The Pennsylvania State University The Graduate School Department of Chemical Engineering

#### COLLOIDAL THERMAL FLUIDS

A Dissertation in Chemical Engineering by Saba Lotfizadeh

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Submitted in Partial Fulfillment of the Requirements

for the Degree of

Doctor of Philosophy

May 2015

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## Abstract

Fluids have very low thermal conductivity in compare to solid material. Improving heat transfer properties in many heating/cooling industrial process where common fluids such as water are used has been a great concern. Adding solid particles even at low volume fraction to a fluid, increases thermal conductivity of the fluid significantly. Maxwell's mean field theory is the basic theory evaluating conduction in such complex suspensions. However, there is a discrepancy between the theory and many experimental measurements and also a large variability among experimental measurements themselves. Larger thermal enhancement, beyond Maxwell prediction, has questioned the accuracy of the classical models to describe conduction in colloidal suspensions. However, it has been proposed that uncontrolled aggregation, which nearly exists in all the experimental systems could be responsible of this inconstancy. This hypothesis originates from Maxwell's theory because in fact, the theory has two limiting bounds depending on the configuration of the phases, providing a range where thermal conductivity may fall. However no experiment has yet directly shown the effect of aggregation on thermal properties of colloidal suspensions. This is mainly because controlling the degree of aggregation

in colloidal suspensions is quite a challenge: once an aggregate forms, it grows unbeatably until precipitates out the solution or reaches a large size where further aggregation becomes very slow.

In this dissertation, a reversible system with well controlled degree of aggregation of the particles was developed. By surface modification of colloidal silica with aminosilanes, interactions among the particles were tuned in a controlled way to produce stable sized clusters at different pH values ranges from well disposed to a colloidal gel. N-[3-(trimethoxysilyl)propyl]ethylenediamine (TMPE) monolayer on particle surface not only removes all the reactive sites to prevent chemical aggregation, also provides steric stabilization in the absence of any repulsion. After surface modification, electrokinetic behavior of silica particles were changed to that of amino groups, positive in acidic pH and neutral at basic pH values. By tuning the pH, the balance between electrostatic repulsion and hydrophobic interactions was reversibly controlled. As a result, clusters with different sizes were developed.

The effect of clustering on the thermal conductivity of colloidal dispersions was quantified using silane-treated silica, a system engineered to exhibit reversible clustering under well-controlled conditions. Thermal conductivity of this system was measured by transient hot wire, the standard method of thermal conductivity measurements in liquids. We show that the thermal conductivity increases monotonically with cluster size and spans the entire range between the two limits of Maxwell's theory. The results, corroborated by numerical simulation, demonstrate that large increases of the thermal conductivity of colloidal dispersions are possible, yet fully within the predictions of classical theory.

Numerical calculations were performed to evaluate the importance of struc-

tural properties of particles/aggregates on thermal conduction in colloidal particles. Thermal conductivity of non-spherical particles including hollow particles, cubic particles and rods was studied using a Monte Carlo algorithm. We show that anisotropic shapes, increase conductivity above that of isotropic particles where Maxwell's theory is reliable. This method also provides an accurate tool for evaluation of conductivity in colloidal suspensions between Maxwell's limits where theory is inadequate and experiments are limited due to colloidal difficulties. The effect of cluster configuration and degree of aggregation was investigated and showed that clusters of about the same size, but with different structures increases conductivity by different degree. We also showed that even small structural details such as the size of the neck that particles form during aggregation, can change the enhancement significantly.

Colloidal clusters conduct heat more efficiently compared to fully dispersed particles at the same volume fraction. We present a predictive model to calculate the thermal conductivity of clusters by extending Maxwell's theory to non-spherical particles. We treat the clusters as spheres with effective thermal conductivity  $k_c$  and volume fraction  $\phi_c$ . We calculate conductivity of the cluster from the upper bound of Maxwell's theory, and the conductivity of a dispersion of such clusters from the lower limit of the theory. We show that structural effects can be represented by a single parameter and a method was provided to obtain this parameter from numerical simulations. We test the theory against simulations as well as dispersions of colloidal cluster and find it to be in very good agreement with both. The results suggest that the variability of literature data and the unusually high values of thermal conductivity that have been reported in the literature can be fully accounted by the presence of clusters.

Gelation occurs at the isoelectric point of silane-treated silica where no repulsion among the particles exists and hydrophobic interactions push the system into gelation. We experimentally studied the kinetics of both aggregation and deadggregation rate. At the isoelectric point, gelation time can be varied from seconds to months by controlling the silane concentration, particle concentration and temperature. Small increase in the silane concentration at constant volume fraction of the particles, causes disproportional decrease in aggregation rate. Temperature also has a significant effect: particles aggregate much faster at higher temperatures. However, regardless of different aggregation rates all the samples will eventually gel. We show that the unattached silanes swimming freely in the solution are responsible for the observed behavior. Particles are just physically bonded and this weak attraction can be broken either by lowering the pH of the suspension to induce repulsion among the particles or with sonication. Stable clusters form by pH deaggregation but sonication only produces unstable clusters. At constant pH, the rate of deaggregation can be controlled by particle/silane concentration in the same way that aggregation rate was controlled. Higher silane concentration well dispersed suspension in favor and higher degaggregation rates are observed.

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## Acknowledgments

I have had the great pleasure working with Dr. Themis Matsoukas as my PhD advisor over the past 4 years. He is a wonderful advisor, kind person and great researcher. I have learned many things from him and he has always been very supportive and helpful throughout these years. I would like to sincierly thank him for his advices, encouragement and patience. I also thank my committee members, Dr. Jim Adair, Dr. Robert Rioux, and Dr. Darrell Velegol for their encouragement and support throughout my research.

I started my project in Matsoukas group with Dr. Carl Marshall and Dr. Anaram Shahravan as my lab mates. Carl was very helpful during the short time that we worked together and Anaram was always very supportive not only as my lab mate, but also as a wonderful friend, I experienced my best years of PhD while working besides her. I also had the pleasure working with You-Han Chen and Farzad Mohajerani, graduate student that joined our group later on. I had a great opportunity to work with a number of undergraduate students in the lab including Dan Raily, Alec Myers, Andrew Ferguson, Dionna Janay Littles and Salem Ahmed. I also would like to thank Dr. Kiarash Vakhshoori, and Payam Khodaparast for their consult, support and great friendship. I would like to acknowledge technical and administrative staff in Millennium science complex (MSC) at Penn State and Advance Cooling Technology Inc. in Lancaster, specially Trevor Clark, Dr. Tapan Desai, Matt Flannery and Angie Fan for their consult and technical collaborations. I am thankful to the members of Dr. Velegol, Dr. Zydney, Dr. Adair and Dr. Colby group for sharing their experimental instruments and laboratory equipments.

I would also like to express my gratitude to Dr. Borhan for his kind support during these years.

My brother, Sam Lotfizdeh who has always supported me in every possible way. He has always been my encouragement to take each and any successful step in my life. Most importantly, Navid Sharif, my fiancé, for his unlimited love. He has always been supportive in all the greatest and hardest parts of this journey. I am very grateful for that.

# Dedication

I would like to dedicate this work to my father, Ahamd Lotfizadeh, and my mother, Nasrin Jahangiri. Their unlimited love and support has always been the greatest motivation for me to take each one of my steps toward success and happiness.



## Introduction

## 1.1 Motivation

The thermal properties of colloidal dispersions have only recently come under the scope of investigators and several reviews have appeared on this topic [6, 7, 7-19]. The motivation is quite practical. The heat transfer fluids used in common heat exchangers (but all liquids in general) have low thermal conductivity when compared to solids (Figure 1.1). Among common thermal transfer liquids, water (k = 0.608 W/m K) is about the most conductive. Ethylene glycol and most other organic liquids have conductivities that are lower by a factor of 2 or more. The thermal conductivity of solid materials is typically much higher. Silica, a poor conductor of heat, has twice the conductivity of water; the conductivity of alumina is almost an order of magnitude higher, while that of metals is larger by yet another order of magnitude. This large difference implies that a solid dispersed in a thermal fluid can lead to significantly higher thermal conductivity, even at very small amounts. It is for this reason that the thermal properties of colloidal dispersions are of interests. There are advantages in using particles



Figure 1.1: Thermal conductivity of selected pure liquid and solid materials at 20  $^{\circ}$ C [1,2].

in the nanometer range for such applications. Most importantly, small particles remain well dispersed avoid difficulties associated with settling, a problem that becomes more severe as the material density of the particles increases. Producing colloidally stable dispersions can be a challenge, especially in non-aqueous thermal systems. One of the most powerful tools for enhancing stability, suspensions's pH, is not of much practical use because most industrial heat transfer operations require near-neutral pH conditions. Despite these problems, a small number of commercial heat transfer fluids enhanced by colloidal additives are currently available [20]. Over the past 15 years there has been growing interest in thermal characterizations of nanoparticle suspensions and in the mechanisms that control their thermal behavior. Alumina (Al<sub>2</sub>O<sub>3</sub>,  $k_p = 35$  W/m K) [21–34] and copper oxide (CuO,  $k_f = 77$  W/m K) [21, 24, 26, 29, 32, 33, 35–38] are among the most widely used materials because they are rather inexpensive to obtain in nanometersize particles. Moreover, even though their conductivity lies in the mid-range for solids (see Figure 1.1), it is high enough that it can deliver the very high enhancement. There are some practical difficulties associated with copper colloids: with a density of 8.96 g/cm<sup>3</sup>, settling becomes a serious problem. Colloidal silica, though not a good conductor, is often the subject of investigations primarily because of its availability in monodisperse form over a range of particle sizes [37,39] but more important, it serves as a model colloid for well-controlled studies [40,41]. Though silica offers a small advantage in thermal conductivity, enhancements of the order of 20% are possible but this requires volume fractions that are relatively high. With non-aqueous systems the enhancement of the thermal conductivity can be higher because of the larger solid-to-fluid ratio of conductivities. Among nonaqueous systems ethylene glycol is the most commonly used base fluid [30,42,43]. Some studies have considered less well-defined liquids such as engine oil and pump fluid, as a means of improving heat transfer in actual machinery. Nonetheless, the formation of stable suspensions in non-polar liquids remains a challenge that has limited both the practical application of colloidal thermal fluids, as well as the study of their thermal properties.

Colloidal dispersions are inhomogeneous media consisting of solid phase dispersed within a continuous fluid. Their transport properties are quite complex and a general theory for simple theoretical calculations is not available. If the mobility of the phases is neglected, the system may modeled as a static inhomogeneous dispersion. The theory for this model was developed by Maxwell [44] in the context of electrical conduction, which translates directly into thermal conductivity (Eq. 1.4) and applies to the dispersion of spherical inclusions in a continuum medium at volume fractions sufficiently low that each particle may be treated independently of the rest. This theory makes several explicit or implicit assumptions. Particles are spherical and immobile and the temperature profile at the fluid-solid interface is continuous, i.e., surface (Kapitza) resistance is not present,

$$\frac{k}{k_f} = \frac{k_p + 2k_f + 2\phi(k_p - k_f)}{k_p + 2k_f - \phi(k_p - k_f)},$$
(1.1)

where k,  $k_p$  and  $k_f$  are the conductivities of the dispersion, of the particle and of the base fluid, respectively and  $\phi$  is the volume fraction of the dispersed phase. Maxwell's theory, therefore, may still apply and indeed represents the benchmark by which to analyze experimental results.

#### Beyond Maxwell's Limit

The measured conductivity of colloids is often highly variable and found to exceed Eq. 1.4. This has led to various speculations about possible nanoscale mechanisms that could explain effects that are stronger than those predicted by classical continuum theories and are not well controlled. Major studied effects includes, Brownian motion, a liquid layering around the particles and particle clustering [2, 6, 42, 45–47]. Large amount of these studies has addressed this inconsistency to ignorance of Brownian motion of the particles. Diffusion of the high conductive particles within the low conductive material was proposed to have an additive contribution in heat conduction through the fluid. However this effect is small. Particles in a temperature gradient develop a thermophoretic drift velocity,  $u_T = D_T \nabla T$ , where  $D_T$  is the thermal diffusion coefficient. Under no slip conditions, the thermophoretic velocity is essentially the characteristic velocity for the transport of heat via microconvection induced by the prepense of the particles. For typical colloids,  $D_T \sim 10^{-12} m^2/s$  K, yielding thermophoretic that are far too



Figure 1.2: Maxwell's model for the conductivity of a dispersed phase.

low to have an appreciable effect [40]. On the other hand, clustering is the most plausible hypothesized mechanism behind this unpredicted behavior of experimental systems, however there is no direct evidence of aggregation effect. Aggregated particles may provide a connected network of high conductive phase, performing more efficient than single particles in conducting heat. Aggregates exist in nearly all colloidal suspensions and can explain the variability in experimentally measured conductivities where aggregation state is not well controlled. This hypothesis originates from Maxwell's theory itself and will be discussed in details in the following section.

## 1.2 Maxwell's Theory

#### 1.2.1 The Lower Limit

Maxwell first addressed the problem of conduction in an inhomogeneous medium idealized in the form of two concentric spheres (Figure 1.2a), an inner sphere with

radius  $R_1$  and conductivity  $k_1$ , and outer one with radius  $R_2$  and conductivity  $k_2$  [44]. Maxwell shows that this system is equivalent to a homogeneous sphere of radius  $R_2$  whose conductivity is

$$k = k_2 \frac{k_1 + 2k_2 + 2(R_1/R_2)^3(k_1 - k_2)}{k_1 + 2k_2 - (R_1/R_2)^3(k_1 - k_2)}.$$
(1.2)

If the inner sphere is replaced by a collection of N smaller spheres of radius  $R'_1$ with any random configurations, Maxwell showed that the conductivity of the new arrangement can be obtained as an extension of the above result, if one assumes the distances between the spheres to be large enough such that effects in disturbing the course of the phonons may be taken as independent of each other (particles not touching) [44]. Maxwell's result for this case is

$$k = k_2 \frac{k_1 + 2k_2 + 2N(R'_1/R_2)^3(k_1 - k_2)}{k_1 + 2k_2 - N(R'_1/R_2)^3(k_1 - k_2)}.$$
(1.3)

It is the standard model for the conductivity of a colloidal dispersion with particle conductivity  $k_p = k_1$  and a fluid conductivity  $k_f = k_2$ . This result is usually expressed as an enhancement ratio in the form

$$\frac{k}{k_f} = \frac{k_p + 2k_f + 2\phi(k_p - k_f)}{k_p + 2k_f - \phi(k_p - k_f)},$$
(1.4)

where k,  $k_p$  and  $k_f$  are the conductivities of the dispersion, of the particle and of the base fluid, respectively, and  $\phi = N(R'_1/R_2)^3$  is the volume fraction of the dispersed phase. With  $k_p > k_f$ , as is the case with most solid dispersions, the conductivity of the dispersion is always higher than that of the fluid. To a first-order approximate in  $\phi$  the above result simplifies to

$$\frac{k}{k_f} \approx 1 + 3\phi \left(\frac{k_p - k_f}{2k_f + k_p}\right),\tag{1.5}$$

and clearly shows that the fractional enhancement is proportional to the difference between the conductivity of the two phases. Upon increasing the conductivity of the solid the conductivity of the dispersion increases but not indefinitely. Setting  $k_p \gg k_f$ , Eq. (1.4) gives

$$k_{\max} = \left(\frac{1+2\phi}{1-\phi}\right) k_f \approx (1+3\phi)k_f.$$
(1.6)

This gives the maximum possible conductivity in a system of well-dispersed spheres at fixed volume fraction. In this limit the enhancement ratio  $k/k_f$  depends only on the volume fraction but not on the conductivities of the two phases. The conductivity itself (k) is a function of the conductivity of the fluid and also of the volume fraction, but is independent of the conductivity of the solid phase. For example, at  $\phi = 0.05$  the maximum enhancement that can be expected is  $k/k_f = 1.158$ . The result can be explained as follows. When the solid phase is infinitely conductive, the rate of heat transfer is limited by the conductivity of the less conductive phase, which occupies a fraction  $1 - \phi$  of the total volume. Thus the result depends only on  $k_f$  and  $\phi$ . This behavior is reached for relatively small ratios of  $k_p/k_f$ . For example, with  $k_p/k_f = 10$ , the actual enhancement of the thermal conductivity is 93% of the  $k_{\text{max}}$ . This means that even materials with conductivities in the mid-range of Figure 1.1 can deliver practically the same enhancement as materials with much higher conductivity. Alumina and copper oxide, for example, produce enhancements of the order of 20% at volume fraction of about 5%. Even though copper has higher conductivity, it does not lead to significantly better enhancements, due to this path dependent conduction effect. Effect of particle volume fraction is always more pronounced than the magnitude of the particle thermal conductivity.

#### 1.2.2 The Upper Limit

Maxwell's result makes two important predictions. The first one is that the enhancement is independent of the size of the dispersed phase and depends only on its volume fraction. A dispersion, regardless of particle size, reduces to the core-shell system of Figure 1.2, in which the core represents the dispersed phase coalesced into a single sphere with the same volume fraction. A second, less obvious consequence is that the order of the layers in the core-shell model is important. In the basic model depicted in Figure 1.2, the core represents the phase with the higher conductivity. If the order is switched such that the more conductive phase is in the *outside*, the conductivity of the new arrangement is obtained from Eq. (1.4) by interchanging  $k_p$  and  $k_f$  and replacing  $\phi$  by  $1 - \phi$ :

$$\frac{k}{k_f} = \left(\frac{k_p}{k_f}\right) \left(\frac{3k_f + 2\phi(k_p - k_f)}{3k_p - \phi(k_p - k_f)}\right).$$
(1.7)

The linearization of equation 1.7 with respect to  $\phi$  gives

$$\frac{k}{k_f} = 1 + \frac{\phi}{3} \left( \frac{2k_p}{k_f} - \frac{k_f}{k_p} - 1 \right) + o[\phi^2]$$
(1.8)

In the limit of high particle conductivity  $(k_p \gg k_f)$  Eq. (1.7) simplifies to

$$k'_{\max} = k_p \left(\frac{2\phi}{3-\phi}\right). \tag{1.9}$$

The conductivity in this case depends on that of the solid (now the continuous phase), and in contrast to Eq. (1.6), it increases continuously with increasing  $k_p$ .

Equation (1.7) predicts conductivities that are *higher* than those from Eq. (1.4)at the same volume fraction. To understand why, we return to Figure 1.2(a), which represents the dispersion as a core-shell structure. When the less conductive phase is placed in the shell, the system has lower overall conductivity because the exterior of the core-shell structure partially insulates the conductive core. In the limit that the conductivity of the shell goes to zero, the conductivity of the core-shell system goes to zero as well. On the other hand, if the more conductive phase is placed at the shell, the core-shell system will remain conductive even if the core is a perfect insulator. Therefore, given two phases with different conductivities, the most conductive core-shell structure is the one that places the more conductive material on the outside. Equations (1.4) and (1.7) are known as the lower and upper limits, respectively, of the Maxwell theory. They are often referred to as the Hashin-Shtrikman (H-S) bounds after the two authors who obtained them in the context of magnetic permeability [48]. The two bounds of Maxwell's theory are shown in Figure 1.3. Accordingly, the lower limit refers to a system of well-dispersed particles (the more conductive phase is dispersed within the less conductive phase) and the upper limit to a system in which the fluid is dispersed within the solid phase.



Figure 1.3: Upper and lower bounds of Maxwell's theory of thermal conductivity with  $k_p/k_f = 10$ . The dashed line represents the conductivity from simple mixing rule in parallel systems.

#### **1.2.3** Effect of Clustering and Maxwell Limits

The relevance of the Maxwell limits to colloidal systems has been elaborated in a series of papers by Eapen, Yi and coworkers [18, 40, 49]. The lower limit clearly represents a well-dispersed system of spherical particles at low volume fractions. The upper limit may be viewed as an idealized model for aggregated nanoparticles (Figure 1.4). Colloidal clusters are typically fractal in structure that can be loosely modeled as interconnected chains. These provide a network of high-conductivity pathways that transfer heat over longer distances compared to well dispersed spheres. In the extreme case that the colloid forms a gel, the solid phase is truly continuous throughout the entire structure (Figure 1.4c). This situation approximates the conditions of the upper limit in Maxwell's theory. The analogy is not exact because the liquid forms also a continuous rather than a dispersed



Figure 1.4: Schematic of (a) Well-dispersed particles; (b) colloidal clusters; (c) colloidal gel; (d) fluid dispersed within solid matrix.

phase as Maxwell's model assumes (Figure 1.4d) [50–53]. Therefore the two limits, shown in Figure 1.3, represent the range of enhancement that can be expected from a colloidal dispersion and may be viewed as mixing rules for the conductivity of the two-phase system that depend on the degree of aggregation. Both Maxwell limits are below the diagonal that connects the conductivities of the pure phases and whose equation is

$$k_{||} = (1 - \phi)k_f + \phi k_p. \tag{1.10}$$

This expresses the conductivity of the system as a simple volumetric average of the conductivities of the two phases and corresponds to a system of resistances in parallel. The upper limit of the theory comes close to the parallel resistance model but it still lies below it. Clustered colloids are predicted to exhibit conductivity that is higher than that of the well-dispersed system. Maxwell's upper limit in Eq. (1.7) offers an upper bound, albeit approximate, of the maximum effect due to clustering. The two Maxwell limits strictly apply to the core-shell structure of Figure 1.2 with the more conductive phase placed in the inner core (lower limit) or in the shell (upper limit). In applying these to colloidal dispersions we must



Figure 1.5: Experimental conductivities of selected aqueous colloidal systems (Alumina, Copper oxide and copper particles). Solid lines are the lower and upper bounds of Maxwell's theory.

require the volume fraction to be small enough such that the effect of the dispersed phase may be treated as additive. For the lower limit this implies low volume fractions. This is usually interpreted to mean that Eq. (1.4) is exact to the first order in  $\phi$  [18], however, direct calculation shows Maxwell's result to hold up to surprising high volume fractions as long as particles are not touching [54]. Since most colloidal systems in thermal applications are at low volume fractions, this requirement is normally met and Maxwell's result is applicable. For the upper limit the requirement is  $\phi \to 1$  because in this case the liquid forms the dispersed phase. This condition is never met in experimental systems. Equation (1.7) therefore must be viewed as a qualitative upper limit for the fully gelled colloid.

Based on this hypothesis adapted from Maxwell's theory, aggregation of the particles which nearly occurs in all experimental systems, can explain the inconsistency observed in the literature. Figure 1.5 demonstrates that the experimental data lie indeed within the two classical limits. An extensive review of literature given by [18] shows this to be invariably the case. However, no direct measurements have yet confirmed the significant effect of aggregation, as formation of aggregates with well controlled sizes is quite a challenge. Aggregation is a kinetically driven process which, once started, usually proceeds uncontrollably until either the aggregates precipitate out solution, or the size and concentration of aggregates reaches such levels that further aggregation proceeds slowly.

#### **1.3** Research Goals

The main objective of this dissertation is to address the thermal behavior of colloidal suspensions and investigate the effect of clustering and structural properties of particles on heat conduction experimentally, theoretically and by numerical simulation. In examining these, we explore the following research goals:

1) Formation of stable silica nanoclusters in water with well controlled degree of aggregation at constant volume fraction of primarily particles.

2) Investigate the effect of particle clustering on thermal conductivity by employing the developed experimental system of silica nanoclusters.

3) Employ numerical simulations to study thermal conductivity of non-spherical particles and also evaluate the effect of particle aggregation and cluster configuration on heat transfer.

4) Develop a theory to quantify the effect of aggregation on thermal conductivity of nanocolloids.

5) Study the kinetics of reversible gelation and equilibrium cluster formation.

### **1.4** Dissertation Outline

In chapter 2, a reversible colloidal system with well controlled degree of aggregation was developed. This chapter reviews the formation of stable clusters of inorganic nano particles in aqueous solution. These cluster are formed as a result of the balance between hydrophobic and electrostatic interactions. Surface of silica particles were treated with different silane coupling agent with the aim of identifying an aminosilane capable of forming a monolayer on particle surface without causing chemical aggregation during the coating process. Silane monolayer prevents permanent aggregation by surface passivation and steric stabilization. By full surface treatment, the zeta potentials of particles were changed to that of amino groups which are positive at acidic pH and neutral at alkaline pH values. Therefore electrostatic interactions and consequently cluster size were controlled as a function of pH. This system exhibits reversibility as aggregation among the particles is not permanent and degree of aggregation can continuously and repeatedly be varied from a well dispersed suspension to a colloidal gel by changing the pH.

In chapter 3, the effect of aggregation on thermal properties of colloidal suspensions was directly evaluated for the first time. At constant volume fraction of silica particles, thermal conductivity increases monotonically with increase in the cluster size between the limits of Maxwell's theory. This result shows that aggregation which normally is neglected can fully be accounted for discrepancy among experimental measurements. The results also confirm that Maxwell's theory can accurately predict the limits of conductivity. Effect of silane monolayer on thermal conductivity of the particles was also investigated experimentally and numerically. Conductivity of silica particles decreased as the surface coverage of the coating was increased. The silane with very low thermal conductivity acts like an insulator on particles surface and decreases their conduction efficiency. The effect of the silane layer was more pronounced in well dispersed suspensions compared to aggregated systems.

In chapter 4, a numerical method was employed to generally address conductivity of non-spherical particles. Monte Carlo simulation was employed to study the effect of particle size and shape as well as clusters with different degrees of aggregation and configuration on thermal conductivity of the suspension. This method provides an accurate tool to evaluate conductivity between Maxwell's limits where the theory is inadequate. Thermal conductivity of spherical particles, hollow particles, rods and different model aggregates was evaluated and compared with different theoretical models. We show that Maxwell's lower limit can be employed for well dispersed suspensions of symmetric particles. However for asymmetric particles, this is not a reliable theory. The effect of neck formation between aggregated particles on conductivity of the aggregated suspensions was studied. We show that as long as the clusters, regardless of the size of the neck that is formed, are placed in a conductive medium, conductivity enhances above singlets at constant volume fraction of solid material. Resistance created by the neck only changes the percentage by which this enhancement increases.

In chapter 5, a predictive model was developed to quantify the thermal conductivity in nanocolloids. Maxwell's continuum theory was extended to capture the effect of clustering and give the entire conductivity profile between the limiting bounds. Clustered colloids were modeled as suspensions of equivalent spheres with effective conductivity and volume fraction. Maxwell's upper limit was used as an estimate to model the effective conductivity of the clusters themselves. Thermal conductivity of the suspension was then evaluated by Maxwell's lower limit as a function of cluster volume fraction. Fractal clusters were generated numerically using diffusion limited cluster-cluster aggregation and the model was validated against conductivity of the fractals (measure by simulations) and experiments in chapter 2 with a very good agreement.

In chapter 6, the kinetics of the reversible gelation process and cluster formation of silica particles coated with a trifunctional silane were studied. We show that at the isoelectric point of the suspension, gelation rate can be varied from seconds to month by changing the silane concentration, particle concentration and temperature. However, these effects are only kinetic and with different rates, all the samples eventually gel. Interestingly increasing the silane concentration or particle concentration, decreases gelation rate subsequently. Rate of deaggregation process can also be controlled. The gel dissociates to smaller sized clusters as a function of pH. Particles reach their final size with different rates depending on both pH and particle concentration. Similar to the gelation, the higher the concentration, the more the particles are prone to remain separated, therefore faster deaggregation rate. We show that the unattached excess silane in the solution is responsible for this unusual behavior. Chapter 7 summarizes the dissertation and gives detailed recommendations for future works.



# Reversible Gelation: Route to the Formation of Stable Clusters with Controlled Size

## 2.1 Introduction

The formation of nanoclusters has recently become of great interest due to their high potential to be used in wide range of applications including biotechnology, medical imaging, sensors and catalysts [55–57]. Clusters may exhibit enhanced physical properties relative to primary particles or provide features that do not exist in monomers [58,59]. Improved optic, electronic, magnetic properties have been reported in the literature for clusters of inorganic nanoparticles [60–63]. Therefore, by controlling the degree of aggregation, a suspension with tunable properties can be produced. The mechanism by which cluster formation occurs, has been studied extensively in the literature [64]. Kinetically driven aggregates are difficult to control because once a stable colloid is colloidally destabilized, particle growth continues uncontrollably until either the aggregates precipitate out solution, or the size and concentration of aggregates reaches such levels that further aggregation proceeds slowly due to slower diffusion. In these processes, aggregation is usually induced by pH change, increase in ionic concentration, manipulation of steric interactions or inducing depletion attraction between particles [65–69]. Gilber et al. [65] investigated the formation of stable iron oxhydroxide clusters in aqueous solutions. By changing the pH, particle's surface charge and as a result electrostatic repulsion among the particles were tuned to form different sized aggregates. However without any surface modification, particles will eventually aggregate permanently.

Aslan et al. [66] controlled the size of biotinylated gold nanoclusters by using the strong bimolecular interactions that exist among biotinyl and streptavidin molecules. Streptavidin has two biotinyl binding sites that can connect at least two biotinylated gold particles. As the concentration of streptavidin in the solution increases, the number of particles entangled together also enhances. Therefore, by controlling the concentration of the binding agent they were able to create finite sized clusters. Tan et al. [68] also investigated cysteamine/carboxymethyl cellulose treated gold (CA/CMC AuNP) cluster formation at different pH by UV-Vis spectroscopy. This system was developed based on the chain conformation change of CMC at different pH values along with the electrostatic interactions among anchored CA to the surface of the particles and CMC which is weakly absorbed to the surface. However large aggregates were formed by this method. There are other assemblies which have been developed by solvent evaporation. Usually after addition of a polymer to a particle suspension, concentration of both are increased by evaporation [69, 70]. Attraction created due to depletion is much faster than polymer adsorption onto the surface. As a result, clusters grow in
size until finally a steric layer provided by adsorbed polymers prevents further aggregation [69]. However as it is not possible to control the cluster size precisely in kinetic-base aggregation, usually large aggregates with wide distributions form that limits their use. In many cases short term stability or small ranges of cluster sizes are reported [67, 68].

On the other hand, clusters form via reversible equilibrium route are expected to behave differently. A number of theoretical studies have discussed mechanisms leading to development of long lived clusters by having long range repulsive and short ranged attractive interactions [71–73]. Formation of a potential well enables stable cluster formation and sometimes reversibility in the system. Experimentally, reversible equilibrium clusters have been studied mostly in suspensions of organic nanoparticles and proteins [74]. In aqueous solutions of protein nanoclolloids, tunable short range depletion repulsion is usually present along with weak long range electrostatic repulsion. High concentration of protein is needed to create strong enough attraction to balance high repulsion between these particles.

For inorganic particle however there are few reported reversible assemblies [70]. Murthy et al. used evaporation quenching method to develop equilibrium assembly of gold nanoclusters [70]. These cluster are formed as a result of a weak adsorption of triblock copolymer on surface of gold particles bounded to citrate and cystine. Upon hydrolysis and pH decrease the polymer starts degrading from the surface. The citrate/cystain monolayer prevents permanent aggregation and help clusters dissociation to single particles as a result of carrying slightly negative charge. In this method, surprisingly, the size of the clusters is widely distributed and particles are so closely packed that the boundary of individual particles could not be recognized by TEM. However unlike kinetic assemblies with very packed structures [69], large gold spacing has been mostly reported in equilibrium assemblies of this particle [75].

Here we develop a system which undergoes reversible gelation responsive to pH where we were able to develop equilibrium nanoclusters with a well controlled degree of aggregation at different pH values. Cluster size can be continuously and reversibly changed from fully dispersed to fully gelled by controlling pH as an external stimuli. We study the colloidal behavior of silica particles modified with three different amino silanes. These studies are essential to identify a silane capable of fully modifying the surface of the particles without causing irreversible aggregation. By full surface treatment of silica nanoparticles, a monolayer on particle surface was developed to prevent chemical reaction and permanent aggregation among the particles at close spacings. A complete study on electrophoretic behavior of coated particles at different pH was done to assess the electrostatic interaction among the particles. In this system, in contrast to other studies, the degree of aggregation was controlled via tuning the long range electrostatic repulsive force. By complete surface coverage of silanes, particles are expected to obtain electrokinetic behavior of amino groups, neutral at high pH and positively charged at low pH. Therefore by tuning the pH, the balance between electrostatic repulsion and hydrophobic/van der Waals attraction can be controlled to tune the size of the clusters.

## 2.2 Experimental

### 2.2.1 Materials

LUDOX TM-40 colloidal silica, 40 wt.% suspension in water supplied by Sigma Aldrich CO., ST. Louis, MO was used. Initial size of the particles were 30 nm

determined by dynamic light scattering and confirmed by transmission electron microscopy. Three different silane coupling agents supplied by Aldrich Co., Milwaukee, WI, were studied: 3-aminopropyltriethoxysilane (APES), aminopropyldimethylethoxysilane (APMS), and N-[3-(trimethoxysilyl)propyl]ethylenediamine (TMPE). Hydrochloric acid (HCl) was employed for pH adjustments.

#### 2.2.2 Characterization Techniques

Particle sizes were measured by dynamic light scattering (Brookhaven model A2039 AT using a He-Ne laser with  $\lambda = 632.8$  nm). Samples were diluted in water and the autocorrelation function was recorded at 25°C and at a scattering angle  $\theta = 90^{\circ}$ . The average hydrodynamic diameter was obtained by cumulant analysis based on 5 independent measurements. Particles and clusters were also studied under transmission electron microscopy(TEM) using Philips 420 with min resolution of 3.4 Å. Zeta potential was measured in a Brookhaven ZETAPALS analyzer and the results were analyzed using the Smoluchowski equation [76]. Values reported in the paper are the average of 10 measurements.

#### 2.2.3 Surface Modification

Ludox was diluted to 12 wt.% with deionized water. pH of the suspension was around pH= 9.5 after dilution. The prescribed amount of each silane was added drop-wise to the diluted Ludox under vigorous stirring. Upon addition of the full amount of the silane, the sample was stirred at room temperature for 24 hours (stirring speed =1000 RPM).



Figure 2.1: Chemical structure of silanes used in this study.

#### 2.2.4 Gelation and Cluster Formation

Surface modification with TMPE concentration of 0.096 g/g silica was done. pH of the suspensions was increased to around pH= 10.8 and zeta potential was slightly negative. pH adjustments were done by addition of HCl to pH= 9.8 ( $\pm 0.1$ ) where zeta potential reached zero and the gel formed. For cluster formation, pH was adjusted to five different values (3, 4, 5.6, 7, 8.6 and 9.2) using hydrochloric acid and were sonicated for 20 min at 25°C in a bath sonicator. Their sizes were monitored after redispersion over one month of storage at room temperature. Reversibly test was done without any sonication at pH= 3.

## 2.3 Results and Discussion

The colloidal behavior of bare silica is determined by the amphoteric character of surface hydroxyls, whose isoelectric point is in the pH range 1.5 - 3.5 [77]. Except in strongly acidic environments, the silica surface is negatively charged and colloidally stable to a moderate degree by electrostatic repulsion. If colloidal stability is destroyed by shifting the pH to near the isoelectric point, the system undergoes

irreversible and uncontrollable aggregation via condensation of hydroxyl groups among particles. Surface modification with aminosilanes resolves the irreversible aggregation by simultaneously removing the reactive sites that are responsible for chemical aggregation and providing a steric layer on the surface. A substantial body of literature exists on the surface modification of colloidal silica nanoparticles via chemical attachment of a variety of molecules. Typical silane coupling agents (SCA) contain silane group  $-Si(OR)_x(x=1, 2, 3)$ . This type of reaction has been studied extensively in the literature [78,79]. Silicon alkoxides attach to the silica surface via hydrolysis of the siloxane bond and subsequent condensation with reaction with hydroxyl groups on the silica surface. Condensation reactions may also take place between the alkoxides themselves and this increases the risk of forming siloxane oligomers with the potential of causing the aggregation of particles. Experimentally, the challenge is to graft the silane at high surface coverage onto nanocolloidal silica (30 nm) without causing aggregation. Aggregates that form during the coating process are chemically bonded through uncovered parts of the surface and can not be redispersed. This issue is commonly neglected in studies done with silanes in this area [80–82]. As shown in figure 2.2, the three silanes of this study perform quite differently with respect to this objective. APES causes aggregation even when added at small amounts. Pham et al. [83] suggested that cross linking of silanes (with more than one reactive site) among the particles could explain this significant aggregation. Higher coverages was achieved using APMS. With this molecule well dispersed particles with surface coverages up to 40% were attained but at higher coverages yet again caused growth by aggregation. APMS with only one ethoxy group minimizes the effect of self reactions because these stop at the dimer, but it potentially forms less packed coating on the surface. By



Figure 2.2: Size of silica particles after coating with different concentrations of APES, APMS, TMPE. Concentrations are reported as surface coverages are estimated theoretically by taking the area of the silane to be 20 Å<sup>2</sup> [3] and a surface area of 110 m<sup>2</sup>/g as reported by the manufacturer. Aggregation during coating process is irreversible and undesirable for this study.

occupying the same volume on the particle, APMS contains only a single hydroxyl group that can attach to the surface. On the other hand TMPE, which like APES hydrolyses to three hydroxyls groups showed a much better performance and allowed full coverage on particle surface without causing significant aggregation in the system. This silane with a longer tail and containing two aminogroups provides higher steric interactions along with the stronger electrostatic repulsion in compare to APES and APMS. Stability of the particles during the coating process with TMPE is contributed to the higher steric protection, as the coating process was done at high pH where amino groups were mostly neutral and the electrostatic repulsion contribution was minimal. Note that the amount of silane is reported as surface coverage and is estimated by taking the area of the silane to be 20 Å<sup>2</sup> [3]

and a surface area of  $110 \text{ m}^2/\text{g}$  as reported by the manufacturer. Reaction with aminosilanes inverts the electrokinetic profile of silica to that of amines, namely, positive below the  $pK_a$  conditions, neutral above. Upon increasing the surface coverage of the coating, a higher number of hydroxyl groups (negatively charged) are replaced with the amino groups (positive or neutral) on the particle surface. Therefore zeta potential can be continuously shifted by systematically increasing the treatment on particle surface. By these studies not only real surface coverage on particles can be assessed but also, the primary knowledge to control the surface charge and electrostatic repulsion between particles at different pH can be obtained. Figure 2.3 shows the zeta potential of the particles, before and after each treatment with the silanes at different pH. For partially covered surfaces, zeta potential represents the net charge arising from both the coated and uncoated. In all three cases after each treatment, zeta potential shifted systematically towards positive values at all pHs and the isoelectric point moved to higher pH. Reaction with aminosilanes inverts the electrokinetic profile of silica to that of amines, namely, positive below the  $pK_a$  conditions, neutral above. Upon increasing the surface coverage of the coating, a higher number of hydroxyl groups (negatively charged) are replaced with the amino groups (positive or neutral) on the particle surface.



Figure 2.3: Zeta potential of unmodified silica and coated silica with various surface coverages of (a) APES, (b) APMS and (c) TMPE at different pH.

Reaction with aminosilanes inverts the electrokinetic profile of silica to that of amines, namely, positive below the  $pK_a$  conditions, neutral above. Upon increasing the surface coverage of the coating, a higher number of hydroxyl groups (negatively charged) are replaced with the amino groups (positive or neutral) on the particle surface. Therefore zeta potential can be continuously shifted by systematically increasing the treatment on particle surface. By these studies not only real surface coverage on particles can be assessed but also, the primary knowledge to control the surface charge and electrostatic repulsion between particles at different pH can be obtained. Figure 2.3 shows the zeta potential of the particles, before and after each treatment with the silanes at different pH. For partially covered surfaces, zeta potential represents the net charge arising from both the coated and uncoated. In all three cases after each treatment, zeta potential shifted systematically towards positive values at all pHs and the isoelectric point moved to higher pH. At low pH values this shift was more dramatic even at low surface coverages. At acidic pH values, not only surface hydroxyls are near their isoelectric point, but also amino groups are highly ionized and positively charged, leading to this substantial change. By increasing surface coverage, particles acquired more positive charge, zeta potential became higher.

At high pH, zeta potential was more resistant to change. At basic pH, hydroxyl groups are highly ionized and in contrast, amino groups are mostly non charged, therefore high portion of the surface should be covered to induce significant changes in zeta potential. For APES and APMS no remarkable changes were observed while with TMPE by moving toward full coverage, zeta potential increased to a point (figure 2.3-c, 88% surface coverage) where no negative value was measured and isoelectric point was shifted to the native pH of the suspension. This confirms that

TMPE is capable of providing a monolayer coverage on particle surface, eliminating all the reactive sites to prevent irreversible aggregation and providing controllable electrokinetic behavior to control repulsion among the particles. The focus of the study is therefore on the particles fully coated by TMPE silane.

Following surface modification, a hydrophobic interaction is created between particles due to desirable attraction among hydrophobic tails of the silanes floating in aqueous medium. The size of the clusters is set by the balance between hydrophobic/van der Waals attractive, and electrostatic repulsive interactions and solely depends on pH which characterizes the strength of the repulsion among the particles. Figure 2.4 shows the size of these cluster as a function of pH, ranges from 39  $\pm 1$  nm (well dispersed) at pH=3 to micron sized clusters at pH=10. At higher pH, hydrophobic interactions are more dominant resulting in a higher degree of aggregation. Toward acidic pH, repulsion increases and dispersibility becomes more favorable to the system and smaller sized clusters are formed until a complete ionization of amino groups promotes well dispersed nanoparticles. These measurements were repeated after a month and size measurements were consistent with earlier values confirming the long term stability of these clustered suspensions. These clusters were also studied under TEM at pH = 5.6, 7.1 and 8.6 (figure 2.4). As the pH increases from 5.6 to 8.6 the degree of aggregation enhances. At high pH, zeta potential is so low that the strength of repulsion is not sufficient to prevent large aggregate formation. Suspension of particles with their final size distribution at different pH (figure 2.4) was sonicated for 40 minutes in water bath. Sonication assists particle redispersion and breaks weak and physical bonding among particles. Following sonication at all pH, complete redispersion to monomers was observed. However, with different rates of aggregation (based on



Figure 2.4: Hydrodynamic diameter of the silica nanoclusters at different pH with particle volume fractions of  $\phi = 0.06$  and  $\phi = 0.08$ . Measurements were repeated after a month to ensure stability of the clusters. Vertical dashed line represents the isoelectric point of the suspension (pH= 9.8) and horizontal dashed line represents the well dispersed suspension of particles. TEM images at pH = 5.6, 7 and 8.6 representing different degree of aggregation. The sizes obtained by DLS are 100, 150, 300 nm, respectively.

pH), clusters with same size distribution as their initial distribution were obtained. This behavior confirms that at any pH the suspension reached an equi-



Figure 2.5: Reversible gelation responsive to pH. Size of the clusters are monitored after pH change from pH=3 with highly repulsive particles to pH=9.7 at isoelectric point, and vice versa.

librium and size of the cluster reached their equilibrium distribution. No further aggregation or redipersion takes place.

At the isoelectric point of the suspension, due to the lack of repulsion, the state of the suspension is dominated by the interaction among the hydrophobic chains and the surrounding fluid (water) causing the colloid to gel. However, surface passivation along with steric stabilization of the particles prevented permanent aggregation. Therefore the gelation can be reversed and particles can fully redisperse simply by inducing repulsion among physically connected particles. By setting the pH to pH=3, particles became highly charged and the repulsion among particles, constructing the gel network, increased significantly. As a result the gel was destabilized and completely dissociated to monomers. Figure 2.5 summarizes the reversible behavior of this colloidal gel, simply by changing the pH from 9.7 to 3 and back, aggregation state was altered from fully gelled (pH=9.7) system to a well dispersed suspension (pH=3) repeatedly. Reversibility is held throughout all pH values. Therefore degree of aggregation can be in situ and continuously changed by controlling pH of the suspension.

## 2.4 Conclusions

In this study it was shown that not every silane is suitable for surface modification as they behave differently during the coating process. Aggregation during coating process is irreversible and therefore uncontrollable. Surface modification of silica particles with TMPE, provided a system with well controlled interactions which enables formation of clusters with controlled sizes. TMPE monolayer in this system functioned as the passivating agent, steric protection and also provided a zeta potential behavior which enabled the aggregation degree to change from a colloidal gel (zeta=0) to a well dispersed suspension (zeta > 40 mv) reversibly. In this system, electrostatic repulsion between the particles was tuned via pH to balance the hydrophobic attraction between the particle. Competition between short range hydrophobic interaction and long range repulsion creates a potential well which enables reversible equilibrium formation of stable sized clusters. Therefore clusters with equilibrium size distribution were developed as a function of pH. In extreme cases, at high pH, repulsion between the particles is screened, therefore, hydrophobic attraction is dominated and the system gels. However steric layer prevents very close spacing between particles and permanent aggregation. At low pH, repulsion becomes very high that no potential is created and cluster formation is impossible.



# The Thermal Conductivity of Clustered Nanocolloids

The majority of the work presented in this chapter was previously published in the Journal of APL Materials (Lotfizadeh, Desai and Matsoukas, 2012) [84].

# 3.1 Introduction

The presence of solid particles in a fluid is known to increase the thermal transport properties of the dispersion over that of the base fluid and the generally large difference between the conductivity of the two phases leads to significant improvements even at low volume fraction of the solid [6, 19]. This has suggested a remarkably simple way to improve the thermal conductivity of thermal fluids (which is generally low), through the dispersion of small amounts of a dispersed solid. The energy savings that could be achieved by colloidal thermal fluids (nanofluids) has prompted several investigations into their thermal properties, and particularly into the enhancement of the thermal conductivity of the base fluid in the presence of colloidal particles [7,85–89]. The precise magnitude of the enhancement has generated a debate in the literature that has centered on reports of anomalously large enhancements relative to those predicted by standard theories [6], and on the possible mechanisms that could explain such large enhancements [40,90]. The classical theory of heat conduction in inhomogeneous media was developed by Maxwell, originally in the context of electrical conduction, and gives the thermal conductivity of a two-phase system that consists of a dispersion of non-interacting spheres in a continuous medium [44]. At fixed volume fraction of phases, Maxwell's theory predicts in fact two limits [18,48]:

$$1 + \frac{3\phi_p(k_p - k_f)}{3k_f + (1 - \phi_p)(k_p - k_f)} \le \frac{k}{k_f} \le \frac{k_p}{k_f} \left(1 - \frac{3(1 - \phi_p)(k_p - k_f)}{3k_p - \phi_p(k_p - k_f)}\right).$$
(3.1)

Here, k is the conductivity of the dispersion,  $k_p$  and  $k_f$  are the conductivities of the solid and liquid, respectively, and  $\phi_p$  is the volume fraction of the solid phase. The lower bound corresponds to a dispersion of the phase with the higher conductivity into a continuum formed by the phase with the lower conductivity and represents the standard model for a well-dispersed colloid. The upper bound corresponds to a system in which the phases are inverted, such that the highconductivity phase forms the continuous medium into which the low-conductivity phase is dispersed. The upper limit has been proposed as a model for colloidal clusters based on the idea that the interconnected structure of an aggregated colloid establishes continuous pathways of high thermal conductivity [18,91]. In this view, the conductivity of a colloidal dispersion at a fixed volume fraction may range from the lower limit, for a fully dispersed system, to the upper limit, for a colloidal gel. Accordingly, experimental reports of thermal conductivities that exceed the lower bound of the theory could likely be accounted for by the presence of colloidal clusters. In an extensive review of the experimental literature over the past 15 years, Eapen and coworkers showed that measured conductivities are found to lie between these two bounds [18]. The clustering hypothesis expands the range of thermal conductivities that are acceptable within the classical view, but this fact alone does not prove that clustering is indeed the mechanism responsible for enhancements that fall in this range. In fact, the aggregation state of the colloid was not controlled in the studies reviewed by [18]. The ability of clusters and colloidal networks to increase the conductivity above that of the well-dispersed state has been predicted by simulation [86] and observed experimentally, [87,89, 92] but the magnitude of the enhancement falls short of Maxwell's predictions [92]. The uncertainty that continuous to surround the magnitude of the thermal conductivity of colloidal dispersions and the precise effect of clustering is due to the experimental difficulty in preparing systems whose aggregation state is well characterized and precisely controlled.

In this letter we show that clustering increases the conductivity of the dispersion and is capable of bridging the entire region between the two bounds of Maxwell's theory. To achieve control of the cluster size we have engineered a colloidal system that allows the production of colloidally stable clusters whose degree of clustering can be varied reversibly from the fully dispersed state to a colloidal gel. We fix the volume fraction of the primary particles and measure the thermal conductivity of the suspension as a function of cluster size to demonstrate systematic increases between the lower and upper bounds of Maxwell's theory.



Figure 3.1: Enhancement of the thermal conductivity of silane-treated silica suspensions as a function of the amount of silane at fixed volume fraction of particles  $\phi_p = 22.4\%$ . The inset graph shows the conductivity of the silane-treated silica particles, extracted from the conductivity of the suspension. The thermal resistance of the silane layer results in a 25% drop of the conductivity of the particle.

## **3.2** Result and Discussion

We begin with 30 nm (diameter) Ludox<sup>TM</sup> silica in water and graft onto their surface a silane, in this case N-[3-(trimethoxysilyl)propyl]ethylenediamine (TMPE). At pH < 4, the aminogroups are positively charged and result in a well-dispersed colloid stabilized by electrostatic and steric repulsion. At basic pH the amino groups are neutral and the lack of repulsion, along with the hydrophobic interaction between the grafted chains and the aqueous environment causes aggregation and even gelling, if the volume fraction is sufficiently high. In the intermediate region the cluster size is set by the balance between electrostatic and hydrophobic interaction and is fully determined by pH. These transformations are reversible because the silanized surface prevents the silica particles from binding irreversibly. Thus by control of the pH this system can span the entire range from fully dispersed nanospheres to a percolated colloidal gel, and back. Using this process we produce dispersions with volume fraction in the range 11 - 22% and measure the thermal conductivity as a function of cluster size using the hot wire transient method. Cluster sizes are measured by dynamic light scattering.

First we assess the effect of TMPE coating on the conductivity of silica. We functionalize silica with varying amounts of silane and measure the conductivity of dispersions at constant volume fraction  $\phi_p = 22.4\%$  and pH= 4, such that the colloid exists in a fully dispersed state. To avoid aggregation that usually occurs when particles are dried and then redispersed, thermal conductivities are measured in the liquid medium that is obtained after reaction with the silane. This medium consists of mostly water with small amounts of methanol produced by the hydrolysis of TMPE. Its conductivity was measured separately and was found to range from 0.70 W/m K to 0.676 W/m K, depending on the amount of methanol. Figure 5.1 shows the conductivity of the dispersion as a function of the amount of TMPE. At concentration 0.05 g/ml of TMPE we obtain practically full coverage of surface hydroxyls, as determined by measurement of the zeta potential pH range 2 to 12, which matches the ionization behavior of the amino groups (positive potential at acidic pH, neutral in the basic region). Note that all the thermal conductivities are measured with transient hotwire method described in appendix-A in more details. The conductivity decreases with increasing silane coverage, indicating that the silane adds thermal resistance to the particle. The conductivity of organic molecules is generally low. Monoethyl amine, for example, has a conductivity of 0.240 W/m K, [93] about one sixth of the conductivity of silica. It is therefore not surprising that a monolayer of surface silane has such strong effect on thermal conduction. We back-calculate the effective conductivity of the modified silica by solving the lower bound of Maxwell's prediction for  $k_p$ at volume fraction  $\phi_p = 22.4\%$  using the measured conductivity  $k_f$  of the base fluid. The results are shown in the inset graph in figure 5.1. At 0% TMPE we obtain  $k_p = 1.43$  W/m K, in excellent agreement with the literature value  $k_{\rm SiO_2} = 1.4$  W/m K for silica, [18] indicating that the lower bound of Maxwell's theory is indeed obeyed in the fully dispersed state. At the other end, full surface coverage by TMPE reduces the conductivity of silica by 25%.

To study the effect of clustering we prepare suspensions of silanized silica at full surface coverage at three volume fractions, 11%, 16.5% and 22%. At each volume fraction we adjust the pH to obtain clusters that range from 39 nm in diameter (fully dispersed) up to 300 nm, as measured by dynamic light scattering. The conductivity of the suspension is plotted in figure 3.2 as a function of cluster size. The conductivity increases approximately linearly with increasing aggregate size and the effect is more pronounced at higher volume fractions. At  $\phi_p = 0.22$ , for example, the conductivity of the dispersion nearly doubles as the cluster size is increased from 39 nm to 200 nm. We examine this behavior in the context of Maxwell's theory by replotting the data as a function of the volume fraction of the primary particles as shown in figure 3.3. Here, each data set represents contours of constant cluster size at fixed volume fraction, obtained from the data in figure 3.2. The lines marked (a) and (b) show respectively the lower and upper



Figure 3.2: Enhancement of thermal conductivity of aggregated nanoparticles. Each line represents a fixed volume fraction of nanoparticles. The dashed line marks the size of unmodified Ludox. Coated particles have a hydrodynamic radius that is 5 nm larger.

bounds of Maxwell's theory calculated with  $k_p = 1.063$  W/m K, corresponding to the decreased conductivity of silane-coated silica. The corresponding solid-to-fluid ratio of conductivities,  $k_p/k_f = 1.56$ , is too close to 1 and produces an extremely narrow range between the lower and upper limit of the theory. For this system, theory predicts no appreciable effect of cluster size. This is at odds with the experimental results. While this apparent conflict seems to suggest "anomalous" enhancement, we show that this is not the case.

The upper limit, labelled (b) in figure 3.3, treats the silane layer as a rigid film whose poor thermal properties makes it an insulator that decreases the effective conductivity of the particle. Clusters make contact at the surface of the insulating



Figure 3.3: Enhancement of thermal conductivity of aggregated nanoparticles as a function of the volume fraction of silica (size of aggregates increases in the direction of the arrow). (a) lower Maxwell bound based on conductivity of modified silica; (b) upper Maxwell bound assuming the silane coating to form a low-conductivity solid shell that prevents thermal contact between silica cores; (c) upper Maxwell bound assuming that silane coating permits thermal contact between silica cores.

layer and the chains they form are poor conductors because the most conductive phase, the silica core of individual spheres, remains isolated inside the insulating phase (shown schematically by the doublet labelled b in figure 3.3). In reality, the silane layer is neither rigid, nor does it provide a complete physical barrier over the solid core. It consists of short flexible chains that are attached to surface hydroxyls, while leaving silicon and oxygen atoms that belong to surface siloxane bonds exposed. [94] With all surface hydroxyls capped by the silane, the exposed surface is estimated to be approximately 50% of the total area [95]. In this picture, particles are capable of making thermal contact between silica cores even when silane is present such that their clusters form chains in which the continuous phase is the core material (depicted by the doublet labelled c in figure 3.3). The conductivity of these chains are clearly higher than that predicted under the assumption of no thermal contact between silica cores (line (b) in figure 3.3). In fact, the thermal behavior of these clusters is expected to be much closer to that of unmodified silica because thermal transport is dominated by the conductivity of the core material, whereas the resistance of the silane layer matters only at the entry and exit points of the heat path through the solid network. According to this model, we expect the conductivity of the clusters to reach as high as the upper limit of Maxwell's theory for unmodified silica. This limit is shown by the line labelled (c) in figure 3.3. The experimental data are seen to span the entire region between the two bounds of the theory. More importantly, the largest clusters approach very close to the upper limit of the theory.

We test this interpretation by numerical calculation. We model silanized silica as a spherical core that contains surface patches of silane domains that cover 34% of the particle surface. The conductivity of the core is set to  $k_p/k_f = 2.5$ , whereas the conductivity of the patches is set to half that of the core  $(k_{\text{silane}}/k_p = 0.5)$ , resulting in a decrease of the conductivity of the coated particle by 29%. These values closely match those in the experiment but are somewhat higher to avoid difficulties associated with larger numerical error when  $k_p/k_f \rightarrow 1$ . We form dispersions of single spheres and linear chains ranging from trimers to pentamers, and calculate their thermal conductivity by a Monte Carlo algorithm [96]. We discretize each particle into 787 volume elements (shown as small spheres in the inset image in figure 3.4) with 102 of them representing silane patches on the particle surface (shown in gold). A single particle or chain placed inside a cubic lattice whose size



Figure 3.4: Numerical simulation of the conductivity of dispersion composed of clusters of patchy spheres. The Maxwell bounds labelled (a), (b), (c) are the same as in figure 3.3. The patchy particle is shown on the bottom right corner, with each sphere representing a Monte Carlo lattice site of either silica (blue) or silane (yellow).

is adjusted to produce a volume fraction  $\phi_p = 8.2\%$ , the surrounding space is filled with a fluid, also represented by discrete volume elements, and the conductivity of the system is calculated using the method of [96]. According to this method, a number of walkers is launched on a random walk that is biased by the conductivity of the local site. The conductivity of the simulated dispersion is obtained from the evolution of the mean-squared displacement of the walk. This method is described more in detail in chapter 4.

The results of this calculation are are shown in figure 3.4 along the predictions of Maxwell's theory. The lower bound (a) and upper bound (b) are calculated using the conductivity of a silane covered particle  $(k'_p/k_f = 1.775)$ , whereas case (c) is the upper limit for the unmodified particle  $(k_p/k_f = 2.5)$ . The fully dispersed spheres are in excellent agreement with the lower bound of the theory. Upon increasing the length of the chains formed by these patchy particles, the conductivity increases systematically and approaches the upper limit of the theory. The pentameric chain is the largest linear cluster that can fit into the simulation volume. This chain forms a continuous conducting path between two opposing faces of the simulation volume and reaches to within 89.5% of the upper limit of the theory. These calculations are in agreement with the experimental observations and confirm that the thermal behavior of silane-treated silica is upper-bounded by the conductivity of unmodified silica, and that this bound can be reached if the size of the clusters is sufficiently large.

## **3.3** Conclusions

This study answers unambiguously the question as to the effect of clustering on the thermal conductivity of colloidal dispersions. This effect is strong and gives rise to conductivities in the entire region between the two classical limits of Maxwell's theory. This demonstrates that the conductivity of nanocolloidal systems can be understood completely within the classical view, as suggested by [49] and [18]. While this does not preclude the presence of other mechanisms that are microscopic in nature, their effects cannot be assessed experimentally unless the colloidal state of the system is controlled. The practice of producing suspensions by dispersing dry powders in a base fluid under stirring and sonication is inadequate because the presence of aggregates can be neither avoided nor controlled. Equally important is the observation that thermal conductivity is very sensitive to the chemistry at the

particle surface. Even partial coverage of the silica surface by silane produces a measurable drop in the conductivity of the particle. Surfactants and other common additives likely have a similar effect, therefore, their use in thermal applications must be assessed. The surface effect is not necessarily a detriment and could also be engineered to produce a colloid with improved thermal properties. If one deposits a highly conductive material as a surface layer on a core particle that is not necessarily a good conductor, the resulting system would be a better thermal medium than either the core particle alone, or a well-dispersed colloid made of the highly conductive material. This follows directly from Maxwell's classical theory (upper limit in Eq. (3.1)), which shows that an inhomogeneous two-phase system exhibits its highest conductivity when the more conductive phase surrounds the one that conducts less.



# Numerical Simulations of Thermal Conductivity

# 4.1 Introduction

Adding nanoparticles to a fluid results in considerable improvement of the fluid thermal properties and the standard theory by which this enhancement is predicted is Maxwell's mean field theory. Maxwell developed this theory for a dispersion of spherical particles [97] and it predicts two limiting bounds for thermal enhancement depending on whether the dispersed phase is the higher conductive (particles) or the lower conductive (fluid) material respectively. At any volume fraction of the solid material, we have the minimum enhancement by having a well dispersed dispersion of colloidal particles and the maximum values can be achieved with a colloidal gel. This suggests that the enhancement depends on the configuration and degree of aggregation of the particles, though such effects are not captured by Maxwell's theory [18]. In our previous chapter we confirmed this hypothesis by developing a reversible colloidal system capable of reversible gelation. Reversibility was essential to create controlled sized stable aggregated suspensions ranging from well dispersed particles to a fully gelled system. We distinctly showed that aggregated nanoparticles have higher conductivity compared to fully dispersed particles at the same volume fraction. However, the structure and configuration of the aggregates, as well as, shape and surface properties of the primary particles can effect thermal enhancement. To study such detailed structural effects one must go beyond experimental limitations to ovoid colloidal complications. Although Maxwell's theory provides a baseline calculation for an idealized system of well dispersed spheres in the limit of low volume fraction, for nearly all other cases, theory is inadequate and one must resort to numerical simulation. Macroscopic simulations are capable of capturing large scale structural effects, in particular clustering. The system is essentially modeled as a macroscopic object of different shapes by solving the macroscopic conduction equation. This can be done by any standard method (for example, finite differences, finite elements) but Monte Carlo methods are especially suited to handle complex geometries and one such algorithm will be discussed in greater detail.

In this study we present a systematic investigation of the thermal conductivity of non-spherical particles with special interest in identifying structures that maximize conductivity at fixed volume fraction of the solid and explore the range of validity of Maxwell theory for different particle shapes. We evaluate thermal conductivity of solid particles, hollow particles as well as rods , cubical particles, linear and nonlinear aggregates using Monte Carlo algorithms.

## 4.2 Monte Carlo Algorithm

Monte Carlo (MC) methods take advantage of the mathematical similarity between diffusion and heat conduction to calculate the thermal conductivity of a composite phase using random walks. Compared to classical numerical methods that solve the steady-state conduction equation, MC is much simpler to implement, straightforward to program, and does not require numerical libraries beyond access to a random number generator. This makes MC particularly appealing for the study of complex structures such as aggregated colloids, colloidal gels, nanofiber networks [98–103] and two-phase systems in general [54,96,104–109]. The theoretical foundation of the algorithm was given by [96] and its implementation is as follows. The simulation volume is discretized in cubic elements of equal size, each element representing either fluid or particle (Fig. 4.1). A walker is launched to perform a random walk of unit steps that is biased by the conductivity in each phase. Starting at a site, the walker on the discretized 3-*d* lattice can move in one of 6 directions. A direction is chosen at random and the walker is advanced to a neighbor site with probability,

$$p_{i \to j} = \frac{k_j}{k_i + k_j}$$

where  $k_i$  is the conductivity of the current site, and  $k_j$  the conductivity of the neighbor. If the target site is of the same material  $(k_i = k_j)$  the walker has a 50% chance to make the move. For dissimilar materials, the walker always has higher probability to remain in the more conductive phase. Time is advanced by  $1/k_i$  and the process is repeated to produce a trajectory in time,  $\mathbf{r}(t)$ . The thermal diffusivity D of the composite material is obtained from the Einstein relationship [99],



Figure 4.1: Schematic of Monte Carlo simulation of thermal conductivity. The volume is discretized into cubic elements and the conductivity is calculated by analyzing the trajectory of random walkers whose steps are biased by the conductivity of the phases.

$$D = \lim_{\tau \to \infty} \frac{1}{6t} \left\langle |\mathbf{r}(t+\tau)\mathbf{r}(t)|^2 \right\rangle, \qquad (4.1)$$

and the conductivity is finally calculated from its relationship to the thermal diffusivity,  $k = \rho C_P D$ . A large number of trajectories is generally required, especially if the difference in the conductivities of the two phases is large, in order to obtain results of sufficient accuracy. In practice, a large number of independent walkers is launched and the results are averaged to obtain the mean squared displacement. The method is very simple to implement and is capable of handling complicated structures such as non-spherical particles and colloidal aggregates. This algorithm was used in many studies to evaluate thermal conductivity of composite materials [110, 111]. Evans et al. [99] employed this method to study thermal conductivity of fractal cluster to confirm their proposed model of conductivity. Such studies highlight the fact that the structure of the clusters is an important factor, for example, clusters that contain a higher percentage of their particles along the backbone of the network exhibit higher conductivity than those composed of more compact arrangements [91]. This further emphasizes the importance of characterizing the colloidal state and structure of aggregates of a system when interpreting its thermal properties.

These studies were conducted with  $(k_p/k_f)$  in range of 4-100 which is characteristic of oxide particles like, silica or alumina or  $(k_p/k_f) > 100$  for metallic particles such as copper or aluminum. The precise value of  $k_p/k_f$  is changed for numerical however qualitatively the results are the same for all values of conductivity

## 4.3 Result and Discussion

#### 4.3.1 Effect of Lattice Number

To create colloidal suspensions and investigate their thermal properties, first we need to find the minimum number of lattice sites that a single particle should be composed of. A common way to create colloidal suspensions is to randomly pick single sites representing single particles [99]. To determine the minimum number of lattice sites, we evaluated thermal conductivity in suspensions of single spherical particles at fixed volume fraction made of different number of primary sites. Figure 4.2 shows that as the number of sites increases, enhancement increases and reaches a plateau. Therefore to capture the true value of conductivity, a minimum number of seven primary sites are needed for particle formation. Simulation method was validated by Maxwell's lower bound theory. Suspensions of well dispersed spherical particles each made with  $n_{\rm site} = 7$  at different volume fractions with  $k_p/k_f = 4$  were generated and compared with Maxwell's lower bound which is the standard model to evaluate enhancement in well dispersed suspensions. Figure 4.3 shows the excellent agreement between the simulated values and theory prediction and validates our numerical simulation.



Figure 4.2: Effect of the number of lattices a single spherical particle is composed of numerical simulations, on thermal conductivity of suspensions with with  $k_p/k_f = 20$  at constant solid volume fraction of  $\phi = 0.1$ . The dashed line represents conductivity predicted by Maxwell's theory.

#### 4.3.2 Effect of Particle Size

Before investigating the conductivity of particle with different structures, we aimed to answer some experimentally unsolved issues such as the effect of particle size on thermal conductivity. There are few theoretical and experimental studies claimed that primary size of the particles are important while Maxwell's prediction only depends on the volume fraction [112, 113]. Chen et al. measured thermal conductivity of silica suspensions with different particle sizes. According to their measurements, particles with larger nominal size had significantly higher thermal conductivity [113]. However there is no report on the degree of particle aggregation in the system leaving the doubt that this enhancement could be probably due to the higher degree of aggregation in larger particles. To distinctly evaluate the effect of particle size, thermal conductivity of suspensions with the same volume fraction of  $\phi = 0.05$  and conductivity ratio of  $k_p/k_f = 4$ , but with different par-



Figure 4.3: Comparison of thermal conductivity between simulations (points) and Maxwell's theory (dashed line) for a well dispersed suspension of spherical particles at different volume fractions with  $k_p/k_f = 4$ . Particle are each composed from seven number of primary lattices.

ticle sizes was simulated. As shown in figure 4.4 as long as the volume fraction is constant, whether we have just one single large particle or many tiny spheres, size of the particles does not matter and conductivity is enhanced by the same percentage. The dashed line is the calculated enhancement from Maxwell's theory which correctly excludes the effect of size in well dispersed spherical particles.

### 4.3.3 Cubic Particles

We have also calculated the thermal conductivity of a cubic particle with the same volume fraction of of  $\phi = 0.05$  and conductivity ratio of  $k_p/k_f = 4$  to evaluate the range of Maxwell's lower limit validity for non-spherical particles. We can see in figure 4.4, that in the case of cubic particles, same enhancement (last point) as



Figure 4.4: Effect of particle size of spherical particles on thermal conductivity of the solution at fixed volume fraction of  $\phi = 0.05$  and  $k_p/k_f = 4$ . This graphs also shows conductivity of a cubic particle at the same volume fraction. The dashed line represents conductivity predicted by Maxwell's theory.

spherical particles is reached and shape of the particles does not have an impact on conductivity enhancements. As a result, Maxwell's theory is still valid for conductivity of these particles.

#### 4.3.4 Hollow Particles

Maxwell's upper bound corresponds to two concentric spheres where the low conductive material (liquid) is completely entrapped in a continuous phase of a high conductive material (solid). Hollow particles with a solid shell and fluid filled core are a true representation of the upper bound. Therefore understanding their thermal behavior helps reaching closer to higher conductivities and Maxwell's upper limit. We have studied thermal properties of suspensions containing hollow



Figure 4.5: Thermal conductivity of hollow particles as the core radius increases while the mass concentration is constant at 6wt.% with  $k_p/k_f = 20$ . The dashed line represent conductivity predicted by Maxwell's theory with a two step calculations : (1) Thermal conductivity of hollow spheres, (2) Thermal conductivity of the suspension using step 1 calculations.

particles and compared it with the Maxwell's theory. Figure 4.5 shows thermal conductivity of hollow particles at 6wt.% and  $k_p/k_f = 20$ . By moving from a dispersion of solid particles to that of hollow particles we can increase thermal enhancement from 20% up to around 40% while keeping the solid mass fraction constant. A hollow particle itself has lower thermal conductivity relative to a solid particle because it contains the same mass of solid and increasing amount of the low conductive phase (liquid) within. But in a suspension, these particles occupy more volume and as a result heat can travel a greater distance in the high conductive region and enhances the conductivity more efficiently. In fact, between the effect of higher volume fraction and lower conductivity, enhancement is more influenced by the volume fraction, as a result, higher enhancement is reached finally. When the hollow particles become larger, the enhancement becomes more pronounced. Maxwell's upper bound can be reached if we assume that just one single hollow particle occupies the entire space in the system. This results suggest that in practical thermal applications, specially where expensive materials like gold or silver are needed, developing hollow particles is a exceptional way to significantly improve heat transfer beyond that of solid particles with same mass of the material. This enhancement was also compared with the theory. We first employed Maxwell's upper bound to calculate thermal conductivity of the hollow particle itself  $(k_h)$ ,

$$k_h = k_p \frac{k_f \left(3 - 2\phi_i\right) + 2\phi_i k_p}{k_f \phi_i + k_p \left(3 - \phi_i\right)}.$$
(4.2)

where  $\phi_i$  is the volume fraction of solid material inside the hollow particle. Then, Maxwell's lower bound was employed to calculate conductivity of dispersed hollow particles with conductivity  $k_h$  and volume fraction  $\phi_h$ ,

$$k = \frac{2k_f + k_h + 2\phi_h \left(k_h - k_f\right)}{2k_f + k_h - \phi_h \left(k_h - k_f\right)}.$$
(4.3)

As figure 4.5 shows, simulations and theory matches very well. Therefore, conductivity in suspension of hollow particles can be predicted accurately by the two step calculation of Maxwell's theory. This also suggests that, Maxwell's lower bound can be used for any suspension of dispersed particles as long as effective conductivity and volume fraction of the particles are known. This issue is discussed in more details in following chapter.
### 4.3.5 Rods

Among the many other materials that have been studied, carbon nanotubes (CNT) and nanofibers are of special interest. CNTs consist of graphitic sheets that form multiwall nanotubes with diameter 20-500 nm and length that can be several micrometers. They are characterized by very high thermal conductivity and their anisotropic shape makes them potentially excellent additives to thermal fluids. Several studies have reported on the thermal properties of these systems [28, 51, 89, 114–122]. Maxwell theory which was developed for spherical particles fails to predict thermal behavior of these suspensions. For non-spherical particles, the most common model is that of Hamilton and Crosser [123], which is based on the work of [124]. This model modifies Maxwell's lower limit as follows:

$$k = \frac{(n-1)k_f + k_p + (n-1)\phi_p \left(k_p - k_f\right)}{(n-1)k_f + k_p - \phi_p \left(k_p - k_f\right)}.$$
(4.4)

The shape of the particle is incorporated into the parameter n, whose general form is

$$n = 3/\psi^a,\tag{4.5}$$

where  $\psi$  is the sphericity of the particle, defined as the surface area of an equal volume sphere over the surface area of the particle. In [124] the exponent *a* is 1 for spheres, 2 for prolate ellipsoids, and 1.5 for oblate ellipsoids but the experiments of [123] were better described with a = 1 regardless of shape. With  $\psi = 1$ , and the above results reverts to Maxwell's lower limit for spherical particles.

For non-spherical particles ( $\psi < 1$ ) Eq. (4.4) gives conductivities that are higher than that of spheres. To study Maxwell range of validity for asymmetric particles, investigate thermal behavior of these particles and also validate Hamilton model,



Figure 4.6: Thermal conductivity of suspensions of rods with aspect ratios in the range of R/L = 0.1 to R/L = 1 and, therefore, shape factors between n = 3 to n = 6 in compare to Maxwell's limiting bounds (dashed lines) at volume fractions of  $\phi = 0.02$  and  $\phi = 0.04$ . The inset graph shows the comparison between these simulated values (point) to the Hamilton's model (dotted line).

we established simulations on suspensions of rods with aspect ratios in the range of R/L = 1 to R/l = 0.1 and conductivity of  $k_p/k_f = 10$  at particle volume fractions of  $\phi = 0.02$  and  $\phi = 0.04$ . This results are summarized in figure 4.6. This figure shows that enhancement at fixed volume fractions depends on the aspect ratio of the rod and as the aspect ratio decreases (sphericity decreases), conductivity increases above Maxwell's lower limit. Elongated particles such as rods and fibers facilitate heat transport along their primary axis. Upon increasing the aspect ratio at constant volume the enhancement along the backbone increases further and, even though transport along the perpendicular axis is decreased compared to the isotropic particle of the same volume, the overall conductivity of the suspension increases. At constant volume fraction, maximum enhancement is reached when the rod becomes long enough to connect two opposite sides of the cubical lattice. Although Maxwell's lower limit fails to predict enhancement in this system, all simulated conductivities including the maximum, fall between limits of this theory. Conductivity of rods with n ranges from 3 to 5 were compared to Hamilton Model as shown as subfigure in figure 4.6. Excellent agreement was observed with a = 1. Simulations also suggest that regardless of shape of the non-spherical particles, Hamilton model works best with a = 1.

While the thermal performance of these systems is superior to those involving spherical nanoparticles, the difficulties associated with the preparation of stable dispersions with acceptable flow characteristics represent challenges that must be overcome before thin/long nano rod suspensions can fulfill their potential in thermal applications involving liquid media.

Investigating thermal conductivity of suspensions of both spherical and nonspherical particles leaded us to the conclusion that Maxwell's lower limit can be employed for suspension of monomers as long as we have symmetric shaped particles like cubical, spherical even hollow particles. Anisotropic shapes including rods, cylinders, ellipsoids and etc. enhances conductivity higher than what predicted by Maxwell's lower limit specially when their sphericity decreases. However this enhancement always lies between Maxwell's predicted bounds.

### 4.3.6 Linear and Nonlinear Model Aggregates

Aggregation is the dominated mechanism to increase thermal conductivity of colloidal suspensions beyond expectation as discussed before. However while we were able to control the degree of aggregation in our experimental system and evaluate the effect of aggregation, configuration of the aggregates can not be controlled precisely. In fact clusters with the same size can have different configurations such as linear, packed, fractal or any other structures. Although many different studies have been investigating ways of creating assemblies with controlled configurations, this is still an experimental challenge. On the other hand, MC simulations enable us to create different model aggregates and investigate thermal conductivity of such systems. This capability provides not only a tool to find the exact conductivity in system with any aggregated structure and size but also a way to investigate the effect of particle configuration in an aggregated structure on conductivity.

Figure 4.7 shows thermal conductivity of different model aggregates with  $\phi = 0.1$  and  $k_p/k_f = 20$ . The first four bars represent the thermal conductivity of suspensions containing linear clusters ranging from monomer to pentamer which is the largest linear aggregate to fit in our cube and actually makes contact with the side of the box. Conductivity increases as the cluster grows in length as expected and yet pentamers can enhance conductivity about 20% above Maxwell's lower bound. This shows the significant effect of aggregation on thermal enhancements. Even by making doublets or triplets, thermal conductivity can be improved remarkably. Likewise rods, the maximum enhancement that is possible to reach with a linear cluster is when it becomes long enough to connect two sides of the lattice. By this connection heat can be transferred to the other side without any interruption of low conductive phase.

Although these linear clusters can increase conductivity remarkably, we are still well below the upper bound of Maxwell theory. In order to find simple aggregated structure with closer conductivity to upper limit, cross-linked structures were developed. As shown in figure 4.7, higher enhancements are observed for



Figure 4.7: Effect of aggregation state and cluster configuration on conductivity enhancement. Thermal conductivity of different model aggregates at  $k_p/k_f = 20$ and solid volume fraction of  $\phi = 0.1$  is presented. The last bar of the chart represent a structure created from hollow particles with the same mass concentration of the other configurations (10wt.%).

these structures in compare to linear clusters. Different configurations of these solid particles can increase the enhancement differently between the bounds. Maximum enhancement (up to 30%) is reached with a three way cross aggregate that connects all sides of the system to each other. In these aggregated structures, more pathways are provided through high conductive phase in all directions. Therefore, conductivity enhances beyond linear aggregates. Maxwell upper bound represents a system where the fluid is completely embedded within the solid which is not the case for any of these model configurations. Therefore to improve conductivity enhancement in these simple model aggregates, even one step further, we have created clusters of hollow particles. Since a well dispersed system of hollow particles has much higher thermal conductivity of solid particles, we can imagine the same behavior in aggregated structures of hollows. As shown in the last bar of figure 4.7, at constant solid fraction, by making the exact configuration as the three way cross with hollow particles, higher thermal conductivity is achieved. Therefore any configuration of particles recreated by hollows, has higher conductivity because, not only pockets of low conductive phase are trapped within each particle and separated but also high conductive phase is continuous throughout the system.

### 4.3.7 Necking

There are few studies which address the effect of aggregation completely different from the previously reported behavior, due to the necking effect [125, 126]. A neck will form between the particles as they aggregate. Since the neck has a very small surface area, thermal resistance between the particles becomes high and as a result, thermal conductivity decreases. With this analogy conductivity is much lower in suspension of clusters compared to singlets as Jie et al. concluded in their study [125]. They developed a theoretical model based on this analogy and the effect of necking and aggregation on thermal enhancement. Desai et al. [126] also studied thermal conductivity of clusters in vacuum using molecular dynamic simulations and showed that small necks build high resistance against heat transfer leading to less conduction in aggregates. To address the necking effect between aggregated particles, we investigate the effect of the neck size between two aggregated particles with  $k_p/k_f = 160$  and  $\phi = 0.09$ .

Figure 4.8 shows thermal conductivity of two separated particles as they aggregate and merge further. By decreasing the center-to-center distance between



Figure 4.8: Effect of the size of the neck formed between particles after formation of a doublet, on thermal conductivity with  $k_p/k_f = 160$  and  $\phi = 0.09$ . Size of the neck is represent by particle's center-to-center distance (d). Dashed line represents conductivity of well dispersed suspension (Maxwell's theory).

the particle we merge them further while maintaining the volume fraction constant. When the particles touch, the thermal conductivity suddenly increases and reaches a maximum. By merging further, enhancement decreases moderately until the particles completely merge into a single particle where enhancement reaches Maxwell's lower limit for well dispersed systems. This shows that although aggregated structures have lower intrinsic conductivities than single particles, when are placed in a fluid medium, they conduct heat much more efficiently. As the doublet forms with any neck size, the thermal conductivity of the suspension increases above that of singlets (lower limit). Existence of a maximum in this system is due to the competition between the length and the area which heat can travel through the system. This competition is more dominated by the length of the doublet, as we infer from the fact that maximum earlier in the merging process.



Figure 4.9: Simple model of series and parallel resistances formulating the behavior of heat transfer in suspension of (a) singlets and (b) doublets. (c) Conductivity calculated based on the simple model as the slabs distance  $(d/d_o)$  decreases [4].

This behavior can be modeled as a set of series and parallel resistances to capture the importance of having a conductive medium and explain the effect of necking on thermal conductivity [4]. When the particles are separated, heat encounters three resistances  $R_p, R_f$  and again  $R_p$  with respect to particle, fluid and particle (figure 4.9-a). In the case of a doublet the intermediate resistance becomes more complicated and can be modeled as a parallel set of resistances.  $R_f$ ,  $R_n$  and again  $R_f$  with respect to resistance of fluid, neck and fluid (figure 4.9-b). In parallel systems the overall resistance is always smaller than each individual resistance ( $R < R_f, R_n$ ). Therefore, because of the medium, which enables parallel transfer of heat, smaller resistance exists between a doublet and finally smaller overall resistance compared to the separated particles. A simple model based this analogy was developed and as the figure 4.9-c shows its general behavior agrees very well with the simulations. A sudden enhancement is predicted when the particles touch with a slower decrease to the initial value as they merge into a single particle.

### 4.4 Conclusions

Numerical simulations provide an accurate tool to investigate the effect of particles/aggregates structure on conductivity of the colloidal suspensions which is neither captured by theory nor simply possible to investigate by experiments. We employed a MC method to study the effect of particle size and shape as well as aggregation and necking effect. We showed that Maxwell's model provides a good prediction for well dispersed suspensions as long as the particles are symmetric. Asymmetric particle enhances conductivity above Maxwell's prediction, however, the limits still provide a valid range. We investigated thermal conductivity of hollow particles and showed that at the same mass fraction, hollow particles are significantly better conductors than solid particle as Maxwell proposed. MC simulations enable evaluation of the exact enhancement in suspensions of clustered particles including linear and nonlinear clusters. At the same volume fraction, degree of aggregation and the structure of the clusters affect thermal conductivity significantly. The higher the degree of cross linking or the lower the density of the structures, the higher the thermal conductivity. We also showed that necking effect does not have a negative impact on thermal conductivity as long as a conductive medium exists. As a doublet form, thermal conductivity enhances in the system beyond singlets by different amounts depending on the neck size.



# A Continuum Maxwell Model for the Thermal Conductivity of Clustered Nanocolloids

# 5.1 Introduction

The addition of solids into liquids increases the thermal conductivity of the base fluid, since solids typically have much higher conductivity than liquids [18]. The magnitude of this enhancement is given by Maxwell's theory, a continuum theory for the conductivity of inhomogeneous systems developed originally for electrical conduction [97]. Several experimental studies have reported enhancements that are much higher than those predicted by the theory, giving rise to various hypotheses as to the origin and precise magnitude of this enhancement [7,19]. The role of clusters has been presented as a major factor controlling the conductivity of colloidal suspensions as demonstrated in chapter 3 that colloidal clusters indeed enhance the conductivity above that of well dispersed spheres with the same volume fraction. Qualitatively, this enhancement is due to the longer paths for heat transfer that emerge along the backbone of the solid matrix that forms the cluster. The qualitative prediction of the thermal conductivity of clustered colloids has been investigated in a number of studies. In a different approach Prasher et al considered structural properties of clusters and developed a model that includes contributions from particle chains forming the backbone of the cluster, and dead-end particles attached to the backbone [91]. The model gave good agreement with simulated aggregates. Wang et al. [127] applied a fractal model to calculate the conductivity of clustered colloids. They calculated the conductivity of the cluster using an empirical model that reduces to the classical Maxwell at low volume fractions and included the effect of size polydispersity appeared to match the experimental measurements. The model, however, includes multiple simultaneous contributions (clustering, polydispersity, surface adsorption) to isolate the effect of clustering alone. Prasher et al. [86] developed a model that treats the dispersion of clusters as a dispersion of equivalent spheres and used the model of Wang et al. [127] to obtain the intrinsic conductivity of the cluster. This model predicts that between the fully dispersed and fully gelled system the conductivity reaches a maximum. However this behavior has not been confirmed experimentally.

The basis for analyzing experimental measurements of the thermal conductivity is given by the classical model of Maxwell, a mean field theory originally developed for electrical conduction in inhomogeneous media [97]. Maxwell obtained the conductivity k of a solid/liquid dispersion in terms of the conductivity of the two phases and the volume fraction  $\phi$  of the solid

$$k\Big|_{\rm L} = \frac{2k_f + k_p + 2\phi \left(k_p - k_f\right)}{2k_f + k_p - \phi \left(k_p - k_f\right)},\tag{5.1}$$



Figure 5.1: Maxwell model of solid dispersion (top), and of dispersion of finite-size clusters (bottom).

where  $k_p$  and  $k_f$  are the conductivities of the solid phase, and the fluid, respectively. According to Maxwell's result the size of the dispersed phase is not important, conductivity depends only on the volume fraction of the two phases. In fact, Maxwell's original derivation is for an arrangement of two concentric spheres, an inner sphere with conductivity  $k_p$  enclosed in a sphere of fluid with conductivity  $k_f$  (figure 5.1a). This system is thermally equivalent to a dispersion of spheres of same volume, as long as they are not close enough to interact. The order of layers is important, however. Thermal conduction is dominated by the phase that provides continuous paths to heat transfer. It follows that the maximum conductivity is obtained when the most conductive phase is continuous and the least conducting phase is fully enclosed within. The order of the phases, however, matters. By placing the most conductive phase as an outer shell that encloses the least conductive phase as an inclusion leads to higher conductivity. This is obtained from Eq. (5.1) by swapping  $k_p$  and  $k_f$ , and replacing  $\phi$  with  $1 - \phi$ :

$$k\Big|_{\rm U} = \frac{k_f + 2k_p - 2(1-\phi)(k_p - k_f)}{k_f + 2k_p + (1-\phi)(k_p - k_f)}.$$
(5.2)

Equations (5.1) and (5.2) establish two limits for the thermal conductivity of a composite two-phase system at fixed volume fraction of the phases, indicated by the subscripts L and U, respectively. The lower limit corresponds to well dispersed particles and represents the standard equation by which experimental results are analyzed in the literature. The upper limit may be viewed as a model for aggregated structures. Colloidal particles form interconnected chains that provide paths of high conductivity while trapping the liquid phase, which is less conductive, into pockets inside the clustered structure. This hypothesis was advanced by Eapen and coworkers [18, 49], who reviewed a large body of data and showed them all to fall between these two limits. More recently, we demonstrated under controlled aggregation conditions that the conductivity of a colloidal suspension at constant volume fraction increases with aggregation and reaches the upper limit when the system forms a gel. This suggests that the upper limit of Maxwell's theory represents a realistic model for the conductivity of a cluster suspension.

Here we develop an analytic model for the conductivity of suspended clusters based on Maxwell's theory. We calculate the conductivity of clusters using the upper limit, and the conductivity of their dispersion using the lower limit. We fine-tune the model by comparison with simulations and finally demonstrate that it captures the observed experimental behavior very well.



Figure 5.2: Thermal conductivity of clusters as a function of solid fraction  $\phi_i$  of clusters  $(k_p/k_f = 10)$ .

# 5.2 Theory

Clusters, and non-spherical particles in general, may be represented by an equivalent sphere with conductivity  $k_c$  and effective volume fraction  $\phi_c$  such that the conductivity of the dispersion can be calculated from the lower bound of Maxwell's theory in Eq. (5.1), with  $\phi_p$  and  $k_p$  replaced by the cluster parameters  $\phi_c$  and  $k_c$ , respectively. The goal is to obtain the effective parameters of the cluster and relate them to structure. We view the cluster as a continuous solid network that contains a volume fraction  $\phi_i$  of primary particles with the remaining  $1 - \phi_i$  corresponding to fluid entrained inside the cluster. The internal volume fraction  $\phi_i$  characterizes the structure of the cluster and is a measure of its density. It ranges from  $\phi_i = 1$ , corresponding to a completely solid cluster that contains no fluid, to  $\phi_i = \phi_p$ , corresponding to a colloidal gel with a macroscopically continuous solid backbone. By balance on the solid phase, the volume fraction of clusters is  $\phi_c = \phi_i \phi_p$ . Therefore, either  $\phi_i$  or  $\phi_c$  is sufficient to describe the clustered state since  $\phi_p$  is assumed known. To calculate  $k_c$ , we treat the cluster as a composite structure in which the solid forms the continuous phase and the liquid is dispersed. The conductivity of this structure may then be obtained from the upper Maxwell limit with  $\phi_p$  replaced with  $\phi_i$ :

$$k_c = k_p \frac{k_f \left(3 - 2\phi_i\right) + 2\phi_i k_p}{k_f \phi_i + k_p \left(3 - \phi_i\right)}.$$
(5.3)

The conductivity of the clustered suspension is then calculated from the lower bound with  $k_c$  in place of  $k_p$ , and  $\phi_c = \phi_p/\phi_i$  in place of  $\phi_p$ :

$$k = k_f \frac{k_c \phi_i + 2k_c \phi_p + 2k_f \phi_i - 2k_f \phi_p}{k_c \phi_i - k_c \phi_p + 2k_f \phi_i + k_f \phi_p}$$
(5.4)

In the context of the Maxwell theory, this two-step calculation is represented by a three-layer concentric structure (figure 5.1b): the outer layer represents the suspending fluid, the solid shell represents the clustered particles, and the inner sphere represents the liquid that is trapped inside the clusters. This arrangement has higher thermal conductivity than the dispersed colloid (figure 5.1b) because the more conductive phase (solid) is now closer to the outer radius. The conductivity from Eqs. (5.3) and (5.4) is plotted in figure 5.2 and shows the enhancement ratio  $k/k_f$  as a function of  $\phi_p$  for various values of  $\phi_i$ . Recall that  $\phi_i$  characterizes the solid fraction in the cluster and ranges from 1 (the cluster in this case is a solid sphere) to  $\phi_p$  (a single cluster that spans the entire volume). All contours of constant  $\phi_i$  start from the lower limit of Maxwell's theory at  $\phi_p$  and terminate at the



Figure 5.3: Fractal clusters with N = 40, 80 and 160 produced by diffusion-limited cluster-cluster aggregation. Circles represent the size of the equivalent sphere with the same conductivity.

upper limit at  $\phi_i = \phi_p$ . The effect of aggregation can be followed along a path of constant  $\phi_p$ . Starting with a fully dispersed system, the conductivity is given by point A ( $\phi_i = 1$ ). For fractal colloidal aggregates, the solid fraction scales with size as  $\phi_i \sim r^{-(3-d_f)}$ , where  $d_f$  is the fractal dimension. Since  $d_f < 3$ ,  $\phi_i$  decreases with increasing cluster size, and the conductivity of the system moves towards point B. This behavior was confirmed experimentally in [128].

## 5.3 Simulations

Implicit in the model is the assumption that the liquid entrained by the cluster is dispersed, i.e., fully entrapped inside the solid, which allows us to obtain the conductivity of the cluster from the upper bound of Maxwell's theory. In reality clusters are bicontinuous with respect to both phases and their thermal conductivity must be less than the maximum predicted by Maxwell. How much less depends on morphology and inner structure. To address this point quantitatively we turn to simulation. We generate clusters by diffusion-limited cluster-cluster aggregation (DL-CCA) (appendix-B) and calculate  $k_c$  and  $\phi_i$  numerically. We perform the calculations on a cubic lattice to produce fractal clusters ( $D_f = 1.87$ ) containing 40 to 160 primary particles. We calculate the thermal properties of the cluster by Monte Carlo following the method of [96]. We place the cluster in a lattice and fill the unoccupied sites by fluid to produce a suspended cluster at volume fraction  $\phi_p = N_p/L$ , where  $N_p$  is the number of primary particles in the cluster and L is the size of the lattice. We then launch a number of walkers that perform a random walk that is biased by conductivity such that the walker moves from site i to neighboring site j with probability  $p = k_i/(k_i + k_j)$ , where  $k_i$  and  $k_j$  are the corresponding conductivities. We obtain the thermal diffusivity from the Einstein relationship [49],

$$D = \lim_{T \to \infty} \frac{1}{6T} \left< |r(t+T) - r(t)|^2 \right>,$$
 (5.5)

and finally the thermal conductivity from  $k = D/\rho C_p$ , where  $\rho$  is the density and  $C_P$  is the heat capacity of the dispersion.

This calculation produces the thermal conductivity of the suspended cluster at the specified  $\phi_p$  but does not resolve  $k_c$  and  $\phi_i$  separately. To obtain these two parameters we first note a characteristic property of Maxwell's theory for a suspension of spheres: when  $k_p$  is increased indefinitely, the conductivity of the suspension reaches a plateau that depends only on the volume fraction of the dispersed phase (and the conductivity of the fluid):

$$\left(\frac{k_p}{k_f}\right)_{\max} = 1 + 3\phi_p. \tag{5.6}$$

Clustered spheres show the same behavior. Figure 5.7 shows the conductivity of suspended clusters from the simulation, plotted as a function of the conductivity of the solid. We see that clusters of all size a plateau in conductivity as  $k_p \to \infty$ . We use this analogy between dispersed and clustered spheres to define the effective

volume fraction of clusters as the volume fraction of suspended spheres with the same maximum conductivity k in the limit  $k_p \to \infty$ :

$$\phi_c = \frac{1}{3} \lim_{k_p \to \infty} \left( \frac{k}{k_f} - 1 \right). \tag{5.7}$$

With  $\phi_c$  known and  $\phi_i = \phi_p/\phi_c$ , we calculate the conductivity of the dispersion from Eqs. (5.3) and (5.4). This is shown by the dashed line in figure 5.4. As anticipated, the calculation overestimates the conductivity of the dispersion everywhere except in  $k_c \to \infty$ . The predicted conductivity will be reached only when the solid fraction of the cluster fully encloses the liquid fraction. This is not the case for the clusters studied here, which is to say that the solid fraction  $\phi_i$  contributes less to the conductivity of the cluster than theory predicts. To correct for this behavior we introduce an empirical morphological factor  $\alpha$  and rewrite Eq. (5.3) in the form

$$k_c = k_p \frac{k_f \left(3 - 2\alpha\phi_i\right) + 2\alpha\phi_i k_p}{k_p \left(3 - \alpha\phi_i\right) + \alpha\phi_i k_f}.$$
(5.8)

For  $\alpha < 1$  the effect of this factor is to reduce the contribution of  $\phi_i$  and decrease the overall conductivity of the cluster. With  $\alpha = 1$  we recover Eq. (5.3), which corresponds to a core-shell particle with the solid in the shell and the liquid in the core; the case a > 1 is not physically possible under Maxwell's model. The value of  $\alpha$  is characteristic of the internal structure of the cluster and must be evaluated for the specific cluster. Here, we obtain  $\alpha$  by fitting the conductivity obtained by simulation to the corrected model represented by Eqs. (5.8) and (5.4). These results are shown by the solid lines in figure 5.4. We find that a common value  $\alpha = 0.34 \pm 0.01$  represents all three cluster sizes and provides excellent agreement between theory and simulation.



Figure 5.4: Comparison of the conductivity of suspended clusters by theory (lines) and simulation (points). The dashed line is obtained from Eq. (5.4) with  $k_c$  from Eq. (5.3), while the solid line calculates  $k_c$  from Eq. (5.8) with  $\alpha = 0.34$ .

Once the true effective properties of the generated fractal clusters are known, Maxwell's lower limit, as theory states, can be employed to predict conductivity of the suspension at any particle volume fraction. Therefore we recreated the parametric graph(figure 5.2) representing the theory for  $k_p/k_f = 200$ , and compared conductivity of fractal suspensions at different volume fraction of primary particles. As shown in figure 5.5, theory agrees very well with the simulation. At constant particle concentration, by moving toward larger aggregates, conductivity increases. As these clusters are fractal in nature, larger clusters have lower particle densities. At fixed cluster size, enhancement follows the dashed line relative to the cluster density as the concentration increases.



Figure 5.5: Comparison of conductivity at different volume fractions with  $k_p/k_f =$  200 between theory (dotted lines) and simulation (points) with  $N_p = 40, 80, 160$  and  $\phi_i = 0.335, 0.298, 0.245$  respectively. Enhancement follows different lines depending on  $\phi_i$  of the clusters

We return to the effective volume fraction of the cluster, which defines the



Figure 5.6: The radius of the equivalent sphere of the cluster  $(R_c)$  plotted as a function of the radius of gyration  $(R_g)$ . The radii are normalized by the size of the lattice  $(R_0)$ .

radius of the equivalent sphere,  $R_c = R_p (\phi_c/\phi_p)^{1/3}$ , where  $R_p$  is the radius of the primary particle. The effective radius correlates very well with the radius of gyration (figure 5.6). We note that the volume fractions calculated from  $R_g$  have much higher uncertainty that those calculated from figure 5.4, nonetheless, the radius of gyration provides a very good estimate of the effective thermal radius of the particle.

# 5.4 Comparison with Experiment

The ultimate test of any theory of conduction in aggregated nanostructures is in comparison to experiment. Such comparison presents a challenge, however, as in most experimental systems colloidal aggregation is an uncontrollable process that leads to an unsteady population of a wide distribution of cluster sizes. Even when the aggregation rate is slow enough to permit thermal measurements, the distribution of sizes is too wide to resolve the effect of cluster size on the conductivity of the dispersion. We recently reported on a model colloidal system that allows us to overcome these difficulties [128]. We have coated colloidal silica (Ludox,  $30\pm1$  nm in diameter) with a monolayer of N-[3-(trimethoxysilyl)propyl]ethylenediamine that offers steric repulsion against permanent aggregation. At pH < 4, these particles produce a well-dispersed colloid that is stabilized electrostatically via repulsion of the ionized amino groups. At pH near 11, the amino groups are neutral and the hydrophobic interaction between the silane layer and the aqueous solvent causes aggregation and the formation of a colloidal gel, which, however is not permanent and can be redispersed by acidification. At intermediate pH the system exists in clusters whose size is solely determined by the pH. The reversible nature of the aggregation/redispersion of this silanized silica produces clusters in a range of sizes that is much narrower compared to aggregation induced by colloidal destabilization. The inset in figure 5.7 shows a TEM image of these particles at pH=5.6. At these pH particles exist as small clusters with an average of 7 primary particles per cluster. The thermal conductivity of these clusters were measured experimentally using the transient hot wire method at three different volume fractions of the primary particles,  $\phi_p = 0.11, 0.166$  and 0.22. To compare with theory, we first run a simulation of the thermal conductivity of clusters with  $N_p = 7$  particles, shown as triangles in figure 5.7. We then used the simulation results to obtain  $\alpha = 0.8$  and the corresponding value of  $\phi_c$ , then used theses values to calculate the conductivity of the suspension from Eqs (5.8) and (5.4), shown by the solid line. The agreement with the experimental measurements is very good. The dashed lines represent the two bounds of the Maxwell's theory. The conductivity



Figure 5.7: Comparison with experimental measurements of thermal conductivity. On average, clusters contain 7 primary particles.

of the clusters falls between these limits and the magnitude of the enhancement is captured very accurately by this model. We note that  $\alpha$  for these small clusters  $(N_p = 7)$  is found to be higher than that of larger  $(N_p > 40)$  clusters produced by the same DLA algorithm. We attribute this to the fact that clusters containing a small number of primary particles do not exhibit the fractal character of larger clusters.

# 5.5 Conclusions

In summary, we have formulated a two-step model based on Maxwell's continuum theory to obtain the thermal conductivity of a suspension of clustered nanoparticles. The model treats clusters as equivalent spheres whose conductivity is modelled after the upper limit of Maxwell's theory, and the conductivity of their dispersion is modelled after the lower limit. The model requires two inputs, the thermal conductivity of the clusters, and their effective volume fraction. The volume fraction correlates fairly well with the volume of a sphere with radius equal to the radius of gyration of the cluster. The conductivity of the cluster is intimately related to morphology and structure and cannot be predicted *a priori*. We do find, however, that this dependence can be condensed into a single empirical parameter,  $\alpha$ , and have provided a methodology for its calculation by numerical simulation. Chapter 6

# The Kinetics of Reversible Gelation

# 6.1 Introduction

Gelation occurs in many colloidal suspensions with attractive forces through equilibrium and non-equilibrium routes. The mechanism by which gelation happens depends on the volume fraction and intermolecular interactions between particles [129, 130]. Strong attraction between the particles results in permanent bonding, fractal growth and finally irreversible gelation [131,132]. In chemical gels where covalent bonds are formed, rate of bond formation limits the rate of irreversible aggregation (reaction limited cluster aggregation, RLCA) [133]. In other irreversible gels, aggregation is kinetically driven and governed by diffusion of the particles (diffusion limited cluster aggregation, DLCA) [131]. On the other hand, physical gels are a result of weak short ranged attractions where bonds are non-covalent like hydrogen bonding, hydrophobic attraction or entropic interactions [134–136]. As a result, dissociation is possible and gels are reversible. In these systems both kinetic-base and equilibrium-base models has been developed [131, 133, 137, 138]. In kinetic models, clusters grow very fast in volume due to their fractal structure to a point where the occupied volume reaches the close packing volume fraction  $(\phi = 0.58)$ . They become locally arrested and a single connected network throughout the system forms [133]. At mild attractions and moderate volume fractions, gelation happens near equilibrium. Gelation starts with a phase separation following percolation or glass transition [139]. Although there are different scenarios proposed for colloidal gelation, a consistent conclusion among neither theories, nor experimental measurements has been reached. Experimentally, many colloidal gels has been developed through different mechanisms [139–141]. Thermoreversible gels are among the most studied where non-equilibrium, steady state gelation happens [142]. These reversible gels have attracted a lot of attention due to the potential they have in drug delivery and medical applications.

Equilibrium gels have been usually developed in suspensions with short range depletion attraction. Induced attraction between the particles initiates aggregation, phase separation and finally gelation. By controlling the deplete concentration and size, interaction between the particles can be controlled so as the gelation kinetic and phase boundary [136, 139].

Interactions between the particles set the gelation time and the dissociation rate. There are different models developed to capture the master kinetic equation of gelation with different attraction energies [143]. In short ranged attractive systems, where the attractive range can be neglected, association rate is independent of the size of the particles and the interaction between them. It is limited by diffusion and expressed by Smulochowski equation as  $k_a = (8/3)k_BT/\mu$  [144], where  $k_B$ is Boltzman constant, T is the temperature and  $\mu$  is the viscosity of the solvent. On the other hand, dissociation rate is a function of internal interactions (V) and is expressed by  $k_d \sim e^{(-V/k_BT)}$ . The higher the attraction (deeper the potential well), the slower the dissociation rate [145]. Therefore by increasing temperature, particle's thermal energy increases so as the association rate. This enhances gelation rate in cases where particle's interaction is not affected by temperature. Therefore, understanding the mechanism of gelation enables development of an appropriate kinetic model.

Here in this chapter, we study the kinetics of gelation/deaggregation of the colloidal system capable of reversible gelation, which was previously discussed in chapter 2. We monitor cluster growth and dissociation at different conditions to directly measure kinetics of this process. We investigate the effect of particle concentration, temperature, pH, sonication and coating concentration gelation/deag-gregation rate with the aim of understanding the mechanism behind the gelation of this reversible system and the effect of internal forces. These studies can bring an extrusive knowledge about gelatin mechanism and parameters affecting the rate of this process either equilibrium or non-equilibrium.

# 6.2 Results and Discussion

### 6.2.1 Gelation rate

The surface of colloidal silica was coated with TMPE as discussed in chapter 2 to a full extent. At the isoelectric point of the coated particles (pH=9.7), there is no long distance electrostatic repulsion between the particles and hydrophobic interactions push the system into gelation. Upon reaching the isoelectric point by pH adjustment, where no electrostatic repulsion exists, we expect the system to be unstable and lead to quick gelation. However the rate of gelation is highly influenced by different parameters. Gelation time can vary from seconds to months by changing particle concentration, coating concentration and temperature. Here



Figure 6.1: Effect of TMPE concentration on the gelation rate at the isoelectric point of the suspension (pH = 9.7). All the samples have constant particle volume fraction of  $\phi = 0.084$ . TMPE concentrations are 0.086, 0.091, 0.096 and 0.1 gr/gr(silica).

we quantified the effect of each parameter on gelation rate.

### 6.2.1.1 Effect of TMPE and Particle Concentration

Figure 6.1 shows the aggregation rate for suspensions at fixed particle volume faction of  $\phi = 0.084$ , coated with silane concentrations of 0.086, 0.091, 0.096 and 0.1 gr/gr(silica) respectively. These measurements were all conducted at room temperature and at the suspension's isoelectric point via dynamic light scattering (DLS). The change in silane concentration was small enough that no considerable change in the isoelectric point was measured. Small changes in the silane concentration, led to disproportional large changes of gelation time. At lower TMPE concentration gelation occurred in seconds. Upon increasing TMPE concentration aggregation was slowed down and the gel point was reached after a month. This dramatic change in gelation rate is very sensitive to the concentration of TMPE.

Particle concentration has a similar effect on aggregation rate. In the experiments we fixed the amount of TMPE (coating) at 0.086 gr/gr(silica) and varied the particle volume fraction from  $\phi = 0.04$  to  $\phi = 0.084$ . To keep the surface coverage constant, higher amount of TMPE was added to the suspensions with higher particle volume fractions. As shown in figure 6.2, at a fixed coating concentration, as the volume fraction of the particles increases, gelation rate decreases significantly. The high concentrated sample (8v.%) remained in dispersed phase much longer (about 1000 times) than the low concentrated one (4v.%). This behavior is in contrast with the usual reported behavior of colloidal suspensions where higher concentrated suspensions aggregate much faster due to the higher rate of collision among the particles.

With respect to particle growth in both figures 6.1 and 6.2, aggregation process can be divided into three distinctive steps. The shock due to the elimination of electrostatic repulsion results in a sudden rise of particle size. Initial blocks of clusters form in seconds right after moving to the isoelectric point. The initial sizes depends on the conditions: larger clusters are formed in samples with low particle or silane concentration. Following the jump, clusters growth continues with much slower rate. This process continues to a point where further growth is not possible as the volume occupied by the clusters reaches the close packing concentration and undergoes kinetic arrest or percolation. This is the maximum size that each individual cluster reaches while remaining as the dispersed phase in the solution and possible to be measured experimentally. Afterward, the suspension will jam into a single huge connected network throughout the system with infinite size.



Figure 6.2: Effect of particle volume fraction on the gelation rate of the suspension at isoelectric point (pH = 9.7). All the samples have same surface coverage with TMPE concentration of 0.086 gr/gr(silica).

For constant volume fractions of particles (figure 6.1), regardless of the silane concentration and association rate, all the samples grow to the same size (400nm < d < 500nm) right before the arrest takes place. As shown in figure 6.2, the higher the particle concentration, as expected, the smaller the final cluster size.

In this process, the second step determines the overall aggregation rate as it is the slowest step. Unexpectedly, larger formed clusters after screening the electrostatic repulsion, grow faster in the second step. This suggests that either the process is not limited by diffusion or a repulsive barrier exists against aggregation in samples with smaller formed cluster (high concentrated samples). To further investigate the limiting process in this step, the effect of temperature was studied.

#### 6.2.1.2 Effect of Temperature

Aggregation behavior of this colloidal system was studied under different temperatures. pH of the a suspension with particle volume fraction of  $\phi = 0.08$  and TMPE concentration of 0.091 gr/gr(silica) was set to the isoelectric point and size of the clusters was monitored at two different temperatures. Samples were placed in a water bath to keep the temperatures constant at  $T = 25^{\circ}$ C and  $t = 55^{\circ}$ C. As we can see in figure 6.3, increasing temperature has a significant effect on gelation rate. Gelation time was shortened from about 10 days at room temperature to couple of minutes at  $T = 55^{\circ}$ C. This process is thermodynamically driven and all the samples, with different rates, will eventually gel. Increasing temperature improves the kinetics of the process and decays the delay in gelation. This experiments confirms that growth of the clusters is governed by diffusion and limited by a repulsive barrier. By increasing temperature we basically provide individual clusters with higher kinetic energy to overcome the barrier very fast and grow in size significantly.

### 6.2.1.3 Origin of the Repulsive Barrier against Gelation

At high TMPE concentrations the repulsive barrier seems to be high enough to delay the gelation time significantly. On the other hand at low concentrations, the barrier is extremely weak that second phase is almost skipped and instant gelation occurs. It seems that the effect of particle volume fraction also lies within the fact that higher concentrated samples contain higher TMPE concentrations as well. TMPE is a silane with three hydrolyzable group that may attach to the surface of silica particle or it may react in the solution with other silane molecules to produce oligomeric structures. At high concentrations of TMPE, the concentration



Figure 6.3: Effect of temperature on gelation rate. This graph presents gelation rate at particle volume fraction of  $\phi = 0.084$  coated with 0.096 gr /gr(silica) TMPE at temperatures of  $T = 25^{\circ}$ C and  $T = 55^{\circ}$ C.

of excess TMPE unattached to the particle surface increases so does the probability of forming self aggregated silanes in the solution. To further investigate the effect that TMPE may cause, we prepared a suspension of coated silica particles in which instant gelation occurs at the isoelectric point. Different concentrations of N-Ndimethyldipropylne-triamine (DMDPTA) was added systematically to the coated suspensions. This molecule has similar structure to TMPE but is non-reactive, it can react neither with the particles nor itself. As shown in figure 6.4, at zero concentration of DMDPTA, particles gel instantly (white color) however as the concentration increases (from left to right), aggregation rate significantly decreases and the suspension becomes completely clear (no aggregation). This observation qualitatively confirms that excess TMPE is responsible for longer stability of the



Figure 6.4: Effect of N-N-dimethyldipropylne-triamine (DMDPTA) on aggregation state of the suspension with concentration of 0, 0.06, 0.1, 0.14, 0.2, 0.3 g/ml. At zero concentration a gel is formed instantly and solution is completely white. As the concentration increases the solution becomes clear with well dispersed particles in the solution.

particles or in other words delay in the time for gelation.

We considered various possible mechanisms that might be responsible for this behavior caused by TMPE. Concentration of excess TMPE may increase to a point where depletion repulsion between the particles is developed. High concentration of TMPE between the particles creates a structural barrier against aggregation and pushes the particles apart. However adsorption of these molecule onto the surface should be slower than particle diffusion. TMPE molecules in water can self react to form tiny silica particles with sizes of about few nanometer. This process also rises the possibility that halo process is providing the stabilizing mechanism. Second possible explanation could be an increase in the steric protection caused by adsorption of multilayer TMPE onto the surface of the particles. At the isoelectric point, TMPE becomes neutral and more prone to adsorb to the particle surface. At higher concentrations, a thicker steric layer and as a result a smaller potential depth is formed. The deaggregation rate increases and gelation time can be delayed. Finally the effect of TMPE may contribute to the fact that the hydrophobic interactions among the coated particles are decreased. The environment surrounding particles becomes more compatible with the surface of the particles as the concentration of TMPE in the solution increases.

### 6.2.2 Deaggregation Rate

The gel is reversible as TMPE monolayer provides steric stabilization and prevents permanent bonding. Particles are physically attracted due to hydrophobic interactions between TMPE monolayer on particles surface. This attraction can be overcome either by repulsion (pH change) or an external force/shear (sonication). At different pH values, stable clusters with controlled size form due to the competition between hydrophobic interactions and electrostatic repulsion between the particles.

The final cluster size is only a function of pH which determines the strength of repulsion. The reversibility locks-in the size of the cluster and at any pH, the system reaches an equilibrium and the size distribution of the particles reaches the equilibrium distribution. However by sonication we temporarily separate the particles and unstable clusters form. In this section cluster formation was monitored as a function of pH and also after sonication.

### 6.2.2.1 Effect of pH

By decreasing the pH from the gel point (pH=9.7), particles gain positive charge due to ionization of amino groups and repulsion breaks weak attraction between the particles to some degree. Therefore the rate which dissociation occurs, clearly depends on the pH. Figure 6.5 shows deaggregation rate of the clusters at pH= 4, 5.6 and 7 for suspensions with volume fractions of 0.06 and 0.084. At pH=4,



Figure 6.5: Deaggregation rate of silica suspensions at volume fraction of  $\phi = 0.06$ and  $\phi = 0.084$  and TMPE concentration of 0.096 gr/gr(silica) at (a) pH= 4, (b) pH= 5.5 and (c) pH= 7

the gel was redispersed very fast to suspension clusters with final size of around 50 nm. Dissociation was fast at this pH and followed the same trend for both volume fractions ( $k_d = 0.86 \pm 0.1 \ 1/hr$ ). However, at pH= 5.5 different behavior was observed for different particle volume fractions. Redispersion was easier for the higher concentrated samples ( $\phi = 0.084$ ) and it reached the same final size of 100 nm in much shorter time. ( $k_{d8}/k_{d6} = 6$ ). At pH=7, redispersion was only possible for at  $\phi = 0.08$ . Samples with lower volume fractions were not capable of redispersion without the additional aid with sonication.

The lower the pH, the higher the repulsion between the particles and thus the shorter time for clusters to reach their final size. As the pH becomes higher, rate of deaggregation decreases. Likewise aggregation, low concentrated samples are more prone to gelation, therefore more difficult to be redispersed. Such effect is less significant at low pH: repulsion is high enough that the strength of the hydrophobic attraction is incomparable and clusters will dissociate to monomers very fast.

To redisperse the particles, the pH must be low enough to provide sufficient repulsion. Maximum pH that provides self deaggregation depends on particle concentration. As it is easier for higher concentrated samples to deaggregate, the maximum needed pH (pH < 7) is also higher than that for low concentrated samples (pH < 5.5). At pH > 7, as electrostatic repulsion becomes inadequate, redispersion is only possible with a help of sonication for both studied volume fractions.

### 6.2.2.2 Effect of Sonication

By applying a force, the gel network will collapse into smaller clusters and the suspension becomes flowable. The higher the concentration of the particles, the


Figure 6.6: Size of the clusters (initially distributed as the dotted line) at different pH right after 40 min sonication and later. Each symbol represents the size of the clusters after different number of days pass the sonication time(as listed). Size of the clusters increase until they reach back to the dotted line which represents equilibrium size distribution of the clusters. Particle volume fraction is (a)  $\phi = 0.22$  and (b)  $\phi = 0.06$ . TMPE concentration is 0.096 gr/gr Silica.

stronger the network is against the applied force. Since these particles are weakly connected, in low concentrated samples, simple shaking of the vial can simply disperse the gel. However as soon as the force is removed, particles start aggregating to reform the gel. This process can be done at any pH where stable clusters are formed. We sonicated the stable nanoclustered samples at their final size distribution at different pH for 40 min in a bath sonicator. After sonication, smaller clusters in compare to the initial distribution were formed. For 20% particle volume fraction (figure 6.6-a) we were able to dissociate particles to monomers at almost any pH. On the other hand, with the same sonication time, for 6% particle volume fraction (figure 6.6-b), deviation from equilibrium size was less and particle dissociation was less responsive to sonication. After sonication, particles grew over days until they reached their initial distribution as shown in figure 6.6. The rate which they achieve their final size depends on pH and TMPE concentration. Similarity in aggregation rate was observed: lower concentrated samples grew faster to their final size. This process is reversible, by re-sonication at any pH, same behavior was observed. This behavior of the particles confirms that the size distribution is only a function of pH, and regardless of the initial aggregation state, a gel or fully dispersed monomers, final distribution of particles with any volume fraction or TMPE concentration will be the equilibrium distribution.

### 6.3 Conclusion

We developed a reversible system where the kinetics of gelation/redisperion is controlled extensively. The rate of gelation can be changed dramatically by changing the coating concentration and temperature. This extensive control is due to a delay that excess TMPE (coating agent) causes. A barrier against aggregation develops that slows the cluster aggregation rate very slow. The system wants to gel thermodynamically however the rate which this happens depends on the strength of the barrier. Higher the concentration of the silane, higher the barrier and therefor longer gelation time. The delay is kinetically driven and therefore by increasing the temperature in which this process is happening we are able to increase the aggregation rate to overcome the barrier much faster. Deaggregation rate also be controlled by pH or particle concentration. The lower the pH, the higher the inter-particle repulsion and therefore, the faster the dissociation process. However at a constant pH, particles with different volume fractions deaggregate with different rates to the same final size. At any pH the system reaches the equilibrium clusters with final sizes form. The gel or the formed clusters can be dissociated further by sonication. Sonication only breaks the weak bond between the particles and as soon as it's remover, particle growth initiates until cluster with equilibrium distribution form.



# Conclusions and Recommendation for Future Works

## 7.1 Conclusions

Colloidal suspensions with improved thermal properties in comparison to liquids, have been under investigation for many years. However their thermal behavior and the mechanism by which conduction occurs has not been well studied. The classic theory to predict conductivity of such complex suspensions is Maxwell's mean field theory with two limiting bounds. The lower bound which evaluates conductivity of well dispersed suspension of spherical particles, is well quoted in the literature and has been employed as a basic theory of conduction in colloids. However, inconsistency between the theory and experiments and also large variability in experimental measurement themselves has questioned the validity of this theory. Different models has been developed to explain this discrepancy and justify unusually higher reported conductivities in compare to this theory. Between proposed mechanism, aggregation is the most plausible event that can effect conductivity and also exists in nearly all colloidal suspensions which was neglected during conductivity measurements. However there is no direct evidence of such effect. The main focus of this dissertation was on thermal characterization of colloidal suspensions with the aim of directly quantifying the effect of aggregation, surface properties and structure of the solid phase and providing a comprehensive knowledge on conduction in such complex fluids, experimentally, theoretically and by numerical simulations.

Controlling the degree of aggregation in experimental systems is usually a challenge. In order to overcome difficulties associated with this issue, in chapter 2, we developed a system with well controlled interactions, capable of forming reversible equilibrium clusters with tunable size. Surface of silica particles were coated with different amino silanes to identify a silane capable of forming a monolayer on surface of the particles without causing irreversible aggregation. Full surface treatment with TMPE, enabled us to tune the electrostatic repulsion between the particles via pH, and therefore, the balance between attractive and repulsive interactions. As a result, stable clusters were formed as a function of pH. This monolayer prevents permanent aggregation between silica particles which usually occurs via chemical reaction. Therefore the cluster size can be reversibly changed from monomers up to a gel.

By developing such system we were able to quantify the effect of aggregation experimentally for the first time in a controlled way. In chapter 3, we showed that at fixed volume fraction of the particles, conductivity enhances monotonically with cluster size and lies between the limits of Maxwell's theory. This result removes any ambiguity about Maxwell's theory validity and also clarifies the importance of aggregation in experimental measurements where usually is neglected. Conductivity of coated silica particles was also investigated and it was shown that even though TMPE monolayer is very thin, it has a significant effect on conductivity of particles due to its low conductivity. Therefore, in order to predict conductivity in colloidal suspensions, extensive knowledge on the system is essential such as degree of aggregation, structure and surface properties, concentration of any additives or surfactants. Without these information, prices prediction and control is not possible.

In Chapter 4, Monte Carlo simulations were employed to address conductivity of non spherical particles and investigate the effect that structural details of the solid material may cause. We showed that Maxwell's theory is accurate for well dispersed suspensions of symmetric particles while it only provides a range for conductivity of anisotropic shapes like rods. Particles with asymmetric shapes enhances conductivity considerably above spheres. Aside from the difficulties arise from synthesis and stability of these particles, they are excellent candidates to be used as nanofluids. Numerical simulation provided a tool to avoid experimental limitations and a method to evaluate conductivity between Maxwell's limiting bounds for any model aggregate. Configuration of aggregated structures play an important role. As the degree of cross linking increases, conduction improves in the system. We showed that even small details of particle's structure such as the neck size that form during aggregation, affect thermal conductivity significantly.

In chapter 5, a theoretical model was developed to quantify effect of aggregation. Although Maxwell's theory provide a baseline for conductivity of colloids, it is inadequate for non-spherical particles and nanoclusters. This three layer model gives the entire profile between Maxwell's limiting bounds based on the degree of aggregation. We showed that aggregated structures can be treated as spheres with effective properties and conductivity of such system can be evaluated by Maxwell's lower limit. Thermal conductivity of aggregates themselves were estimated by the upper bound of the theory since clusters can be visualized as micro gels. We showed that Maxwell's upper limit which gives conductivity of a system, where the fluid is dispersed within the solid material, is an overestimation for colloidal gels where the system is truly bi-continuos. The effect of aggregation on thermal properties of colloidal suspensions obtained by experimental groundwork in chapter 3 was successfully correlated with analytical calculations and numerical simulations.

In chapter 6, we addressed the kinetic behavior of reversible colloidal gelation of silica suspension developed in chapter 2. We showed that gelation rate can be controlled extensively. By small changes in TMPE concentrations used to coat the particles surface, we were able to change the gelation time significantly. Increasing temperature on the other hand, has the opposite effect. Samples with gelation times of about a week, were gelled in 3 minutes by increasing temperature from 25°C to 55°C. Deaggregation rate was also controlled by pH, sonication time and TMPE concentrations. It was shown that if the particles were sonicated away (down to monomers) from their initial size distribution, they would grow in size until they reach their equilibrium distribution. It was shown that excess TMPE in the solution is responsible for the unusual aggregation behavior. Particles with higher TMPE concentration, are more prone to remain stable in the solution, as a result, they aggregate slower and deaggregate much faster. However the mechanism by which this dramatic change occurs it still not fully understood.

### 7.2 Recommendation for Future Work

### 7.2.1 Thermal Conductivity

The use of colloidal particles as additives for thermal fluids is an attractive way to improve the heat transfer characteristics of the base fluid. The most significant observation is that improvements between 10% and 40% can be achieved with less than 10% by volume of the solid phase. Many challenges remain, however. While it has been established that large enhancements are possible, it has also become clear that a substantial part of it is due to clustering, an effect that is undesirable in practical settings. Indeed, providing sufficient stability under temperature swings and flow conditions in aqueous and organic solvents remains the key obstacle to commercial development. On the other hand, the potential benefits, particularly with respect to more efficient utilization of energy, are quite substantial. In this respect, this relatively new area provides colloidal scientists with new opportunities. We showed that configuration of aggregated structures can change conductivity significantly, therefore providing new designs of stable clusters with the aim of maximizing conduction in experimental systems can lead to a great energy saving. However size of these nanocluster should be small enough to minimize difficulties associated with aggregated particle like settling down, viscosity and etc. in practical applications. By designing particles with desired structures we can optimize both conduction and stability in the system. Assembling particles into specific structures has been a great interest and a challenging area. Between inorganic particles, gold assemblies has been among the most studied [146]. Most of the techniques used in colloidal solutions, however, result in uncontrolled configurations.

In chapter 5 we developed a continuum model of conductivity. This model needs

two pieces of information, cluster volume fraction and  $\alpha$ , the correction factor that accounts for the structure of the aggregates, in order to predict conductivity of colloidal suspensions. Although we showed that effective volume fraction can be estimated by radius of gyration of the aggregates, computer simulation is still needed for the calculation of  $\alpha$  for new structures. It would be very interesting to elaborate this factor with real structural characteristics of the dispersed phase like its fractal dimension, to avoid extra simulation work. By designing different configuration of aggregates and evaluating their thermal behavior, this correlation can be found. However, simple correlation is needed to avoid implication to real experimental measurements.

### 7.2.2 Reversible Gelation of Silica

#### 7.2.2.1 Application

In chapter 2 and 6, we presented an interesting colloidal system with the capability of reversible gelation. This unique system can be employed in many different potential applications including drug delivery, sensors and etc. with further investigations. For example, it can be used as a switch responsive to pH of the environment or as a carrying agent in medical applications even at high temperatures. The important feature of this system is transforming from a fluid to a solid like network and back, instantly or with a controlled rate. Loading capacity and release rate of different molecules, dyes and biological agents can be measured in this system to provide enough information on the ability of these gels to be used in potential applications. This gels are also reversible due to shear. Rheological studies can provide information of the nature, strength and lifetime of the interactions between the particles.

### 7.2.2.2 Routes to Gelation

Route to physical gelation, result of short range attractive forces has been studied extensively and numerous models have been developed [133]. However not a consistent conclusion has been reached so far. Gelation can be a result of an equilibrium or kinetically driven process. Most of the studies that were done on equilibrium gelation has been carried out on systems with short range depletion attraction and inconsistent conclusions on the gelation mechanism has been proposed [136, 139]. Therefore investigation of this matter for our system where the attraction is originated by hydrophobic interactions can bring new insights and provide significant information on gelation in colloidal suspensions. Different experimental techniques including, in situ rheology, dynamic and static light scattering can monitor the phase behavior of the system and may provide the needed information.

### 7.2.2.3 Nature of TMPE Effect on Kinetics of Gelation

As discussed in chapter 6, TMPE has a significant effect on kinetics of reversible aggregation. However the mechanism is still not fully understood. In order to clarify the dramatic role of TMPE in the system series of controlled experiments are needed. Any possible mechanism including depletion repulsion, steric effect or reduction in attraction should be tested separately. For depletion repulsion, it is needed to add non-reactive molecules soluble in water with structures different in compare to TMPE. By this experiment, it will become clear whether large oligomers are responsible for delaying gelation or not. Another effective way would be to find a way to separate particles from all the excess TMPE in the solution. Centrifuge may work, although, these particles are small in size with density close to water which makes centrifuging not very effective. Any kind of drying is not effective since TMPE will stick to the particles in the evaporation process. However washing the particles through a membrane may help removing unrelated silanes.

### 7.2.2.4 Kinetic Model

This system can also be modeled kinetically. By extracting the strength of the attractive force and the repulsive barrier, a model can be developed where not only gives rate constant, also provides the final size of the clusters at any pH. With this model we will be able to tune the exact size of the clusters to desired value.

Appendix .

# The Transient Hot Wire Method

The most direct way to measure conductivity is through application of Fourier's law under steady state across a layer of fluid that is subjected to known heat flux. Steady-state methods, however, produce convective flows that interfere with the measurement and are difficult to control [147]. Transient methods avoid these problems. The technique most commonly used is the transient hot wire (THW) method, which applies a short heat pulse to a conductive wire immersed in the sample and extracts the conductivity from the transient response of the fluid. The transient nature of the experiment, its brief duration and small perturbation ensure that convection does not arise during the measurement [148, 149]. The technique has been proven highly accurate for both liquid and solid materials [147, 150–152]. It is by far the most common method used for the conductivity of colloidal dispersions [2, 5, 22, 27, 28, 30, 33–37, 42, 43, 92, 112, 114–118, 120, 147, 150–167].

The basic setup of the THW apparatus is shown in Fig. A.1. It consists of a thin metal wire, typically Pt, that runs along the axis of a cylindrical vessel that contains the liquid of interest. The wire is subjected to a step change of the applied voltage and its temperature rise is recorded as a function of time. The electrical



Figure A.1: Schematic of the transient hot wire (THW) apparatus (adapted from [5]).

circuit forms a Wheatstone bridge between the wire and three known resistances. By adjusting the resistance of the potentiometer  $R_3$  such that no current runs between points 1 and 2, the resistance of the wire is calculated from the balance condition  $R_w = R_1 R_3/R_2$ . This measurement produces both the resistive heat that is delivered through the wire as well as its temperature. The heat per unit length (W/m) is

$$\dot{q}_L = i^2 \rho_w / A_w, \tag{A.1}$$

where *i* is the current through the wire, and  $\rho_w$ ,  $A_w$ , are the resistivity ( $\Omega m$ ) and cross sectional area (m<sup>2</sup>) of the wire. The temperature is obtained through the relationship between resistance and temperature, which is quadratic in T [164],

$$R_w = a_0 + a_1 T + a_2 T^2. (A.2)$$

The calculation of conductivity requires a theoretical model for the temperature rise of the wire under a step change in the heat that is delivered through it. The model assumes a linear source of heat of infinite length, uniform temperature along the wire and within its cross section, and an infinite medium around the wire that transports heat by conduction only. These assumptions must be matched by the design of the apparatus. The characteristic time for establishing uniform temperature across the wire is of the order  $r_w^2/\alpha_w$ , where  $\alpha_w$  is the thermal diffusivity of the wire. Using  $\alpha_w = 2.6 \times 10^{-5} \text{ m}^2/\text{s}$  [5], and  $r_w = 50 \ \mu\text{m}$ , this time is of the order of 0.1 ms. Typical measurements last several s, therefore the above condition is well met.

The conduction equation in the medium that surrounds the wire is [5]

$$\frac{\partial T}{\partial t} = \frac{\alpha_f}{r} \frac{\partial}{\partial r} \left( r \frac{\partial T}{\partial r} \right), \tag{A.3}$$

where  $\alpha = k/\rho C_p$  is the thermal diffusivity of the medium,  $\rho$  (kg/m) is its density and  $C_p$  (J/kg K) is its heat capacity. This is solved under the following conditions:

$$\left(r\frac{\partial T}{\partial r}\right)_{r_w} = -\frac{\dot{q}_L}{2\pi k},$$
$$T(t=0,r) = T_0.$$
$$T(t,r\to\infty) = T_0.$$

The first of these is the boundary condition at the fluid-wire interface and expresses the heat flux in terms of the temperature gradient on the fluid side of the interface. The second equation is the initial condition before the step change, and the third equation gives the far-field condition for temperature at all times. An analytic solution is obtained using the substitution  $x = r_w^2/4\alpha t$  [5]. The final form is

$$T - T_0 = \frac{\dot{q}_L}{4\pi k} \operatorname{Ei}\left(\frac{r_w^2}{4\alpha t}\right) \tag{A.4}$$

where Ei(x) is the exponential integral

$$\mathrm{Ei} = \int_{x}^{\infty} \frac{e^{-x}}{x} dx. \tag{A.5}$$

This equation can be expanded in terms of  $r_w^2/4\alpha t$  to produce a simple expression for experimental analysis,

$$T - T_0 = \frac{\dot{q}_L}{4\pi k} \left[ -\gamma + \ln\left(\frac{4\alpha t}{r_w^2}\right) + \cdots \right]$$
(A.6)

where  $\gamma$  is Euler's constant. The omitted terms are of the order of  $r_w^2/4\alpha t$  and higher, an approximation that is acceptable over several s of the transient, provided that  $r_w$  is sufficiently small. The conductivity is then calculated from the slope of a linear graph of T versus  $\ln t$ :

$$k = \frac{\dot{q}_L}{4\pi} \frac{\Delta(\ln t)}{\Delta T},\tag{A.7}$$

which assumes that the physical properties of the fluid do not vary much with temperature. With a wire of length l, below a critical time,  $t \ll l/U$ , that depends on Prandtl number, convection can be neglected.  $U \sim g\alpha l^2 \Delta T/\nu$  for very short wires and  $U \sim (g\alpha l\Delta T)^{1/2}$  for long wires where  $\alpha$  and  $\nu$  are the thermal expansion coefficient and kinematic viscosity of the fluid respectively. Our measurements are done in a setup with l = 0.138m and within t = 2s to avoid natural convection.

The basic setup described here, originally developed for gases, must be modified to accommodate liquids that are electrically conductive. The difficulty arises from partial flow of current through the liquid, polarization effects at the surface of the wire and poor signal-to-noise ratio [165]. These problems are generally avoided by applying a thin insulating layer on the wire. In one approach the wire is coated by a thin layer of polyester [165]. Other designs implement anodized tantalum wires in which a thin layer of metal oxide serves as the insulator [115, 118, 152, 160], and the use of a mercury capillary in which case mercury replaces the wire and the borosilicate glass offers the insulation [12, 156, 166]. Various corrections may be necessary to account for radiation losses, finite size of the apparatus, and other assumptions that are not matched by the experimental design. These can be found in the specialized literatures (see for example references [12] and [165]) but essentially they apply corrections to the value of  $\Delta T$  that is used in Eq. (A.7).



# Diffusion Limited Cluster Cluster Aggregation

Clusters with different fractal dimensions can be generated by computer simulations through various methods including Eden models, Ballistic model, diffusion limited particle cluster aggregation, diffusion limited cluster cluster aggregation and also reaction limited methods [168]. In diffusion limited methods, cluster formation is limited by the random motion of the species and aggregates form as soon as any two particles touch.

In diffusion limited cluster cluster aggregation, particles/aggregates which are represented by occupied lattice sites in a cubical lattice are picked with a probability that scales as 1/r, where r is the number of primary particles in a cluster. If the suspension is fully dispersed the probability of each individual particle to be picked are equal. On the other hand, as the particles grow and form larger cluster, 1/r decreases so as their probability to be picked. This function accounts for the fact that larger clusters diffuse much slower in the solution than smaller particles.

The chosen particle/aggregate is moved randomly in one of the six directions

by one unit. After the movement if the particle/aggregate contacts any of the neighboring particles, they aggregate permanently and treated as single unit. This process continuous until one final cluster remains. However keep in mind that the larger the aggregate, the slower that it can diffuse in the solution.

This simulations are done with periodic boundary condition and result in clusters with  $d_f = 1.7 - 1.9$ .

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### Publications

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• Themis Matsoukas, <u>Saba Lotfizadeh</u>, Encyclopedia of Surface and Colloid science, Second Edition, (2014)

• <u>Saba Lotfizadeh</u>, Themis Matsoukas, "A Continuum Maxwell Model for the Thermal Conductivity of Clustered Nanocolloids", Submitted to Journal of Applied Physics Letter, February (2015)

• <u>Saba Lotfizadeh</u>, Dan Railly, Hassan Aljama, Themis Matsoukas, "Equilibrium Cluster formation of Silica nanoparticles," In preparation to be submitted to Langmuir, March (2015)

• <u>You-Han Chen</u>, Saba Lotfizadeh, Themis Matsoukas, "Effect of Aggregation on Thermal Conductivity; Microscopic View," In preparation to be submitted to Journal of Nanoparticle Research, March (2015)

• <u>Saba Lotfizadeh</u>, Alec Myers, Dionna Janay littles, Themis Matsoukas, "Kinetics of pH-Reversible Gels", In preparation to be submitted to Journal of colloid and interface science, March (2015)

### Conference presentations

• "A Predictive Model for the Thermal Conductivity of Clustered Nanocolloids," Colloid and Surface Science Symposium, Philadelphia, June 2014.

• "Reversible Gelation Responsive to pH with Controlled Size of aggregates," AIChE National Meeting, Atlanta GA, November 2014.

• "A Model to Predict Thermal Conductivity in Colloidal Dispersions. AIChE National Meeting," AIChE National Meeting, Atlanta GA, November 2014.

• "Monte Carlo Simulation of Nanofluids to Evaluate the Effect of Aggregation. AIChE National Meeting," AIChE National Meeting, San Francisco CA, November 2013.

 $\bullet$  "Stabilization of silica nanofluids at neutral pH and evaluate the effect of coating concentration", AIChE National Meeting, San Francisco CA, November 2013, Conference poster ,

• "Effect of Clustering in the Thermal Properties of Colloidal Suspensions," AIChE National Meeting, Pittsburg PA, October 2012.

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