CHAPTER ONE

INTRODUCTION
CHAPTER - 1

INTRODUCTION

I.A LIGHT SCATTERING

The study of electromagnetic wave scattering from condensed matter is a topic of long standing and used by different groups from different disciplines. In different discipline, workers used different electromagnetic waves (of different wavelength) to study different phenomena. But the same basic scattering principles govern all the different phenomena, as long as the wavelength of the electromagnetic radiation is comparable to the dimension of the scatterers.

The first observation of the light scattering phenomena was reported by J.B. Richter way back in 1802. But probably the first scientific work of light scattering was done by Tydall in 1869 [Chu, B., 1974 ; Crosignani, B., et.al., 1975]. Couple of years after that, in 1871, Lord Rayleigh, explained the theoretical principle of light scattering for the first time. Originally, Rayleigh thought light as mechanical vibrations and based his theory on elastic theory of light. But later on he deduced the same results [Rayleigh, J.W.S., 1881 ; 1889] from Maxwell's electromagnetic wave theory for noninteracting, nonabsorbing and optically isotropic particles having sizes very small compared to the incident radiation. His result shows, scattered intensity is inversely proportional to the 4th power of wavelength of incident light. This result exactly explained why the color of the sky and sea is blue, but not red, green or yellow. Since then Rayleigh's approach has been modified a great deal to accommodate absorbing, anisotropic particles having dimension comparable to that of wavelength of incident light. In the early work one was modeling the scattering theory from noninteracting molecules (from a gas), which were incoherent and randomly located. In order to find the total scattered intensity at a point, one has to simply add up all the intensities scattered from different molecules [Bendek, G.B., 1968 ; Pike, E.R., 1976]. But in the case of a condensed media like liquids and solids, the molecules are no more noninteracting. So solids and liquids should require different
concepts. In an ideal crystalline solid (perfectly ordered solid) there should be no scattering because of the completely destructive interference. And liquids should be intermediate between solids and gases. But in reality both solids and liquids do show significant scattering. The explanation to this was given by Smoluchowski [1908] and Einstein [1910]. Smoluchowski argued that under normal condition, all the thermodynamic state variables of the system will show some fluctuation due to the finite heat content of the system. And these fluctuations in thermodynamic state variables are responsible for giving a nonzero scattered intensity. Einstein [1910] was able to by pass the difficulties inherent in Rayleigh's analysis as applied to a collection of interacting particles. He assumed that the local density fluctuations in neighboring volume elements could be independent of one another and carried out a quantitative calculation of the mean square amplitude of density fluctuations from a statistical mechanics approach. Although Einstein's theory was good enough to explain the scattering from pure liquids and do predict the enormous increase in scattering as the liquid-gas critical point was approached (critical-opalescence), it failed to account for the angular dissymmetry of the scattered intensity in critical apalescent systems. But, his theory remains valid for \( \frac{\Delta q}{q} = 0 \) (\( \Delta q = k_i - k_s = (4\pi n/\lambda)\sin(\theta/2) \)) even in critical region. Ornstein and Zernike [1914; 1915; 1916; 1926] tried to account for the scattering behavior at \( \frac{\Delta q}{q} = 0 \) by stressing the effects of correlation between fluctuations of neighboring volume elements.

In quasi-elastic laser light scattering, one generally studies the changes in number (density) and direction (momentum) of each type of photon in the incident and scattered light beams [Porto, S.P.S., 1969; Chu, B., 1968]. Whereas the angular dissymmetry and the polarization of the scattered intensity can give information about static properties like: isothermal compressibility of liquid and shapes and sizes of macromolecules in solution. These changes in number and momentum are contained in the central Rayleigh broadened spectrum of the scattered light.

The fluctuations in the thermodynamic variables of the system have a finite life time and relax back by diffusive processes with a simple time dependence given as, \( e^{-\Gamma t} \). In order to study the time-dependent behavior of these fluctuations, one has to measure the Rayleigh broadening quite accurately. But the thermal fluctuations of dielectric constant of fluid produce spectrum having width as narrow as 100 Hz
[Porto, S.P.S., 1969 ; Chu, B., 1968]. So to study this, one has to have instruments having resolution as high as $10^{12}$ or $10^{13}$. But the conventional dispersive spectrometers can have maximum resolution limit of $10^7$. Even the best of Fabry-Perot can not provide the sufficient resolution to measure the narrow central component in critically opalescent systems. In addition to this one faces the problem of incident light used in the scattering experiments having substantially big natural linewidth whereas it should be as small as possible. So with the invention of lasers, both the quality and quantity of the experiments undergo a sea change. With laser, high resolution spectroscopic methods started appearing and optical mixing spectrometers took the lead [Javan, A., et.al., 1967 ; Arecchi, F.T., et.al., 1967 ; Lastovka, J.B., 1967]. And during the past couple of decades several types of laser related spectroscopic devices, with very high resolution have been developed.

The next most universally accepted technique used to analyze the signal at optical frequency is the digital-photon correlation technique. The first digital intensity correlation (photon correlation) was observed by Hanbury Brown and Twiss in 1954, at radio frequencies [1954]. The same workers Brown and Twiss [1956] in 1956 observed the intensity correlation at optical frequencies. Since then it has been modified a lot. In a photon correlation experiment one is interested in finding the evaluation of the conditional probability of detecting at least a single photon at a particular instant of time provided it has been already detected at an earlier time. This can be written as [Mandel, L., 1963],

$$P(t, \tau/t) = \frac{\langle I(t)I(t+\tau) \rangle}{\langle I \rangle^2}$$  \hspace{1cm} (I.1)

But generally it is written as

$$P(t, \tau) = \frac{\langle I(t)I(t+\tau) \rangle}{\langle I \rangle^2}$$ \hspace{1cm} (I.1-a)

where $I(t)$ is the intensity at a particular instant of time $t$ and $I(t+\tau)$ is the intensity at a later time $(t+\tau)$. The angular bracket represents the ensemble average.

If one is interested in counting the number of photons, $n(t)$ instead of the intensity $I(t)$, then the above Eq.(I.1-a) can be written as,
\[ P(t,\tau) = \frac{\langle n(t)n(t+\tau) \rangle}{\langle n \rangle^2} \] (1.2)

where \( \langle I(t)I(t+\tau) \rangle \) and \( \langle n(t)n(t+\tau) \rangle \) are commonly known as intensity correlation function and photon correlation function respectively. This term contains the dynamic information like: diffusion coefficient, hydrodynamic radius, etc., of the system.

In contrast the angular distribution of scattered light intensity is analyzed through Zimm plots to deduce molecular weight, radius of gyration, interaction parameters, etc., of the diffusing particles dissolved in a solvent.

Both chemists and physicists use the light scattering techniques extensively to study polymers and macromolecules in solution. Chemists use it to study sizes, shapes of the polymers where as physicists use it to study scaling concepts, phase transformation, etc. In this thesis we are using this to study scaling concepts, phase and conformational transitions in a polymer system.

I.B. POLYMER

Polymer has always been considered a strong hold of chemists, particularly of organic chemists. But recently (last couple of decades), it has developed into more of an interdisciplinary area rather than strong hold area of any particular discipline. Both, chemists, physicists, biologists, etc., are actively involved in this area of research. Researchers are involved in both experimental and theoretical studies. Apart from doing research in their respective fields, they have also engaged themselves in cross-disciplinary area. This is an area which brought together scientists from different discipline to study this vastly rich area of science. Some of the reasons, why it is so popular among the scientists and researchers are its wide application in industry, its uses in day-to-day life and of course the most important one being it holds the key to the life. All the living beings are build up of proteins which are biopolymers. This protein, gets synthesized in nature from simple chemical compounds like: methane, ammonia and carbon-dioxide. Polymers are so widely used that, it is difficult to name a branch of industry and transport, culture and consumer’s goods production, agriculture and medicine, the defense industry and astronautics where it would be possible to do without polymers. It appears for a moment that it has no drawbacks at all, only
advantages. But one of the biggest problem of this polymer industry is its rational utilization and the disposal of obsolete polymeric materials. Polymers are generally non degradable materials. So one should start thinking immediately in the line of reutilization of the rejected polymers and rational utilization of them. Otherwise it will be very soon be a threat to environment pollution. So the specialists in the field of physics, chemistry and technology of polymers and materials should join together to solve this problem as soon as possible.

I.B.1 Definition of Polymer

Polymer is a Greek word meaning many (poly) parts (mer). They are basically large molecules composed of many small molecules (building units called monomers). Due to their largeness in size, they are sometimes called as macromolecules. Now the question arises how big is big? The molecular weight of an ordinary polymer is 5 to 10 thousand and they can be as high as several millions. In comparison to this the molecular weight of a low molecular weight compound will not more then few hundred Daltons. For example the molecular weight of NaCl is 58.5 and that of CH₄ is 16. As described above a polymer is basically composed of many small molecules. Each small molecule in the polymer is called as a monomer (meaning, single part). If 5 to 10 monomers combine together to form a bigger molecule (but not big enough to be called as polymer), the resultant molecule is called as an oligomer. The number of monomers present in the polymer is called as the degree of polymerization (D.P.). So the molecular weight of the polymer is roughly the molecular weight of the single monomer times the degree of polymerization. A polymer can have one, two and sometimes three or more types of monomers.

I.B.2 Structure and Classification of Polymers

Depending on whether a polymer already exists in nature or is synthesized in a laboratory, it is either called as a natural or a synthetic polymer. If the backbone of the polymer is made up of carbon atoms, then the polymer is called as an organic polymer otherwise it is called an inorganic polymer. Some of the natural organic polymers exhibit some biological activity and they are called as biopolymer.

If the backbone of a polymer contains a single type of monomer, then it is called as a homopolymer. On the other hand if it contains more than one type of monomers,
then it is called a copolymer. If two type of monomers combine randomly in a polymer it is called a random copolymer. When they occur alternatively, then are called alternating polymer. If in a copolymer a group of monomers of one type clubbed together and joined with another group of monomers of another type then polymer is called as a block copolymer. Whereas if the blocks of one of the monomers are joined to the backbone of a polymer consisting of different type of monomers, the polymer is called as a grafted copolymer. The structure of all these polymers are shown in the Fig.(1.1).

![Fig.1.1 Schematic representation of structure of polymers: (a) homopolymer; (b) random polymer; (c) alternating copolymer; (d) block polymer; (e) grafted polymer.](image)

I.B.3 How are Polymers made?

One of the the basic requirement for a polymer to be formed is that the monomers should be at least bi-functional (i.e., they should have at least two reactive sides). If the monomers of a polymer is bi-functional, then the polymer resulting out of it will be a linear polymer. On the other hand if some of the monomers will have functionality more than two, the polymer formed will be a branched polymer. Under certain special conditions a branched polymer can form a cross-linked or network polymer. All these different type of polymer are sketched in the Fig.(1.2).

![Fig.1.2 Schematic representation of different types of macromolecules: (a) linear polymer; (b) branched polymer; (c) cross-linked or network polymer.](image)
A synthetic polymer can be made in the laboratory from monomers by one of the two methods called *polycondensation* and *polyaddition*. In the case of *polycondensation* in each step of polymerization a low molecular weight substance will be liberated. So in this case the molecular weight of the polymer is exactly not equal to the molecular weight of the monomer times the degree of polymerization, whereas in the case of *polyaddition* no such low molecular weight substances are liberated. In the polymerization process the degree of polymerization of the polymers may vary. This will result in polymers of different molecular weights.

**1.B.4 Molecular Weight of Polymer and its Distribution**

If some one asks a question what is the molecular weight of a low molecular weight substance like NaCl or CH₄, one with a little bit of knowledge of chemistry will come up with a definite answer each time (58.5 and 16 respectively). But if one asks the same question about a polymer, one might come up with different answers each time and each time he may be right. How is this possible? Actually a polymer with 500 degree of polymerization will have the same name as a polymer consisting of same monomers with 1000 degree of polymerization. But definitely they will have different molecular weights, i.e.,

\[
R-\left[\begin{array}{c} 
\text{CH}_2 \\
\text{CH}_2 \\
\end{array}\right]-R_{500} : \text{Polyethylene} \quad \text{molecular weight} = 14,000
\]

\[
R-\left[\begin{array}{c} 
\text{CH}_2 \\
\text{CH}_2 \\
\end{array}\right]-R_{1000} : \text{Polyethylene} \quad \text{molecular weight} = 28,000
\]

so to describe a polymer, it is absolutely necessary to mention the molecular weight of it along with its name.

The molecular weight of a polymer is not a definite quantity but an average statistical quantity. There are several different averages of molecular weight which are important in their respective way. Out of which the two most common and experimentally verifiable methods of averaging are called *number average molecular weight* and *weight average molecular weight*. 

1.0.5 Number Average Molecular Weight

The number average molecular weight \( \bar{M}_n \) is the total weight of all the molecules in a polymer specimen related to one mean statistical molecule. Mathematically it is given as,

\[
\bar{M}_n = \frac{\sum N_i M_i}{\sum N_i}
\]  

(I.3)

where \( N_i \) is the number of molecules with molecular weight \( M_i \).

1.0.6 Weight Average Molecular Weight

The weight average molecular weight is the sum of the products of the mass of each polymer fraction and its molecular weight related to total mass of the polymer sample. Mathematically this is given as

\[
\bar{M}_w = \frac{\sum W_i M_i}{\sum W_i} = \frac{\sum N_i M_i^2}{\sum N_i M_i}
\]  

(I.4)

where \( W_i \) is the mass of a fraction with molecular weight \( M_i \), i.e., \( W_i = N_i M_i \).

In general a polymer solution consists of same type of polymer with different molecular weights. So they give rise to a molecular weight distribution of a polymer solution. This molecular weight distribution of a polymer substantially affects the mechanical and physical properties of the polymer. A typical sketch of a molecular weight distribution of a polymer is given in Fig.(I.3). The number average molecular weight is generally situated at the peak of the distribution, whereas the weight average molecular weight is shifted to the right along the axis of abscissa (Fig.I.3). If a solution contains polymers having single molecular weight value, the solution is called a monodisperse solution. In this case the molecular weight distribution is like a delta function and the number average molecular weight coincides with the weight average molecular weight. But if
it contains polymer with different molecular weight the solution is called a polydisperse solution. More the solution is polydisperse more will be separation between $\bar{M}_n$ and $\bar{M}_w$. The ratio of $\bar{M}_w/\bar{M}_n$ measures the polydispersity of the solution.

Many polymers exhibit a phenomena called sol-gel transition in solution with the variation of temperature, concentration and many other thermodynamic parameters affecting the environment. In the gel state the individual chains get entangled through the formation of primary covalent bonds, through the secondary forces like hydrogen bonding. Physical entanglement can also contribute to gelation dynamics alike it happen in a variety of biopolymers. If a sol is cooled very rapidly to avoid the crystallization zone, it can form an amorphous glass trapped in a metastable state. For any desired application and use of polymers one needs to ascertain the phase diagram of the system apriori.

I.C. GEL

Like polymer science was not a subject of physicists, the study of gels was also not traditionally a subject for physicists either. This subject was more familiar to chemists or physical chemists. Physicists got interested in this area of research to mainly study the phase transition in polymers and to know the dynamics of phase transition (1st or 2nd order) it belongs to. In this process they have learned much about the great richness of this field. Now-a-days scientists with different backgrounds, i.e., physicists, chemists, chemical engineers, biologists, medical researchers are studying different types of gels having widely different structure. So it is not quite surprising for not reaching at a consensus decision as to what constitutes a gel and how to define a gel? This makes the communication between the researchers in different field much more difficult and frustrates the newcomers to this field who want to know the exact meaning of a gel.

There are many natural and artificial gels. A most common and familiar gel is the dessert jello, where in the network (see definition of a gel) is comprised of polymers derived from animal protein gelatin and the solvent whose volume constitutes ~ 90 to 98% of the total volume, is colored, flavored and sweetened water. The vitreous humor that fills interior of the eye is a gel, as is the material of the cornea. Blood vessel walls, connective tissues and the synovial fluid lubricating skeleton joints contain gel. In such biological gels, the liquid
component allows the free diffusion of oxygen, nutrients and other molecules, whereas the polymer network provides a structural network to hold the liquid in space. The surface of internal tracts such as the stomach and intestine is covered by mucopolysaccharide gels. The epithelial cells in the stomach are protected from externally acidic gastric juice by a gel. The lung surface is also covered by a similar gel. Some plants roots are covered by gels produced by bacteria, which affect the plant metabolic functions. All these are natural gels. There are also many artificially made gels which are equally important. To name few, gels are important intermediates in manufacture of polymers such as rubber, plastics, glues, films and membranes. They are used as absorbent in disposable diapers, for water purification, in chromatography and electrophoresis, where molecules are separated according to the speed with which they pass through or are expelled by the pores. Gels are also used as implants in plastic surgery and for artificial and soft contact lenses. The gel consistency is also appreciated in food technology where a particular texture or structure is required by the consumer and related to the test of the product. Clear and soft gels are appreciated for cosmetic and pharmaceutical purposes. They are used in paints and pastes where they are spreadable gels. They are also used as glues also in photography and many other things. After saying so much about different types of gels (both natural and artificial) and its application, now the question arise what exactly a gel is? Which materials should be considered as gels and which should not be? What it is consists of? and so on.

I.C.1 What is a Gel?

This is a question asked a long ago and different people kept on defining and redefining this term again and again at different time. There are many good review articles on this topic 'gel' [Hermans, P.H., 1949; Djabouroff, M., 1988; 1991; Ross-Murphy, S.B., 1991; Almdal, K., et.al., 1993] and all of them tried to answer the same century old question "What is a gel?" and "What it constitutes of?".... Despite this, scientist are yet to find a common answer to this. The reason for this being scientist and researchers working in different discipline try to bring in more and more materials into this according to their own convenience and define it accordingly. In the process they introduced a number of related terms, i.e., ‘weak gel’, quasi-gel, ‘temporary-gel’, pseudo-gel’, hetero-gel, iso-gel, micro-gel, nano-gel, xero-gel, etc. In a simplest way a gel is defined as a cross-linked polymer network swollen in a liquid medium. The properties depend very strongly on the interaction of two components. In a gel the liquid prevents the polymer network
from collapsing into a compact mass and the network in turn retains the liquid.

Probably the originator of the term gel is Thomas Graham [1861]. He proposed a different class of substances according to their 'diffusive power': the colloidal substances are slowly diffusing substances which are held in solution by "feeble forces". Among colloidal materials, he grouped together hydrated sililic acid, hydrated alumina, starch gelatin, albumen, gum and so on. Following Graham, a rich literature developed in the colloid field. Then this idea about gel arose progressively that a gel is a continuous solid state extending throughout the liquid and forming a frame work for the liquid. But it was not very clear whether the frame work was purely amorphous or purely crystalline. The x-ray diffraction and calorimetric study could not give a clear cut answer to this. D. Jordan Lloyd [1926] started her survey on gels with the famous word: "Gel is one which is easier to recognize than to define". But this recognition of a gel is not free from difficulties. This confused by the facts that limits between gel and sol in one hand and gel and what may termed as curd on other hand, which is not precised but consists of gradual change. This is exactly the reason why some workers considered some substances as gel whereas others not. Only one common rule seems to accepted by everybody is that they must built up from two components, one of which is a liquid and the otherone is a solid under the temperature considered. The solid one often called as a gelator. The gel itself is a solid-like having the mechanical properties of a solid. Later in that paper she wrote that all the gels might have not got the same molecular architecture, but all of them posses a solid-phase. About 20 years after that P.H. Hermans addressed the same question in the chapter entitled "Gels" in the famous book Colloid Science Vol.II [1949]. This chapter is even now-a-days an excellent introduction to this subject. In this chapter he mentioned the gel name should be given to the systems having following features.

a. They should be coherent, two component systems formed by a solid substance finely dispersed or dissolved in a liquid phase.

b. They should exhibit solid-like behavior under the action of mechanical forces.

c. Both the dispersed component and the solvent should extend continuously throughout the whole system, each phase being interconnected.

Both these definitions clearly exclude the one component systems such as fully cross-linked linear polymer. So both these two definitions are not in agreement with the Flory-Stockmayer [Flory, P.J., 1942 ; Stockmayer, W.H., 1944] gelation
theory. However, *Hermans* qualifies his definition by mentioning that all those single component substances which are capable of swelling in the second component are often included in the family of gels (Hermans, P.H., 1949).

Later on *Flory* [1974] proposed a classification of gels on the basis of structural criteria. He divided gels into four groups.

a. **Well ordered-lamellar structure including gel mesophases.**
b. **Covalently polymeric networks; completely disordered.**
c. **Polymer networks formed through physical aggregation; predominantly disordered, but with regions of local order.**
d. **Particulate, disordered structure.**

So unlike *Herman's* definition, *Flory* does not stress on minimum number of components in the system. So the undiluted cross-linked rubber, which is consists of one giant molecule is also considered as a genuine gel. Although *Flory's* structural classification contains no requirement of solid-like behavior, Flory carefully stated in the general section of this paper that the solid-like behavior is an essential characteristic of a gel. *Ferry* [1980] considered gel to be diluted system which exhibits no steady-state flow, i.e., Ferry excludes all the visco-elastic liquids irrespective of the magnitude of the largest relaxation time. But it was felt that this condition of true solid may be too restrictive. *Djabourov* [1991] came up with a proposal of putting a limiting value of storage modulus as a measure of gel rigidity:

\[
E = \lim_{\omega \to 0} G'(\omega)
\]  

where '\(\omega\)' is the angular frequency and 'E' is termed as relaxed shear modulus. But it is well known that \(\omega \to 0\) is an unattainable limit. A transition from plateau region to the liquid state may occur at a frequency lower than an experimental achievable value, i.e., \(10^{-2}\) rad/sec. *Burchard* and *Ross-Murphy* [1990] make a general statement about gel: "that they all possess one common property, i.e., they possess a plateau in the real part of the complex modulus extending over an appreciable window of frequencies", i.e., they can be converted into visco-elastic solid under appropriate condition. There is a recent article by *Almdal*, et.al., [1993] on "Towards a Phenomenological Definition of the term Gel". They suggests a gel should have following properties
a. A gel is a soft solid or solid-like material of two or more components one of which is a liquid, present in substantial quantity.

b. Solid-like gels are characterized by the absence of an equilibrium modulus, by a storage modulus, \( G'(\omega) \) which exhibits a pronounced plateau extending to times at least to the order of seconds and by a loss modulus, \( G''(\omega) \) which is considerably smaller than the storage modulus in the plateau region.

Gel resulting from an outstanding variety of mechanism can be broadly divided into two categories.

1. Chemical gel.
2. Physical gel.

A chemical gel is formed by chemical reactions (like: copolymerization, polycondensation, vulcanization) leading to formation of a branched network (cross-linked network) made up of linear flexible chains attached by covalent bonds and surrounded by large quantity of solvents. These are sometimes called as strong gels. The network can be called the 'fishing net gels'. On the other hand a physical gel can be formed by the formation of weak bonds like hydrogen bonds, Vander Walls forces or hydrophobic and ionic interactions. This is the reason why they are sometimes termed as 'weak gels'. Gelatin gel, Agarose gel, etc., are come under this type of gel. Some structures of gels are schematically drawn in Fig.(1.4).

![Fig.1.4](image-url) Different structures of gels: (a) fishing net type (chemical gels); (b) triple-helices of gelatin gels; (c) egg-box structure of proteins and alginates in presence of calcium ions; (d) bundles of double helices in agarose gels; (e) shish-kabab structure of high molecular weight polyethylene.
1.C.2 Sol-Gel Transition

Gels are characterized by their equilibrium, dynamic and kinetic properties. These properties depend on the gel state represented by osmotic pressure, temperature, solvent composition, the degree of swelling, pH value, ionic strength, etc. A gel can go into a sol phase with slight alternation in above parameters. A sol is distinguished from a gel by its fluidity nature. So a sol is one which changes its shape with the tilt of the container but gel is one which can sustain some mechanical stress (like a solid). All most all the physical gels are thermo-reversible gel. That is, they can go from a gel state to sol state or the vice-versa with the change in temperature. This transition from sol-state to gel state or gel state to sol state is called as sol-gel transition.

There exists several excellent review papers [Clark, A.H. and Ross-Murphy, S.B., 1987; Burchard, W. and Ross-Murphy, S.B., 1988; Russo, P.S., 1987; Chandau, S.J., et.al., 1982] on classification of different types of gels and different mechanism of gelation (sol-gel transition) in particularly for polymeric gels. In spite of this, there still exists a lot of open questions in this field. In the recent past a lot of people started asking the question, are there any common universal laws exist which govern the gelation phenomena, no matter how different the microscopic processes may be? In the last decade or so theoreticians have come up with a very encouraging answer to it. They consider gels as part of the large family of disordered systems. A lot of approaches have been proposed to deal with such systems. In 1976, both P.G. De Gennes [1976] and D. Stauffer [1976] suggested analogy between gelation and percolation. This has been supported by a great number of theoretical and experimental studies, including an overwhelming contribution of computer simulations

1.C.3 The Percolation Model

The percolation model is one of the theoretical techniques which deals with severely disordered systems. This theory was invented by a mathematician J.M. Hammersely in 1957 to describe a statistical geometrical situation which reminds one of the passage of fluid through networks of channels, some of them being blocked. The percolation theory deals with the effects of varying the number of interconnections in a random systems [Stauffer, D., 1985]. A popular image that one can find for this process is the vandalized grid [Zallen, R.S., 1983]. Let us
imagine a 2-d grid made up of a network of resistors forming a regular lattice. Let the network be connected to an external voltage source and to an ammeter measuring the intensity of electrical current (Fig.1.5-a). Imagine a saboteur starts cutting the bonds (resistors) randomly. Then the current will start decreasing and for certain number of uncut bonds below a threshold value $p_c$ ($p < p_c$) the current will stop flowing. That is to say the network loses its long range connectivity (Fig.1.5-b). Apart from transport properties, the mechanical aspects of the grid will also be affected. Cutting the bonds will weaken the grid and below $p_c$ the grid will disintegrate into disconnected pieces. $p_c$ is called as the "percolation threshold". This type of experiment has been repeatedly simulated in computers to get main characteristic parameters of percolation transition.

A bond percolation simulation on square lattice is shown in Fig.1.6: this sketch can be considered similar to sol-gel transition. Let us say all the sites situated at the intersections are occupied by molecules and are capable of forming bonds (chemical and physical) with the nearest neighbor molecules at random. Let $p$ be the

![Image](image_url)
fraction of reacted bonds. When 'p' is small, clusters of different but finite sized will be formed (Fig.1.6-a). With increase in 'p', the clusters size will increase and above certain threshold $p_c$, a "infinite cluster" will form along with some finite clusters. An infinite cluster is one, which extends through the lattice and connects four edges of the lattice (Fig.1.6-b). If 'L' the size of the cluster

![Diagram](image)

**Fig.1.6** A bond percolation simulation: (a) below the percolation threshold, only clusters of finite size are present; (b) above the percolation threshold, an infinite cluster connects the four edges of the lattice.

is very large compared to 'a' the size of a bond, i.e., $L/a \to \infty$ (thermodynamic limit), the threshold $p_c$ is sharply defined and only depends on the geometrical shape of the lattice. For example for bond percolation and square lattice $p_c = 0.5$.

The analogy between a simulated percolation transition and a gelation process can be imagined in the following way: let the macromolecules dissolved in the solution establish increasing number of links in the course of a chemical reaction. Macromolecules are linked within clusters. From the above analysis it appears that at a certain stage of the process a dramatic change to the connectivity will occur, which is called as "percolation threshold" or "gel point". The renomalization group theory [De Gennes, P.G., 1979] suggested the percolation transition is equivalent to a second order phase transition or critical phase transition, where temperature plays the same role as the amount of reacted bonds 'p'. The analogy of percolation theory to sol-gel transition suggests that, sol-gel transition is a 2nd order phase transition. As in a second-order phase transition, one would expect that a certain number of characteristic features must be common to all the percolation or gelation processes.
One of the important parameters is the fraction of reacted bonds which belong to the *infinite cluster* 'P'. This is also called as the "gel fraction" and, it is the *order parameter* of the transition. As expected, this parameter is equal to zero below the *gel point* \((p < p_c)\) and rapidly increases with the number of reacted bonds above \(p_c\). 'P' is a function of \((p - p_c)\). As \((p - p_c) \to 0\), 'P' follows a power law with an exponent 0

\[
P \sim (p - p_c)^\beta; \quad p > p_c
\]

\[
P = 0; \quad p < p_c
\]

(1.6)

Below the gel point, i.e., \(p < p_c\), clusters with finite molecular weight \((\bar{M}_w)\) will be formed and it will start diverging as one approaches \(p_c\). As \((p_c - p) \to 0\), \(\bar{M}_w\) will show a power law with an exponent 0

\[
\bar{M}_w \sim (p_c - p)^\gamma; \quad p < p_c
\]

(1.7)

A similar power law will be seen in the case of average radius of the clusters with an exponent 0,

\[
R_{av} \sim (p_c - p)^\nu; \quad p < p_c
\]

(1.8)

The critical exponents \(\beta\), \(\gamma\) and \(\nu\) are connected to each other. They have non-integer values and they depend on the space dimension of the system.

Measuring of these exponents \(\beta\), \(\gamma\) and \(\nu\) of a *sol-gel transition* would be a direct evidence of the *percolation model*. But these can be done only on limited number of samples.

There are some other important features which characterize the *sol-gel transition* and are common to a large number of gelling systems. These are the mechanical properties of the system. Two parameters of importance are the *Newtonian viscosity* '\(\eta\)' below the gel point \((p < p_c)\) and the *relaxed shear modulus* '\(E\)' above the gel point \((p > p_c)\).

Both the *Newtonian viscosity* '\(\eta\)' and relaxed shear modulus are experimentally measurable quantities. They can be given as,
\[ \eta = \lim_{f \to 0} \frac{G''}{2\pi f} \]  
\[ E = \lim_{f \to 0} \frac{G'}{f} \]

where \( G' \) and \( G'' \) are the shear modulus and loss modulus measured in the dynamical regime.

As expected the Newtonian viscosity will have finite value below the gel point and start diverging as one approaches \( p_c \), i.e., \( (p_c - p) \to 0 \). This obey a power law with an exponent \( k > 0 \)

\[ \eta \sim (p_c - p)^{-k} ; \quad (p < p_c) \]  
\[ \eta \sim (p - p_c)^{-t} ; \quad (p > p_c) \]

As oppose to this the shear modulus 'E' will have value equal to zero below the gel point and starts appearing above the gel point, i.e., \( p > p_c \). This also show a power law with an exponent \( t > 0 \)

All these behavior of various parameters (\( P, M_w, R_{av}, \eta \) and \( E \)) in the vicinity of gel point are shown in Fig.(1.7).

But all these theoretical predications made are for cross-linked gels (chemical gels). Now the question arises are these predictions applicable to physical gels or not? Almost all the physical gels are thermo-reversible gels and they are formed by weak forces like: hydrogen bond, Vander Walls force, ionic interactions, etc. From enthalpy study it is clearly observed that the sol-gel transition in physical gels are like first order like phase transition. All of them show a first-order-like enthalpy change as one goes from sol state to gel state. So this

\[ \text{Fig.1.7 Behaviour of the different parameters } M_w, R_{av}, \eta, P \text{ and } E \text{ in close vicinity of sol-gel transition.} \]
is still an open question, whether the physical gels belongs to some universality class as chemical gels or not?

I.D CONTRIBUTION OF THIS THESIS

In this thesis, we study the conformational path change undertaken by gelatin gel at different thermodynamic environments like: temperature, concentration, etc. We have also tried to answer the question, the type of phase transformation involved in physical gels (our sample system is gelatin gel) and the scaling relations it obeys. We have addressed the question of occurrence of spinodal line in gelatin gel. All these things are studied by different experimental techniques like: Differential Scanning Calorimetry (DSC), Dynamic Light Scattering (DLS), Static Light Scattering (SLS), Dielectric Relaxation Measurements, Optical Rotation Measurements, Viscometry, Desitometry, Refractive Index Measurements and Electrical Conductivity Measurements. We have proposed an alternative theory to cumulant analysis to get parameters like: polydispersity, weight average molecular weight, Mark-Houwink exponent of high molecular weight polymers from DLS data. In this theory the correlation function has been expanded about mean molecular weight as oppose to linewidth as is normally done in cumulant analysis. The chapter wise organization of this thesis is as follows:

Chapter-II describes why gelatin as a biopolymer is important, its utility and applications. It also contains the information about the chemical composition of the collagen which is the parent protein of gelatin and the processes of extraction of gelatin from the parent collagen.

Chapter-III describes the thermodynamics of polymer solutions and theory of polymer gels. In the part thermodynamics of polymer solutions the expression for entropy of mixing for ideal and non-ideal solutions of simple liquids are given. The entropy of mixing according to liquid lattice theory for both simple liquids and polymers are described in detail. Also the heat and free-energy of mixing for polymers are described in great detail. Combining this with partial molar quantities, expression for osmotic pressure has been derived. From this the information like, molecular weight, second virial coefficient can be obtained. It also describes about the type of interaction exists between polymer and solvent, which gives an indication about the quality of the solvent. In the part, theory of polymer gels, the critical condition for the formation of polymer gels have been described in great detail.
The relation between the branching coefficient and the extent of reaction has been derived.

Chapter-IV describes the basic theory of quasi-elastic light scattering (both SLS and DLS). It also contains the proposed alternative theory to the cumulant analysis. In SLS part the basic Rayleigh relation (i.e., the scattered intensity is inversely proportional to the 4th power of wavelength of incident of light) for a dilute gas has been derived extensively from the electromagnetic theory. This has been further extended to absorb the interaction terms to get information like: molecular weight, radius of gyration, second virial coefficients, etc. In DLS part the expression for temporal auto-correlation function has been derived from the fluctuation theory. From this how to get information like: diffusion coefficient, hydrodynamic radius, etc. is described. In the last part the proposed alternative method to cumulant analysis is described. This theory based on the expansion of correlation function around mean molecular weight whereas the same has been done around linewidth in cumulant analysis. This method can give information like: polydispersity parameter, molecular weight, Mark-Houwink exponent. From the knowledge of all these things one can construct the Schulz distribution function. This theory has been tested on some model systems.

Chapter-V describes the theory of dielectric relaxation and optical rotation dispersion. The sample was subjected to these experiments to investigate relaxation properties of the gel network. Quantification of the helix content of the gel at different temperatures in the gelling sol state constituted the second objective of this study.

Chapter-VI is the experimental chapter. It contains all the experimental details (procedure, results and discussions) carried out in this thesis by various experimental techniques to study the sample system gelatin gel. Both the sol-state and gel-state properties of the gelatin gel have been studied quite extensively by different techniques. The phase diagram for this system is also established. The phase transition, the scaling relations it obeys has been described. The observation of spinodal line is mentioned and described.

Finally in chapter-VII the concluding part of this thesis is given. The success and failure of the thesis is talked about and the open questions to be addressed are mentioned.