic distribution of molecules, but what about liquids? Liquids lie in between two extremes in between the structure that a solid crystal possesses and a structure that gas possesses. That is why this comment is made over here liquids lie in between two extremes some short range order, but little long range order. Specifically if we talk about liquids gases we have derived so many equations and most of the time when we are dealing with the systems of biological interest or non biological interest there is solvent and sometimes the solvent specifically when we talk about biological systems the solvent is water. So, therefore, understanding the structure of liquid becomes very very important. As I just mentioned this liquid structure can be in between solid and that of the gas and then there can be additives. For example, consider this dissolution of an ionic crystal by action of solvent.

See Slide Time: 3:38

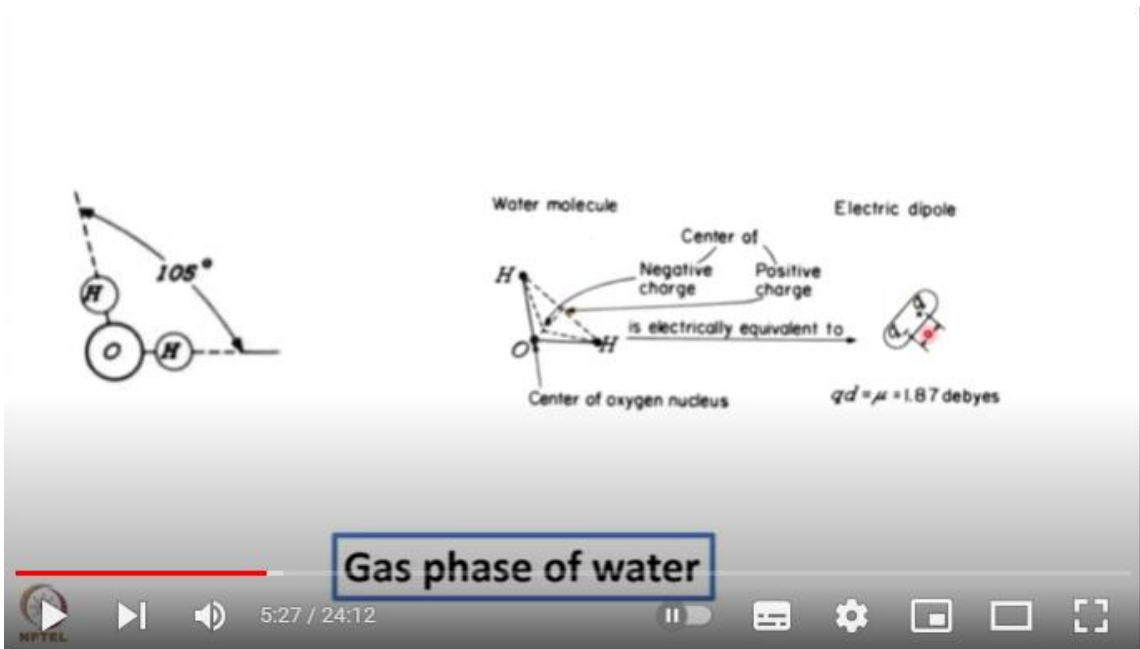


### Chemical method of producing ionic solutions



When this crystal this is what I was telling you that in the crystal there is an order well defined order and when it is dissolved in water molecules which are represented as quarter pole over here you can treat water molecules as dipole also and then we see that the solvent molecule is surrounding ions ions there is a dissolution here we are dealing with the liquids. First consider the gas phase of water I will explain one by one the structural differences which come when you move from gas to liquid to solid. This is the structure of gaseous water HOH with about 105 degree angle. Then if you look at this structure HOH there is a center of negative charge there is a center of positive charge so this is equivalent to a dipole. So therefore, what is the structure of a gaseous water or gas phase of water this is just individual H<sub>2</sub>O molecules. When you talk about this solid state of water ice for example, the arrangement of water molecules in ice is like puckered hexagonal ring and a section for example, this section if you zoom as that shown on the right hand side you see that each oxygen is surrounded by four other oxygen there is a tetrahedral arrangement and in between two oxygen there is a hydrogen this can be hydrogen bonded or this can be a covalent bond. Now you see the structural difference between gaseous water molecule and ice this is gaseous is gas phase ice is solid phase huge structural difference.

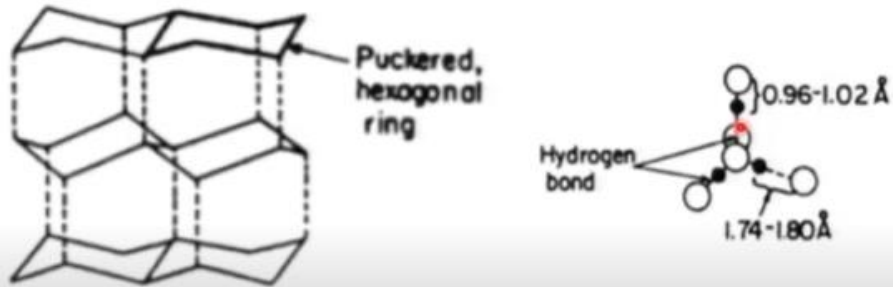
See Slide Time: 5:27



There is let us see there is a well arranged order of the molecules you can assign coordinates also for example, you can choose one of the corner and assign coordinates whereas, in the gas phase these are mobile very mobile you cannot assign coordinates because they are moving.

See Slide Time: 6:05

## ICE



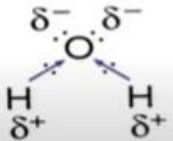
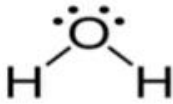
The oxygen atoms in ice which are located at the intersections of the lines in the figure lie in a network of open puckered hexagonal rings

Now let us look at the structure of liquid water compare these three gaseous water molecule ice and liquid.

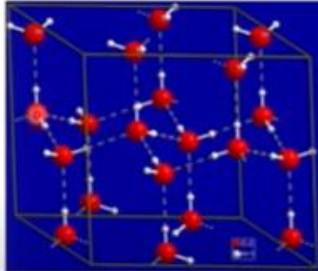
Liquid what happens is if you look at the structure which is in between and consider this red circle red sphere as an oxygen molecule each oxygen is surrounded by four other oxygens and with this arrangement there are voids in between. In liquid water what happens some of the water molecules which are hydrogen bonded in this network structure occupy the interstitial spaces and then there is an equilibrium fast equilibrium between this monomeric water molecules and the tetrahedral associated network this is the structure of liquid water. So gas individual water molecules ice regular tetrahedral network liquid water which is and in between structure.

See Slide Time: 7:21

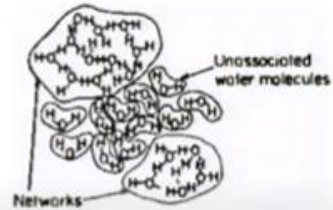
## Structure of water



Gaseous water



Ice



Liquid water

The statistical thermodynamics which largely we discussed earlier was for the gaseous system. Can we apply statistical thermodynamics to the condensed systems? Condensed system means either we talk about liquid or further condensed or compact system which is solid. With this difference in the structure between the gas and ice and liquid water let us see what kind of further treatment can be done. Now any alteration in the structure of water will be reflected in the form of volume changes this is one important contribution. The mean oxygen oxygen distance in ice is 276 pico meter and in liquid water is 292 pico meter that means the molecules are in water are more mobile than in ice. Number of nearest neighbors in ice it is 4 and in liquid water it is 4.4 to 4.6 and this additional number to 4 for example, initially it is 4 now 4.4 or 4.6 that is because the some of the water molecules which are occupying the lattice points have entered into interstitial spaces.

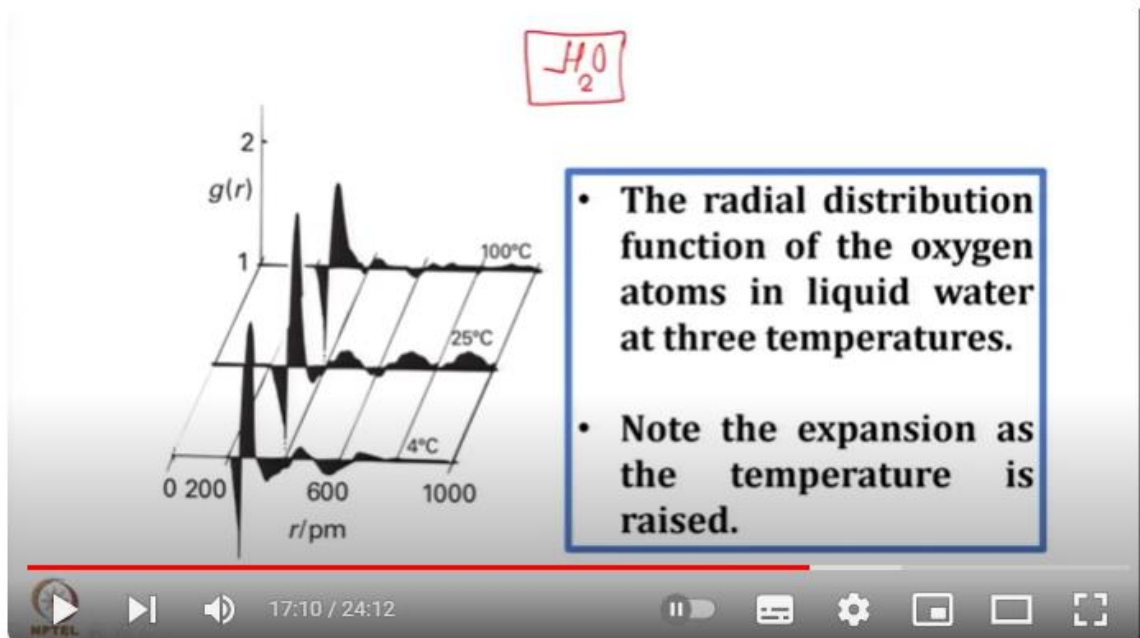
See Slide Time: 9:20

**The Structure of Ice and Liquid Water**

	Ice	Liquid Water
Mean O–O distance	276 pm	292 pm
Number of oxygen nearest neighbors	4	4.4–4.6

The structure of water around any additive can alter a solute can be a structure maker and a solute can be a structure breaker. Around hydrophobic groups water is strengthened because hydrophobic groups they do not like water. If they do not like water then the hydrophobic groups will like to come close form clusters and they want to avoid water that means the more hydrogen bonding will be introduced in the surrounding water molecules. Structure strengthening also means increase in heat capacity very obvious. Now to deal with the condensed phases to deal with the liquids how it is done is to introduce the radial distribution function.

See Slide Time: 17:10



As I just said that we will not go too much deep into this subject, but we will introduce what radial distribution function is what does it give. Since we are talking about liquid the particles of a liquid are held together by intermolecular forces. Obviously when you have gas these gas molecules have to come close to each other and when they form this intermolecular interactions the condensed phase appears one of that condensed phase is liquid state. So in the liquid state the kinetic energies are comparable to their potential energies you have water molecules. If you just talk about let us say if the solvent is water there is an equilibrium between the monomer and tetrahedral network. So therefore, the kinetic energies are comparable to their potential energy in the liquid state. So as a result the whole structure is very mobile. As a backup example you can again consider ice versus liquid water versus gas. How to deal with it? The mathematical description of the average locations of the particles is expressed in terms of radial distribution function and we will call that radial distribution function as  $G$ . It's a mathematical description of the average locations of particles. So you have to define the function in such a way that you can talk about the probability of finding the molecule. So this radial distribution function is defined in such a way that this  $G R^2 dR$  this is the probability that a molecule will be found in the range  $dR$  at a distance  $R$  from the other one. So now we have started talking about the probability of finding the molecule in a small range at a distance  $R$  from the other particle. So once again we can start with the crystal. In a perfect crystal this  $G$  this is a periodic array or sharp spikes. Why sharp spikes? Because their coordinates are fixed and there is a certainty they represent certainty that means if there is no defect there is no thermal motion then you can have certainty. As a result the  $G$  radial distribution function can show sharp spikes. Once again the reason is because as the particles lie at specific locations to help you understand



this I go back to the structure of ice here you look at this is solid form. These locations in 3D structure are fixed whereas when you talk about the gaseous state they are not fixed they are mobile very mobile. In liquid state also there is a fast exchange between monomeric and tetrahedral structure of water.

So such kind of regularity continues out to the edges of the crystal thus the crystals have long range order. In the crystal when we just talk about we talk about unit cell then those unit cell are repeated and then forms the whole solid structure. So such regularity continues out to the edges of the crystal thus the crystals have long range order. If you take sodium chloride and you keep on raising the temperature eventually sodium chloride will melt. You talk about conductivity of solid sodium chloride crystal and you talk about conductivity of molten sodium chloride obviously molten sodium chloride will have more conductivity compared to the perfect or pure crystal of sodium chloride because there the molecules are not mobile.

So that means when the crystal melts this long range order is lost. Once the long range order is lost there will be an equal probability of finding a second particle from a given particle. When you talk about the solid the coordinates are fixed. When you talk about liquid the molecule other molecules can be mobile. So that means then there will be an equal probability of finding a second particle from a given particle.

So thus close to the first particle it is possible to detect a sphere of nearest neighbors at a distance  $r_1$  and perhaps beyond them is sphere of nearest neighbors  $r_2$ . Now moving over from solid to liquid means now we are acknowledging the existence of short range order. This existence of short range order means that the radial distribution function can be expected to oscillate at short distances and there will be peaks one peak at  $r_1$  and then there can be another smaller peak at  $r_2$  and perhaps there can be more structures beyond that. So depending upon the structure. So the question is how to determine the shape of radial distribution function.

Once again we cannot go into that much details over here, but just to understand the shape of radial distribution function can be determined by axial deflection. Before that let us take the example of water. So the shelves of local structure of water we will consider for further elaboration. What do we have in water? We have water may we have  $H_2O$  and since we are talking about water in the liquid state here that means we are talking about the fast equilibrium between monomer and tetrahedral network and in between structure between that of the gaseous water molecule and the solid water molecules. So since liquid water has this equilibrium between monomer and tetrahedral network of structure it should be temperature dependent that means if you keep on increasing the temperature in that case this hydrogen bonding must be affected. In this figure what you see is the radial distribution function of oxygen atoms in liquid water at 4 degree centigrade, 25 degree centigrade and 100 degree centigrade. Note that

the expansion here as the temperature increases. You can also notice the peaks here at certain values of  $R$ . Next is a closer analysis of water molecule the radial distribution function of water molecule. A closer analysis shows that any given water molecule is surrounded by other molecules at the corners of a tetrahedron similar to the arrangement in ice.

But as I said that in liquid state there is a fast exchange any water molecule which is a monomer at a given instant next instant it will be a part of the regular tetrahedral network structure. And obviously when you increase the temperature this is also going to change because even the hydrogen bonding is dependent upon temperature if you keep on increasing the temperature this hydrogen bonding is also weakened. So the form of radial distribution function at 100 degree Celsius shows that the intermolecular forces are strong enough to affect the local structure right up to the boiling point. This is based upon the comparison at three different temperatures. Here I have talked about a very complicated situation.

This complicated situation means we are talking about water molecule. There are variety of solvent molecules. Water becomes peculiar here in the sense that liquid water presents anomalous properties whereas if you take solvents like DMSO carbon tetrachloride etcetera etcetera there this issue of hydrogen bonding does not arise to that much. Even when you compare the physicochemical properties of the liquids for example, the density of ice versus density of liquid water. Density of ice is lower than density of liquid water. The reason is in ice there is extensive hydrogen bonding and as a result of extensive hydrogen bonding the distance between one oxygen and the other oxygen increases and that is the reason because of the low density ice floats in water. Therefore the liquids in which the extent of association is large will offer different physicochemical properties than the liquids in which the intermolecular interactions or association is not that large. Therefore radial distribution functions become very important parameter or properties specifically when you talk about systems in the condensed phase. You will see in literature so many publications on the radial distribution functions focused on biologically important system. Whether you talk about the interaction of one molecule with another or you talk about the conformational changes in the biological macromolecules or similar other issues radial distribution function its variation gives very very important information.

In this lecture we have sort of addressed how to deal with the liquid systems. We have not done elaborate treatment because elaborate treatment is not in the purview of this course, but at least we should know what a radial distribution function is. I would like to reiterate repeat over there that most of the treatment that we have done while addressing various concepts of statistical thermodynamics pertain to gaseous systems.

You need to include other parameters other discussion when you extend it to liquid system because liquid systems because of the short-range disorder you need to involve all those

points into the discussion. Similarly long range order which is present in the solids will also require similar treatment.

So I hope that the radial distribution function what it is what it can do is important and you also understand that the variation in radial distribution function can also or also tells us about the structure of the solvent close to a given molecule or away from the given molecule. This area is very very important therefore, I recommend that with this little background if you are interested you should read more and more about it. Thank you very much. Thank you.