Light Scattering Studies of Phase Transition in Polymer Gels

By

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Abstract

A protocol of embedding a holographic grating into a hydrophobic N-isopropylacrylamide (NIPA) gel was presented. The holographic grating was incorporated as an interpenetrating polymer network. Discontinuous changes in the grating spacing occurred at two temperatures. Both of the transition temperatures were within 1 °C of the transition temperature of the pure NIPA hydrogel. This holographic grating embedded in a NIPA gel has many prospective applications, including information storage and optical actuator. The colloidal micro-gels with hydrophobic and hydrogen bonding interactions were prepared by emulsion polymerization of NIPA and acrylic acid (AAc) monomers. We observed continuous albeit drastic volume changes of the micro-gels in response to the pH or temperature changes using light scattering technique. In response to pH changes, the degree of swelling was on the order of two thousand times. The existence of glass phase transition of the hydrogen bondable gel made of methacrylic acid (MAAc) and dimethacrylamide (DMAAm) was investigated using dynamic light scattering technique. Below certain temperature, the time correlation function of the scattered light by this heteropolymer gel can be characterized by the stretching exponent $\beta$ of the kohlrausch-Williams-Watts relaxation function. The characteristic delay time of this correlation function increased some three orders of magnitudes as temperature decreases. These observations suggested the existence of the glass phase transition of the heteropolymer gel. In addition, the intensity ratio of the static component to the dynamic component of the scattered light increased drastically as temperature was decreased. This was consistent with the existence of the glass transition.
I WOULD LIKE TO DEDICATE MY THESIS
TO MY PARENTS:

YANG, ZESEN
AND
ZHANG, FENGSHU
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1. Introduction

1.1. Gels

A polymer gel is consisted of a three dimensional polymer network, or cross-linked polymer chains, and the solvent in contact with the network. Because of this unique structure, polymer gels have both liquid-like and solid-like properties [1-8]. The liquid-like properties come from the solvent within the polymer network. For example, a standard (700mM) N-isopropylacrylamide (NIPA) gel contains more than 98.7% of water and less than 1.3% NIPA polymers upon gelation. On the other hand, a polymer gel retains its shape by a shear modulus, which is due to the cross-linking among the polymer chains. The cross-linking can be covalent chemical bonds or physical contacts (such as entanglements, hydrogen bonding). In this thesis, I consider only the chemically cross-linked gels.

A schematic representation of the microscopic structure of a polymer gel is shown in figure 1.1.1
Because of the cross-linking among the polymer chains, a polymer gel can be viewed as a single polymer molecule of macroscopic size [9,10]. To some extent, a polymer gel represents a single polymer behavior on a macroscopic scale. A single polymer chain can undergo phase transition between disordered (coil) and ordered (globule) states[9], given an overall attraction among the composite monomers of a single polymer chain. In the disordered phase, the entropy is maximized by a random walk like behavior of the polymer. Therefore the mean variance of the polymer size scale $R \sim N^{\nu}$, where $N$ is the number of monomers of the polymer. In the ordered phase, the polymer collapses into a completely dense state due to an overall attraction among the monomers. Thus $R \sim N^{\nu_d}$, where $d$ is the dimension of the space. A polymer gel can change its volume drastically -- more than a thousand folds in some cases -- in response to an infinitesimal change of environmental intensive...
variable, such as temperature or pH of the solvent. This volume phase transition of polymer gels is, in a sense, a macroscopic manifestation of a coil-globule transition [9,10] of its composite polymer chains.

Polymers also undergo phase glass transition, which refers to the loss of ergodicity in liquid as temperature decrease [11]. One expects polymer gels undergo glass phase transition as temperature decreases. An important part of this thesis will deal with the studies that explore the existence of glassy transition in gels.

Gels are of importance in both scientific research and technological applications[1-8]. Traditionally, gels are used as molecular sieves for molecular separation, such as gel permeation chromatography and electrophoresis. Recent applications include adding gels in disposable diapers as super-water absorbents. Gels that undergoes volume phase transition triggered by external stimuli, such as temperature, pH, photons, ions, and electric current(field), etc. have potential applications as controlled drug release systems, information storage (holographic memories), actuators, sensors, switching devices, and so on. I will discuss the studies of holographic memories and volume phase transitions of colloidal microgels that can be used in controlled drug delivery.
1.2. **Volume Phase Transitions of Gels**

The volume phase transition of a polymer gel refers to a reversible discontinuous change in the volume of the gel in respond to an infinitesimal change of the environment, such as temperature, ions, pH, solvent composition, etc. Figure 1.2.1 illustrates such a reversible transition between the swollen and collapse states of a gel. Solvent is pulled into or expelled from the polymer networks in the process of a volume phase transition. Therefore the confirmation and density of the polymer chains (the ratio of polymers to the solvent within the network) changes, but the topology of the polymer network remains the same.

**Fig 1.2.1** Reversible volume phase transition of gels between collapsed and swollen states. The confirmation and density of the polymer chains change while the topology of the network remains the same.
The theoretically prediction of the volume phase transition of gels was made by Dusek and Patternson in 1968 [12]. And the experimental discovery was done ten years later by Tanaka using a partially ionized acrylamide gel in a solvent of mixture of acetone and water[13]. In addition to the change of the composition of the solvent [14-16], other environmental changes that can induce volume phase transition were also observed experimentally: temperature [17-21], ionic and pH changes [22-24], irradiation of light [25,26], electric fields [27-29] and so on.

Phase transition results from the changes in the attractive and repulsive interactions among the composite molecules. I will briefly discuss the fundamental molecular interactions responsible for volume phase transition of polymer gels in session 1.2.1. In session 1.2.2, the Flory-Huggins theory will be introduced to qualitatively describe the volume phase transition of polymer gels.

1.2.1. Fundamental Molecular Interactions in Gels

There are four fundamental molecular interactions (including both polymer-polymer and polymer solvent interactions) responsible for volume phase transition of polymer gels that have been studied: van der Waals,
hydrophobic, hydrogen bonding, and electrostatic. Each interaction will be discussed briefly.

**1.2.1.1. van der Waals Interaction**

The van der Waals interaction exists between any two atoms that are 3 to 4 Armstrong apart. It is an attraction due to the asymmetry in electron distributions of the two atoms. The attraction increases as the pair of atoms gets closer, accompanied by short range excluded volume repulsion. Due to the existence of the water, van der Waals interaction (about 1kcal/mol) between polymer chains of gel is normally much smaller than other interactions. Nevertheless, such interaction can be strengthened by adding non-polar solvent. The first volume phase transition observed experimentally[13] was induced by van der Waals attractions between polymer chains.

**1.2.1.2. Hydrophobic Interaction**

The hydrophobic interaction is an attraction between non-polar molecules in water. Similarly, this attraction also exists between polymer chains with non-polar hydrocarbon group. It results from entropy maximization of the combined system of the polymer network and water. Water molecules form a more ordered structure (ice structure) in the vicinity of a non-polar hydrocarbon group than that in pure water. Therefore the entropy of the water is reduced. To
maximize the entropy of the whole system at high temperature, the polymer chains are forced to aggregate. The entropy loss of polymer chains is less than the entropy gain of water. Therefore hydrophobic interaction become stronger as temperature increases. Although the energy of hydrophobic interaction is only on the order of sub kcal/mol to a few kcal/mol, it plays an important role in the stabilization of biopolymers. Opposite to the temperature dependence of volume phase transition induced by van der Waals interaction, gels with hydrophobic interaction collapse at high temperature [17-21].

1.2.1.3. Hydrogen Bonding

When hydrogen atom is located between two closely separated atoms with high electronegativity, such as oxygen or nitrogen, a hydrogen bond can be formed. Hydrogen bonding is an attractive interaction resulting from the formation of hydrogen bonds among the polymer network of a gel. Hydrogen bond has directional preference, therefore it stabilizes the characteristic confirmation of the polymer network. The energy of a hydrogen bond is on the order of 5 kcal/mol. Although this energy is substantially smaller than that of a covalent bond, which is about 50–100 kcal/mol, hydrogen bonding is important in the physical and chemical properties of biopolymers. Hydrogen bonding becomes weaker as pH or temperature increases due to the increase of thermal energy kT or disassociation of hydrogen ion. Therefore gels with hydrogen bonding tend to collapse at low pH and low temperature[22-24].
1.2.1.4. Electrostatic Interaction

Volume phase transition of gels can be induced by electrostatic interactions among charged polymer chains and the counter ions in the solvent[22-24]. If the polymer network carries net charge, the mobile counter ions in the solvent are localized around the charges attached to the network. As a result, the osmotic pressure of the counter ions tends to swell the gel. The strong Coulombic repulsion between same charges attached to the network is usually screened by water. In a polyampholyte gel, which has both cationic and anionic groups on the polymer networks, long range attraction is presented in addition to short range repulsion.

1.2.2. Flory-Huggins Theory

The volume phase transition of polymer gels was first predicted by Dusek and Patterson using the Flory-Huggins theory for polymer solution[12]. This is a mean-field lattice theory, and only gives a qualitative description of the volume phase transition.
1.2.2.1. Free Energy and Flory Parameter

In the process of volume phase transition of gels, the topology of the polymer network remains the same but the confirmation and density of polymer chains changes. The change of free energy between two state due to those changes of polymer chains is of our interest. In the Flory-Huggins theory [9], the free energy relative to a reference state can be decomposed as follows:

\[\Delta F = \Delta F_{\text{mixing}} + \Delta F_{\text{elasticity}} + \Delta F_{\text{counterion}}.\]  

\(\Delta F_{\text{mixing}}, \Delta F_{\text{elasticity}}\) and \(\Delta F_{\text{counterion}}\) represent the mixing, elastic and counter ion mobility contributions to the free energy respectively.

The free energy of mixing between monomer and solvent molecules is

\[\Delta F_{\text{mixing}} = k_B T \frac{V}{v_{\text{site}}} (1 - \phi) \left[ \ln(1 - \phi) + \chi \phi \right].\]  

where \(V\) is the gel volume, \(v_{\text{site}}\) the lattice site volume, \(\phi\) the polymer volume fraction, \(k_B\) the Boltzmann's constant, \(T\) the absolute temperature. The Flory parameter \(\chi\) is a measure of monomer-solvent interaction and is given by
\[ \chi = \frac{1}{k_B T} \left( \frac{f_{mm} + f_{ss}}{2} - f_{ms} \right) = \frac{\varepsilon}{k_B T}, \]  

(1.2.2.1.3)

where \( f_{mm} \), \( f_{ss} \), and \( f_{ms} \) are free energy of a pair of adjacent monomer-monomer, solvent-solvent, and monomer-solvent molecules, respectively. Therefore \( \varepsilon \) represents the average difference in free energy between a pair of molecules at separate and mixing state. If the monomer-solvent interaction depends on temperature, so does \( \varepsilon \). Therefore the temperature dependence of \( \chi \) can be complicated. The Flory parameter \( \chi \) plays a very important role in the volume phase transition induced by change of temperature.

The network elasticity contribution to the free energy is

\[ \Delta F_{\text{elasticity}} = \frac{3k_B T}{2}\frac{V\phi}{N_x v_{\text{site}}} \left[ \left( \frac{\phi_0}{\phi} \right)^{\chi_3} - 1 - \frac{1}{3} \ln \left( \frac{\phi_0}{\phi} \right) \right], \]

(1.2.2.1.4)

where \( N_x \) is the average number of monomers between crosslinks, \( \phi_0 \) the polymer volume fraction in the reference state. Note that \( V\phi / N_x v_{\text{site}} \) is the effective number of chains in the network and \( \phi_0 / \phi \) is the swelling ratio of gel volume. The volume change in a polymer gel is uniform in each dimension upon equilibrium due to the shear modules. Therefore the following equalities hold:
\[
\frac{\phi_0}{\phi} = \frac{V}{V_0} = \left(\frac{d}{d_0}\right)^3,
\]
(1.2.2.1.5)

where \( V_0 \) and \( d_0 \) are the gel volume and diameter in the reference state, respectively. The note \( d \) represents gel diameter.

If the network carries net charge, some mobile counter ions in the are localized around the charges to keep the electroneutrality. As a result, the osmotic of the counter ions tend to swell the gel. The free energy from the counter ion mobility can be modeled as that of ideal gas:

\[
\Delta F_{\text{counter}} = k_BT \frac{V\phi}{N_x v_{\text{site}}} f \ln \phi,
\]
(1.2.2.1.6)

where \( f \) the average charges per chain.

### 1.2.2.2. Prediction of Volume Phase Transition

In the case of free-swelling of gels in solution, the osmotic pressure should be zero at equilibrium states. The osmotic pressure \( \Pi \) can be calculated by

\[
\Pi = \phi^2 \left( \frac{\partial F}{\partial \phi} \right)_T.
\]
(1.2.2.2.1)
Carrying out the calculation and imposing $\Pi = 0$, the following equation can be obtained

$$\tau = \left( \frac{1}{2} - \chi \right) = \frac{1}{\phi^2} \left\{ \frac{\phi_0}{N_r} \left[ \left( f + \frac{1}{2} \right) \left( \frac{\phi}{\phi_0} \right) - \left( \frac{\phi}{\phi_0} \right)^2 \right] - \phi \ln(1 - \phi) - \frac{\phi^2}{2} \right\}, \quad (1.2.2.2.2)$$

where $\tau$ is defined as reduced temperature[30-32]. The correspondence of the reduced and real temperature varies with different type of gels. In the case of N-isopropylacrylamide (NIPA) gel, the reduced temperature decreases as the real temperature increases due to the hydrophobic interaction.

Figure 1.2.2.2.1 [30] shows a set of theoretical isobar ($\Pi = 0$) curves for gels with different ionization, $f$. With no ionization, the curve is monotonous of degree of swelling, $(\phi_b/\phi)$, which indicates continuous volume change with that of temperature. By increasing $f$, a Maxwell loop appears indicating that the gel undergoes a volume phase transition between swollen and collapsed state in response to the change of temperature. There exist a critical volume, $f_c$, of ionization at which the phase transition appears. The experimental swelling curve of hydrophobic N-isopropylacrylamide (NIPA) gel with varies degree of ionization [18] is shown in Figure 1.2.2.2.2.
Fig. 1.2.2.1 Theoretical swelling curves of gels with varies degree of ionization $f$, the number of ions per chain. The degree of swelling, $\frac{V}{V_0}$, is plotted as a function of reduced temperature $\tau$. The shaded area is the region of coexistence of swollen and collapsed states.
Fig. 1.2.2.2.2 Experimental swelling curves of ionized N-isopropylacrylamide (NIPA) gels in water. The degree of swelling, $V/V_o$, is plotted as a function of temperature. The ionization values shown in the graph are the amount of ionized group (sodium acrylate) incorporated in 700mM NIPA gel. The shaded area is the region of coexistence of swollen and collapsed states.

Given the fact that the reduced temperature $\tau$ runs in opposite directions with real temperature, this set of experimental swelling curves shown in Figure 1.2.2.2.2 are qualitatively agree with the theoretical prediction shown in Figure 1.2.2.2.1.
1.3. Glass Transition of Gels

An overview of glass transition in polymers and polymer gels will be provided in section 1.3.1; and the canonical features associated with the glass transition will be discussed in section 1.3.2.

1.3.1. Overview
Glass transition refers to the loss of ergodicity in liquid as temperature decrease. If crystals do not form during cooling of a liquid, the glassy state is entered as the temperature decreases even more. The average relaxation time increases by some two to three orders of magnitude as the temperature decreases from the crystallization temperature to the entry of the glassy state[11]. As a result, liquid degrees of freedom become kinetically inaccessible. Therefore macroscopically glass maintains its shape like a solid, but its microscopic structure is barely distinguishable from the fluid substance it was before it passes into the glassy state.

The liquid states of polymers correspond to globule state, which can be melted polymers or globular polymers in a solvent. Due to the kinetic constraint, it is easier to get glassy state than crystals in polymers and any other matters with heavy molecular weight. In compact states, the constraint from cross-links of a gel should make crystallization even more difficult. Therefore we expect that polymer gels undergo glass transition at low temperature.
1.3.2. Departure from the Arrhenius law

The loss of liquid degree of freedom is manifested most directly by a rapid decrease of heat capacity $C_p$ from liquid-like to crystal-like. Correspondingly, the viscosity departure from the Arrhenius law is perhaps the most important canonical feature of glass-forming liquids [11]. The viscosity $\eta(T)$ around the glass transition temperature $T_g$ can be empirically described by a modified Vogel-Tammann-Flucher[11] equation

$$\eta(T) = \eta_0 \exp \left( \frac{D T_0}{T - T_0} \right).$$ (1.3.3.1)

As $D \to \infty$ (and $T_0 \to 0$ so that $D T_0$ remains finite), the viscosity obeys Arrhenius law

$$\eta(T) = \eta_0 \exp \left( \frac{E_A}{k_B T} \right),$$ (1.3.3.2)

where $E_A$ is activation energy, $k_B$ is Boltzmann's constant. The viscosity deviation from the Arrhenius law for different liquids can be considerably different, so is the change of heat capacity $\Delta C_p$. Liquids with little deviation from an Arrhenius viscosity, which are classified as strong liquid, also have very small
jumps of $\Delta C_p$. The other extreme is fragile liquids, viscosity of which vary in strongly non-Arrhenius fashion, with large jumps of $\Delta C_p$. Therefore, fragile liquids have more pronounced glass transition than the strong liquids. Strong liquid can be converted to more fragile behavior by changing their densities. Hydrogen bonding seems to make a special contribution to $\Delta C_p$ [11].

I will discuss the investigations of the existence of glass transition in a hydrogen bondable heteropolymer gel in chapter 6.

Before I leave this subject, it is interesting to mention the similarity between the unfolding transition in a single protein molecule and the transition from strong to fragile liquid. The globular denatured protein has quite pronounced glass transition (considerable large $\Delta C_p$), and the dry native protein shows little or none. With increasing water content, the thermal effect of native protein becomes somewhat pronounced but is never comparable with the denatured sample nor with that of simple polypeptides of comparable molecular weight and water content [11].

1.4. About This Thesis

The remaining five chapters of this thesis will cover the studies of the four research projects on phase transitions of polymer gels and their applications.
In chapter 2, I will report our studies on holographic imprinting in hydrogels, gels with water as solvent, with hydrophobic interactions. We incorporated holographic gratings in the form of inter-penetrating polymer (IPN) network into a hydrophobic hydrogel, using dye-sensitized photo-polymerization. We obtained the spacing of this holographic grating by measuring the diffraction angle of a laser beam from the gratings. As we discussed in chapter 1, hydrophobic gels can undergo a reversible discontinuous volume phase transition in response to temperature changes. We have observed reversible discontinuous changes in the spacing of the holographic gratings as the gel underwent the phase transition in response to the temperature changes. While similar holographic experiments were conducted before[33], it is the first experiment to incorporate holographic gratings into a gel so that one can change the spacing with external stimuli. This system can be used as an information storage or an optical actuator.

In chapter 3 and chapter 4, I will discuss our studies on volume phase transitions of colloidal micro-gels with both hydrogen bonding and hydrophobic interactions using light scattering methodology. These studies include two research projects: dynamic light scattering and static light scattering by the colloidal micro-gels. Light scattering methodology will be discussed in chapter 3. As we discussed in chapter 1, polymer gels with these interactions can undergo
discontinuous volume phase transition in response to changes in the pH value and temperature. Such volume phase transition in bulk gels has been observed in many studies before [34,35]. The characteristic time for bulk gels to reach equilibrium can be long. For many applications it is important to reduce this characteristic time, which can be achieved by reducing the size of the polymer gel (see chapter 4). Therefore, we focused on micro-gels with less than 1 micron meter in diameters. We obtained the average size by measuring the angular distribution and time-correlation function of the scattered light intensity. We observed drastic but continuous volume changes of the micro-gels in response to the temperature and pH value changes.

I will cover our studies on exploring the glass transition of hetero-polymer gels with strong hydrogen bonding interactions in chapter 5 and chapter 6. As we discussed in chapter 1, glass transition occurs when the attractive molecular interactions are getting so strong that the liquid degrees of freedom become kinetically inaccessible. The loss of liquid degree of freedom is manifested most directly by a rapid decrease of heat capacity $C_p$ from liquid-like to crystal-like. Correspondingly, the departure from the Arrhenius law (see equation 1.3.3.2) of viscosity as a function of temperature is perhaps the most important canonical feature of glass transition. The attractive molecular interaction in the gels for our studies is hydrogen bonding, which can be strengthened by lowering temperature and pH. We kept low pH value during the measurements so that the gel remained collapsed. The gel was rubbery at high temperature, and
became as rigid as a plastic when the temperature decreased. This observation indicates that there might be a glassy transition at some temperature. We measured the time correlation function of the scattered light from this gel, and estimated the visco-elasticity of the gel from the average decay time of this correlation function. We observed deviations in the visco-elasticity from Arrhenius law (see equation 1.3.3.2). Some mechanical measurements also suggested the existence of glass transition in this hetero-gels with hydrogen bonding interactions.
Part I

Holographic Imprinting in a NIPA Gel
ABSTRACT

Holographic grating was incorporated into a hydrophobic N-isopropylacrylamide (NIPA) gel as an interpenetrating polymer network, using dye-sensitized photo-polymerization. Discontinuous changes in the grating spacing occurred at two temperatures in response to the temperature changes. These two transitions appear to represent that of the pure NIPA gel and that of the interpenetrating polymer network, respectively. Both of the transition temperatures were within approximately 1 °C of the transition temperature of the pure NIPA hydrogel. The swelling degrees calculated from the changes in the grating spacing were less than those of the pure NIPA hydrogel. The discontinuous changes in the holographic grating spacing were demonstrated by the first-order diffraction angle from an argon laser beam. Same holographic gratings were also incorporated into a copolymer gel of NIPA and Acrylamide (AAm) with the same method. The changes in the spacing were sharp but continuous near the NIPA gel transition temperature. This confirmed that the hydrophobic property of NIPA was responsible for the discontinuous spacing changes.
INTRODUCTION

Over the past twenty years, intensive research has been conducted to explore the new external stimuli that cause the volume phase transition of gels and the new applications of this phase transition [30-32]. In parallel, many studies have been done on holographic memories [36]. The study I will present in this chapter was inspired by the studies in both fields. The result has potential applications in information storage or optical actuator.

This study presents an experimental protocol for incorporating holographic grating into a hydrophobic N-isopropylacrylamide (NIPA) hydrogel. The grating was in the form of an interpenetrating polymer network. We used the same method, dye-sensitized photo-polymerization, as Sugawara et al. [36] did in his research on holographic recording [37-40] within an acrylamide solution.

There are unique advantages of using a hydrogel as the “carrier” of the holographic gratings. In contrast of the gratings formed in a solution, the gratings embedded in a hydrogel maintain their regularities. Also, the excess photo-polymerizable solution (see section 2.3) in the gel can be washed out after the formation of gratings so that the sample can be maintained under prolonged light exposure. As we will discuss below, the most distinguishable advantage was that we can control the spacing of the gratings by changing external stimuli such as temperature.
Hydrogels with hydrophobic interactions can undergo reversible discontinuous volume phase transition in response to the change in temperature. The spacing of the embedded holographic gratings should reflect the volume phase transition of the NIPA gel. In other words, we expect the spacing of the embedded holographic gratings undergo a discontinuous change as the temperature across the phase transition temperature of the NIPA gel. We have observed the discontinuous changes in the grating spacing by measuring the first-order diffraction angle from an argon laser beam passing through the holographic gratings embedded in the hydrogel.

To confirm that the volume phase transition of NIPA caused the discontinuous spacing changes of the holographic gratings, we incorporated the same holographic gratings into a copolymer hydrogel of NIPA and Acrylamide (AAm). The NIPA/AAm hydrogel undergoes a sharp but continuous volume change in response to the changes in temperature. Similarly, we observed that the spacing changes of the holographic gratings were sharp but continuous. This confirmed that the hydrophobic property of NIPA was responsible for the discontinuous spacing changes.
2. Discontinuous Phase Transition of Holographic Imprinting in a NIPA Gel

I will present our study on holographic imprinting in a hydrophobic gel using dye-sensitized photo-polymerization. This imprinting was in the form of interpenetrating polymer network. We observed the discontinuous volume phase transitions of this holographic imprinting in response to temperature changes. This result has potential applications in information storage or optical actuator.

The sample preparation will be described in section 2.1. The experiment setup will be described in section 2.2. The experiment results and analyses will be discussed in section 2.3.

2.1. Sample Preparation

The sample was a thin slide of gel made of two interpenetrating polymer networks. We prepared one polymer network using free radical polymerization. We then embedded the second polymer network into the first one using dye-sensitized photo-polymerization. I will refer the former polymer network as the “carrier” gel. This polymerization of the embedded network was induced by interference electric field of two coherent helium-neon ion laser beams. The spatial distribution of intensity of the interference electric field was three-dimensional grating and can be expressed as
\[ I_f(x) = 2I_0 \left\{ 1 + \cos \left[ (k_1 - k_2) \cdot x + \varphi_0 \right] \right\}, \quad (2.1.1) \]

where \( I_0 \) is the intensity of individual laser beam, and \( k_1, k_2 \) are the wave vectors of the two laser beams. The constant \( \varphi_0 \) is the phase difference of the two beams at the origin of the space coordinate. Since the light was sufficient weak and the exposure time was sufficient short, the response (polymerization) can be assumed to be linear. The density distribution of the embedded polymer network should share the same profile as the right hand side of equation 2.1.1. Therefore I refer the embedded copolymer network as holographic imprinting or holographic grating.

The “carrier” NIPA gel was prepared by free radical polymerization. We dissolved 7.9 g (700 mM) NIPA (the main polymer constituent), 0.133 g N,N'-methylenbisacrylamide (cross-linker), 240 \( \mu \)l tetraethylmethylenediamine (accelerator), and 40 mg of ammonium persulphate (initiator) in 100 ml of water. This solution was degassed for 40 minutes. To make a thin sheet gel, we transferred this solution between two microscope glass slides. The slides were separated by plastic spacers on both ends. The thickness of the spacers was 0.7 mm. The polymerization temperature was fixed at 20 °C by circulating water from a Brinkmann Lauda RC-3 for over twelve hours.
We prepared a copolymer gel of NIPA and Acrylamide (AAm) as the “carrier” for the control experiment. The formulation was the we used 7.1 g (630 mM) NIPA and 1g (70 mM) AAm in instead of 7.9 g of NIPA. The polymerization process was the same.

The next step was to embed the second polymer network into the “carrier” gel. The pre-gelation solution was prepared by dissolving 2.3 g NIPA (monomer), 0.35 g N,N'-methylenebisacrylamide (cross-linker), 0.53 ml triethanolamine (initiator), and 0.6 mg methylene blue (dye) in 3.4 ml dimethacrylamide (DMAAm, monomer). Because of dye, light exposure can easily trigger the polymerization of this solution. I will refer this pre-gelation solution as dye-sensitized photo-polymerizable solution.

We immersed the “carrier” gel in the dye-sensitized photo-polymerizable solution for half an hour without light exposure. After the “carrier” gel was saturated with this solution, we transferred it into a temperature controlled cell as shown in figure 2.2.1. We then applied the two coherent laser beams to trigger the polymerization. I will discuss the experiment setup and measurements in section 2.2 and 2.3.
2.2. Experiment Setup

I will describe the experiment setup for the formation and monitoring of holographic grating, and for measurements of temperature dependence.

Figure 2.2.1 shows the optical setup for the holographic imprinting in the “carrier” gel. The beam splitter divided a helium-neon laser beam into two orthogonal beams. One beam was applied to the sample in the temperature controlled cell at an incident angle of $0^\circ$. An adjustable mirror directed the second beam to form an interference electric field with the first beam within the “carrier” gel. The angle, $\theta$, between the two incident beams was set at $10^\circ$ and the temperature was fixed at $25^\circ$C during the polymerization. The observation screen was used to monitor the polymerization.
Figure 2.2.1 The schematic representation of the optical apparatus for forming and controlling the holographic gratings in the hydrophobic hydrogel. A helium-neon laser is used to polymerize the dye-sensitized photo-polymerizable solution within NIPA hydrogel, which is situated in the temperature controlled cell.

Prolonged exposure to the helium-neon laser light can destroy the holographic grating because the polymerization would no longer linearly depend on the intensity distribution. Thus it was important to monitor the formation of the grating and stop the polymerization in time. We applied a single argon laser beam in addition to the helium-neon laser beams serve this purpose. The argon laser did not interfere the polymerization because the dye (methylene blue) absorbs little blue light. When the holographic grating was formed, the scattered
argon light by this grating resulted in diffraction spots on the observation screen. The optical setup for monitoring is shown in figure 2.2.2. The mirror was used to direct an argon laser beam to the sample at an incident angle of $0^\circ$. The first-order diffraction spot appeared on the observation screen after the holographic gratings were formed. The first order diffraction angle is denoted by $\beta$.

Figure 2.2.2 Schematic representation of the optical apparatus for monitoring the formation of the holographic gratings and measuring the first-order diffraction angle $\beta$. The term $L$ denotes the distance between the sample and the observation screen, and $l = L \tan \beta$ the distance between the zero-order and first-order diffraction spots on the observation screen.
It took approximately 5 seconds of helium-neon laser irradiation to form the holographic gratings. The irradiation was then stopped and the sample gel slide was immersed in a large amount of deionized distilled water to wash away the excess pre-gelation solution. Water was replaced repeatedly until the gel color changed from blue to clear. The sample was then placed back to the temperature controlled cell, and the argon laser was re-applied for the measurement of temperature dependence of the diffraction angle $\beta$ (see figure 2.2.2). The temperature was controlled within 0.04 °C by circulating water from a Brinkmann Lauda RC-3 during the measurements. The spacing of the grating can be calculated from the diffraction angle.

### 2.3. Measurement and Analyses

We observed discontinuous volume phase transition of the holographic grating in response to temperature changes. This observation was from the experimental data and some calculations. I will present our measurements on temperature dependence of diffraction angle of the argon light scattered by the holographic grating. I will then discuss the calculations of the spacing of the holographic grating as a function of temperature. Finally, I will compare the transition temperature and the degree of swelling of the holographic grating with those of the pure NIPA gel.
Figure 2.3.1(a) shows the temperature dependence of the first order diffraction angle of the scattered light by the holographic grating in NIPA “carrier” gel. Figure 2.3.1(b) shows the same measurements for the holographic grating in NIPA/ AAm “carrier” gel.

![Graph showing temperature dependence of diffraction angle](image)

Figure 2.3.1(a) The first order diffraction angle $\beta$ as a function of temperature for the holographic grating in the pure NIPA gel. The parameter $L$ denotes the distance between the sample and the observation screen (see figure 2.2.2). Filled circles represent the values of $L \tan \beta$ on raising the temperature and open circles the values of $L \tan \beta$ on lowering the temperature.
Figure 2.3.1(b) The first order diffraction angle $\beta$ as a function of temperature for the holographic grating in the NIPA/AAm gel. The parameter $L$ denotes the distance between the sample and the observation screen (see figure 2.2.2).

As shown in figure 2.3.1 (a) and figure 2.3.1 (b) we measured $l = L \tan \beta$ (see figure 2.2.2), where $\beta$ is the diffraction angle and $L$ the distance between the sample and the observation screen. This distance $L$ was fixed in this experiment. I will refer sample1 to the combined system of the embedded holographic gratings and the NIPA gel; and sample2 the combined system of the embedded holographic gratings and the NIPA/AAm gel.
The measurement results for holographic grating in NIPA gel (sample 1) is shown in figure 2.3.1 (a). The temperature was raised from 20 °C gradually. Discontinuous increases in $\tan \beta$ occurred at two temperatures. At about 33.2 °C, $\tan \beta$ suddenly increased by approximately 1.3 times. The second discontinuity occurred at about 34.3 °C, where $\tan \beta$ increased again by approximately 1.2 times. When the temperature was lowered starting from 37 °C, $\tan \beta$ decreased discontinuously at approximately 33.5 °C and 31.2 °C. The transition temperatures upon raising and lowering the temperature were different by 2.0 °C and 0.8 °C, respectively.

The measurement results for holographic gratings in the NIPA/AAm gel (sample 2) is shown in figure 2.3.1 (b). The temperature was raised from 20 °C gradually. The increase in $\tan \beta$ was drastic but continuous between 38 °C and 40 °C.

The initial grating spacing upon polymerization, $\delta_0$, can be calculated according to the Bragg condition

$$\delta_0 = \frac{\lambda_l}{\sin \theta}, \quad (2.3.1)$$

where $\lambda_l (=.633 \ \mu \text{m})$ denotes the wavelength of the helium-neon laser, and $\theta$ the angle between the two incident laser beams (see figure 2.2.1).
The diffraction angle, \( \beta \), of the scattered argon laser light scattered by the holographic grating (see figure 2.2.2) can be expressed as

\[
\sin \beta = \frac{\lambda_2}{\delta},
\]  

(2.3.2)

where \( \lambda_2 \) \((= 0.488 \, \mu m) \) denotes the wavelength of the argon laser, and \( \delta \) the grating spacing. Both the diffraction angle \( \beta \) and spacing \( \delta \) are temperature dependent. Since the diffraction angle \( \beta \) less than 15° even at the most collapsed state, thus the measured quantity \( L \tan \beta \) (see figure 2.2.2) can be expressed in terms of the spacing \( \delta \) as

\[
L \tan \beta \equiv L \sin \beta = \frac{L \lambda_2}{\delta}.
\]  

(2.3.3)

Thus the measurement \( L \tan \beta \) (see figure 2.3.1 (a) & (b)) showed discontinuous phase transitions in sample 1 and continuous volume change in sample 2. Note that there exist two transition temperatures in sample 1. I will present a hypothesis to explain this observation.

Now let us focus on sample 1 – the combined system of the embedded holographic gratings and the “carrier” NIPA gel. The two transition temperatures calculated from the experimental measurements for sample 1 are shown in Table
2.3.1. The term $T_1$ denotes the transition temperature at which the measured quantity $L \tan \beta$ changed discontinuously from about 30 mm to about 40 mm. Similarly, $T_2$ represents the transition temperature at which the measured quantity $L \tan \beta$ changed discontinuously from about 40 mm to about 50 mm.

The term hysteresis describes the difference between the transition temperatures that resulted from raising and lowering the temperature. The presence of hysteresis indicates that both are the first-order phase transitions. The transition temperature in this study refers to the mean value of the transition temperatures upon raising and lowering the temperature. Both of the observed transition temperatures were within 1 °C of the NIPA hydrogel transition temperature (33.2 °C). This observation suggests that the hydrophilic property of NIPA hydrogel was the dominant cause of the discontinuous changes in the holographic grating spacing.
Table 2.3.1
Phase Transition Parameters of Sample1

<table>
<thead>
<tr>
<th></th>
<th>$T_1$ (°C)</th>
<th>$T_2$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>lowering temperature</td>
<td>33.2</td>
<td>34.3</td>
</tr>
<tr>
<td>raising temperature</td>
<td>31.2</td>
<td>33.5</td>
</tr>
<tr>
<td>hysteresis</td>
<td>2.0</td>
<td>0.8</td>
</tr>
<tr>
<td>transition temperature</td>
<td>32.2</td>
<td>33.9</td>
</tr>
</tbody>
</table>

To explain the presence of two transition temperatures in sample1, let us consider the "carrier" NIPA gel and the grating separately. The pure NIPA hydrogel undergoes a phase transition at about 33.2 °C. The holographic gratings were made of copolymer network of NIPA and DMAA, and the molar ratio of NIPA and DMAA was 1/1.13. Therefore the polymer network of the holographic gratings was partially hydrophobic, and may undergo a sharp volume change within a small temperature range or even a discontinuous volume change. The corresponding transition temperature should be higher than that of the pure NIPA hydrogel. The reason for this was that the hydrophobic interactions in the polymer network of the gratings were weaker due to the presence of DMAA.

Table 2.3.2 provides a comparison between the holographic gratings and NIPA hydrogel pre-gelation solutions.
Table 2.3.2
Composition of Pre-Gelation Solutions for NIPA and Holographic Gratings

<table>
<thead>
<tr>
<th>polymer networks</th>
<th>monomer molar concentration</th>
<th>cross-linker to monomer ratio</th>
<th>initiator to monomer ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>NIPA</td>
<td>7%</td>
<td>1.2%</td>
<td>0.25%</td>
</tr>
<tr>
<td>Gratings</td>
<td>90.7%</td>
<td>3.7%</td>
<td>6.5%</td>
</tr>
</tbody>
</table>

The cross-linker to monomer ratio in the gratings pre-gelation solution was higher than that of the pure NIPA hydrogel. Therefore, the polymer network of the holographic gratings was stiffer than that of the pure NIPA hydrogel. This elastic constraints imposed by the gratings on the NIPA hydrogel made a significant contribution to the overall swelling behavior. The observed swelling degree of sample1 was in fact less than that of the pure NIPA hydrogel (see figure 2.3.2).

This elastic constraints also shined some lights on the understanding of the presence of two transition temperatures in sample1. The following explanation is my hypothesis. As the temperature was increased towards the NIPA transition temperature, the NIPA hydrogel started to shrink drastically and therefore the grating network was forced to shrink. This process resulted in the first phase transition of sample1. However, the NIPA hydrogel might not reach its completely collapsed state as a result from the resistance of the grating polymer network. As I mentioned before, the polymer network of the gratings
undergoes a sharp volume change around certain temperature. And this
temperature should be higher than the phase transition temperature of a NIPA
gel. This leads to the explanation of second phase transition of sample1. As the
temperature was raised further after the first transition, the volume of sample1
shrank gradually until the temperature around which the polymer network of the
gratings underwent a sharp decrease in volume. In the other words, the
resistance of the grating polymers was suddenly disappeared. Therefore the
second phase transition occurred.

The degree of swelling of a polymer hydrogel is usually represented by
the ratio \( V/V_0 \), where \( V \) denotes the volume of the hydrogel and \( V_0 \) the original
hydrogel volume upon gelation. Because of the existence shear modulus \( T \) of the
hydrogel, the swelling process of a hydrogel is isostropic. Therefore the degree of
swelling of sample1 can be determined by \( (\delta/\delta_0)^3 \), where \( \delta \) denotes the grating
spacing and \( \delta_0 \) denotes the original spacing when the gratings were formed.
Equation 2.3.3 shows that the inverse of our quantity \( L \tan \beta \) (see figure 2.2.2), is
proportional to \( 1/\delta \). Thus the following equality holds,

\[
\frac{V}{V_0} = \left(\frac{\delta}{\delta_0}\right)^3 \equiv \left(\frac{\tan \beta}{\tan \beta_0}\right)^{-3}
\]

(2.3.4)

Figure 2.3.2(a) shows the degree of swelling for sample1; and figure
2.3.2(b) shows the degree of swelling for pure NIPA gel. Both curves are plotted
on a logarithmic scale so that the shape of the curve does not depend on the reference volume $V_0$. The curve plotted in figure 2.3.2 (a) is $\left(\frac{\tan \beta}{\tan \beta_0}\right)^{-3}$ (see equation 2.3.4). The value of $\tan \beta_0$ chosen in this plot does not correspond to the initial grating spacing $\delta_0$. Thus only the shape of the curve tells us the relative degree of swelling.

As shown in figure 2.3.2 (a) and figure 2.3.3 (b), the overall swelling degree of the sample1 was smaller than that of the pure NIPA. At each of the two transition temperatures, the volume of sample1 increased by about a factor of 2. Thus the total volume changed discontinuously by about a factor of 4 in sample1. The pure NIPA gel showed a volume increase by about 8 times. As we mentioned in session 2.4.3, this result is due to the elasticity constraint imposed by the polymer network of the holographic gratings in sample1.
Figure 2.3.2(a) Swelling degree of sample 1, the combined system of embedded holographic gratings and the NIPA gel. The two transition temperatures are denoted as \( T_1 \) (32.2 °C) and \( T_2 \) (33.9 °C). The term \( T_x \) (33.2 °C) represents the transition temperature of pure NIPA. Filled and open circles give the degree of swelling on raising and lowering the temperature, respectively.
2.4. Conclusions and Future Work

We provided an experimental protocol for implanting holographic grating into a hydrophobic N-isopropylacrylamide (NIPA) hydrogel. This holographic grating embedded in a NIPA gel has many prospective applications, including information storage and optical actuator.
The grating was incorporated into the NIPA gel as an interpenetrating polymer network, using dye-sensitized photopolymerization. Discontinuous changes in the grating spacing occurred at two temperatures that were within 1 °C of the pure NIPA hydrogel transition temperature. A controlled experiment also confirmed that the hydrophobic property of the NIPA hydrogel was essential for the discontinuous change of the holographic grating spacing.

Further exploration of the interactions between the holographic polymer network and the NIPA gel may provide deeper understanding of the existence of the two phase transitions of the system.
Part II

Light Scattering by Colloidal Micro-gels
ABSTRACT

The colloidal micro-gels with hydrophobic and hydrogen bonding interactions were prepared by emulsion polymerization of N-isopropylacrylamide (NIPA) and acrylic acid (AAc) monomers. We observed continuous albeit drastic volume changes of the micro-gels in response to the pH or temperature changes using light scattering technique. The average size of the micro-gels was calculated from correlation function and angular dependence of the scattered light. At low pH and high temperature, the micro-gels were collapsed and virtually mono-dispersed. The micro-gels became poly-dispersed with the increase in the pH or decrease in the temperature. As the pH was increased from 2.5 to about 10.3, the volume of the micro-gels was increased drastically and the degree of swelling was in the order of two thousand times. When the pH was increased further, the micro-gels started to shrink. The volume of the micro-gels was decreased as the temperature was increased from 15 °C to 75 °C, and the corresponding degree of swelling was in the order of ten times at pH=5.8.
INTRODUCTION

The volume phase transition of gels is of great importance in both scientific research and technological applications. Many studies have shown the volume phase transition of bulk gels with hydrophobic and hydrogen bonding interactions [17-24]. The characteristics time for a bulk gel to reach equilibrium during phase transition can be long. For the applications such as switching device controlled drug delivery, it is important to reduce this characteristic time. Since volume phase transition of a gel is closely related to the diffusion process of certain molecules from the solution into the gel, the increase of this characteristic time is quadratic as the increase of the gel size. Therefore the phase transition time can be shortened drastically by reducing the gel size.

Several recent studies have been focus on the property of sub-micron gels [34,35]. The average diameter of the micro-gels in this study was about 300 nano-meters (nm) under room temperature and neutral pH, and the time for the micro-gels to reach equilibrium was less than a few minutes. In this study, we employed a new method to better control the pH value and achieve better measurement accuracy.

Traditionally the pH value was controlled by placing the sample directly in the pH solution. Because the samples were the colloidal micro-gels in this case, it would have been difficult to change the pH value without changing the sample.
Consequently, it would have been difficult to change the pH value continuously and reversibly. To overcome these problems, we used a different approach to control the pH value. We injected the colloidal micro-gels into a micro-dialysis tube, and then placed this micro-dialysis tube into a cylindrical micro-pipette. The pH value of the micro-gel is controlled by flushing pH solution through the micro-pipette (see figure 4.3.2.1). Because the sample was physically separated with the ever flowing pH solution, we can change the pH value without changing the sample. Therefore the pH value can be controlled continuously and reversibly.

The pH and temperature dependence of the colloidal micro-gels were measured with both dynamic and static laser scattering technique. In the dynamic light scattering experiments, we measured the time-correlation function of the intensity of the scattered light by the colloidal micro-gels in a given direction. From the characteristic decay time of this correlation function, we calculated the average size of the micro-gels. The results of this calculation showed continuous albeit drastic volume changes in the micro-gels in response to pH value and the temperature changes. In the static light scattering experiments, we measured the angular dependence of intensity of the scattered light by the colloidal micro-gels. From the local minimums of this angular dependence, we calculated the average size of the micro-gels. Again, the results of this calculation show continuous albeit drastic volume changes in the micro-gels.
3. Light Scattering Methodology

This chapter serves as the theoretical background for the experiment work presented in chapter 4. Readers who are familiar with light scattering methodology can skip this entire chapter.

Electromagnetic radiation is one of the most important probes of the structure and dynamics of matter. When light impinges on matter, the electric field of light induces an oscillating polarization of the electrons in the molecules. The molecules then serve as a secondary light source and radiate (scatter) light. The intensity, polarization, angular distribution, and frequency shifts of the scattered light are determined by the size, shape and molecular interactions in the scattering medium. Therefore from the light scattering characteristics, it should possible to obtain information about the structure and molecular dynamics of the scattering medium. This chapter is devoted to the basic theory (see section 3.1) and techniques (see section 3.2) of light scattering. This will provide the basis of the setup and analyses for the light scattering experiments of polymer gels presented in later chapters.

A schematic representation of light scattering experiment is shown in figure 3.1.
Fig. 3.1  
A schematic representation of the light-scattering experiment. Light from a laser passes through a polarizer with polarization $n_i$, and impinges on the scattering medium. The scattered light then passes through an analyzer which selects a given polarization $n_f$, and finally enters a detector. The position of the detector determines the scattering angle $\theta$. In addition, the intersection beam the incident beam and the scattered beam intercepted by the detector defines a scattered region, which is represented by the gray shaded region, of volume $V$. The term $k_i (\lambda_i)$ and $k_f (\lambda_f)$ are the wave vectors (wave length) of the incident and scattered light, respectively. The reflection index is denoted by $n$. 

$\text{Laser}$

$\text{Polarizer}$

$\text{Scattering Medium}$

$\text{Analyzer}$

$\text{Detector}$

$k_i = 2\pi n/\lambda_i$

$k_f = 2\pi n/\lambda_f$
3.1. Basic Light Scattering Theory

The theory of light scattering can be developed on the basis of quantum field theory. Since the major results differ little from the classical theory, the discussions in this chapter will be based on the classical theory. The scattered electric field can be calculated as the superposition of scattered electric fields from equal-sized sub-regions of the illuminated volume. If the sub-regions are optically identical (with same dielectric constant), the scattered lights from the sub-regions cancel each other in all the directions except the forward direction. If, however, the sub-regions are optically different (with different local dielectric constants), then the amplitudes of the light scattered from different sub-regions are different. Complete cancellation will no longer take place, and there will be scattered light in other than forward direction. Therefore in this semi-macroscopic view, originally introduced by Einstein, light scattering is a result of local fluctuations in the dielectric constant of the medium [41-43].

3.1.1. Fluctuations and Time-Correlation Function

In light scattering experiments, the molecules of the scattering medium are perpetually translating, rotating and vibrating due to the thermal interaction. In the case of gels, the thermal fluctuation of the polymer network can be described as diffusion process [42]. As the response from the erratic thermal molecular motion of the scattering medium to the incident light, the scattered
electric field at the detector fluctuates in time. In light scattering experiments, the incident light is sufficiently weak that the scattering medium can be assumed to respond linearly to it. According to linear response theory [42] for two weakly coupled systems, the way in which one system responds to the other can be described by the behaviors of both system in the absents of coupling. Also, the response of one system to the other can be completely described in terms of time-correlation functions of the dynamic variables. The time-correlation function of the scattered light can be measured by using optical mixing techniques; and the Fourier-transform of this correlation function, the spectrum density, can be measured by using filter techniques. These light scattering techniques will be discussed later in this section.

The time correlation function of scattered light can be interpreted directly in terms of dynamic property of the medium, given the medium is fluid-like fluctuating medium (see chapter 4 discussions about solid-like amorphous media). Section 3.1.1.1 will provide an overview of properties of time-correlation function. The relations between time-correlation function of scattered light and the fluctuations will be derived in section 3.1.1.2. An example of obtaining the size of spherical particles from this correlation of scattered light will be given in section 3.1.1.3.
3.1.1.1. Overview of Time-Correlation Function

One of the common seen time-correlation function is auto-correlation function. In light scattering experiment, the term time-correlation function generally refers to auto-correlation function. Let us consider a property $A$ of a system at stationary condition, that is, the time average of $A$ over a long time period does not depend on the initial time. In other words,

$$\overline{A}(t_0) = \lim_{T \to \infty} \frac{1}{T} \int_{t_0}^{t_0+T} dt A(t) = \lim_{T \to \infty} \frac{1}{T} \int_0^T dt A(t).$$

(3.1.1.1)

We denote this time average as $\langle A \rangle$. In the light scattering experiment of gels, all the measurements are done at equilibrium states. Therefore the stationary condition is automatically satisfied. The auto-correlation function of property $A$ is defined as

$$\langle A(0)A(\tau) \rangle = \lim_{T \to \infty} \frac{1}{T} \int_0^T dt A(t) A(t + \tau).$$

(3.1.1.2)

For a non-periodic fluctuated property, we would expect $A(t + \tau)$ to be very close to $A(t)$ when the time $\tau$ is very small compared with the typical fluctuation time in $A$. As $\tau$ become very large, $A(t + \tau)$ and $A(t)$ would be totally independent. Therefore,
\[
\lim_{\tau \to 0} \langle A(0)A(\tau) \rangle = \langle A(0)^2 \rangle = \langle A^2 \rangle,
\]
and
\[
\lim_{\tau \to \infty} \langle A(0)A(\tau) \rangle = \langle A(0)\langle A(\tau) \rangle \rangle = \langle A \rangle^2
\]

In other words, the auto-correlation function of a non-periodic property \( A \) decays from \( \langle A^2 \rangle \) to \( \langle A \rangle^2 \). This is shown in Figure 3.1.1.1, where \( \tau_c \) represents the correlation time, beyond which the correlation function decays appreciably.

Fig.3.1.1.1  The auto-correlation function of property \( A \), \( \langle A(0)A(\tau) \rangle \). This function decays from initial value \( \langle A^2 \rangle \) to \( \langle A \rangle^2 \) as time \( \tau \) becomes very long compared with the correlation time \( \tau_c \).
In many applications the auto-correlation function decays like a single exponential so that

\[ \langle A(0)A(\tau) \rangle = \left\{ A^2 - \langle A \rangle^2 \right\} \exp \frac{-\tau}{\tau_c} + \langle A \rangle^2. \]  

(3.1.1.5)

If we define

\[ \delta A(t) = A(t) - \langle A \rangle, \]  

(3.1.1.6)

we can obtain

\[ \langle \delta A(0)\delta A(\tau) \rangle = \langle \delta A^2 \rangle \exp \frac{-\tau}{\tau_c} \]  

(3.1.1.7)

for a single exponential decay auto-correlation function. In general cases, we can define the correlation time as

\[ \tau_c = \int_0^\infty d\tau \frac{\langle \delta A(0)\delta A(\tau) \rangle}{\langle \delta A^2 \rangle}. \]  

(3.1.1.8)

3.1.1.2. Relations between Correlation of scattered light and Fluctuation of Dielectric Constant

Considering a medium with average dielectric constant \( \varepsilon_0 \) (and refractive index \( n = \sqrt{\varepsilon_0} \)). The local dielectric constant can be expressed as
\[ \varepsilon(r, t) = \varepsilon_0 \bar{I} + \delta \varepsilon(r, t), \] (3.1.1.2.1)

where \( \delta \varepsilon(r, t) \) is the dielectric constant fluctuation tensor at position \( r \) and time \( t \) and \( \bar{I} \) is the second-rank unit tensor.

Let the incident electric field be a plane wave

\[ E_i(r, t) = n_i E_0 \exp(ik \cdot r - \omega_i t), \] (3.1.1.2.2)

where \( n_i \), \( E_0 \), \( k_i \) and \( \omega_i \) are the polarization, field amplitude, wave vector and angular frequency respectively. The scattered electric field can be calculated as the supervision of scattered electric fields from equal-sized sub-regions of the illuminated volume. The spatial and momentum scattering geometry are shown in figure 3.1.1.2.1 and figure 3.1.1.2.2, respectively.
Fig. 3.1.1.2.1 The spatial scattering geometry. The total scattered electric field at the detector is the superposition of the fields from all infinitesimal sub-regions $d^3r$ at position $r$ with respect to the center, $O$, of the illuminated volume $V$. The detector is at position $R$ with respect to the center of the illuminated volume.
\[ q^2 = k_i^2 + k_f^2 - 2k_i \cdot k_f = 4k_i^2 \sin^2(\theta/2) \]

Fig. 3.1.2.2 The wave-vector (momentum) scattering geometry. Incident light of polarization \( n_i \) and wave vector \( k_i \) is scattered in all directions. Only the scattered light with wave vector \( k_f \), which points in the direction from the center of illuminated volume to the detector, and polarization \( n_f \) arrives at the detector. The scattering vector \( q = k_i - k_f \) is defined by the geometry. Only the quasi-elastic scattering is of our interest, namely, \( k_f \equiv k_i \). Therefore \( q = 2k_i \sin \theta/2 \).

From the electromagnetic theory, the component of the scattered electric field at a large distance \( R \) from the center of the illuminated volume \( V \) with polarization \( n_f \), wave vector \( k_f \) and frequency \( \omega_f \) may be expressed as

\[
E_s(R,t) = \frac{-k_i^2 E_0}{4\pi R \varepsilon_0} \exp(\imath k_f R - \omega_f t) \delta\epsilon_{if}(q,t), \tag{3.1.2.3}
\]
where the vector $q$, tensor $\delta \tilde{\varepsilon}(q,t)$ and its component $\delta \varepsilon_{ij}(q,t)$ are defined in terms of scattering geometry as

$$q = k_i - k_r,$$  \hspace{1cm} (3.1.2.4)

$$\delta \tilde{\varepsilon}(q,t) = \int d^3r \exp(iq \cdot r) \delta \tilde{\varepsilon}(r,t),$$  \hspace{1cm} (3.1.2.5)

$$\delta \varepsilon_{ij}(q,t) = n_r \cdot \delta \tilde{\varepsilon}(q,t) \cdot n_i.$$  \hspace{1cm} (3.1.2.6)

Therefore the auto-correlation function of the scattered field can be expressed as

$$\langle E'_s(R,0) E_s(R,t) \rangle = \frac{k_f^4 |E_0|^2}{16\pi^2 R^5 \varepsilon_0^2} \langle \delta \varepsilon_{ij}(q,0) \delta \varepsilon_{ij}(q,t) \rangle \exp(-i\omega t).$$  \hspace{1cm} (3.1.2.7)

From equation 3.1.2.3 and 3.1.2.7, we can see clearly that light scattering is a result of local fluctuations of the dielectric constant. The auto-correlation function of the scattered field is measured in optical mixing experiments (see section 3.2).

### 3.1.1.3. Time Correlation Function of Scattered light by Particle Diffusion

In this section, an example will be provided to obtain information of the medium from time-correlation function of the scattered light. Let us consider scattered light from mono-dispersed colloidal spherical particles in suspension. The particles perform Brownian motions, or self-diffusion, in the solvent. The
"solution" is dilute enough so that the particles are uncorrelated. The scattered light by the small solvent molecules is negligible since it is either much weaker compared with the scattered light by the particles, or the decay time is much faster. As we will see at the end of this section, the diffusion coefficient of the particles can be calculated from the characteristic decay time of the scattered light correlation function; and the size of particles can be calculated from this diffusion coefficient.

The time-correlation function of scattered, \( \langle E_s^*(R,t) E_s(R,t) \rangle \), is proportional to that of the momentum Fourier transform of the fluctuation in the medium's dielectric constant, \( \langle \delta \varepsilon_f(q,0) \delta \varepsilon_f(q,t) \rangle \) (see equation 3.1.1.2.7). Thus our goal is to express \( \langle \delta \varepsilon_f(q,0) \delta \varepsilon_f(q,t) \rangle \) in terms of the properties of our interests (the diffusion coefficient in this case).

For this particular medium, the fluctuation of the dielectric constant results mainly from the difference between the dielectric constant of the particles and that of the solvent. Let us assume they are different by value \( \alpha_p \). If there are \( N \) particles in the scattering volume and each particle can be viewed as a point scatter, the fluctuation of the dielectric constant \( \delta \varepsilon_f(r,t) \) and its momentum Fourier transform \( \delta \varepsilon_f(q,t) \) can be written as (see equation 3.1.1.2.5 and 3.1.1.2.6)
\[ \delta \varepsilon_{i, f}(r, t) = (\mathbf{n}_i \cdot \mathbf{n}_r) \alpha_p \sum_{j=1}^{N} \delta \left( r - r_j(t) \right), \quad (3.1.1.3.1) \]

\[ \delta \varepsilon_{i, f}(q, t) = \int_V d^3 r \exp(iq \cdot r) \delta \varepsilon_{i, f}(r, t) = (\mathbf{n}_i \cdot \mathbf{n}_r) \alpha_p \sum_{j=1}^{N} \exp iq \cdot r_j(t) \quad (3.1.1.3.2) \]

where \( r_j(t) \) represents the position of particle \( j \) in the scattering volume \( V \); the prime denotes the sum is over the particles within the scattering volume. To make this constraint of the sum explicit, let us define the following variable, of which the value depends on whether particle \( j \) is the scattering volume \( V \)

\[ b_j(t) = \begin{cases} 1 & j \in V \\ 0 & j \notin V \end{cases} \quad (3.1.1.3.3) \]

Now equation 3.1.1.3.1 and 3.1.1.3.2 can be written as

\[ \delta \varepsilon_{i, f}(r, t) = (\mathbf{n}_i \cdot \mathbf{n}_r) \alpha_p \sum_j b_j(t) \delta \left( r - r_j(t) \right), \quad (3.1.1.3.4) \]

\[ \delta \varepsilon_{i, f}(q, t) = \int_V d^3 r \exp(iq \cdot r) \delta \varepsilon_{i, f}(r, t) = (\mathbf{n}_i \cdot \mathbf{n}_r) \alpha_p \sum_j b_j(t) \exp iq \cdot r_j(t). \quad (3.1.1.3.5) \]

Since the particles are uncorrelated, the time-correlation of \( \delta \varepsilon_{i, f}(q, t) \) can be expressed as the superposition of self-correlation of each particle
\[
\langle \delta \epsilon^*_j(r,0) \delta \epsilon^*_j(r,t) \rangle = (\mathbf{n}_i \cdot \mathbf{n}_j)^2 \alpha^2 \sum_j b_j(0)b_j(t) \exp iq \cdot (\mathbf{r}_j(t) - \mathbf{r}_j(0)) \right]. \tag{3.1.1.3.6}
\]

For the times when particle \( j \) leaves the scattering volume, this particle will not contribute to the correlation function presented in equation 3.1.1.3.6. Also, \( \exp iq \cdot (\mathbf{r}_j(t) - \mathbf{r}_j(0)) \) becomes considerably different from value 1 for the times when the displacement \( \mathbf{r}_j(t) - \mathbf{r}_j(0) \) is comparable to \( q^{-1} \). We can use diffusion theory to estimate these two time scales.

According to the diffusion theory, the mean-square displacement \( L^2 \), of a particle along a given dimension at time \( \tau \) can be expressed as

\[
L^2 = 2D\tau, \tag{3.1.1.3.7}
\]

where \( D \) is the diffusion coefficient of the particle. Let us denote the characteristic dimension of the scattering volume as \( L \). The two time scales for a particle to travel a distance of \( L \) and \( q^{-1} \) can be expressed as

\[
\tau_L \sim L^2/D, \tag{3.1.1.3.8}
\]

\[
\tau_q \sim (q^2D)^{-1}. \tag{3.1.1.3.9}
\]

Thus the ratio of these two time scales is
\[ \frac{\tau_L}{\tau_q} = (qL)^2. \quad (3.1.1.3.10) \]

In light scattering experiments, \( q \approx 10^5 \text{cm}^{-1} \) and \( L \approx 0.01 \text{ to } 0.1 \text{ cm}, \) so that \( \frac{\tau_L}{\tau_q} \) ranges from \( 10^4 \) to \( 10^6. \) This means that \( \exp iq \cdot (r_j(t) - r_j(0)) \) decays considerably well before the particle \( j \) leaves the scattering volume. Thus \( b_j(0)b_j(t) = b_j(0)b_j(0) \) is a good approximation for equation 3.1.1.3.6. We know that \( b_j(0)b_j(0) = b_j(0) \) since \( b_j(0) \) can only be 0 or 1. Therefore

\[
\langle \delta e^*_q(r,0) \delta e_q(r,t) \rangle = (\mathbf{n}_i \cdot \mathbf{n}_j)^2 \alpha_p^2 \left\langle \sum_j b_j(0) \exp iq \cdot (r_j(t) - r_j(0)) \right\rangle = (\mathbf{n}_i \cdot \mathbf{n}_j)^2 \alpha_p^2 \left\langle \sum_j \langle b_j(0) \rangle \langle \exp iq \cdot (r_j(t) - r_j(0)) \rangle \right\rangle, \quad (3.1.1.3.11)
\]

where we assume the displacement of a particle is independent of whether this particle is initially in the scattering volume.

Since \( \langle \exp iq \cdot (r_j(t) - r_j(0)) \rangle \) is an ensemble average, it should be the same for all the particles. Also note that \( \sum_j \langle b_j(0) \rangle = \langle N \rangle, \) where \( \langle N \rangle \) is the average number of particles in the scattering volume \( V. \) Therefore, equation 3.1.1.3.11 can be simplified as
\[
\langle \delta \varepsilon_g^* (r,0) \delta \varepsilon_g (r,t) \rangle = \left( \mathbf{n}_i \cdot \mathbf{n}_j \right)^2 \alpha_p^2 \langle N \rangle \left( \exp i \mathbf{q} \cdot (r(t) - r(0)) \right).
\] (3.1.1.3.12)

This equation implies that the characteristic decay time of \( \langle \delta \varepsilon_g (q,0) \delta \varepsilon_g (q,t) \rangle \) and \( \langle E_s^*(R,t) E_s(R,t) \rangle \) is of the same order of \( \tau_q \sim (q^2 D)^{-1} \). In fact, it can be shown that [42]

\[
\left\langle \exp i \mathbf{q} \cdot (r(t) - r(0)) \right\rangle = \exp(-q^2 D t).
\] (3.1.1.3.13)

Combine equation 3.1.1.3.12, and 3.1.1.3.13

\[
\langle \delta \varepsilon_g^* (r,0) \delta \varepsilon_g (r,t) \rangle = \left( \mathbf{n}_i \cdot \mathbf{n}_j \right)^2 \alpha_p^2 \langle N \rangle \exp(-q^2 D t).
\] (3.1.1.3.14)

Therefore, the characteristic decay time of \( \langle \delta \varepsilon_g (q,0) \delta \varepsilon_g (q,t) \rangle \) and \( \langle E_s^*(R,t) E_s(R,t) \rangle \) can be expressed in terms of the diffusion coefficient of the particles

\[
\tau_c = (q^2 D)^{-1}.
\] (3.1.1.3.15)

According to the Einstein relation and Stokes approximation,
\[ D = \frac{K_B T}{\zeta}, \quad (3.1.1.3.16) \]
\[ \zeta = 6\pi \eta a, \quad (3.1.1.3.17) \]

where \( \zeta \) is the friction constant, \( \eta \) the viscosity of the solvent, and \( a \) the radius of the spherical particle.

Thus from the characteristic decay time of the correlation time of the scattered light, one can calculate the diffusion coefficient and the radius for mono-dispersed spherical particles

\[ D = \frac{1}{q^2 \tau_c}, \quad (3.1.1.3.18) \]
\[ a = \left( \frac{k_B T q^2}{6\pi \eta} \right) \tau_c . \quad (3.1.1.3.19) \]

3.1.1.4. The Spectral Density

The spectral density of the time-correlation function of the scattered light is defined as

\[ I_E(\omega) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} dt e^{-i\omega t} \langle E_s^*(0) E_s(t) \rangle, \quad (3.1.1.4.1) \]
and Fourier inversion of this equation yields

\[ \langle E_s^*(0) E_s(t) \rangle = \int_{-\infty}^{\infty} d\omega \ e^{i\omega t} I_\omega (\omega) . \]  

(3.1.1.4.2)

The spectral density \( I_\omega (\omega) \) is also referred as scattered-intensity spectrum because the average intensity, \( I_s \), of the scattered light can be expressed as

\[ I_s = \frac{c}{8\pi} \left| \langle E_s(0) \rangle \right|^2 = \frac{c}{8\pi} \int_{-\infty}^{\infty} d\omega \ I_\omega (\omega) . \]  

(3.1.1.4.3)

Recall that the time-correlation function of the scattered field (see section 3.1.2) can be expressed as

\[ \langle E_s^*(R,0) E_s(R,t) \rangle = \frac{k_f^4 |E_0|^2}{16\pi^2 R^2 \epsilon_0^2} \left\langle \delta \varepsilon_{ij}(q,0) \delta \varepsilon_{ij}(q,t) \right\rangle \exp(-i\omega t) . \]  

(3.1.1.2.7)

The spectral density of light scattered in to that detector such that

\[ (n_s,k_s,n_s) \rightarrow (n_f,k_f,n_f) \]

can be written as
where $I_0 = |E_0|^2$. The spectrum density of the scattered light is measured in filter experiments (see section 3.2).

### 3.1.2. The Static Structure Factor

The time-correlation function and spectrum density of scattered light reveal the dynamic information of the scattering media (such as diffusion coefficient we discussed in section 3.1.1.3). The structural information of the media, such as the shape and size of the scatters, can be obtained from the scattered light intensity and its angular dependence. In this section, I will introduce the static structure factor obtained from scattered light intensity. To simplify the discussion, we will again consider mono-dispersed spherical particles in suspension as we did in section 3.1.1.3. The “solution” is dilute enough so that the particles are uncorrelated. The scattered light by the small solvent molecules is negligible since it is much weaker compare with the scattered light by the particles.
The intensity of the scattered light, with scattering vector \( q \) and long distance \( R \) from the center of the scattering volume, for a medium with isotropic scatters can be expressed as (see equation 3.1.2.4)

\[
I(q, R) = \left\langle |E_0(q, R)|^2 \right\rangle = (n_1 \cdot n_r)^2 \frac{k^4|E_0|^2}{16\pi^2 R^2 \varepsilon_0^2} \left\langle |\delta \varepsilon(q)|^2 \right\rangle , \tag{3.1.2.1}
\]

where \( \delta \varepsilon(q, t) \) are the momentum Fourier transformation of the fluctuation of the local dielectric constant \( \delta \varepsilon(r, t) \) (see figure 3.1.1.2.1 and 3.1.1.1.2)

\[
\delta \varepsilon(q, t) = \int_V \, d^3 r \exp(iq \cdot r) \delta \varepsilon(r, t). \tag{3.1.2.2}
\]

Note the integral in equation 3.1.2.2 is over the scattering volume \( V \). The fluctuation of the dielectric constant \( \delta \varepsilon(r, t) \) results mainly from the difference between the dielectric constant of the particles and that of the solvent. Let us assume they are different by value \( \alpha \). Intuitively, we know that \( \delta \varepsilon(r, t) \) will have value \( \alpha \) inside any particles and value 0 outside the particles (in the solvent).

Therefore if the radius of the particles is \( a \), \( \delta \varepsilon(r, t) \) can be written as

\[
\delta \varepsilon(r, t) = \alpha \sum_j f\left(r - r_j(t)\right), \tag{3.1.2.3}
\]
where $\mathbf{r}_j(t)$ is the center of mass position of particle $j$, and $f(\mathbf{r} - \mathbf{r}_j(t))$ is defined as

$$
f(\mathbf{r} - \mathbf{r}_j(t)) = \begin{cases} 
1 & \text{if } |\mathbf{r} - \mathbf{r}_j(t)| \leq a \\
0 & \text{if } |\mathbf{r} - \mathbf{r}_j(t)| > a 
\end{cases}.
$$

Since the particles are uncorrelated, $\langle |\delta \varepsilon(\mathbf{q})|^2 \rangle$ can be expressed as a superposition of the contribution from each particle in the scattering volume

$$
\langle |\delta \varepsilon(\mathbf{q})|^2 \rangle = \langle N \rangle \left\langle |\delta \varepsilon'(\mathbf{q})|^2 \right\rangle,
$$

where $\langle N \rangle$ is the average number of scatters in the scattering volume, and $\delta \varepsilon'(\mathbf{q}, t)$ is the integral over the volume $v_i$ of individual scatter ($v_i = \frac{4}{3} \pi a^3$ for a spherical particle)

$$
\delta \varepsilon'(\mathbf{q}, t) = \alpha \int_{v_i} d^3 r \exp(i\mathbf{q} \cdot \mathbf{r}),
$$

$$
\langle |\delta \varepsilon(\mathbf{q})|^2 \rangle = \langle N \rangle \alpha^2 \left\langle \int_{v_i} d^3 r \exp(i\mathbf{q} \cdot \mathbf{r}) \right\rangle^2.
$$

If we define the static structure factor $S(\mathbf{q})$ as
The scattering intensity can be expressed as

\[
I(q, R) = \left| \left\langle \mathbf{E}(\mathbf{q}, R) \right\rangle \right|^2 = (n_i \cdot n_t)^2 \frac{k^4 |E_0|^2}{16\pi^2 R^2 \varepsilon_0^2} \langle N \rangle \alpha_p^2 S(q),
\]  

where

\[
\alpha_p = \alpha v_1.
\]

After the integration in equation 3.148 is carried out for spherical particles with radius \(a\), we obtain

\[
S(q) = \frac{\sin (qa)}{qa} - \cos (qa) \left( qa \right).
\]

If we express the scattering vector \(q\) in terms of the scattering angle \(\theta\), wave length \(\lambda\), and define \(x\) as

\[
x = qa = \frac{4\pi a}{\lambda} \sin \left( \frac{\theta}{2} \right),
\]

the structure factor can be written as

\[
S(x) = \left[ \frac{3}{x^2} \left( \frac{\sin x}{x} - \cos x \right) \right]^2.
\]
Figure 3.2.4.1 shows the structure factor as a function of $x$. When $x \to 0$, either the scattering angle $\theta$ is very small or $\lambda \gg a$, $S(x) \to 1$. As $x$ increases (as $\theta$ increases), $S(x)$ becomes less than 1 and experiences several local minimums and maximums. This means that the intensity of the scattered light will experience several local minimums and maximums as the scattering angle increases (the scattering intensity is proportional to $S(x)$). The radius of the particles can be calculated from the scattering angles that correspond to the local minimums of the scattered light intensity (see chapter 5 for detailed discussion).

For particles of arbitrary shape, the definition of static structure and its relation with scattered light intensity (equation 3.1.2.8 and 3.1.2.9) still hold. The ensemble average in equation 3.1.2.8 should be an average over all orientation of the particles relative to the scattering vector $q$. The radius of gyration $R_g$ of a particle can be calculated from the structure factor at $q \to 0$ (see reference 1 for detailed discussion).
3.1.2.1 The structure factor for spherical particle \( x = 4\pi a \sin(\theta/2)/\lambda \). The scale of \( S(x) \) in the second plot is reduced 100 fold to show the local minimums and maximums.

3.2. Optical Mixing Techniques

In modern light scattering experiment, both the intensity and the spectral distribution (or the equivalent, auto-correlation function) of the scattered light are measured. A photo-multiplier is the main detector, but the pre and post photo-multiplier systems differ depending on the frequency change of the scattered light. The three different method known as filter, homodyne, and heterodyne methods, are shown in Figure 3.2.1.
The filter experiments (see figure 3.2.1 (a)) measure the spectrum density of the scattered light, and the optical mixing experiments measure the time-correlation function of the scattered light. Filter technique is used when the relaxation time is less than $10^{-6}$ sec. This technique does not have enough resolution for slower process. For fluctuations with relaxation time from $10^{-6}$ to 1 sec, optical mixing techniques (see figure 3.2.1 (b) & (c)) must be used.
Optical mixing techniques are the optical analogs of the beating techniques developed in radio-frequency spectroscopy (Forrester, 1961). They are used to study the dynamics of relatively slow processes such as macro-molecular diffusion, the dynamics of fluctuations in the critical region, and the motility of micro-organisms.

3.2.1. Homodyne and Heterodyne Method

In optical mixing methods, the scattered light impinges directly on the photo-multiplier cathode (see Figure 3.2(b) & (c)). In the homodyne (or self-beat) method only the scattered light impinges on the photo cathode, while in the heterodyne method a small portion of unscattered light is mixed with the scattered light on the cathode surface. The instantaneous current output, \(i(t)\), is proportional to the intensity of the incident light, or square of the incident electric field, i.e. \(i(t) \propto \left|E(t)\right|^2\).

The output from photo-multiplier cathode is then passed through an auto-correlator, which calculates the time auto-correlation function

\[
\langle i(0)i(t) \rangle = B \langle |E_0(0)|^2 |E_0(t)|^2 \rangle ,
\]

where \(B\) is a proportionality constant.
To illustrate the difference of homodyne and heterodyne method, let us define two time auto-correlation of scattered light $E_s(t)$

$$I_1(t) = \langle E_s^*(0)E_s(t) \rangle, \quad \text{(3.2.1.2)}$$

$$I_2(t) = \langle |E_s(0)|^2 |E_s(t)|^2 \rangle. \quad \text{(3.2.1.3)}$$

If $E_s$ is a Gaussian stochastic variable, it can be shown that (see appendix in section 3.2.3)

$$I_2(t) = |I_1(0)|^2 + |I_1(t)|^2. \quad \text{(3.2.1.4)}$$

In homodyne method (see Figure. 3.2(b)), auto-correlation function of the photo-multiplier output can be expressed as

$$\langle i(0)i(t) \rangle = BI_2(t). \quad \text{(3.2.1.5)}$$

In heterodyne method, a small portion of the unscattered light, $E_{LO}(t)$, is mixed with the scattered light, $E_s(t)$, at the photo-multiplier cathode (See Figure. 3.2(c)). Therefore the auto-correlation function of photo-multiplier output can be expressed as
\[ \langle i(0) i(t) \rangle = B \left\langle \left| E_{\text{LO}}(0) + E_s(0) \right|^2 \left| E_{\text{LO}}(t) + E_s(t) \right|^2 \right\rangle. \]  (3.2.1.6)

Simplifications of this equation can be made under the following three conditions:

1. The fluctuations of the unscattered light are negligible;

2. The experimental condition can be adjusted to satisfy \( |E_{\text{LO}}(t)| >> |E_s(t)| \), so that the term \( \left\langle \left| E_s(0) \right|^2 \left| E_s(t) \right|^2 \right\rangle \) is negligible;

3. The unscattered and scattered light are statistically independent so that

\[
\left\langle \left| E_{\text{LO}}(t) \right|^2 \left| E_s(t) \right|^2 \right\rangle = \left\langle \left| E_{\text{LO}}(t) \right|^2 \right\rangle \left\langle \left| E_s(t) \right|^2 \right\rangle.
\]

The auto-correlation function of the output from photo-multiplier cathode can be estimated as

\[
\langle i(0) i(t) \rangle \equiv B \left[ I_{\text{LO}}^2 + 2I_{\text{LO}} \text{Re} I_i(t) \right], \quad (3.2.1.7)
\]

where \( I_{\text{LO}} = \left\langle \left| E_{\text{LO}} \right|^2 \right\rangle \).

In summary, homodyne method measures the time-correlation function of the intensity of the scattered light; and heterodyne measures the time-correlation function of the scattered electric field. These two correlation functions yields the same information about the scattering medium if the scattered electric field is a Gaussian stochastic variable.
3.2.2. Gaussian Approximation

The mathematical proof of equation 3.2.1.4 will be provided in this section. This equation leads to the well known conclusion that homodyne and heterodyne method obtain the same information about the scattering medium if the scattered electric field is a zero-mean Gaussian stochastic variable (see equation 3.2.1.4).

The auto-correlation function of scattered light $E_s$ and intensity $|E_s|^2$ defined in section 3.2.1 can be written as follows

$$I_1(t) = \langle E_s^*(0), E_s(t) \rangle = \int dE_s(0) \int dE_s(t) E_s^*(0) \, \rho[E_s(0), E_s(t)] \, E_s(t); \,
\quad (3.2.2.1)$$

$$I_2(t) = \langle |E_s(0)|^2, |E_s(t)|^2 \rangle = \int dE_s(0) \int dE_s(t) |E_s(0)|^2 \, \rho[E_s(0), E_s(t)] \, |E_s(t)|^2, \quad (3.2.2.2)$$

where $\rho[E_s(0), E_s(t)]$ is joint density distribution function for $E_s(0)$ and $E_s(t)$.

Our mission is to prove

$$I_2(t) = |I_1(0)|^2 + |I_1(t)|^2. \quad (3.2.1.4)$$

To simplify our discussion, let us define a two-dimensional Gaussian random vector $x$ as
\( x = \begin{pmatrix} E_s(0) \\ E_s(t) \end{pmatrix} \).  

(3.2.2.3)

The joint density distribution function for \( E_s(0) \) and \( E_s(t) \) can be expressed as

\[
P[E_s(0), E_s(t)] = p_x(x) = \frac{\exp[-\frac{1}{2} x^T \Lambda_x^{-1} x]}{2\pi \left| \Lambda_x \right|^\frac{1}{2}},
\]

(3.2.2.4)

where \( \Lambda_x \) is the correlation matrix of \( x \) defined as

\[
\Lambda_x = \langle xx^T \rangle = \begin{pmatrix} \langle |E_s|^2 \rangle & \langle E_s^*(0)E_s(t) \rangle \\ \langle E_s(0)E_s^*(t) \rangle & \langle |E_s|^2 \rangle \end{pmatrix} = \begin{pmatrix} 1 & \hat{I}_1(t) \\ \hat{I}_1^*(t) & 1 \end{pmatrix}.
\]

(3.2.2.5)

where \( \hat{I}_1(t) \) is the normalized correlation of scattered light as

\[
\hat{I}_1(t) = \frac{\langle E_s^*(0)E_s(t) \rangle}{\langle |E_s|^2 \rangle}.
\]

(3.2.2.6)

From equation 3.2.2.5, we can obtain the inverse of \( \Lambda_x \) as
\[ \Lambda_1^{-1} = \frac{1}{\langle |E_s|^2 \rangle \left[ 1 - \left| \hat{I}_1(t) \right|^2 \right]} \begin{pmatrix} 1 & -\hat{I}_1(t) \\ -I_1^*(t) & 1 \end{pmatrix}. \]  

(3.2.2.7)

Combine equation 3.2.2.4, 3.2.2.5 and 3.2.2.7, the joint density distribution function for \( E_s(0) \) and \( E_s(t) \) can be expressed as

\[
P[E_s(0), E_s(t)] = \frac{\exp\left\{ -\frac{|E_s(0)|^2}{2\langle |E_s|^2 \rangle} - \frac{|E_s(t) - \hat{I}_1(t)E_s(0)|^2}{2\langle |E_s|^2 \rangle} \right\}}{2\pi \langle |E_s|^2 \rangle \left[ 1 - \left| \hat{I}_1(t) \right|^2 \right]^{\frac{3}{2}}}. \]  

(3.2.2.8)

Substitute this in the intensity correlation function defined in equation 3.2.2.2,

\[
I_2(t) = \frac{1}{2\pi \langle |E_s|^2 \rangle \left[ 1 - \left| \hat{I}_1(t) \right|^2 \right]^{\frac{3}{2}}} \int dE_s(0) \int dE_s(t) 
\exp\left\{ -\frac{|E_s(0)|^2}{2\langle |E_s|^2 \rangle} - \frac{|E_s(t) - \hat{I}_1(t)E_s(0)|^2}{2\langle |E_s|^2 \rangle \left[ 1 - \left| \hat{I}_1(t) \right|^2 \right]} \right\} |E_s(t)|^2. \]  

(3.2.2.9)

If we define \( E_s'(t) \) is defined as
\[ E_s'(t) = E_s(t) - \hat{I}_1(t) \times E_s(0), \quad (3.2.2.10) \]

then equation 3.2.2.9 can be written as

\[
I_2(t) = \frac{1}{2\pi \left< |E_s| \right> \left( 1 - |\hat{I}_1(t)|^2 \right)} \int dE_s(0) \int dE_s(t) \left| E_s(0) \right|^2 \\
\times \exp \left\{ -\frac{|E_s(0)|^2}{2 \left< |E_s|^2 \right>} - \frac{|E_s'(t)|^2}{2 \left< |E_s|^2 \right> \left( 1 - |\hat{I}_1(t)|^2 \right)} \right\} \\
\times \left\{ |E_s'(t)|^2 + 2 \Re \left( \hat{I}_1(t) E_s(0) E_s'(t) \right) + \hat{I}_1(t)^2 |E_s(0)|^2 \right\}. \quad (3.2.2.11)
\]

\( E_s' \) should be a zero-mean Gaussian variable since \( E_s \) is a zero-mean Gaussian variable. Furthermore, \( E_s(0) \) and \( E_s'(t) \) are independent because

\[
\left< E_s^*(0) E_s'(t) \right> = \left< E_s^*(0) \right> \left< E_s'(t) \right>. \quad (3.2.2.12)
\]

The right hand side of equation 3.2.2.12 equals zero because both \( E_s \) and \( E_s' \) are zero-mean random variables. And the left hand side of equation 3.2.2.12 equals zero because
\[
\langle E_s^*(0) E_s'(t) \rangle = \langle E_s^*(0) E_s(t) \rangle - I_1(t) \langle |E_s|^2 \rangle = \langle E_s^*(0) E_s(t) \rangle - \frac{\langle E_s^*(0) E_s(t) \rangle}{\langle |E_s|^2 \rangle} \langle |E_s|^2 \rangle = 0.
\]

(3.2.13)

Using equation 3.2.12 and 3.2.13, we can simplify the intensity correlation function calculated in equation 3.2.11 as

\[
I_2(t) = \frac{1}{2\pi \langle |E_s|^2 \rangle \left[ 1 - |I_1(t)|^2 \right]^2} \int dE_s(0) \int dE_s(t) \left[ \left| E_s'(t) \right|^2 |E_s(0)|^2 + \left| I_1(t) \right|^2 |E_s(0)|^4 \right] \\
\times \exp \left\{ -\frac{|E_s(0)|^2}{2\langle |E_s|^2 \rangle} - \frac{|E_s'(t)|^2}{2\langle |E_s|^2 \rangle \left[ 1 - |I_1(t)|^2 \right]} \right\} \\
= \left( \langle |E_s|^2 \rangle^2 + |I_1(t)|^2 \langle |E_s|^2 \rangle^2 \right) = |I_1(0)|^2 + |I_1(t)|^2.
\]

(3.2.14)

Therefore, the homodyne and heterodyne method obtain the same information about the scattering medium if the scattered electric field is a zero-mean Gaussian stochastic variable.
4. Light Scattering by Colloidal Micro-gels

I will present our studies on volume phase transition of hydrophobic and hydrogen bondable micro-gels using dynamic and static light scattering techniques. The sample preparation will be described in section 4.1. The experiment setup will be described in section 4.2. The experiment results and analyses will be discussed in section 4.3.

4.1. Sample Preparation

We used emulsion polymerization method to prepare the colloidal micro-gels. We dissolved the monomers, the cross-linkers, and the initiators in a huge amount of hot water. The solution was stirred and heated continuously during the polymerization. These monomers are with hydrophobic and hydrogen bonding interactions upon gelation. As we discussed in chapter 1, polymer-gels with hydrophobic interactions tend to collapse at high temperature. Thus as the polymerization proceeded, the polymer chains scattered in the solution collapsed and became the cores colloidal micro-gels.

There were two types of colloidal micro-gels in this experiment: pure N-isopropylacrylamide (NIPA) micro-gels and copolymer of NIPA and acrylic acid (AAc). The latter colloidal micro-gels were prepared [35] by emulsion
polymerization of 450 mg NIPA (monomer), 50 mg AAc (monomer), and 50 mg N,N'-methylenebisacrylamide (BIS, cross-linker) in 100ml of de-ionized water at 70°C under a nitrogen atmosphere. The pure NIPA micro-gels were prepared by inverse suspension polymerization [34] by professor Haruma Kawaguchi of Keio University.

The schematic representation of this polymerization process is shown in figure 4.1.1(a). We heated 95 ml de-ionized water in a three necked round bottom flask up to 70°C. The water was saturated with nitrogen gas and stirred at 120 round per minute. In the mean time, we dissolved 450 mg NIPA, 50 mg AAc and 50 mg BIS in 5 ml de-ionized water. After the water temperature in the three necked round bottom flask was stabilized at 70 °C, we added in this solution and 50 mg ammonium persulfate (APS, initiator). A few minutes later, the solution in the flask started to turn opaque. This indicated the formation of the colloidal micro-gels. The polymerization temperature was maintained at 70° C by circulating water from a Brinkmann Lauda RC-3. Typical reaction yields are of the order of 95% after 6 hours.

The next step was to remove any remaining monomers. We transferred the solution of colloidal poly (NIPA/AAc) micro-gels from the three necked round bottom flask into a dialysis tube and immersed this dialysis tube into a huge amount of de-ionized water. The water was stirred continuously, and replaced every half an hour for twelve hours. This process is shown in figure 4.1.1(b).
Fig. 4.1.1  (a) Schematic representation of the emulsion polymerization process of the colloidal micro-gels. In the three necked round bottom flask, a small amount of monomers, cross-linkers, and initiators are dissolved in a large amount of de-ionized water. Nitrogen gas saturates the solution in the flask through a pipette; and the solution is stirred with a magnetic stirrer. The flask is set in a bath of 70 °C water (the temperature is controlled by circulating the water from a Brinkmann Lauda RC-3, which is not shown here). (b) Schematic representation of removing the remaining monomers from the colloidal micro-gels. The colloidal micro-gels are filled into a dialysis tube. This dialysis tube is then immersed into a huge bath of de-ionized water, which is stirred slowly with a magnetic stirrer.

4.2. Experiment Setup

In our studies of the volume phase transition of the colloidal micro-gels, we conducted both dynamic and static light scattering experiments. I will describe the setup of these two experiment separately.
4.2.1. Dynamic light Scattering Setup

I will first describe the optical setup. Then the sample holder and the method to control the pH value and temperature will be discussed.

The dynamic light scattering setup for this experiment is a Microscopic Laser Light Scattering (MLLS) setup built by Dr. Michal Orkisz [44] (see figure 4.2.1.1). It is a modification of the conventional homodyne setup (see figure 3.2.1). A microscope was added to improve measurement precision for small samples. In addition, a stepping motor was installed to allow the systematic measurements from many independent scattering volume. These changes were mainly for the measurements of phase transition of bulk gels. I will discuss the advantages of this setup over the conventional one in section 6.2.

Figure 4.2.1.1 demonstrates Microscopic Laser Light Scattering (MLLS) setup. The source of the light was a Spectra Physics Helium-Neon laser (model 127) with an output power of about 50 mW. The light was transmitted through a single-mode optic fiber and then focused on the sample by a GRIN (Graded Refraction Index) lens. The distance between the lens surface and the sample is 4 mm. The focused waist of the light was under 10 μm. The output power from the GRIN lens is reduced to about 50 mW. The 90° scattered light traveled through and focused by the eyepieces of a Nikon OPTIPHOT microscope, and was than detected by a built-in optical fiber in the focal plane. The microscope had a Leitz L32 long working distance objective lens with adjustable aperture
and Gamma Scientific 10x eyepieces. There were two built-in optic fibers (model 700-10-36A with 50 \( \mu \text{m} \) fiber and 700-10-37A with 150 \( \mu \text{m} \) fiber). The larger fiber was often used; and the 50 \( \mu \text{m} \) fiber was only used when the scattering intensity was too high. The optic fiber transmitted the scattered light to a photo-multiplier (PMT) for the intensity measurements. The intensity signal was then passed to an auto-correlator as the traditional homodyne setup (not shown in Figure 4.2.2.1, see figure 3.2.1).

Fig. 4.2.1.1 Schematic representation Microscopic Laser Light Scattering (MLLS) setup. The incident light, transmitted through a single mode optic fiber, was focused on the sample by a GRIN lens. The 90 \( ^\circ \) scattered light was focused by the eyepieces of the microscope and then detected by an optic fiber, which is connected to a PMT.
The pH value and temperature control method and the sample holder is shown in figure 4.2.1.2. The colloidal micro-gels was injected into a micro-dialysis tube. The inner diameter of dialysis tube is only 150 micro meters. We then tightened both ends of the micro-dialysis tube and place it into a 100 micro liter micro-pipettes, the inner diameter of which was 1.31 miler meters. The pH value of the colloidal macro-gels were controlled by circulating pH solution through the micro-pipette. Since the micro-gels were confined in the micro-dialysis tube, the pH value can be changed continuously and reversibly. We finally place the micro-pipette into a glass cuvette. The temperature was controlled by circulating water from a Brinkmann Lauda RC-3 through the glass cuvette.
Fig. 4.2.1.2 A schematic representation of the sample holder and the control of pH value and temperature for the micro-gels. (a) The colloidal micro-gels were filled into a micro dialysis tube; (b) The dialysis tube was placed inside a micro pipette, and pH solution was circulated through the micro pipette; (C) The micro pipette was fixed in a glass cuvette, and temperature controlled water was circulated through the glass cuvette.

4.2.2. Static Light Scattering Setup

Figure 4.2.2.1 shows the schematic representation of the setup of the static light scattering experiment. The source of the light was a Spectra Physics Argon laser with the output power set at about 200 mW. The sample holder was a 100 micro-liter micro pipette, which was fixed in the center of a cylindrical cuvette. The direction of the incident light was perpendicular to the cuvette and the micro-pipette. The temperature was controlled by circulating water through the cuvette. A optic fiber transmitted the scattered light to a photo-multiplier (PMT) for the intensity measurements. The angular dependence was obtained
by rotating the PMT. The range of the scattering angle was from $31^\circ$ to $130^\circ$, with the average increment of $2^\circ$. Note that our static scattering setup was not designed to control pH value easily. We only measured the temperature dependence of the size of the micro-gels in the static light scattering experiments.

Fig. 4.2.2.1 A schematic representation of the static light scattering experiment. (a) The side view (b) The top view.

4.3. Measurements and Analyses

As discussed in section 3.1.1.3 and section 3.1.2, the size of small particles in suspension can be determined from the time correlation function and
angular dependence of the scattered light by them. The time correlation function of the scattered light by the micro-gels was measured in the dynamic light scattering experiment; whereas the angular dependence of which was measured in the static light scattering experiment. I will present the results and analyses in section 4.3.1 and 4.3.2.

4.3.1. Dynamic Light Scattering Experiments

The time correlation function of the scattered light by the micro-gels is a single exponential decay, and the size of the colloidal micro-gels can be calculated from the characteristic decay time of this correlation (see section 3.1.1.3). In this experiment, we measured the intensity correlation function instead of the correlation function of the scattered light. I will describe the equivalency of these two correlation functions, and present the experimental measurements and analyses.

The equivalency of the intensity correlation function and scattered light correlation function comes from the Gaussian approximation (see section 3.2.2). Since the colloidal micro-gels are fluid-like fluctuating media, in which the scattering matter can diffuse throughout the system. Thus the scattered light can be described by a zero-mean complex Gaussian random variable. In fact, the normalized intensity correlation function $g^{(2)}(t)$ can be expressed directly in terms of the normalized scattered light correlation function $g^{(1)}(t)$ as follows
The definitions of the normalized correlation functions can be found in section 5.1.2. The normalized correlation function of the scattered light from the microgels is single exponential decay (see section 3.1.1.3). Considering the measurement errors from the instrument and random noise, the normalized intensity correlation function can be expressed as

\[ g^{(2)}(t) - 1 = \left| g^{(1)}(t) \right|^2. \]  

\[ \text{Equation 4.3.1.1} \]

where \( r' \) is the characteristic decay time of the scattered light correlation function, \( \beta \) is an instrument parameter, \( R \) is the ratio of dynamic component to total intensity (see section 6.2 for detailed discussion). In this experiment, \( \beta \approx 0.8 \) and \( R \) should be very close to 1.

From equation 3.1.1.3.19, the average diameter \( d \) of the micro-gels can be expressed as

\[ d(pH, T) = \left[ \frac{k_B T q^2}{3 \pi \eta(T)} \right] \tau_c^{(1)}(pH, T), \]

\[ \text{Equation 4.3.1.3} \]
where \( k_B \), \( T \), \( q \), and \( \eta \) are the Boltzmann's constant, the temperature, the scattering vector and the viscosity of water. Note the viscosity of water is a function of temperature. The viscosity decreases as the temperature increases. The scattering vector \( q \) can be expressed in terms of wavelength \( \lambda (=633 \, \mu m) \) of the incident light, the reflection index \( n_w (=1.333) \) of water and the scattering angle \( \theta (=90^\circ) \) as follows

\[
q = \frac{4\pi n_w \sin(\theta/2)}{\lambda} = \frac{4\pi (1.333) \sin(\pi/4)}{.633} = 18.712 (\mu m)^{-1}.
\] (4.3.1.4)

The diameter of the micro-gels depend on both temperature and pH value. The temperature was set at certain value when we measured the pH dependence. To reduce the errors of measurement from random noise, we measured the intensity correlation functions of two hundred independent scattering volumes. We then calculated the average over these two hundred independent measurements. Figure 4.3.1.1 shows an example of the normalized intensity correlation functions for three pH values we measured at temperature \( T = 35.5^\circ C \). The formulation of the fitting curves is shown in equation 4.3.1.2.
Fig. 4.3.1.1 The normalized intensity correlation function of the scattered light by the NIPA-AAc micro-gels at various pH values. The temperature was fixed at 35.5 °C. (a) logarithm time scale. (b) linear time scale.
From figure 4.3.1.1, the intensity correlation function at pH = 10.33 decayed much slower than both of those at pH = 3.16 and pH = 12.4. Since the temperature was fixed, slower decay indicated larger particle size (see equation 4.3.1.2). One can also see that the fitting was better for the correlation functions that decayed faster, which correspond to the collapsed states. I will address the implications of the fitting after the discussion of the pH dependence of the size of the micro-gels.

Figure 4.3.1.2 shows the calculated diameter as function of pH from all the measurements at temperature $T = 35.5 \, ^\circ C$. As the pH increased from 2.5 to 12.4 the size of the micro-gels experienced steady increase, drastic increase, peak, and decrease. The size peaked at pH $\approx 10.5$.

The pattern of the pH dependence of the gel size can be explained by the changes in hydrogen bounding and electrostatic interactions. At low pH the strong hydrogen bounding collapsed the micro-gels (see section 1.2.1.3). As we increased the pH, the micro-gels became swollen due to the weakened hydrogen bounding as well as the osmotic from the counter-ions (see section 1.2.1.4) when pH became higher than 7. When pH became very high, the increased sodium ions provided better shield for the negative charges in the micro-gels. Thus the gel size decreased when pH was higher than 10.5.
Fig. 4.3.1.2 The pH dependence of the diameter of NIPA-AAc micro-gels measured in the dynamic light scattering experiment. The experiment was conducted under a fixed temperature \((T = 35.5 \, ^\circ C)\).

Figure 4.3.1.2 shows the continuous albeit drastic volume changes in response to the pH changes. The diameter increased more than 12-fold (from 0.25 \(\mu m\) to 3.1 \(\mu m\)), which corresponds to more than 1800-fold increases in volume.
The lack of the discontinuous volume phase transition in the micro-gels might be due to the high molar ratio of cross-linker to monomer. This ratio was about 10% for the micro-gels, whereas the ratio for the bulk NIPA gels we used to observe phase transition was on the order of 1%. We attempted to make micro-gels with lower cross-linker to monomer ratio, but the measured correlation function of the scattered light suggested these micro-gels were poly-dispersed (see discussions below). It is difficult to determine the average size of poly-dispersed particles using light scattering technique.

The correlation function of the scattered light by the micro-gels in the swollen states deviated from single exponential decay (see figure 4.3.1.1(b)); whereas in the collapsed states single exponential decay well described this correlation function. This deviation suggested that the micro-gels were not mono-dispersed in the swollen states.

One hypothesis for this poly-dispersity is as follows: the ratio of the cross-linkers or acrylic acid was different among the micro-gels while the total number of composite monomers was the same for each micro-gel. This hypothesis leads to the poly-dispersity in the swollen states and mono-dispersity in the collapsed states. In the collapsed states, the volume of each micro-gel is determined by number of composite monomers. In the swollen states, the volume is determined by the strength of shear modulus and osmotic pressure of
the counter-ions. The shear modulus and osmotic pressure depend on the density of the cross-linkers and acrylic acid, respectively.

We also measured the temperature dependence of pure NIPA micro-gels and NIPA-AAc micro-gels. The temperature dependence of the NIPA gel will be shown in section 4.3.2 with the static scattering measurements. Figure 4.3.1.3 shows the temperature dependence of the NIPA-AAc micro-gels at pH=10.6 and pH=5.8. At pH=10.6, the micro-gel remained swollen even at high temperature (~ 80 °C). At pH=5.8, the volume changes between 35 and 42 were drastic but continuous.
Temperature Dependence of NIPA-AAc Micro-Gels at Different pH

Fig. 4.3.1.3 The temperature dependence of the diameter of the NIPA-AAc micro-gels measured in the dynamic light scattering experiment.

4.3.2. Static Light Scattering Experiments

The angular dependence of the intensity of the scattered light by the micro-gels contains several local minimums and maximums, from which one can calculate the size of the micro-gels (see section 3.1.2).
As shown in figure 4.2.2.1, the temperature of the micro-gels was controlled by circulating water through the sample holder. Each time when we changed the temperature, we waited for about half an hour to allow the micro-gels to reach equilibrium. At each temperature, we measured the angular distribution of the intensity of the scattered light. The range of the scattering angle was from 31° to 130° and the average increment was 2°. In other words, we measured the intensity at 50 different scattering angles at each temperature. To reduce the measurement errors, we measured 30 times at each scattering angle and calculated the average scattering intensity over these 30 data points.

4.3.2.1. Measurements

Note the scattering volume is proportional to $1/\sin \theta$ in our experiment setup (As shown in figure 4.2.2.1), where $\theta$ is the scattering angle. Thus we multiplied the measured intensity by the factor $\sin \theta$ to get the scattered intensity from an equivalent scattering volume for various the scattering angles. This adjustment has been made in all the relevant figures in this section.

Figure 4.3.2.1.1(a) shows the angular dependence of the intensity of the scattered light at the temperature of 33 °C. Compare figure 4.3.2.1.1(a) with figure 3.1.2.1, we can see some similarities between the profiles of these two curves. The detailed analyses will be carried out in section 4.3.2.2.
Angular Dependence of the Intensity of the Scattered Light by NIPA Micro-gels at T = 33°C

Fig. 4.3.2.1.1(a) The angular dependence of the intensity of the scattered light by NIPA micro-gels. The diamond-shaped dots represent the average intensity value over 30 measurements. The value of the error bar is ± the standard deviation of the 30 measurement results.

To easily visualize the local minimums and maximums, we plotted the intensity of the scattered light with the logarithm scale in figure 4.3.2.1.1 (b).
From this plot one can see the two local minimums, around 58° and 108°, within the range of scattering angle we measured.

**Angular Dependence of the Intensity of the Scattered Light by NIPA Micro-gels at T = 33°C**

Fig. 4.3.2.1.1(b) The angular dependence of the intensity of the scattered light by NIPA micro-gels with logarithm scale. The diamond-shaped dots represent the average intensity value over 30 measurements. The value of the error bar is ± the standard deviation of the 30 measurement results.

Figure 4.3.2.1.2 (a) and 4.3.2.1.2 (b) show the angular dependence of the intensity of scattered for various temperatures. Figure 4.3.2.1.2 (a) shows
the measurements as we increased the temperature; whereas figure 4.3.2.1.2 (b) shows those as we decreased the temperature. These two figures demonstrate that the higher the temperature, the larger the scattering angles corresponding with the local minimums. Let us denote $\theta_M$ as the scattering angle corresponding to the first local minimum of the intensity. From figure 4.3.2.1.2 (a) one can see $\theta_M$ is around $50^{\circ}$ at temperature of $20^{\circ}$ C; whereas $\theta_M$ is around $70^{\circ}$ at temperature of $40^{\circ}$ C. The temperature dependence of the micro-gel size calculated from $\theta_M$ will be presented in section 4.3.2.2.
Angular Dependence of the Intensity of the Scattered Light by NIPA Micro-gels as Temperature Increases

Fig. 4.3.2.1.2(a) The angular dependence of the intensity of the scattered light by NIPA micro-gels as temperature increases. The value of scattering angles that correspond to the local minimums increase as temperature increases. The solid lines represent the average intensity value over 30 measurements. The value of the error bar equals ± the standard deviation of the 30 measurement results.
Angular Dependence of the Intensity of the Scattered Light by NIPA Micro-gels as Temperature Decreases

Fig. 4.3.2.1.2(b) The angular dependence of the intensity of the scattered light by NIPA micro-gels as temperature decreases. The value of scattering angles that correspond to the local minimums decrease as temperature decreases. The solid lines represent the average intensity value over 30 measurements. The value of the error bar equals ± the standard deviation of the 30 measurement results.
4.3.2.2. Analyses

I will describe two models we used to calculate the temperature dependence of the average diameter of the micro-gels, and compare these results with the one from the dynamic light scattering experiment. I will first explain the motivation of using these two models, and discuss both models in details.

The motivation to use the two models, the sphere model and the shell model, was to bring consistency between the results calculated from static and dynamic light scattering experiment. The shell model worked better at high temperature, and the sphere model worked better at low temperature. These two models gave us some insights of the structure of the micro-gels at different temperature regions.

The sphere model describes the micro-gels as mono-dispersed spherical particles with uniform density. The shell model describes the micro-gels as mono-dispersed hollow spherical particles. At high temperature region, the calculated diameters from the sphere model are larger than that from the dynamic light scattering experiment (see figure 4.3.2.2.1(a)). The shell model explained the discrepancies reasonably well at high temperature region (see figure 4.3.2.2.1(b)), but introduced new discrepancies at low temperature region.
Temperature Dependence of Diameter of Pure NIPA Micro-Gel

Fig. 4.3.2.1(a) The temperature dependence of the diameter of NIPA micro-gels calculated from the sphere model and the dynamic light scattering experiment.
Temperature Dependence of Diameter of Pure NIPA Micro-Gel

Fig. 4.3.2.2.1(b) The temperature dependence of the diameter of NIPA micro-gels calculated from the sphere model, the shell model, and the dynamic light scattering experiment.

Let us start with the sphere model, where the micro-gels were described as mono-dispersed spherical particles with uniform density. The angular dependency of the scattered light is proportional to the static structure factor, and the structure factor for mono-dispersed spherical particle in suspension can be expressed as (see section 3.1.2)
\[ S(x) = \left[ \frac{3}{x^2} \left( \frac{\sin x}{x} - \cos x \right) \right]^2 \]  

(4.3.2.2.1)

where \( x \) can be expressed in terms of the scattering angle \( \theta \), the radius \( a \) of the particles, the reflective index \( n_w \) of water, and the wave length \( \lambda \) of the incident light as 
\[ x = \frac{4\pi n_w a \sin(\theta/2)}{\lambda}. \]

The static structure factor as a function of \( x \) is shown in figure 4.3.2.2.2. Let us represent the \( x \) value corresponding to the first local minimum by \( x_M \).

From figure 4.3.2.2.2, one can see that \( x_M \) is about 4.5. From numerical estimation, \( x_M = 4.4934 \). The diameter of the micro-gels can be calculate as
\[ d(T) = \frac{x_M \lambda}{2\pi n_w \sin[\theta_M(T)/2]}, \]  

(4.3.2.2.2)

where \( \theta_M(T) \) denotes the scattering angle corresponds to the first minimum of the scattered light intensity. This scattering angle is a function of temperature (see Fig. 4.3.2.1.2(a) and (b)). The wave length of the argon laser \( \lambda = 488 \mu m \), and the reflective index of water \( n_w = 1.333 \). The calculated temperature dependence of diameter is shown in figure 4.3.2.2.1(a).
The diameters calculated from the angular dependence of the intensity showed continuous volume changes as temperature was increased (see figure 4.3.2.2.1(a)). At high temperatures, the diameters were larger than those calculated from the dynamic light scattering experiment results.

To explain the discrepancies at high temperatures, we considered the shell model. The shell model describes the micro-gels as mono-dispersed hollow spherical particles. It may seem strange to assume the micro-gels as hollow particles. The physical meaning of this assumption is the believe that the structures are very different between the surface and the inside of the micro-gels. Because the colloidal NIPA micro-gel was produced by inverse suspension polymerization [34], the surface structure may well be different from the inside structure.

The static structure factor can calculated using.

\[
S(q) = \frac{1}{(4\pi a^2 \Delta a)^2} \left\langle a^2 \Delta a \int_0^{2\pi} d\phi \int_0^{\pi} d\theta \left[ \sin \theta \exp(iqa \cos \theta) \right]^2 \right\rangle
\]

\[
= \left( \frac{\sin(qa)}{qa} \right)^2 ,
\]

(4.3.2.2.3)

where \( a \) and \( \Delta a \) are the radius and the thickness of the hollow spherical particle. The scattering factor \( q \) can be expressed in terms of the scattering angle \( \theta \), the
incident wave length \( \lambda \), and the reflective index of water \( n_w \) as

\[
q = \frac{4\pi n_w \sin\left(\frac{\theta}{2}\right)}{\lambda}.
\]

As shown in figure 4.3.2.2, the local minimums of the static structure factor of the shell model are smaller than those of the sphere model. The local minimums for the shell model is given by \( x_m = m\pi \), where \( m \) can be any integer. From equation 4.3.2.2 the local minimums, we can calculate the temperature dependence of the diameter.

The temperature dependence of the diameter calculated from the shell model is shown in figure 4.3.2.1(b). At high temperature, these results are consistent with the those from the dynamic light scattering experiment. However, at low temperature these diameters are much smaller than those from dynamic light scattering experiment.

Figure 4.3.2.1(b) shows that near the NIPA transition temperature the diameters calculated from dynamic light scattering experiment were in between of those from the sphere and shell model. This indicates that the surface effects might be important.
4.4. Conclusions and Future Work

To accelerate the kinetics and the volume phase transition of gels for applications like drug delivery, we studied the pH and temperature dependence of colloidal micro-gels. We employed a new method to better control the pH value of the micro-gels with both hydrogen bounding and hydrophobic
interactions. The pH and temperature dependence of the micro-gels was measured using dynamic light scattering technique. We observed continuous albeit drastic changes of the volume of the micro-gels. The time for the micro-gels to reach equilibrium was less than a few minutes.

The lack of the discontinuous volume phase transition in the micro-gels might be due to the cross-linker to monomer ratio. This ratio of the micro-gel is ten times higher than that of the standard NIPA gel. The micro-gels with lower cross-linker to monomer ratio were poly-dispersed.

The temperature dependence of the NIPA micro-gels, which were prepared by inverse suspension polymerization, was also measured using the static light scattering technique. The comparison of the results from static light scattering and dynamic light scattering suggested that the density near the surface of the micro-gels was higher than the inner density in collapsed states.

Future work should include exploration of producing mono-dispersed micro-gels with lower cross-linker to monomer ratio. It is also interesting to investigate the surface structure of the micro-gels prepared by inverse suspension polymerization.
Part III

Exploring Glass Phase Transition of Heteropolymer Gels
ABSTRACT

The existence of glass phase transition of a heteropolymer gel with hydrogen bonding interaction was investigated using dynamic light scattering technique. Below certain temperature, the time correlation function of the scattered light by this heteropolymer gel can be characterized by the stretching exponent $\beta$ of the kohlrausch-Williams-Watts relaxation function [45]. The characteristic delay time of this correlation function increase some three orders of magnitudes as temperature decreases. These observations indicate the departure of temperature dependence of the visco-elasticity from the Arrhenius law [46-51], which is perhaps the most important canonical feature of glass-forming liquids [11]. Therefore these observations suggest the existence of the glass phase transition of the heteropolymer gel. In addition, the intensity ratio of the static component to the dynamic component of the scattered light increased drastically as temperature was decreased. This was consistent with the existence of the glass transition.
INTRODUCTION

The glass phase transitions of melted polymers or polymer solutions have been intensively investigated before[11]. Glass transition refers to the loss of ergodicity in liquid as temperature decrease. If crystals do not form during cooling of a liquid, the glassy state is entered as the temperature decreases even more. The glass-transition temperature is actually a range of temperatures over which the system falls out of equilibrium [11]. The average relaxation time increases by some two to three orders during this temperature range. A rapid decrease of the heat capacity \( C_p \) from liquid-like to crystal-like values as the liquid degrees of freedom become kinetically inaccessible. Hydrogen bonding seems to make a special contribution to \( \Delta C_p \) [11].

As we discussed in chapter 1, a gel macroscopically represents a single polymer's behavior to some extent. Thus we expect polymer gels undergo the glass phase transition. The following observations about the MAAc-DMAAm copolymer gel indicate that there might be a glass phase transition at some temperature. Firstly, the MAAc-DMAAm copolymer gel is as rigid as a plastic at low pH and temperature (say, pH = 3 at room temperature) due to the strong hydrogen bonding interaction. As the temperature increases, the gel becomes more rubbery but remains in collapsed state. Secondly, the mechanical measurement conducted by Dr. T. Enoki and Dr. G. Wang showed the ratio of imaginary and real part of the elastic moduli peaks around 60°C (see figure III.1).
Inspired by these observations, we investigated the existence of glass transition of the MAAc-DMAAm copolymer gel using dynamic scattering technique. The correlation function of the scattered light by the copolymer gel is measured. We observed that this correlation function is not a simple exponential below certain temperature. The departure from exponentiality can be
characterized by the stretching exponent $\beta$ of the kohlrausch - Williams - Watts relaxation function [45]:

$$g^{(1)}(t) = \exp\left[-\left(t/\tau_c\right)^{\beta}\right].$$

The value $\beta$ increased from about 0.4 at 20 °C to about 0.8 at 77 °C. The characteristic decay time $\tau_c$ increased from $10^{-4}$ second at 20 °C to 0.1 second at 77 °C. These observations indicate the departure of temperature dependence of the visco-elasticity from the Arrhenius law and the rapid change of heat capacity [46-51]. Thus these observations suggest the existence of the glass transition. In addition, we observed that the intensity ratio of the static component to the dynamic component of the scattered light increases drastically as temperature decreases. This was consistent with the existence of the glass transition.
5. **Light Scattering by Solid-Like Amorphous Medium**

This chapter serves as the theoretical background for the experiment work presented in chapter 6. Readers who are familiar with the issues in light scattering by polymer gels can skip the entire chapter.

We have discussed light scattering from fluid-like fluctuating medium, in which the scattering matter can diffuse throughout the medium. Therefore the scattered field by fluid-like fluctuating medium is a zero-mean Gaussian random variable; and the time-averaged scattered light or intensity correlation function is independent of individual sample (a particular scattering volume). Polymer gels are solid-like amorphous medium, in which the scattering elements are restricted to limited Brownian motions around the fixed average positions. The scattered field will depend on the configuration of the fixed average positions of the scattering elements and the amplitudes of the fluctuations. Therefore the scattered field by solid-like amorphous medium is no longer a zero-mean Gaussian random variable; and the time-averaged scattered light or intensity correlation function will depend on the particular scattering volume.

It can be shown (see discussion in section 5.1.3) that the scattered light by solid-like amorphous medium can be decomposed into the sum of a zero-mean Gaussian dynamic component and a constant static component. The static component depends explicitly on the configuration of the fixed average...
positions of the scatters in the scattering volume. The dynamic component is independent of the scattering volume.

From the properties of these two components, we can show that for solid-like amorphous medium the characteristic decay time of the time-averaged correlation function of the scattered field is independent of the scattering volume. This may seem surprising because we just argued this correlation function depends on the scattering volume. The trick is that the characteristic decay time is determined by the dynamic component of the scattered light, which is independent of the scattering volume. This characteristic decay time can be interpreted as the characteristic relaxation time of the scattering elements fluctuations in the medium (see the discussion in section 5.2 on the collective diffusion modes of polymer gels). Similarly, we can show that this characteristic decay time can be calculated directly from the normalized time-averaged intensity correlation by a single scattering volume.

Section 5.1 will explore the differences between time-average from a single scattering volume and the average over many independent scattering volumes for solid-like amorphous medium. The latter is referred as the ensemble average. The concept of dynamic and static components of the scattered light will also be introduced. In section 5.2, we will discuss the light scattering by collective diffusion modes of polymer gels.
5.1. Time Average and Ensemble Average

The solid-like amorphous medium differs from the fluid-like fluctuating medium by the localization of the scattering elements. Because of this localization, the phase space $\phi_p$ of one scattering volume is different from those of other scattering volumes. The phase space refers to the collection of all possible spatial configurations. If the spatial constraints of solid-like amorphous medium are removed, the corresponding phase space $\Phi_w$ will be independent of the scattering volume. In fact, the phase space $\phi_p$ is a subset of $\Phi_w$. To simplify our discussions, $\Phi_w$ is defined as the entire phase space of a solid-like amorphous medium. Consequently, the ensemble-average is an average over all possible spatial configurations in $\Phi_w$.

I will discuss the general concept ensemble-average vs. time-average in section 5.1.1; and apply these concepts to normalized intensity correlation functions in section 5.1.2. In section 5.1.3, the discussions will be focused on the decomposition of the scattered light into the sum of the static and dynamic component. The discussions in this section are based upon and derived from the theoretical work conducted by P. N. Pusey and van Megen in 1989 [52].
5.1.1. Definition of Ensemble Average

The ensemble average is over all the possible spatial configurations—entire phase space—of a system, as shown in equation 5.1.1.1.

\[
\langle A \rangle_E = \lim_{N \to \infty} \frac{1}{N} \sum_{n=0}^{N} A_n ,
\]  

(5.1.1.1)

where \( A_n \) represents the value of property \( A \) for a spatial configuration \( n \). A fluid-like fluctuating scattering medium evolves through a representative fraction of all possible spatial configurations, thus the time averaged correlation function gives a good estimate of its ensemble average. In other words, for a fluid-like fluctuating medium

\[
\langle A \rangle_T = \langle A \rangle_E .
\]  

(5.1.1.2)

The term \( \langle A \rangle_T \) represents time averaged property \( A \) and is defined as

\[
\langle A \rangle_T = \lim_{T \to \infty} \frac{1}{T} \int_{0}^{T} dt A(t) ,
\]  

(5.1.1.3)

where \( A(t) \) denotes the time evolution of property \( A \) of the system.
In a solid-like amorphous medium like polymer gels, however, the scatters can only undergo limited Brownian motions around their fixed average positions. Thus the system can only evolve a number of restricted spatial configurations, or "sub-ensembles." These configurations are determined by the average positions of the scatters and the magnitudes of their displacements. Different samples prepared under the same conditions will have scatters in different average positions, and should be described by different "sub-ensembles." Therefore, the time averaged correlation function measured from a particular sample is equivalent to the average over a sub-ensemble of spatial configurations. Let us use \( A_p(t) \) to represent the time evolution of a property of a solid-like amorphous sample \( p \) (sub-ensemble). The time average of \( A_p(t) \) can be expressed as

\[
\langle A_p \rangle_T = \lim_{T \to \infty} \frac{1}{T} \int_0^T dt \ A_p(t).
\]  (5.1.1.4)

This is equivalent to an average over the sub-ensemble \( p \), as shown in the following equation

\[
\langle A_p \rangle_T = \frac{1}{N_p} \sum_{n=0}^{N_p} A_n,
\]  (5.1.1.5)

where \( N_p \) is number of spatial configurations accessible to the sample \( p \), and \( A_n \) the value of property \( A \) for a spatial configuration \( n \).
The full ensemble average can be obtained by measuring time average from many independent samples and averaging the results, given approximately the same number of spatial configurations \((N_p)\) is accessible to the every sample. This condition should hold because the samples are similarly prepared and thus macroscopically identical. The average of the time average measurements of a property obtained from many independent samples can be expressed as follows

\[
\lim_{P \to \infty} \frac{1}{P} \sum_{p=1}^{P} \langle A_p \rangle_T = \lim_{P \to \infty} \frac{1}{P} \sum_{p=1}^{P} \left( \frac{1}{N_p} \sum_{n=1}^{N_p} A_n \right) = \lim_{P \to \infty} \frac{1}{P} \sum_{p=1}^{P} \left( \frac{1}{N_p} \sum_{n=1}^{N_p} A_n \right) = \lim_{N \to \infty} \frac{1}{N} \sum_{n=1}^{N} A_n. \tag{5.1.1.6}
\]

Compare equation 5.1.1.6 with equation 5.1.1.1,

\[
\langle A \rangle_T = \lim_{P \to \infty} \frac{1}{P} \sum_{p=1}^{P} \langle A_p \rangle_T. \tag{5.1.1.7}
\]

5.1.2. Normalized Ensemble-Averaged Intensity Correlation Functions

In the light scattering discussions in chapter 3, we have equated the time-averaged and ensemble-averaged correlation function of the scattered light. Since the ensemble-averaged correlation function of scattered light can be

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interpreted directly from ensemble-averaged properties of the medium (see equation 3.1.1.2.7), we can then link the time-average correlation function measured from light scattering experiments to ensemble-averaged properties of the medium. This approach only works for fluid-like fluctuating medium. For solid-like amorphous medium, we need a different way to obtain ensemble-averaged correlation function from the time-averaged one. In this section, we will focus on the definition and behavior of normalized ensemble-averaged and time-averaged intensity correlation function for solid-like amorphous medium.

The normalized time-averaged intensity function the scattered light, homodyne correlation function, with scattering vector $q$ (see figure 3.1.1.2.2 for the scattering geometry) is defined as

$$G_T^{(2)}(\mathbf{q}, \tau) = \frac{\langle I_P(\mathbf{q},0)I_P(\mathbf{q},\tau) \rangle_T}{\langle I_P(\mathbf{q})^2 \rangle_T},$$

(5.1.2.1)

where the label $p$ indicates the sample on which the measurement is performed. The normalized ensemble-averaged intensity correlation function is defined as

$$G_E^{(2)}(\mathbf{q}, \tau) = \frac{\langle I(\mathbf{q},0)I(\mathbf{q},\tau) \rangle_E}{\langle I(\mathbf{q})^2 \rangle_E}.$$  

(5.1.2.2)
Notice that the ensemble average is not dependent on any particular sample, because it should be an average of many independent samples (see equation 5.1.1.7).

The normalized time-averaged and ensemble-averaged intensity correlation functions for fluid-like fluctuating, pure static and solid-like amorphous medium are summarized in figure 5.1.2.1. A pure static medium, where no motions of the scatters are possible, is an extreme case of the solid-like amorphous medium. The normalized ensemble-averaged intensity correlation function starts from the same value 2 for all three type of medium at time 0, but decays to different values for different type of medium when time is much greater than the typical fluctuation time of the scattered light. The normalized time-averaged intensity correlation function starts from different values for different type of medium at time 0, but decays to the same value 1 for all three type of medium when time is much greater than the typical fluctuation time of the scattered light.

Let us assume the scattered light \( E(q, t) \), sampled over the full ensemble, is a zero-mean complex Gaussian random variable. We know from equation 3.2.2.4

\[
\langle I(q,0)I(q,\tau) \rangle_E = \langle I(q) \rangle_E^2 + \left| \langle E^*(q,0)E(q,\tau) \rangle_E \right|^2.
\]  
(5.1.2.3)

Thus
\[ g_E^{(2)}(q, \tau) = 1 + \left| g_E^{(1)}(q, \tau) \right|^2, \tag{5.1.2.4} \]

where
\[ g_E^{(1)}(q, \tau) = \frac{\langle E^*(q,0)E(q,\tau) \rangle_E}{\langle |E(q)|^2 \rangle_E} = \frac{\langle E^*(q,0)E(q,\tau) \rangle_E}{\langle I(q) \rangle_E} \tag{5.1.2.5} \]

is the normalized ensemble-averaged correlation function of the scattered light.

From equation 3.1.1.2.7, \( g_E^{(1)}(q, \tau) \) can be expressed as the ensemble-averaged correlation function of the dielectric constant (or density) fluctuations that cause the scattering
\[ g_E^{(1)}(q, \tau) = \frac{\langle E^*(q,0)E(q,\tau) \rangle_E}{\langle I(q) \rangle_E} = \frac{\langle \epsilon_y^*(q,0)\epsilon_y(q,\tau) \rangle_E}{\langle |\epsilon_y(q)|^2 \rangle_E}. \tag{5.1.2.6} \]

From equation 5.1.2.4 and 5.1.2.6, we see the normalized ensemble-average scattering light correlation function and intensity correlation function yield the same information of the scattering medium. This is consistent with our previous assertion about the equivalence of homodyne and heterodyne experiments, given the scattered light \( E(q, \tau) \) is a zero-mean complex Gaussian random variable (see section 3.2.1).

We can make some observations of \( g_E^{(1)}(q, \tau) \) based on figure 5.1.2.1. For all three types of medium
In the case of fluid-like fluctuating medium the density fluctuations can decay completely, \( g^{(1)}(q, \tau) \) decays to 0. For pure static medium, the density fluctuations are totally “frozen in” and \( g^{(1)}(q, \tau) \) remains as value 1. For an ordinary solid-like amorphous medium \( g^{(1)}(q, \tau) \) decays to a non-zero value \( g^{(1)}(q, \infty) \), which provides a measure of the fraction of density fluctuations that is frozen in [52]. I will re-visit this concept in chapter 6 in the discussion of possible frozen transition of polymer gels.

The discussions for the rest of this section will be focused on the normalized ensemble-averaged and time-averaged intensity correlation function shown in figure 5.1.2.1. To simplify the notions, we use \( g^{(2)}_{\tau, p}(\tau) \) and \( g^{(2)}_{E}(\tau) \) (as opposed to \( g^{(2)}_{\tau, p}(\tau) \) and \( g^{(2)}_{E}(\tau) \)) to represent normalized time-averaged and ensemble-averaged intensity correlation respectively hereafter.
Fig. 5.1.2.1  Normalized time-averaged vs. ensemble-averaged intensity correlation functions of fluid-like fluctuating, pure static, and solid-like amorphous medium. The case of fluid-like fluctuating medium is show in the two plots in the first row. The normalized time-averaged and ensemble averaged intensity correlation functions are equivalent. Their values start from 2 at time 0 and decay to 1 as time increases. The case of pure static medium is show in the two plots in the second row. Both normalized correlation functions are independent of time. The value of normalized time-averaged correlation function is 1; and the value of normalized ensemble-average correlation function is 2. The case of solid-like amorphous medium is show in the two plots in the third row. The values of normalized time-averaged intensity correlation functions from different samples are different. They all start from some values between 1 and 2, and decays to value1. The value of normalized ensemble-averaged intensity correlation function starts from 2 and decays to a value between 1 and 2
Let us consider an amorphous medium, of which the illuminated volume contains many uncorrelated regions. According to central limit theorem, the scattered light in the far field $E(q,t)$, sampled over the full ensemble, is a zero-mean complex Gaussian variable.

In a fluid-like fluctuating medium, the time-averaged correlation function equals the ensemble averaged correlation function (see section 5.1.1). When the delay time $\tau = 0$, the normalized intensity correlation can be calculated as follows

$$g_E^{(2)}(0) = g_T^{(2)}(0) = \lim_{\tau \to 0} \frac{\langle I(q,0)I(q,\tau) \rangle_T}{\langle I(q) \rangle^2_T} = \frac{\langle I(q)^2 \rangle_T}{\langle I(q) \rangle^2_T} = 2. \quad (5.1.2.8)$$

The value 2 results from the zero-mean Gaussian statistical properties of $E(q,t)$, based on which the distribution, $P[I(q)]$, of $I(q)$ is

$$P[I(q)] = \langle I(q) \rangle^{-1}_E \exp\left[-\frac{I(q)}{\langle I(q) \rangle_E}\right]. \quad (5.1.2.9)$$

Notice that $\langle I(q) \rangle = \langle I(q) \rangle_E$ because of the fluid-like fluctuating medium.

When the delay time $\tau$ much greater than the typical fluctuation time of the scattered light, $I(q,0)$ and $I(q,\tau)$ become uncorrelated so that
\[ g_{E}^{(2)}(\infty) = g_{T}^{(2)}(\infty) = \lim_{\tau \to \infty} \frac{\langle I(q,0)I(q,\tau) \rangle_T}{\langle I(q) \rangle_T^2} = \frac{\langle I(q) \rangle_T^2}{\langle I(q) \rangle_T^2} = 1. \]  

(5.1.2.10)

Therefore the normalized intensity correlation of fluid-like fluctuating medium decays from 2 to 1 as time increases, which is shown in the first row of Figure 5.1.2.1.

In a pure static medium, no motion of the scatters is possible. Therefore the intensity correlation of pure static medium is time independent. The normalized time-averaged intensity can be expressed as

\[ g_{T,p}^{(2)}(\tau) = \frac{\langle I_p(q,0)I_p(q,\tau) \rangle_T}{\langle I_p(q) \rangle_T^2} = \frac{\langle I_p(q) \rangle_T^2}{\langle I_p(q) \rangle_T^2} = \frac{\langle I_p(q) \rangle_T^2}{\langle I_p(q) \rangle_T^2} = 1, \]  

(5.1.2.11)

where the label \( p \) indicates the sample. The normalized ensemble-averaged intensity correlation can be expressed as

\[ g_{E}^{(2)}(\tau) = \frac{\langle I(q,0)I(q,\tau) \rangle_E}{\langle I(q) \rangle_E^2} = \frac{\langle I(q) \rangle_E^2}{\langle I(q) \rangle_E^2} = 2 \]  

(5.1.2.12)
The value 2 results from the zero-mean Gaussian statistical properties of $E(q,t)$ (see equation 5.1.2.9 for the distribution of $I(q)$). Notice that the ensemble average is an average over many independent samples, as opposed to only a particular sample $p$ in the time-averaged intensity correlation described in equation 5.1.2.11. The normalized time-averaged and ensemble-averaged intensity correlation function for pure static medium are shown in the second row figure 5.1.2.1.

For a solid-like amorphous medium, the scatters can only executed limited Brownian motion near their average positions. Thus only limited number of spatial configurations are accessible to a particular sample $p$. The normalized time-averaged intensity correlation from sample $p$ (the illuminated volume) differs from normalized ensemble-averaged intensity correlation, which is an average over all possible spatial configurations. Because of the limited Brownian motions of the scatters, the light scattered by a particular sample $p$, $E_p(q,t)$, will constitutes a speckle pattern consisted of both fluctuating and non-fluctuating components.

When decay time $\tau = 0$, the normalized time-averaged intensity correlation function can be expressed as
Notice that $E_p(q,t)$ is not a zero-mean Gaussian variable. The value of time-averaged scattered light $\langle E_p(q) \rangle_T$ is determined by the average positions of the scatters in sample $p$. Therefore initial value of normalized time-averaged intensity correlation function, $g_{T,p}^{(2)}(0)$, is less than 2. As the delay time $\tau$ much greater than the typical fluctuation time of the scattered light, $I_p(q,0)$ and $I_p(q,\tau)$ become uncorrelated. Therefore the normalized time-averaged intensity correlation function decays to value 1, as shown in equation 5.1.2.14

$$g_{T,p}^{(2)}(\infty) = \lim_{\tau \to \infty} \frac{\langle I_p(q,0)I_p(q,\tau) \rangle_T}{\langle I_p(q) \rangle_T^2} = \frac{\langle I_p(q) \rangle_T^2}{\langle I_p(q) \rangle_T^2} = 1. \quad (5.1.2.14)$$

The scatter light $E(q,t)$, sampled over the full ensemble (as opposed to a particular scattering volume), is a zero-mean complex Gaussian variable. Therefore initial value of the normalized ensemble-averaged intensity correlation for solid-like amorphous medium is 2, as shown in the following equation

$$g_E^{(2)}(0) = \lim_{\tau \to 0} \frac{\langle I(q,0)I(q,\tau) \rangle_E}{\langle I(q) \rangle_E^2} = \frac{\langle I(q) \rangle_E^2}{\langle I(q) \rangle_E^2} = 2. \quad (5.1.2.15)$$
It merits some detailed discussion about the value of normalized ensemble-average correlation function for a solid-like amorphous medium as the delay time \( \tau \) much greater than the typical fluctuation time of the scattered light.

As we discussed in section 5.1.1, the ensemble average can be obtained by averaging over the time averages from many independent sample (see equation 5.1.1.7). Therefore the normalized ensemble-averaged intensity correlation function can be written as

\[
\begin{align*}
\langle I(q,0)I(q,\tau) \rangle_E &= \lim_{P \to \infty} \frac{1}{P} \sum_{p=1}^{P} \langle I_p(q,0)I_p(q,\tau) \rangle_T \\
\langle I(q) \rangle_E^2 &= \left[ \lim_{P \to \infty} \frac{1}{P} \sum_{p=1}^{P} \langle I_p(q) \rangle_T \right]^2.
\end{align*}
\]

The label \( p \) in equation 5.1.2.16 denotes a individual sample. When the delay time \( \tau \) much greater than the typical fluctuation time of the scattered light, \( I_p(q,0) \) and \( I_p(q,\tau) \), the intensity from a individual sample, become uncorrelated. From equation 5.1.2.16, we can obtain the value of normalized ensemble-average correlation function for a solid-like amorphous medium as follows

\[
\begin{align*}
g_E^{(2)}(\tau) &= \frac{\langle I(q,0)I(q,\tau) \rangle_E}{\langle I(q) \rangle_E^2} = \frac{\lim_{P \to \infty} \frac{1}{P} \sum_{p=1}^{P} \langle I_p(q,0)I_p(q,\tau) \rangle_T}{\left[ \lim_{P \to \infty} \frac{1}{P} \sum_{p=1}^{P} \langle I_p(q) \rangle_T \right]^2}.
\end{align*}
\]

(5.1.2.16)
The value of $g^{(2)}_E(\infty)$ in equation 5.1.2.17 will always greater than 1 unless

$\langle I_p(q) \rangle_T$ is identical for different samples. In the case of a solid-like amorphous medium, the value of $\langle I_p(q) \rangle_T$ varies from sample to sample ($\langle E_p(q) \rangle$ is determined by the fixed average point of the scatters in sample $p$, thus this mean value varies from sample to sample). Thus for a solid-like amorphous medium, the normalized time-averaged intensity function of a individual sample starts from some value between 1 and 2 and decays to 1; while the normalized ensemble-averaged intensity function starts from a value 2 and decays to some value greater than 1. Both of the normalized intensity correlation functions are shown in the third row of figure 5.1.2.1.

5.1.3. Dynamic and Static Components

The discussions in this section are based on the following assumptions:

1. The sample is amorphous within the scattering volume;
2. The correlation length of the sample is much smaller than the scattering volume;
3. The scattering volume is much larger than the incident wave length
4. There are many scatters in one scattering volume.
The scatters in a solid-like amorphous medium can only execute limited Brownian motion about fixed average positions. Thus the scattered light $E(q,t)$ is not a complex zero-mean Gaussian random variable. Let us decompose $E(q,t)$ into a sum of fluctuating dynamic component $E_F(q,t)$ and non-fluctuating static component $E_N(q)$

$$E(q,t) = E_F(q,t) + E_N(q), \tag{5.1.3.1}$$

where $E_F(q,t)$ and $E_N(q)$ are defined as

$$E_F(q,t) = E(q,t) - \langle E(q) \rangle_T, \tag{5.1.3.2}$$

$$E_N(q) = \langle E(q) \rangle_T. \tag{5.1.3.3}$$

It is apparent that $E_N(q)$ is time-independent, and $E_F(q,t)$ is a zero-mean random variable. The properties of these two components will be discussed in this section. We will find that the dynamic component $E_F(q,t)$ is independent of the scattering volume; while the static component $E_N(q)$ depends directly on the average positions of the scatters in a particular scattering volume.

To simplify our discussion, let us consider a solid-like amorphous and amorphous medium with the discrete scatters. If the scattering volume contains...
N scatters and the center of mass of scatter \( j \) is \( r_j(t) \), the scattered light

\[ E(q,t) \] can be written as

\[ E(q,t) = X b_j \exp i q \cdot r_j(t), \]  

(5.1.3.4)

where \( b_j \) is determined by the scattering vector \( q \), the dielectric constant of scatter \( j \), and distance between the scattering volume and the detector (see equation 3.1.1.2.3). Thus \( b_j \) is independent of time and the position of scatter \( j \).

Let us represent the displacement of the center of mass of scatter \( j \) from its fixed average position \( r_{0j} \) as \( u_j(t) \). Since scatter \( j \) fluctuates about \( r_{0j} \), the position \( r_j(t) \) of the center of mass of scatter \( j \) can be expressed as

\[ r_j(t) = r_{0j} + u_j(t), \]  

(5.1.3.5)

\[ r_{0j} = \langle r_j(t) \rangle_T \]  

(5.1.3.6)

\[ \langle u_j(t) \rangle_T = 0. \]  

(5.1.3.7)

On substituting equation 5.1.3.5 in equation 5.1.3.4, the scattered field can be written as

\[ E(q,t) = X b_j \exp i q \cdot [r_{0j} + u_j(t)]. \]  

(5.1.3.8)
From equation 5.1.3.3, the static component, time-averaged scattered field, can be expressed as

\[ E_N(q) = \left< E(q,t) \right>_T = \sum_{j=1}^{N} b_j \omega_j \exp \left( i q \cdot r_{0j} \right), \]  

(5.1.3.9)

where

\[ \omega_j = \left< \exp \left( i q \cdot u_j \right) \right>_T. \]  

(5.1.3.10)

The dynamic component \( E_F(q,t) \) of the scattering can be written as

\[ E_F(q,t) = \sum_{j=1}^{N} b_j \exp \left( i q \cdot r_{0j} \right) \left[ \exp \left( i q \cdot u_j(t) \right) - \omega_j \right]. \]  

(5.1.3.11)

Note if the fluctuations in time of the phase factor \( \{ q \cdot u_j(t) \} \) are large compare to \( 2\pi \), the value of \( \omega_j \) (see equation 5.1.3.10) becomes zero. This means that there is no the static component (see equation 5.1.3.11) if the displacements of the scatters from their average positions are very large. Thus the static component \( E_N(q) \) of the scattered light results from the spatial restrictions of the scatters in a solid-like amorphous system.
From equation 5.1.3.10, we know that $\exp i \mathbf{q} \cdot \mathbf{u}_j(t) - \omega_j$ is a zero-mean random variable. Given the medium is amorphous, $E_F(q,t)$ is a sum of many zero-mean random variables. If the dimension of the scattering volume is much larger than the correlated range of the displacements of the scatters, $E_F(q,t)$ is a complex zero-mean Gaussian random variable. The time-averaged heterodyne correlation of the dynamic component can be shown as [52]

$$\langle E_F^*(q,0) E_F(q,\tau) \rangle_T = \left| \langle I(q) \rangle_E \left[ \delta_E^{(i)}(q,\tau) - \delta_E^{(i)}(q,\infty) \right] \right|$$

$$= \left| \langle E^*(q,0) E(q,\tau) \rangle_E - \langle E^*(q,0) E(q,\infty) \rangle_E \right|.$$  (5.1.3.12)

where $g_E^{(i)}(q,\tau)$ is the normalized ensemble-averaged correlation function of the scattered light (see equation 5.2.1.5). At $\tau = 0$ and $\tau \to \infty$, equation 5.1.3.12 and 5.2.1.7 give

$$\langle I_F(q) \rangle_T = \left\langle \left| E_F(q) \right|^2 \right\rangle_T = \langle I(q) \rangle_E [1 - g_E^{(i)}(q,\infty)],$$  (5.1.3.13)

$$\langle E_F^*(q,0) E_F(q,\infty) \rangle_T = 0.$$  (5.1.3.14)

Since $E_F(q,t)$ is a zero-mean complex Gaussian variable, $\left\langle \left| E_F(q) \right|^2 \right\rangle_T$ is the variance of $E_F(q,t)$. In equation 5.1.3.13 this variance is expressed as a function of ensemble-averaged quantities, which are independent of the scattering.
volume. Therefore dynamic component of the scattered field $E_F(q,t)$ is independent of the scattering volume. Because of linear relationship between the time-averaged heterodyne correlation function of the dynamic component and the ensemble-averaged correlation function of the total scattered light (see equation 5.1.3.12), they have the same characteristic decay time.

In fact, we can show that the time-averaged heterodyne correlation function and ensemble-averaged of the total scattered light have the same characteristic decay time. Because $E_F(q,t)$ is a zero-mean random variable and $E_N(q)$ is time-independent,

$$
\langle I(q) \rangle_T = \langle I_F(q) \rangle_T + I_N(q) \quad (5.1.3.15)
$$

where $\langle I_F(q) \rangle_T$ is defined in equation 5.1.3.13 and $I_N(q)$ is defined as

$$
I_N(q) = |E_N(q)|^2 \quad (5.1.3.16)
$$

From equation 5.1.3.13 and 5.1.3.15,

$$
I_N(q) = \langle I(q) \rangle_T - \langle I(q) \rangle_E \left[ 1 - S_E^{(1)}(q,\infty) \right]. \quad (5.1.3.17)
$$
The time-averaged heterodyne correlation function of the total scattered light can be written as

\[
\langle E^*(\mathbf{q},0)E(\mathbf{q},\tau) \rangle_T = \langle E^*_F(\mathbf{q},0)E_F(\mathbf{q},\tau) \rangle_T + \langle I_N(q) \rangle^2 + 2\text{Re}\left[ E^*_N(q)\langle E_F(q) \rangle_T \right] \\
= \langle E^*_F(\mathbf{q},0)E_F(\mathbf{q},\tau) \rangle_T + I_N(q). \tag{5.1.3.18}
\]

From equation 5.1.3.14 and 5.1.3.18, we know that \( \langle E^*(\mathbf{q},0)E(\mathbf{q},\tau) \rangle_T \) starts from \( \langle I(q) \rangle_T = \langle I_F(q) \rangle_T + I_N(q) \) at \( \tau = 0 \), and decays to \( I_N(q) \) at \( \tau \to \infty \).

Using equation 5.1.3.12, 5.1.3.17, and 5.1.3.18,

\[
\langle E^*(\mathbf{q},0)E(\mathbf{q},\tau) \rangle_T = \langle I(q) \rangle_T \left[ g_E^{(1)}(q,\tau) + \langle I(q) \rangle_T - \langle I(q) \rangle_E \right]
\]

\[
= \left| \langle E^*(\mathbf{q},0)E(\mathbf{q},\tau) \rangle_E \right| + \langle I(q) \rangle_T - \langle I(q) \rangle_E. \tag{5.1.3.19}
\]

Therefore the time-averaged heterodyne correlation function \( \langle E^*(\mathbf{q},0)E(\mathbf{q},\tau) \rangle_T \) can be written as the sum of the ensemble-averaged correlation function

\[ \langle E^*(\mathbf{q},0)E(\mathbf{q},\tau) \rangle_E \] of the scattered light and a scattering volume dependent constant \( \left\{ \langle I(q) \rangle_T - \langle I(q) \rangle_E \right\} \); and these two correlation functions have the same characteristic decay time.
The time-averaged homodyne correlation function, or the intensity correlation function, $\langle I(q,0)I(q,\tau) \rangle_T$ can be simplified based on that $E_F(q,t)$ is zero-mean Gaussian variable, and $E_N(q)$ is independent of time

$$\langle I(q,0)I(q,\tau) \rangle_T = \left\langle |E_F(q,0)+E_N(q)|^2E_F(q,\tau)+E_N(q)\right\rangle_T$$

$$= \langle I_F(q,0)I_F(q,\tau) \rangle_T + \left[I_N(q)\right]^2 + 2I_N(q)\langle I_F(q) \rangle_T + 2I_N(q)\text{Re}\left\langle E_F^*(q,0)E_F(q,\tau) \right\rangle_T.$$  \hspace{1cm} (5.1.3.20)

Using the Gaussian property (see equation 3.2.2.4) of $E_F(q,t)$ and equation 5.1.3.12, 5.1.3.13

$$\langle I_F(q,0)I_F(q,\tau) \rangle_T = \left\langle I_F(q) \right\rangle_T^2 + \left\langle E_F^*(q,0)E_F(q,\tau) \right\rangle_T^2$$

$$= \left\langle I(q) \right\rangle_T^2 \left\{1-\left|g_E^{(i)}(q,\infty)\right|^2+\left|\left|g_E^{(i)}(q,\tau)\right|-\left|g_E^{(i)}(q,\infty)\right|\right|^2 \right\}. \hspace{1cm} (5.1.3.21)$$

Combining equation 5.1.3.12 to 5.1.3.15, 5.1.3.20 and 5.1.3.21,

$$\langle I(q,0)I(q,\tau) \rangle_T = \left\langle I(q) \right\rangle_T^2 + \left\langle I(q) \right\rangle_T^2 \left|g_E^{(i)}(q,\tau)-\left|g_E^{(i)}(q,\infty)\right|\right|^2$$

$$+ 2I_N(q)\left\langle I(q) \right\rangle_T \left|\left|g_E^{(i)}(q,\tau)\right|-\left|g_E^{(i)}(q,\infty)\right|\right|. \hspace{1cm} (5.1.3.22)$$
From 5.3.1.17 and 5.1.3.22, the normalized time-averaged intensity correlation function $g^{(2)}_T(q,\tau)$ of can be expressed in terms of $g^{(1)}_E(q,\tau)$ and a scattering volume dependent constant $Y \equiv \langle I(q) \rangle_E / \langle I(q) \rangle_T$

$$g^{(2)}_T(q,\tau) = \frac{\langle I(q,0)I(q,\tau) \rangle_T}{\langle I(q) \rangle_T^2}$$

$$= 1 + Y^2 \left[ |g^{(1)}_E(q,\tau)|^2 - |g^{(1)}_E(q,\infty)|^2 \right] + 2Y(1-Y) \left[ g^{(1)}_E(q,\tau) - g^{(1)}_E(q,\infty) \right].$$

To express the normalized ensemble-averaged heterodyne correlation function $|g^{(1)}_E(q,\tau)|$ directly from the normalized time-averaged intensity correlation function, let us define a variable $f_T(q,\tau)$ as in terms of $g^{(2)}_T(q,\tau)$

$$[f_T(q,\tau)]^2 = 1 - \left[ g^{(2)}_T(q,0) - g^{(2)}_T(q,\tau) \right].$$

From equation 5.1.3.23,

$$[f_T(q,\tau)]^2 = \left[ Y|g^{(1)}_E(q,\tau)| + 1 - Y \right]^2.$$

Thus

$$f_T(q,\tau) = Y|g^{(1)}_E(q,\tau)| + 1 - Y,$$

and
\[ g_E^{(0)}(q, \tau) = 1 + \left[ f_T(q, \tau) - 1 \right] / Y. \] (5.1.3.26b)

From equation 5.1.3.24, 5.1.3.26b, even for solid-like amorphous system we can determine the characteristic decay time of the normalized ensemble-averaged heterodyne correlation function \( g_E^{(0)}(q, \tau) \) from the time-averaged intensity correlation function! From equation 5.1.3.26 and 5.1.3.17

\[
f_T(q, \infty) = 1 - \frac{\langle I(q) \rangle_T \left( 1 - g_E^{(0)}(q, \infty) \right)}{\langle I(q) \rangle_T} = 1 - \frac{\langle I_T(q) \rangle_T}{\langle I(q) \rangle_T}.
\] (5.1.3.27)

Thus

\[
\langle I_T(q) \rangle_T = \langle I(q) \rangle_T [1 - f_T(q, \infty)].
\] (5.1.3.28)

\[
I_N(q) = \langle I(q) \rangle_T - \langle I_T(q) \rangle_T = \langle I(q) \rangle_T f_T(q, \infty).
\] (5.1.3.29)

We can express \( f_T(q, \tau) \) in terms of the heterodyne correlation function of the dynamic component. Substituting equation 5.1.3.12, 5.1.3.13, and 5.1.3.15 into 5.1.3.26,

\[
f_T(q, \tau) = R_T g_T^{(0)}(q, \tau) + 1 - R_T,
\] (5.1.3.30)

where

\[
R_T \equiv \langle I_T(q) \rangle_T / \langle I(q) \rangle_T.
\] (5.1.3.31)
and

\[
g^{(1)}_{\tau,F}(q,\tau) = \frac{\langle E^*_F(q,0)E_F(q,\tau) \rangle}{\langle I_F(q) \rangle}. \tag{5.1.3.32}
\]

Since \( g^{(1)}_{\tau,F}(q,\infty) = 0 \), from equation 5.1.3.30

\[
g^{(1)}_{\tau,F}(q,\tau) = \frac{f_F(q,\tau) - f_F(q,\infty)}{1 - f_F(q,\infty)}. \tag{5.1.3.33}
\]

Equation 5.1.3.33 shows that for solid-like amorphous medium the normalized heterodyne correlation function can be obtained directly from the normalized time-averaged intensity correlation function (see 5.1.3.24).

It is worth mentioning that the static component \( E_N(q) \), sampled over many independent scattering volumes, is a zero-mean complex random variable. This is apparent given that the scattered light \( E(q,t) \) and its dynamic component \( E_F(q,t) \) are both zero-mean complex Gaussian variables, sampled over the full ensemble. The variance of \( E_N(q) \) over many independent scattering volumes is

\[
\langle I_N(q) \rangle_E, \text{ which is the ensemble-average of } I_N(q) \equiv |E_N(q)|^2. \text{ From equation 5.1.3.17, we can obtain that}
\]
\[
\langle I_N(q) \rangle_E = \left( \langle I(q) \rangle_T \right)_E - \langle I(q) \rangle_E \left[ 1 - \left| g^{(1)}_E(q, \infty) \right| \right]
= \langle I(q) \rangle_E g^{(1)}_E(q, \infty).
\] (5.1.3.34)

Let us examine equation 5.1.3.34 and 5.1.3.13 under two extreme cases: fluid-like fluctuating and pure static medium. From equation 5.1.2.4 and figure 5.1.2.1, we know that \( g^{(1)}_E(q, \infty) = 0 \) for fluid-like fluctuating medium and \( g^{(1)}_E(q, \infty) = 1 \) for pure static medium. Thus equation 5.1.3.34 and 5.1.3.13 give

\[
\langle I_N(q) \rangle_E \begin{cases} 0 & \text{for ergodic medium} \\ \langle I(q) \rangle_E & \text{for pure static medium} \end{cases}
\] (5.1.3.35)

\[
\langle I_F(q) \rangle_T \begin{cases} \langle I(q) \rangle_E & \text{for ergodic medium} \\ 0 & \text{for pure static medium} \end{cases}
\] (5.1.3.36)

which are consistent with that the scattered light has only the dynamic component for a fluid-like fluctuating medium; and only the static component for pure static medium.

In summary, the scattered light by solid-like amorphous medium can be decomposed into the sum of a sample independent zero-mean Gaussian dynamic component and a constant static component. The static component is sample dependent. From the properties of these two components, we can show that for solid-like amorphous medium the characteristic decay time of the time-averaged correlation function of the scattered field is independent of the
scattering volume. Similarly, we can show that this characteristic decay time can be calculated directly from the normalized time-averaged intensity correlation by a single scattering volume.

5.2. Light Scattering of Collective Diffusion Modes of Gels

In equilibrium states, the structure fluctuations of the polymer network of a gel can be described by collective diffusion modes [43,53]. The diffusion coefficient is determined by the elasticity and the friction coefficient of the polymer network. The diffusion coefficient can be obtained from dynamic light scattering experiment.

5.2.1. Collective Diffusion Modes in a Gel

When we study the structural fluctuations of the polymer network of a gel, the network can be treated as a continuous medium and the solvent as an incompressible fluid. Thus the network structure fluctuations can be uniquely described the displacement, \( u(r,t) \), of polymer network its average location.

The movement of a unit cube of the polymer network centered at the point \( r \) can be expressed as following equation according to Newton's second law:
\[ \rho \frac{\partial^2 u}{\partial t^2} = \nabla \cdot \bar{\sigma} - f \frac{\partial}{\partial t} u, \]  \hspace{1cm} (5.2.1.1)\\

where \( \rho \) is average mass density of the polymer network, \( \bar{\sigma} \) the stress tensor, and \( f \) the friction coefficient between the network and the solvent. The friction coefficient \( f \) should be proportional to the viscosity of the solvent.

In equation 5.2.1.1 the acceleration term on the left hand side is usually much smaller than the two force terms on the right hand side, therefore this term is neglected hereafter. Expressing the stress tensor \( \bar{\sigma} \) in terms of the bulk modulus \( K \) and shear modulus \( \mu \) of the polymer network, equation 5.2.1.1 can be decomposed into three diffusion equations corresponding to one longitudinal mode and two transverse modes:

\[ \frac{\partial u_i}{\partial t} = \frac{K + \frac{4}{3} \mu}{f} \frac{\partial^2 u_i}{\partial x_i^2} \]  \hspace{1cm} (Longitudinal), \hspace{1cm} (5.2.1.2)\\
\[ \frac{\partial u_r}{\partial t} = \frac{\mu}{f} \frac{\partial^2 u_r}{\partial x_i^2} \]  \hspace{1cm} (Transverse), \hspace{1cm} (5.2.1.3)\\

where \( x_i \) is the coordinate along the wave vector of the mode, \( u_i \) and \( u_r \) the components of the displacement vector along and perpendicular to the wave vector, respectively. Therefore the normal modes in a gel can be described as
collective diffusion modes. The diffusion coefficient $D$ can be expressed as the ratio of an appropriate elastic modulus $E$ and the friction coefficient $f$

$$D = \frac{E}{f}, \quad (5.2.1.4)$$

where

$$E = \begin{cases} K + \frac{4}{3} \mu & \text{(longitudinal)} \\ \mu & \text{(transverse)} \end{cases} \quad (5.2.1.5)$$

Let us consider the Fourier transform of $u(r,t)$

$$u(q,t) = \int d^3r \exp(iq \cdot r) u(r,t), \quad (5.2.1.6)$$

$$u_t(q,t) = \hat{q} \cdot u(q,t). \quad (5.2.1.7)$$

From equation 5.2.1.2,

$$\frac{\partial}{\partial t} u_t(q,t) = -q^2 \frac{K + \frac{4}{3} \mu}{f} u_t(q,t), \quad (5.2.1.8)$$

The solution of equation 5.2.1.8 yields

$$u_t(q,t) = u_t(q,0) \exp\left(-q^2 \frac{K + \frac{4}{3} \mu}{f} t\right). \quad (5.2.1.9)$$
The longitudinal displacement \( u_l(r, t) \) can be expressed as the inverse Fourier transform of \( u_l(q, t) \)

\[
\begin{align*}
  u_l(r, t) &= \frac{1}{2\pi} \int d^3q \exp(-iq \cdot r) u_l(q, t) \\
             &= \frac{1}{2\pi} \int d^3q u_l(q, 0) \exp \left( -iq \cdot r - q^2 \frac{K + \frac{4}{3} \mu}{f} t \right). 
\end{align*}
\] (5.2.1.10)

The transverse displacement \( u_t(r, t) \) can be obtained in the similar way.

5.2.2. Light Scattering from Collective Diffusion Modes

The time-averaged heterodyne correlation function of scattered light
\( \langle E^*_s(R, 0) E_s(R, t) \rangle_T \) is proportional to that of the Fourier transform of the spatial fluctuation in the medium's dielectric constant, \( \langle \delta\varepsilon_f(q, 0) \delta\varepsilon_f(q, t) \rangle_T \) (see equation 3.1.1.2.7). Since we only use time averages in this section, we will not specify this hereafter.

The diagonal element of dielectric constant \( \varepsilon(r, t) \) contributes to the polarized scattering \( E_{pol}(R, t) \) while the off-diagonal element \( \varepsilon_D(r, t) \) contributes to the depolarized scattering \( E_{dep}(R, t) \)[43,53]. More explicitly,

\[
\langle E_{pol}(R, 0) E_{pol}(R, t) \rangle \propto \langle \delta\varepsilon^*(q, 0) \delta\varepsilon(q, t) \rangle, \quad (5.2.2.1)
\]
\[
\langle E_{dep}(R,0) E_{dep}(R,t) \rangle \propto \langle \delta \varepsilon^*_\ast(q,0) \delta \varepsilon(q,t) \rangle.
\] (5.2.2.2)

In the light scattering experiments presented in this thesis, only the polarized scattered light was measured. Thus we will only discuss the polarized scattered light in this section.

The local fluctuation of the diagonal element of dielectric constant of a gel can be expressed as the local density fluctuation \( \delta \rho(r,t) \);

\[
\delta \varepsilon(r,t) = \left( \frac{\partial \varepsilon}{\partial \rho} \right) \delta \rho(r,t).
\] (5.2.2.3)

We assume the relaxation of the polymer network is isothermal in equation 5.2.2.3, because the thermal diffusion is much faster than the relaxation of the polymer network structure of a gel. At room temperature the thermal diffusion coefficient of water is on the order of \(10^{-3} \text{ cm}^2/\text{sec}\), while the diffusion coefficient that characterize the density fluctuation of the polymer network of a gel is on the order \(10^{-7} \text{ cm}^2/\text{sec}\) [43,53].

The spatial local density fluctuation, or in-homogeneity, comes from two sources: the fluctuations in time \( \delta \rho_F(r,t) \) resulting from the relaxation of the polymer network structures, and the density in-homogeneity of the network...
configuration $\delta \rho_n(r)$. The latter term is time independent. The term $\delta \rho_F(r,t)$ can be expressed in terms the divergence of the displacement vector $u(r,t)$ and the average density $\rho$ of the polymer network.

\[
\delta \rho_F(r,t) = \rho \nabla \cdot u(r,t),
\]

(5.2.2.4)

\[
\delta \rho(r,t) = \delta \rho_F(r,t) + \delta \rho_n(r) = \rho \nabla \cdot u(r,t) + \delta \rho_n(r).
\]

(5.2.2.5)

Combining equation 5.2.2.3 and 5.2.2.5, the Fourier transform of $\delta \epsilon(r,t)$ can be written as

\[
\delta \epsilon(q,t) = \int d^3r \exp(i \cdot q \cdot r) \delta \epsilon(r,t) = \delta \epsilon_F(q,t) + \delta \epsilon_n(q),
\]

(5.2.2.6)

where

\[
\delta \epsilon_n(q) = \left( \frac{\partial \epsilon}{\partial \rho} \right)_T \rho \int d^3r \exp(i \cdot q \cdot r) \delta \rho_n(r).
\]

(5.2.2.7)

and

\[
\delta \epsilon_F(q,t) = \left( \frac{\partial \epsilon}{\partial \rho} \right)_T \rho \int d^3r \exp(i \cdot q \cdot r) \nabla \cdot u(r,t)
\]

\[
= \left( \frac{\partial \epsilon}{\partial \rho} \right)_T \rho (i\cdot q) \cdot u.q.t).
\]

(5.2.2.8)
The term $u(q,t)$ is the Fourier transform of $u(r,t)$ defined in equation 5.2.1.6 and 5.2.1.7. Using equation 5.2.1.6, we know $\delta \varepsilon_r(q,t)$ is a zero-mean variable

$$\langle \delta \varepsilon_r(q) \rangle = \left( \frac{\partial}{\partial \rho} \right)_T \rho(-i \mathbf{q}) \cdot \langle \mathbf{u}(q) \rangle = 0 \quad (5.2.2.9)$$

It is apparent from equation 5.2.2.6 to 5.2.2.9 that $\delta \varepsilon_r(q,t)$ contributes to the fluctuating dynamic component and $\delta \varepsilon_s(q)$ to the non-fluctuating static component of the scattered field. Because $\delta \varepsilon_r(q,t)$ is a zero-mean variable,

$$\langle \delta \varepsilon^*(q,0) \delta \varepsilon(q,t) \rangle = \langle \delta \varepsilon^*_r(q,0) \delta \varepsilon_r(q,t) \rangle + |\delta \varepsilon_s(q)|^2 + 2 \Re \left[ \delta \varepsilon^*_s(q) \langle \delta \varepsilon(q) \rangle \right]$$

$$= \langle \delta \varepsilon^*_r(q,0) \delta \varepsilon_r(q,t) \rangle + |\delta \varepsilon_s(q)|^2. \quad (5.2.2.10)$$

On substituting equation 5.2.1.9 into equation 5.2.2.8, we get

$$\delta \varepsilon_r(q,t) = (-iq) \left( \frac{\partial}{\partial \rho} \right)_T \rho \ u_i(q,0) \exp \left( -q^2 \frac{K + \frac{4}{3} \mu}{f} t \right). \quad (5.2.2.11)$$

Thus

$$\langle \delta \varepsilon^*_r(q,0) \delta \varepsilon_r(q,t) \rangle = q^2 \left( \frac{\partial}{\partial \rho} \right)_T^2 \left| u_i(q,0) \right|^2 \exp \left( -q^2 \frac{K + \frac{4}{3} \mu}{f} t \right). \quad (5.2.2.12)$$
From equation 5.2.2.10 and 5.2.2.12,

\[
\langle \delta \varepsilon^* (q, 0) \delta \varepsilon (q, t) \rangle = q^2 \left( \frac{\partial \varepsilon}{\partial \rho} \right)_r \rho^2 \left( \mu_r (q, 0) \right)^2 \exp \left( - q^2 \frac{K + \mu}{f} t \right) + |\delta \varepsilon_N (q)|^2 \tag{5.2.2.13}
\]

Combining equation 5.2.2.13 and equation 5.2.2.1, we know that

\[
\langle E_{\text{pol}, R}(q, 0) E_{\text{pol}, R}(q, t) \rangle \propto \langle \delta \varepsilon^*_R (q, 0) \delta \varepsilon_R (q, t) \rangle, \tag{5.2.2.14}
\]

and

\[
I_{\text{pol}, N}(q) = |E_{\text{pol}, N}(q)|^2 \propto |\delta \varepsilon_N (q)|^2, \tag{5.2.2.15}
\]

where the \( E_{\text{pol}, R}(q, t) \) and \( E_{\text{pol}, N}(q) \) are the dynamic component and static component of the polarized scattered field, respectively. The characteristic decay time \( \tau_c \) of the time-averaged heterodyne correlation function of the polarized scattered field can be expressed in terms of the bulk modulus \( K \), shear modulus \( \mu \), and the friction coefficient \( f \) of the polymer network in a gel

\[
\tau_c = \left( q^2 \frac{K + \frac{3}{2} \mu}{f} \right)^{-1} = \left( q^2 D \right)^{-1}, \tag{5.2.2.16}
\]

where \( D \) is diffusion coefficient of the polymer network along longitudinal direction of the scattered light (see equation 5.2.1.4 and 5.2.1.5). From the
discussion in section 5.1.3, the characteristic decay time is the same for the following three heterodyne correlation functions: time-averaged, ensemble average and time-average of the dynamic component.

In summary, in equilibrium states the structure fluctuations of the polymer network of a gel can be described by collective diffusion modes. The diffusion coefficient is determined by the elasticity and the friction coefficient of the polymer network. The time correlation function of the scattered light by the collective diffusion modes is a single exponential decay. The diffusion coefficient can be obtained from the characteristic decay time of this correlation function.

When a polymer gel falls out of equilibrium, time correlation function of the scattered light will depart from a single exponential decay (see section 6.3).
6. Explore Glassy Transition in Heteropolymer Gels

I will present the experimental work and the analyses of the measurement results in this chapter. The sample preparation will be described in section 6.1. The experiment setup in section 6.2. The measurement results and analyses will be presented in section 6.3. Conclusions and future work will be covered in section 6.4.

6.1. Sample Preparation

The sample was the hydrogen bondable copolymer gel in low pH solution. We used an organic solvent to better dissolve the cross-linkers in the pre-gelation solution. Thus there were two more steps in the sample preparation in addition of the polymerization. One step was to replace the organic solvent in the gel with water. The other step was to lower the pH gradually to obtain a transparent gel at low pH.

The hydrogen bondable copolymer gel was prepared by free radical polymerization. The two types of monomers, methyacrylic acid (MAAc) and dimethyacrylamide (DMAAm), were liquid. We dissolved 0.31 g of N,N'-methylenebisacrylamide (BIS, cross-linker) and 0.16 g of 2,2'-azobisisobutyronitrile (AIBN, initiator) in the mixture of 12.9 g MAAc (monomer), 5.0 g DMAAm (monomer), and certain amount methylsulfoxile (DMSO, solvent).
The amount of DMSO was such that the total solution 100 ml. This solution was
degassed and transferred into 10 μl micro-pipettes. The polymerization
temperature was set at 60 °C. This temperature was controlled by a Brinkmann
Lauda RC-3. We allowed more than twelve hours of polymerization.

To wash out the DMSO solvent within the gels, we took the copolymer
gels off the micro-pipettes and immersed them in huge amount of de-ionized
water. The de-ionized water was replaced every half an hour for the first twelve
hours, and then replaced three or four times a day for next few days. Since
DMSO is not soluble in water, the gels became opaque until all the DMSO
diffused out of the gel. The hydrogen bounding is much stronger in DMSO than
it is in the water. Therefore the gels swelled significantly during the washing
process and became increasingly fragile. To make sure all the remaining DMSO
was washed out after the gels became almost clear, we added sodium hydroxide
into the de-ionized water so that the pH value was increased to 9. The gels
swelled even more, and became more fragile.

To obtain transparent gels at low pH for light scattering experiment, we
lowered the pH value gradually. Otherwise the gels would shrink too fast and
become opaque or deformed. We first immersed the swollen gels into de-
ionized water with neutral pH for several hours. The de-ionized water was
replaced every half an hour to wash out sodium and hydroxide ions. The gels
shrunk slightly. After the size of the gels became stabilized, we added some
hydrochloride solution into the water so that pH value was lowered to 6. The pH 6 water solution was replaced every half an hour until the stabilization of the gel size. Then, doubled hydrogen ion concentration. We repeated the washing process and double the hydrogen ion concentration again after stabilization of the gel size. By doubling the hydrogen ion concentration, we lowered the pH value by 0.3 at a time. Thus it took totally 10 times of hydrogen ion doubling to reduce the pH value from 6 to 3. It appeared that the longest time for the gel size to reach equilibrium was lowering the pH value from 3.6 to 3.3. This process took overnight.

6.2. Experiment Setup

The optical set up was the same Microscopic Laser Light Scattering (MLLS) setup shown in figure 4.2.1.1 (see section 4.2.1). It is a modification of the conventional homodyne setup (see figure 3.2.1). A microscope was added to improve measurement precision for small samples. In addition, a stepping motor was installed to allow the systematic measurements from many independent scattering volumes.
Fig. 4.2.1.1 Schematic representation Microscopic Laser Light Scattering (MLLS) setup. The incident light, transmitted through a single mode optic fiber, was focused on the sample by a GRIN lens. The 90° scattered light was focused by the eyepieces of the microscope and then detected by an optic fiber, which is connected to a PMT.

These changes provided important advantages for the measurements on phase transition of gels. It is desirable to measure small sample because the increase of the transition time is quadratic as the increase of the gel size. For example, the speed gain of 100 fold can be achieved by reducing the sample size to one tenth. Since gels are solid-like amorphous media, we can not equate the time-averaged homodyne correlation function with the ensemble-averaged intensity correlation function (see chapter 5.1.2). Our approach to estimate the ensemble-average was to average the homodyne correlation functions
measured from many independent scattering volumes. The limitation of this setup is that the scattering angle is fixed at 90 °, which precludes the measurements of angular dependence.

As we discussed earlier on solid-like amorphous system like polymer gels, the ensemble average can be achieved by averaging the measurement results of many independent samples. The gel samples we used for light scattering experiments are long (~1 cm) and thin (<500 μm) cylinders. The focused waist of the incident light is less than 10 μm. Thus a gel sample contains thousands of independent “samples” of the size of the illuminated region. Therefore the ensemble average can be achieved by moving the sample through a series of positions so that the illuminated region changes within the sample. A stepping motor was installed to achieve this (see figure 6.2.1).

The sample holder is shown in figure 6.2.1. The MAAc-DMAAm copolymer gel was placed in a 100 μL micro-pipette, which was resided in a temperature controlled couvette. The pH value was control by circulating pH=3 solution through the micro-pipette. The temperature was controlled by circulating water from a Brinkmann Lauda RC-3 through the glass cuvette.
6.3. **Measurement and Analyses**

In this experiment, we measured the intensity and the intensity correlation function of the scattered light by the MAAc-DMAAm copolymer gel. I will present the experiment data in section 6.3.1. The analyses will be covered in section 6.3.2.
6.3.1. Measurements

We measured the normalized intensity correlation function $g^{(2)}(\tau)$ (see definition in section 5.1.2) of the scattered light by MAAc-DMAAm gel for a wide range of temperatures, from 19 °C to 77 °C. The pH value was fixed at 3 throughout this experiment. Some measurement results are shown in figure 6.3.3.1 (a).

![Normalized Intensity Correlation Function of Scattered Light by Copolymer MAAc-DMAAm Gel](image)

Fig 6.3.1.1(a) The normalized intensity correlation function $g^{(2)}(\tau)$ of the scattered light by the MAAc-DMAAc copolymer gel at various temperatures (pH = 3). The correlation function is adjusted by a constant so that it starts from 1 at time 0.
If the correlation function of the scattered light is a single exponential decay, the normalized intensity correlation function should follow (see section 6.3.2 for detailed discussion)

\[ g^{(1)}(\tau) = \beta \left[ R \exp\left( -\frac{\tau}{\tau_C} \right) + 1 - R \right]^2 + \text{const.} \]  

(6.3.1.1)

where \( \beta = 0.8 \) is an instrument parameter, \( R \) is the ratio of intensity of the dynamic component \( I_d \) (see section 5.1.3) to the total intensity \( I_T \) of the scattered light.

**Normalized Intensity Correlation Function of Scattered Light by MAAc-DMAAm Gel (T = 27.21°C, 40.14°C, and 77.2 °C)**

Fig 6.3.1.1(b) The fit of the intensity correlation using equation 6.3.1.1. The solid black lines are the fitting curves.
In figure 6.3.1.1(a) & (b) the correlation function $g^{(2)}(\tau)$ was adjusted by a constant (temperature dependent) so that it started from value 1 as time 0. Figure 6.3.1.1 (a) & (b) show that the lower the temperature, the slower the decay of the intensity correlation function $g^{(2)}(\tau)$. The characteristic decay time of the intensity correlation function increased more than 2 orders of magnitude as temperature was increased from 27.27 °C to 77.2 °C.

Figure 6.3.1.1 (b) also shows equation 6.3.1.1 does not fit well with the measurements, and it gets worse at low temperature. This indicates that the correlation function of the correlation function of the scattered light is not single exponential decay. This deviation suggests possible existence of glass transition below certain temperature (see section 6.3.2).

The measurement of the intensity of the static and dynamic component (see section 5.1.3) of the scattered light are show in figure 6.3.1.2 (a) & (b). 6.3.1.2 (a) that the intensity ratio of static component to dynamic component remained pretty much the same from temperature 40 °C to 80 °C. This ratio increased gradually when temperature fell below 40 °C till 30 °C, and increased drastically when temperature was lower than 30 °C. Figure 6.3.1.2 (b) shows that the intensity of both dynamic and static component decreased as temperature was decreased. The intensity of dynamic component decreased more drastically.
Intensity Ratio of Static to Dynamic Component of Scattered light by MAAc-DMAAm Copolymer Hydrogel

\[ \frac{I_{\text{in}}}{I_{\text{f}}} \]

Temperature (°C)

Fig 6.3.1.2(a) The ratio of the intensity of static component to intensity of dynamic component of the scattered light by MAAc-DMAAm copolymer gel.
Intensity of Static and Dynamic Component of
Scattered light by MAAc-DMAAm Copolymer Hydrogel

![Graph showing the intensity of static and dynamic component of scattered light by MAAc-DMAAm copolymer hydrogel as a function of temperature.](image)

Fig 6.3.1.2 (b) The intensity of static component and dynamic component of the scattered light by MAAc-DMAAm. Both intensities increase as temperature increases.

6.3.2. Analyses

The departure of temperature dependence of the visco-elasticity from the Arrhenius law is perhaps the most important canonical feature of glass-forming liquids [11]. This departure from Arrhenius law can be reflected by the departure of time correlation function of the scattered light from single exponential decay
Empirically the departure from exponentiality can be characterized by stretching exponent $\beta$ of the Kohlrausch-Williams-Watts relaxation function [45]:

$$g^{(1)}(t) = \exp\left[-\left(t/\tau_c\right)^\beta\right]. \quad (6.3.2.1)$$

The correlation function shown in the previous equation should be ensemble-averaged. As discussed in section 5.1.3, the correlation function of the dynamic component is linearly dependent of the ensemble-averaged correlation function of the total scattered light (see equation 5.1.3.12). The correlation function of the dynamic component can be calculated from the intensity correlation function (see equation 5.1.3.33). I will use exactly the same reasoning in the analyses, and also take into account of the measurement error from the limitation of the instrument.

The limitation of the setup comes from the finite solid angle of the detector of the scattered light, and the discrete time interval when the time-averaged correlation function is calculated. Dr. Michael Orkisz showed that the measurement error from discrete time interval $\Delta t$ is negligible if $\Delta t/\tau_c << 1$, where $\tau_c$ is the characteristic decay time of correlation function [44]. As shown in figure 5.3.1.1, the opening of the aperture of the objective lens has finite size. The intensity of the scattered light we measured is an integral over finite range of...
the scattering vector $d\mathbf{q} = |\mathbf{q}|^2 dq \, d\Omega$, where $\mathbf{q}$ and $d\Omega$ are the scattering factor and the finite solid angle of the detector. Thus even if we use this setup to measure a fluid-like fluctuating medium, such as colloidal latex micro-spheres of polystyrene, the normalized intensity correlation function is less than 2 at the time $0$. The Gaussian property (see equation 3.2.2.4) can be written as [54]

$$\bar{g}^{(2)}_E(q, \tau) = 1 + \beta |g^{(1)}_E(q, \tau)|^2,$$  \hspace{1cm} (6.3.2.2)

where $\bar{g}^{(2)}_E(q, \tau)$ represents the approximation of the normalized intensity correlation function $g^{(2)}_E(q, \tau)$ (see equation 5.1.2.2) from the measurement; $\beta$ is a instrumental parameter due to the finite solid angle of the detector; $g^{(1)}_E(q, \tau)$ (see equation 5.1.2.5) is the normalized heterodyne correlation function. In our setup, the parameter $\beta = 0.8$ [44].

For solid-like amorphous medium, the average value of the normalized intensity correlation function over finite number of scattering volumes derived follow the same reasoning as in section 5.1.3

$$\bar{g}^{(2)}_M(q, \tau) = 1 + \beta \left[ R_M |g^{(1)}_M(q, \tau)| + 1 - R_M \right]^2 + \frac{\left[ \langle I_N(q)^2 \rangle_M - 2(1 + \beta) \langle I_N(q) \rangle^2_M \right]}{\left[ \langle I(q) \rangle^2_M \right]}^2,$$  \hspace{1cm} (6.3.2.3)
where $g^{(1)}_{T,r}(q,\tau)$ is the normalized correlation function of the dynamic component of the scattered light; $\langle I_N(q) \rangle_M$ is the average intensity of the static component scattered light over the finite number of scattering volume; and $R_M$ is the ratio of the dynamic component intensity to total intensity

$$R_M = \frac{\langle I_F(q) \rangle_T}{\langle I(q) \rangle_M}.$$  \hspace{1cm} (6.3.2.4)

Note that when we increase the number the scattering volumes

$$R = \lim_{P \to \infty} R_M = \lim_{P \to \infty} \frac{\langle I_F(q) \rangle_T}{\langle I(q) \rangle_E} = \frac{\langle I_F(q) \rangle_T}{\langle I(q) \rangle_E}.$$  \hspace{1cm} (6.3.2.5)

Let us define

$$[f_M(\tau)]^2 = 1 - \left[ \tilde{g}^{(2)}_M(q,0) - \tilde{g}^{(2)}_M(q,\tau) \right] / \beta.$$  \hspace{1cm} (6.3.2.6)

From equation 6.3.2.3,

$$f_M(\tau) = \sqrt{1 - \left[ \tilde{g}^{(2)}_M(q,0) - \tilde{g}^{(2)}_M(q,\tau) \right] / \beta} = R_M \left| \tilde{g}^{(1)}_{T,r}(q,\tau) \right| + 1 - R_M.$$  \hspace{1cm} (6.3.2.7)
Since $g_{TF}(q,\infty) = 0$ (see section 5.1.3),

$$R_M = 1 - f_M(\infty).$$  \hspace{1cm} (6.3.2.8)

Thus from equation 6.3.2.7 and 6.3.2.8, the normalized correlation function of the dynamic component of the scattered light can be expressed as

$$\left| g_{TF}^{(i)}(q,\tau) \right| = \frac{f_M(\tau) - f_M(\infty)}{1 - f_M(\infty)}. \hspace{1cm} (6.3.2.9)$$

Equation 6.2.3.6 and 6.2.3.9 allow us to obtain the correlation function $g_{TF}^{(i)}(q,\tau)$ of dynamic component of the from the intensity correlation function.

Figure 6.3.2.1 shows $g_{TF}^{(i)}(q,\tau)$ obtained from the normalized intensity correlation functions shown in figure 6.3.1.1(b). Note the $g_{TF}^{(i)}(q,\tau)$ was not single exponential decay.
The correlation of the dynamic component of the scattered light by MAAc-DMAAc gel at various temperatures.

The next step is to fit $g_{TRF}^{(1)}(q, t)$ with $\exp \left( \frac{t}{\tau_c} \right)$. We made the following transformation

$$\log \log \left[ g_{TRF}^{(1)}(q, t) \right] = \beta \log t - \beta \log \tau_c + \log(\log e)$$

(6.3.2.10)
to make the fitting easier. The value $\beta$ and $\tau_c$ can be obtained by the slope and intercept of plot $\log[\log(g^{(i)}_{T,F}(q,t))]$ vs. $\log t$. If $g^{(i)}_{T,F}(q,t)$ is a single exponential decay, the slope should be one. Such an example is given in figure 6.3.2.2.

![Graph](image)

**NIPA Gel at T=25 °C**

**Fig.6.3.3.2** The fitting of the normalized correlation function of the dynamic component of a NIPA gel at 25 °C. Since this correlation function is a single exponential decay (see section 5.2.1), the slope of the plotted curve is close to 1.

Some examples of fitting $g^{(i)}_{T,F}(q,t)$ for the MAAc-DMAAm gel at various temperatures are shown in figure 6.3.3.3 (a) to (d). These plots compare the fittings with different cut-off decay time. Longer cut-off decay time gives smaller $\beta$. The signal to noise ratio became stronger as the time increased because the
signal decreased. Therefore we used the fittings from shorter cut-off decay time.

Figure 6.3.3.3 (a) to (d) also shows that the measurements were noisy at low temperature. The data became smoother as temperature was increased.

Figure 6.3.3.3 (a) The fitting of the normalized correlation function of the dynamic component of the MAAc-DMAAm gel at $T=23.9 \, ^\circ C$ and $30.09 \, ^\circ C$ under pH=3. The two plots on the same row are from same measurement. The cut-off time for the curve fitting on the left plot was shorter than the one on the right plot.
Figure 6.3.3.3 (b) The fitting of the normalized correlation function of the dynamic component of the MAAc-DMAAm gel at $T=44.46 \, ^\circ\text{C}$ and $54.04 \, ^\circ\text{C}$ under pH=3. The two plots on the same row are from same measurement. The cut-off time for the curve fitting on the left plot was shorter than the one on the right plot.
Figure 6.3.3.3 (c) The fitting of the normalized correlation function of the dynamic component of the MAac-DMAAm gel at T=59.24 °C and 67.94 °C under pH=3. The two plots on the same row are from same measurement. The cut-off time for the curve fitting on the left plot was shorter than the one on the right plot.
Figure 6.3.3.3 (d) The fitting of the normalized correlation function of the dynamic component of the MAAc-DMAAm gel at T=72.82 °C and 77.2 °C under pH=3. The two plots on the same row are from same measurement. The cut-off time for the curve fitting on the left plot was shorter than the one on the right plot.

The fitting parameter \( \beta \) and the characteristic decay time \( \tau_c \) for the MAAc-DMAAm gel with pH=3 are shown in figure 6.3.3.4. As temperature was decreased the characteristic decay time \( \tau_c \) increased and the parameter \( \beta \)
decreased (deviate more from 1). As temperature was decreased from 77 °C to 20 °C, β decreases from 0.8 to 0.4 and $\tau_c$ increased from $10^{-4}$ second to 0.1.

Parameters of Correlation Function of Scattered light by MAAc-DMAAm Copolymer Hydrogel (pH=3)

Figure 6.3.3.4 The parameters of stretched exponential fitting of the normalized correlation function of the dynamic component of the MAAc-DMAAm gel at various temperature under pH=3. The parameter $\tau_c$ is the characteristic decay time and β indicates the deviation from single exponential decay.

Note that β never reached 1 in this experiment, even when temperature was 77 °C. The mechanical measurement (see figure III.1 in page 120) showed that transition temperature was around 60 °C. These results suggested that the
departure from exponentiality of the correlation function might occur before the glassy transition.

Figure 6.3.3.5 shows the logarithm of the characteristic decay time $\tau_c$ as function of $1/T$. The solid line is the fitting curve, the formulation of which is shown on the graph. We expect when temperature increased to certain value, the correlation function of the dynamic component will become single exponential decay and the characteristic decay time $\tau_c$ will not drastically decrease.
Logarism of Decay Time of Correlation Function of Scattered light by MAAc-DMAAm Copolymer Hydrogel (pH=3)

\[ y = 4.5245x - 10.843 \]
\[ R^2 = 0.75 \]

Figure 6.3.3.5 The logarithm of the characteristic decay time \( \tau_c \) as a function of the inverse of temperature. The solid dots are the calculated results from the measurements. The solid line is the linear fitting curve, and the dashed line is the expected behaviour when temperature are increased even further.

6.4. Conclusions and Future Work

To explore the existence of the glass transition in the MAAc-DMAAm gel, we measured the correlation function of the scattered light in the collapsed states at various temperatures. The departure from exponentiality and drastic
increase of the characteristic decay time of this correlation function suggested the existence of the glass transition.

The existence of the glass transition would be more evident if the complete return to exponentiality at high temperature is observed. Thus future work should include the investigation of the behavior of the MAAc-DMAAm gel at higher temperature.
CONCLUSIONS

This thesis presented four experiment projects of exploration of the volume and glassy phase transitions of polymer gels and their applications.

Chapter 2 presented a protocol of embedding a holographic grating into a hydrophobic N-isopropylacrylamide (NIPA) gel. The holographic grating was incorporated as an interpenetrating polymer network (IPN). This system can be used as an information storage or an optical actuator. We obtained the spacing of this holographic grating by measuring the diffraction angle of a laser beam from the gratings. We have observed reversible discontinuous changes in the spacing of the holographic grating as the gel underwent the phase transition in response to the temperature changes. While similar holographic experiments were conducted before[33], it is the first experiment to incorporate holographic gratings into a gel so that one can change the spacing with external stimuli.

Chapter 3 discussed light scattering methodology, which served as theoretical background of the experimental work presented in chapter 4. Chapter 4 covered our studies on volume phase transitions of colloidal micro-gels with both hydrogen bonding and hydrophobic interactions using light scattering methodology. We focused on the micro-gels because the kinetics and the volume phase transition can be accelerated by reducing the gel size. This is important for applications like drug delivery. We employed a new method to
better control the pH value of the micro-gels. The studies presented in chapter 4 include two research projects: dynamic light scattering and static light scattering by the colloidal micro-gels. In the static light scattering study, the average size was obtained by measuring the angular distribution of the scattered light intensity. In the dynamic light scattering experiment, the average size was obtained by measuring the time-correlation function of the scattered light. We observed drastic but continuous volume changes of the micro-gels in response to the temperature and pH value changes. The time for the micro-gels to reach equilibrium was less than a few minutes. The lack of the discontinuous volume phase transition in the micro-gels might be due to the cross-linker to monomer ratio. This ratio of the micro-gel is ten times higher than that of the standard NIPA gel.

Chapter 5 discussed the light scattering by solid-like amorphous medium. A simple data analyses method was derived to extract the dynamic property of solid-like amorphous medium from the light scattering data. The method was derived from the theoretical work conducted by P. N. Pusey and van Megen in 1989 [52], which served as theoretical background of the experimental work presented in chapter 6. The existence of glass phase transition of the hydrogen bondable gel made of methacrylic acid (MAAc) and dimethacrylamide (DMAAm) was investigated using dynamic light scattering technique. We observed that below certain temperature the time correlation function of the scattered light by this heteropolymer gel can be characterized by the stretching
exponent $\beta$ of the kohlrausch-Williams-Watts relaxation function. The characteristic delay time of this correlation function increased some three orders of magnitudes as temperature decreases. These observations suggested the existence of the glass phase transition of the heteropolymer gel. In addition, the intensity ratio of the static component to the dynamic component of the scattered light increased drastically as temperature was decreased. This was consistent with the existence of the glass transition.
REFERENCES


